Effects of NO₂ and C₃H₆ on the heterogeneous oxidation of SO₂ on TiO₂ in the presence or absence of UV irradiation

Biwu Chu 1, 2, 3, Yali Wang 1, 3, Weiwei Yang 1, 3, 4, Jinzhu Ma 1, 2, 3, Qingxin Ma 1, 2, 3, *, Peng Zhang 1, Yongchun Liu 1, 5, Hong He 1, 2, 3

1 State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
2 Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
3 University of Chinese Academy of Sciences, Beijing 100049, China
4 Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, Institute of Environmental and Applied Chemistry, College of Chemistry, Central China Normal University, Wuhan 430079, China
5 Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Correspondence to: Qingxin Ma (qxma@rcees.ac.cn)

Abstract. The heterogeneous reactions of SO₂ in the presence of NO₂ and C₃H₆ on TiO₂ were investigated with the aid of in situ DRIFTS under dark conditions or with UV irradiation. Sulfate formation with or without the coexistence of NO₂ and/or C₃H₆ was analyzed with IC. Under dark conditions, SO₂ reacting alone resulted in sulfite formation on TiO₂, while the presence of ppb levels of NO₂ promoted the oxidation of SO₂ to sulfate. The presence of C₃H₆ had little effect on sulfate formation in the heterogeneous reaction of SO₂ but suppressed sulfate formation in the heterogeneous reaction of SO₂ and NO₂. UV irradiation could significantly enhance the heterogeneous oxidation of SO₂ on TiO₂, leading to a copious generation of sulfate, while the coexistence of NO₂ and/or C₃H₆ significantly suppressed sulfate formation in experiments with UV lights. Step-by-step exposure experiments indicated that C₃H₆ mainly competes for reactive oxygen species (ROS), while NO₂ competes with SO₂ for both surface active sites and ROS. Meanwhile, the coexistence of NO₂ with C₃H₆ further resulted in less sulfate formation compared to introducing either one of them separately to the SO₂-TiO₂ reaction system. The results of this study highlighted the complex heterogeneous reaction processes that take place due to the ubiquitous interactions between organic and inorganic species, and the requirement to consider the influence of coexisting VOCs and other inorganic gases in the heterogeneous oxidation kinetics of SO₂.

1 Introduction

Atmospheric aerosol pollution has attracted widespread attention in recent years because of its adverse effects on human health, visibility and climate (Thalman et al., 2017; Davidson et al., 2005; Pöschl, 2005). In many developing countries, such as China and India, high concentrations of SO₂, NOₓ, and volatile organic compounds (VOCs) coexist in the atmosphere (Zou et al.,
2015; Liu et al., 2013; Yang et al., 2009) and result in “complex atmospheric pollution” (Yang et al., 2011) and heavy haze events. Sulfate was found to play important roles in the occurrence of these haze events (Zhang et al., 2011; Liu et al., 2017) due to both its high mass concentration in fine particles (PM$_{2.5}$) and its strong hygroscopicity. Rapid formation of sulfate was frequently observed in haze episodes in China, in which heterogeneous reactions played important roles (He et al., 2014; Zhang et al., 2006a; Ma et al., 2018). However, the mechanism of the heterogeneous reaction process as well as its contribution to sulfate formation in “complex atmospheric pollution” remain uncertain (Yang et al., 2018a; Ma et al., 2018; Wang et al., 2018; Yu and Jang, 2018). These uncertainties are considered to be the main reason for the inaccuracy of sulfate simulation in air quality models (Wang et al., 2014b; Zheng et al., 2015; Yu and Jang, 2018).

About 1000 to 3000 Tg of mineral aerosols are emitted into the atmosphere every year (Dentener et al., 1996; Shen et al., 2013; Jaoui et al., 2008) and provide abundant surface area for the heterogeneous oxidation of SO$_2$. The heterogeneous uptake of SO$_2$ can form bisulfite (HSO$_3^-$) or sulfite (SO$_3^{2-}$) on γ-Al$_2$O$_3$ and sulfate (SO$_4^{2-}$) on MgO (Goodman et al., 2001a). Similarly, SO$_2$ can be irreversibly converted into sulfite, bisulfite or sulfate on mineral dust such as metal oxides (Zhang et al., 2006b), calcite, and China loess (Usher et al., 2002). The heterogeneous reaction of SO$_2$ on mineral dust can be promoted by gaseous oxidants. For example, SO$_2$ could be oxidized into sulfate by O$_3$ on the surface of CaCO$_3$ particles (Li et al., 2006; Zhang et al., 2018). Similar results were obtained when introducing H$_2$O$_2$ into the heterogeneous oxidation system (Capaldo et al., 1999; Jayne et al., 1990). NO$_2$ can also promote the heterogeneous oxidation of SO$_2$. In our previous studies, it was found that SO$_2$ was oxidized to sulfate on γ-Al$_2$O$_3$ in the presence of NO$_2$ and O$_2$, while it was only converted to sulfite in the absence of them (Ma et al., 2008). Therefore, NO$_2$ was proposed to act as a catalyst to activate O$_2$ in the oxidation, in which the intermediates observed in the spectra, i.e. nitrogen tetroxide (N$_2$O$_4$), might play an important role (Ma et al., 2008). This synergistic effect between SO$_2$ and NO$_2$ was further observed on many other mineral oxides such as CaO, α-Fe$_2$O$_3$, ZnO, MgO, α-Al$_2$O$_3$, and TiO$_2$ (Liu et al., 2012; Ma et al., 2017; Zhao et al., 2018; Yu et al., 2018). These effects were confirmed in smog chamber studies and field observations of heavy haze in China, and were proposed to be an important reason for the rapid growth of sulfate in haze events (He et al., 2014; Ma et al., 2018; Wang et al., 2014a; Chu et al., 2016). Heterogeneous oxidation of SO$_2$ may also be affected by the coexistence of organic compounds. Pre-adsorption of CH$_3$CHO was found to suppress the heterogeneous reaction of large amounts of SO$_2$ on the surface of α-Fe$_2$O$_3$ (Zhao et al., 2015b), while HCHO was proposed to react with SO$_3^{2-}$ and generate hydroxymethanesulfonate (HMS) in the northern China winter haze period (Song et al., 2019). Wu et al. (Wu et al., 2013) found that the synergistic effects between HCOOH and SO$_2$ in the heterogeneous reaction on hematite provide a new source of sulfate, while Zhao et al. (Zhao et al., 2015a) found that sulfate formation on α-Fe$_2$O$_3$ was suppressed by the presence of acetaldehyde (CH$_3$CHO).

Illumination can affect both the properties of particles and heterogeneous reactions (Nanayakkara et al., 2012a; Cwiertny et al., 2008; George et al., 2015). The photooxidation of SO$_2$ in the presence of mineral dust may represent an important pathway for generating sulfate aerosols (Park et al., 2017; Yu and Jang, 2018). TiO$_2$, an n-type semiconductor material, has been widely used for studying heterogeneous photochemical reactions (Chen et al., 2012b). TiO$_2$ can be excited by UV light (λ< 387 nm), resulting in active species (primarily O$_2^-$ and OH) that can participate in atmospheric photochemical...
reactions (Chen et al., 2012b). Shang et al. (Shang et al., 2010) studied the heterogeneous reaction of SO$_2$ on TiO$_2$ particles using *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), and observed that SO$_2$ was oxidized to sulfate on TiO$_2$ with UV illumination while remaining as sulfite under dark conditions. Chen et al. (Chen et al., 2012a) further proposed that the formation of sulfate on TiO$_2$ with UV illumination was related to surface oxygen vacancies acquiring additional charge, followed by forming reactive oxygen species (ROS). Our recent study showed that O$_2$ and H$_2$O have contrary roles in the photooxidation of SO$_2$ on TiO$_2$, where surface water exhibits a competition effect in the reaction of SO$_2$ due to the occupation of surface OH. (Ma et al., 2019) Besides H$_2$O, the co-existence of organics may also suppress the formation of sulfate due to competition with SO$_2$ for reactive oxygen species. For example, Du et al. (Du et al., 2000) studied the photocatalytic reaction of SO$_2$ in the presence of heptane (C$_7$H$_{16}$) and found that the formation of sulfate was suppressed. In spite of these studies involving the heterogeneous oxidation of SO$_2$ under various conditions, it is not fully understood how the heterogeneous oxidation of SO$_2$ is influenced by co-existing pollutants under dark or illumination conditions. Meanwhile, the interactions between organic and inorganic species in the heterogeneous oxidation of SO$_2$ at low concentrations have not been deeply researched yet. In this study, we focus on the effects of co-existing NO$_2$ and propene at low concentrations (200 ppb) on the heterogeneous oxidation of SO$_2$ on TiO$_2$ with *in situ* DRIFTS under both dark and illumination conditions. Propene is selected as a representative VOC since it is a ubiquitous VOC in the atmosphere, and is widely used as an accelerator in photochemical reactions in some smog chamber studies (Jang and Kamens, 2001; Song et al., 2007). Rather than UV lights, a xenon light is used for a better simulation of the UV irradiation from the sun on the earth’s surface. Generally, our study could be helpful for gaining a better understanding of sulfate formation under complex air pollution conditions, in which abundant SO$_2$, NO$_x$, and VOCs as well as mineral dust exist in the atmosphere at the same time.

### 2 Experimental section

#### 2.1 Materials

TiO$_2$ (Degussa P$_{25}$) used in this study was a typical commercially available material, which contains 75% anatase and 25% rutile. It has been widely used in laboratory studies due to its good photocatalytic properties. The surface area of the material in this study was 50.50 m$^2$ g$^{-1}$, measured by an ASAP2010 BET apparatus with multipoint Brunauer-Emmett-Teller (BET) analysis. The average particle diameter was about 20 nm, determined by transmission electron microscopy (H-7500, Hitachi Inc.). For gases, N$_2$ (99.999% purity, Beijing Huayuan) and O$_2$ (99.999% purity, Beijing Huayuan) were introduced as synthetic air (80% N$_2$ and 20% O$_2$) in this study, while SO$_2$ (5.9 ppm in N$_2$, Beijing Huayuan), NO$_2$ (3.9 ppm in N$_2$, Beijing Huayuan) and C$_3$H$_6$ (5.9 ppm in N$_2$, Beijing Huayuan) were used as reactant gases.
2.2 Experimental methods

2.2.1 In situ DRIFTS

In situ DRIFTS spectra were recorded on a Nicolet Nexus 670 FTIR equipped with a mercury cadmium telluride (MCT) detector, scanning from 4000 to 650 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) for 100 scans. Before each experiment, the oxide sample was finely ground and placed into a ceramic crucible in the in situ chamber. Then the sample was pretreated at 503 K and atmospheric pressure for 120 min to remove adsorbed species in 100 mL min\(^{-1}\) synthetic air. All the spectra are presented in the Kubelka-Munk (K-M) scale to improve the linearity of the dependence of signal intensity upon concentration (Armaroli et al., 2004). The UV irradiation was acquired with 500 W xenon light (CHF-XM35, Beijing Chuangtuo) and was introduced into the DRIFTS reaction cell via a UV optical fiber. The intensity of UV irradiation was measured as 478 μW cm\(^{-2}\) by a UV Meter (Photoelectric Instrument Factory of Beijing Normal University).

2.2.1 IC

Sulfate products on the powders after the In situ DRIFTS study were also measured quantitatively using ion chromatography (IC). The powders were firstly weighed, and placed in 8 ml transparent glass jars. After adding 5 ml ultrapure water (specific resistance ≥ 18.2 MΩ cm\(^{-1}\)) containing about 1% formaldehyde (50 μL) to inhibit the oxidation of sulfite to sulfate, the samples were then extracted by sonication at 303K for 120 minutes. After a standing time of 120 minutes, the obtained supernatant was passed through a 0.22 μm PTFE membrane filter and then was analyzed using a Wayee IC-6200 ion chromatograph equipped with a TSKgel Super IC-CR cationic or SI-524E anionic analytical column. An eluent of 3.5 mM Na\(_2\)CO\(_3\) was used at a flow rate of 0.8 mL min\(^{-1}\).

3 Results and Discussion

3.1 Heterogeneous reaction of SO\(_2\) under different conditions

3.1.1 Heterogeneous reaction of SO\(_2\) on TiO\(_2\)

To investigate heterogeneous sulfate formation in complex atmospheric pollution, in situ DRIFTS was used to analyze the products on particle surfaces in the reactions under different conditions. The experiments were carried out under dark conditions or with UV irradiation and the DRIFTS spectra are shown in Fig. 1, while the vibrational frequencies of chemisorbed species formed on the surface of TiO\(_2\) are listed in Table 1. Initially, the TiO\(_2\) sample was flushed with the synthetic air at a total flow rate of 100 mL min\(^{-1}\) at 303K for 2 h. Then the background spectra were recorded when they showed little change with time. After that, 200 ppb SO\(_2\) was introduced to the gas flow and then passed through the reaction chamber for 12 h. In the dark experiment, the reaction products on the surface of TiO\(_2\) were mainly sulfite. As shown in Fig. 1(a), the positive bands observed at 1098, 1078, and 1052 cm\(^{-1}\) can be assigned to monodentate sulfite (Hug, 1997; Peak et al., 1999). Negative peaks
at 3691 and 3630 cm\(^{-1}\) were attributed to hydroxyl on TiO\(_2\) (Primet et al., 1971; Tsyganenko and Filimonov, 1973; Ferretto and Glisenti, 2003). These negative peaks indicated that some SO\(_2\) was absorbed on the surface hydroxyls, and were observed in all the reaction systems in this study, as shown in Fig. 1.

With UV light illumination, SO\(_2\) was oxidized on TiO\(_2\) and resulted in abundant sulfate species, as shown in Fig. 1(b). The main bands in the 1400-1100 cm\(^{-1}\) region became more apparent with increasing exposure time. The spectra in this region were assigned to sulfate in different coordination modes, including aggregation at 1344 cm\(^{-1}\), bidentate at 1290 cm\(^{-1}\) and bridging sulfate at 1177 and 1141 cm\(^{-1}\) (Fu et al., 2007; Hug, 1997; Peak et al., 1999). The sharp band at 1626 cm\(^{-1}\) and the broad bands with maxima at 3316 and 3190 cm\(^{-1}\) in Fig. 1(b) can be assigned to the bending vibration and stretching modes of molecularly adsorbed water. Surface water may be formed in the photochemical reaction or via enhanced adsorption of water due to the increased hygroscopicity induced by sulfate (Ma et al., 2019). Compared with the reaction under dark conditions, i.e. Fig.1 (a), sulfate species rather than sulfite species were generated, indicating a different mechanism for the formation of sulfate with UV irradiation.

### 3.1.2 Heterogeneous reaction of SO\(_2\) and NO\(_2\) on TiO\(_2\)

As reported in previous studies, the presence of NO\(_2\) can promote the heterogeneous oxidation of SO\(_2\) (Ma et al., 2008; Liu et al., 2012; Ma et al., 2017), which was also investigated in this study under both dark and illuminated conditions. The spectra regarding the reaction of SO\(_2\) and NO\(_2\) on TiO\(_2\) under dark conditions are shown in Fig. 1(c). Sulfite, sulfate and nitrate species were observed in this reaction system. Specifically, the bands at 1361 and 1346 cm\(^{-1}\) were assigned to aggregated sulfate; bands at 1163 and 1115 cm\(^{-1}\) were related to bridging sulfate and bands at 1074 and 1010 cm\(^{-1}\) were ascribed to monodentate sulfite (Liu et al., 2012; Yang et al., 2017; Yang et al., 2018b). The other bands in the 1620-1370 and 1300-1240 cm\(^{-1}\) regions were due to nitrate species, including bridging nitrate (1611, 1246 cm\(^{-1}\)), bidentate nitrate (1584, 1284 cm\(^{-1}\)) and monodentate nitrate (1503, 1453 cm\(^{-1}\)) (Goodman et al., 2001b; Qingxin et al., 2010). The consumption of OH groups (negative peaks at 3691 and 3630 cm\(^{-1}\)) and formation of water (3310, 3191, and 3341 cm\(^{-1}\)) on the particle surface were also observed. These results indicated that SO\(_2\) can be partially oxidized to sulfate in the presence of NO\(_2\) under dark conditions, which is consistent with previous studies (Ma et al., 2008; Liu et al., 2012), in spite of ambient concentration levels of SO\(_2\) and NO\(_2\) being used in this study.

The spectra of TiO\(_2\) exposed to SO\(_2\) and NO\(_2\) simultaneously with UV irradiation were recorded and shown in Fig. 1(d). The bands at 1629, 1584, and 1503 cm\(^{-1}\) were related to nitrate species while the bands at 1344, 1284 cm\(^{-1}\) and 1177, 1141 cm\(^{-1}\) were associated with sulfate species. Compared to the dark experiment of SO\(_2\) and NO\(_2\) in Fig 1(c), more sulfate species were generated with UV irradiation, which is consistent with the fact that UV irradiation significantly promotes sulfate formation in the reaction of SO\(_2\) alone. Also, compared with the spectra of TiO\(_2\) exposed to only SO\(_2\) with UV irradiation, the bands of sulfate species decreased in intensity in the presence of NO\(_2\). The effect of NO\(_2\) on sulfate formation with UV irradiation was opposite to that under dark conditions.
3.1.3 Heterogeneous reaction of SO$_2$ and NO$_2$ on TiO$_2$

To investigate the heterogeneous reaction with the coexistence of inorganic and organic gases on TiO$_2$, propene was chosen as a representative volatile organic compound, and its effect on the heterogeneous oxidation of SO$_2$ was studied. Under dark conditions, the *in situ* spectra after introduction of 200 ppb SO$_2$+200 ppb C$_3$H$_6$ were recorded and are shown in Fig. 1(e). No distinguishable products were observed except for the bands at 1074 and 1048 cm$^{-1}$, which were assigned to monodentate sulfite. Compared to the reaction of SO$_2$ alone, the coexistence of C$_3$H$_6$ had no apparent effect in this dark experiment. With UV irradiation, the sulfate bands between 1360-1100 cm$^{-1}$ with peaks at 1343, 1289, 1244, 1177 and 1139 cm$^{-1}$ increased with reaction time, as shown in Fig. 1(f). Compared to the reaction of SO$_2$ alone, the coexistence of C$_3$H$_6$ had no apparent effect with UV irradiation. The similar spectra obtained for the SO$_2$ reaction and SO$_2$+C$_3$H$_6$ reaction indicated that C$_3$H$_6$ had little influence on the heterogeneous reaction of SO$_2$ on TiO$_2$.

3.1.4 Heterogeneous reaction of SO$_2$, NO$_2$ and C$_3$H$_6$ on TiO$_2$

In order approximate the complexity of the real atmosphere, we investigated the heterogeneous reaction of SO$_2$, NO$_2$ and C$_3$H$_6$ on TiO$_2$. Fig. 1(g) and 1(h) show the dynamic changes of the spectra after introducing these three gases together on TiO$_2$ under dark conditions and with UV light, respectively. The concentrations of SO$_2$, NO$_2$ and C$_3$H$_6$ were all 200 ppb. The product species in the reaction of SO$_2$/NO$_2$/C$_3$H$_6$ on TiO$_2$ were quite similar to the sum of SO$_2$/NO$_2$ (Fig. 1(c) and 1(d)) reaction and SO$_2$/C$_3$H$_6$ reaction (Fig. 1(e) and 1(f)), regardless of whether irradiated or not.

3.2 Sulfate formation and the influence of NO$_2$ and C$_3$H$_6$

To obtain the area of an individual band for quantitative analysis, a curve-fitting procedure was used employing Lorenz and Gaussian curves based on the second-derivative spectrum to deconvolute overlapping bands. An example of the analysis for the bands in Fig. 1(b), with a correlation coefficient of 0.992, is shown in Fig. 2. The band at 1070 is attributed to sulfite, while the bands at 1140, 1178, 1240, 1292 and 1346 cm$^{-1}$ are attributed to sulfate. To avoid interference by nitrate species and other surface products in reactions with the presence of NO$_2$, the peaks at 1198-1135 cm$^{-1}$ were chosen for calculation of the sulfate K-M integrated area.

The K-M integrated areas of bridging sulfate in the four reaction systems: (1) SO$_2$; (2) SO$_2$+C$_3$H$_6$; (3) SO$_2$+NO$_2$; (4) SO$_2$+NO$_2$+C$_3$H$_6$ in the dark and with UV light are shown in Fig. 3(a) and Fig. 3(b), respectively. In the dark experiments, no apparent sulfate was generated in the reaction of SO$_2$ alone. The presence of C$_3$H$_6$ had no discernable effect on the formation of sulfate in dark experiments. The presence of NO$_2$ promoted the oxidation of SO$_2$ on TiO$_2$, with the result that mostly sulfate was yielded from the reaction of SO$_2$+NO$_2$. The presence of NO$_2$ seemed to induce the generation of some ROS, which oxidize S(IV) to S(VI) on TiO$_2$ (Ma et al., 2008; Liu et al., 2012; Ma et al., 2017). When SO$_2$ was introduced into the cell with NO$_2$ and C$_3$H$_6$ together, sulfate formation was less than that in the reaction of SO$_2$+NO$_2$, probably due to the competition between SO$_2$ and C$_3$H$_6$ for the ROS due to NO$_2$. In the UV irradiation experiments, on the contrary, both
NO\textsubscript{2} and C\textsubscript{3}H\textsubscript{6} had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO\textsubscript{2}. The opposite effect of NO\textsubscript{2} on sulfate formation relative to dark experiments may be explained by the different influence of NO\textsubscript{2} on the oxidation capacity in the heterogeneous photooxidation, compared to dark experiments. In dark experiments, the contribution of NO\textsubscript{2} to the oxidation capacity is predominant due to the limited availability of ROS, while it becomes of lesser importance when surface ROS are continuously generated in the experiments with UV irradiation. To further probe and analyze the total amounts of sulfate in different systems quantitatively, sulfate in the different reaction systems were also analyzed by IC. The results, which are shown in Fig. 4, are consistent with the results derived from integrated peak areas in Fig. 3. These results confirmed the enhancing effect of NO\textsubscript{2} on the heterogeneous oxidation of SO\textsubscript{2} under dark conditions and the inhibiting effect of NO\textsubscript{2} and C\textsubscript{3}H\textsubscript{6} on heterogeneous photooxidation of SO\textsubscript{2}. Despite the different yields of sulfate under different atmospheres, the presence of UV irradiation always increased sulfate formation significantly. We also observed that the promotion effect of UV irradiation on the heterogeneous oxidation of SO\textsubscript{2} was most significant for the individual reaction of SO\textsubscript{2}, while it became less noticeable under more complex pollution, i.e. in the presence of NO\textsubscript{2} and some VOCs.

### 3.3 Step-by-step experiments with UV irradiation and related mechanisms

To further investigate the effects of NO\textsubscript{2} and C\textsubscript{3}H\textsubscript{6} on the heterogeneous oxidation of SO\textsubscript{2} with UV irradiation, three step-by-step exposure experiments were performed. The concentrations of reactants in the step-by-step exposure experiments were changed from 200 ppb to 200 ppm to strengthen the signals of the products. These step-by-step exposure experiments all included three steps, namely, first exposing the particles to NO\textsubscript{2}, C\textsubscript{3}H\textsubscript{6}, or both for 2 h, then flushing with air for 1 h, and finally exposing them to SO\textsubscript{2} for 2 h. In the first step, the spectra for TiO\textsubscript{2} exposure to 200 ppm NO\textsubscript{2} are shown with the black lines in Fig. 5(a). The nitrate bands at 1611, 1586, 1507, and 1288, 1241 cm\textsuperscript{-1} increased in intensity. When the NO\textsubscript{2} was cut off, the particles were purged with air for 1 h, and the spectrum is recorded as the blue line in Fig. 5(a). Air purging did not noticeably change the spectra, except that the nitrate band at 1611 cm\textsuperscript{-1} shifted to 1637 cm\textsuperscript{-1} due to the absorption of water (Qingxin et al., 2010), indicating a relatively steady adsorption of nitrate species. Then the NO\textsubscript{2}-preadsorbed TiO\textsubscript{2} particles were exposed to SO\textsubscript{2} in the third step, marked by red lines in Fig. 5(a). A new band at 1168 cm\textsuperscript{-1} assigned to sulfate appeared and the bands at 1380-1050 cm\textsuperscript{-1} increased in intensity. When the NO\textsubscript{2} was cut off, the particles were purged with air for 1 h, and the spectrum is recorded as the blue line in Fig. 5(a). Air purging did not noticeably change the spectra, except that the nitrate band at 1611 cm\textsuperscript{-1} shifted to 1637 cm\textsuperscript{-1} due to the absorption of water (Qingxin et al., 2010), indicating a relatively steady adsorption of nitrate species. Then the NO\textsubscript{2}-preadsorbed TiO\textsubscript{2} particles were exposed to SO\textsubscript{2} in the third step, marked by red lines in Fig. 5(a). A new band at 1168 cm\textsuperscript{-1} assigned to sulfate appeared and the bands at 1350-1200 cm\textsuperscript{-1} became broader due to the formation of sulfate. Meanwhile, the nitrate bands at 1586 and 1507 cm\textsuperscript{-1} decreased in intensity and even disappeared. The possible reason might be either the replacement of nitrite with sulfate from SO\textsubscript{2} heterogeneous photooxidation (Park et al., 2017) or the photolysis of nitrate (Ye et al., 2017).

Similarly, the spectra in the 200 ppm C\textsubscript{3}H\textsubscript{6} pre-saturated experiment are shown in Fig. 5(b). After C\textsubscript{3}H\textsubscript{6} was introduced into the reaction cell for 2 h, intense bands at 1582, 1541, 1452, 1379, and 1361 cm\textsuperscript{-1} were observed. These principal bands are assigned to carboxylate (-COO, 1582, 1541 cm\textsuperscript{-1}) methyl (-CH\textsubscript{3}, 1452, 1379 cm\textsuperscript{-1}), and methyne (-CH, 1361 cm\textsuperscript{-1}), respectively (Busca et al., 1987; Idriss et al., 1995). Based on the above bands, the main products could be deemed to be formate and acetate species. After stopping the flow of C\textsubscript{3}H\textsubscript{6} and flushing the cell with synthetic air for 1 h, the surface products were reduced, indicating that these species from C\textsubscript{3}H\textsubscript{6} were not stable and could be removed easily from the surface. The subsequent introduction of SO\textsubscript{2} into the system resulted in sulfate formation, as seen by the bands in the 1380-1050 cm\textsuperscript{-1}
region. Introducing NO2 and C3H6 together before SO2 resulted in both nitrate and organic species on TiO2, as shown in Fig. 5(c). It is interesting that some distinct new bands were observed when the surface was exposed to NO2+C3H6, such as the bands at 1750, 1682, and 1524 cm\(^{-1}\), which could be assigned to CH2O (Liao et al., 2001), HNO3 (Goodman et al., 2001b) and COO groups (Mattsson and Österlund, 2010) respectively. This may indicate some interaction between NO2 and C3H6 and a possible influence of C3H6 on nitrate formation, as well as NO2 on C3H6 oxidation in the heterogeneous photooxidation.

Figure 6 compares the K-M integrated areas of bridging sulfate (1168 cm\(^{-1}\)) formed during these step-by-step experiments under different conditions. Compared to the reaction with SO2 alone, the pre-adsorption of C3H6 on TiO2 did not have any apparent influence. This is consistent with the supposition that the formate, and acetate species from heterogeneous oxidation of C3H6 might be easily removed from the surface. Since introducing C3H6 with SO2 together suppressed sulfate formation in the heterogeneous photooxidation while pre-adsorption of C3H6 had little influence, C3H6 is proposed to compete with SO2 for ROS rather than surface reactive sites in the heterogeneous photooxidation. Instead, the pre-adsorption of NO2 on TiO2 suppressed the formation of sulfate, which might have resulted from the different absorption status of the oxidation products of NO2 and C3H6. Compared to the experiment introducing NO2 and SO2 simultaneously, sulfate formation was more inhibited with pre-adsorption of NO2 in the first hour, while sulfate formation in these two cases became similar after 1.5 h duration. Compared to the individual reaction of SO2, both pre-adsorption of NO2 and introducing NO2 simultaneously suppressed sulfate formation from the beginning of the heterogeneous photooxidation. This indicated competition between SO2 and NO2 for both surface reactive sites and ROS. It is interesting that pre-adsorption with of NO2 + C3H6 resulted in much less sulfate formation compared to the pre-adsorption of NO2 or C3H6, as well as the reaction of SO2+NO2+C3H6. The detailed reason for this phenomenon was not discovered in this study. One possible reason might be that some products were generated when the particles were exposed to NO2 and C3H6 at the same time, and these species seemed to block some reactive sites on TiO2 and suppress sulfate formation in heterogeneous photooxidation.

4 Conclusions and environmental implications

Based on the experimental results obtained in this study, we propose the following possible mechanisms for the reaction of SO2 in the presence of NO2 and C3H6. Under dark conditions at 303K, only a few monodentate sulfite species formed. SO2 could hardly react on the particle surface except for weak adsorption as sulfite-like species. With reaction time increasing, the surface became saturated and prevented SO2 from adsorbing on the particles further. To better represent the real atmosphere, the concentration of the pollutant gases were decreased to ppb levels in this study. It was found that the presence of NO2 could enhance the heterogeneous formation of sulfate with pollutants at close to ambient concentrations. The presence of C3H6 had little effect on sulfate formation in the heterogeneous reaction of SO2 but suppressed sulfate formation in the heterogeneous reaction of SO2 and NO2, indicating that heterogeneous oxidation of C3H6 competes with SO2 for ROS or surface active sites on TiO2 with the coexistence of NO2.
When irradiation was introduced into the system, the surface of TiO$_2$ particles was activated by the light and generated electron-hole (e$^-$/h$^+$) pairs. At the same time, adsorbed O$_2$ could trap an electron, resulting in the formation of O$_2^-$.

Hydroxyl groups are the main reactive sites on metal oxides, and play a big role in the photocatalytic chemistry of TiO$_2$ particles (Fujishima et al., 2008; Diebold, 2003; Henderson, 2002; Liu et al., 2009). Reactive hydroxyl radicals can be generated via trapping of photogenerated holes by surface hydroxyl groups, or via the reaction between absorbed water and photogenerated holes. These ROS such as OH and O$_2^-$ can then initiate photocatalytic reactions, oxidize S(IV) species and result in much more sulfate formation. Sulfate formation was suppressed significantly with the coexistence of NO$_2$ and/or C$_3$H$_6$ in experiments with UV light due to the competition for surface reactive sites or the available ROS. In the step-by-step experiments, presaturation by C$_3$H$_6$ and then flushing had no significant influence on sulfate formation in the heterogeneous photooxidation of SO$_2$, while presaturation with NO$_2$ and then flushing suppressed sulfate formation. These results indicated that C$_3$H$_6$ mainly competes with SO$_2$ for ROS on the surface, while NO$_2$ competes with SO$_2$ for both surface active sites and ROS. The coexistence of NO$_2$ and C$_3$H$_6$ seemed to lead to more organics formation on the surface of TiO$_2$ and suppressed sulfate formation more compared to introducing only one of them.

These results indicated that heterogeneous oxidation of SO$_2$ might be influenced by a number of factors under complex pollution conditions with various gas pollutants. Besides inorganic species, organics could also significantly change the heterogeneous oxidation of SO$_2$. In this study, only one VOC was investigated, while the heterogeneous oxidation of various VOCs has been reported in previous studies (Niu et al., 2017; Du et al., 2000). The competition for ROS and surface reactive sites between these VOCs and SO$_2$ is likely to suppress sulfate formation in the heterogeneous reactions. Due to the different properties of the oxidation products, the influence of coexisting VOCs might be different for different VOC species.

The results of this study highlighted the very complex heterogeneous reaction processes that take place under complex air pollution conditions due to the ubiquitous interactions between organic and inorganic species. For a better estimation of the heterogeneous sulfate formation, kinetics of the heterogeneous oxidation of SO$_2$ must be developed with consideration of the influence of coexisting VOCs and other inorganic gases.

Author contribution

Q.M, B.C and H.H designed the study. Y.W, W.Y and B.C carried out the experiments. B.C, W.Y, J.M, and Q.M analysed the data with input from all co-authors. B.C and Y.W wrote the paper with contribution from Y.L, J.M, W.Y, and P.Z on the editing of the paper.
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References


Goodman, A., Underwood, G., and Grassian, V.: Heterogeneous reaction of NO2: Characterization of gas-phase and adsorbed products from the reaction, 2NO2 (g)+ H2O (a)→ HONO (g)+ HNO3 (a) on hydrated silica particles, The Journal of Physical Chemistry A, 103, 7217-7223, 1999.


Figure 1: Dynamic changes in the *in situ* DRIFTS spectra of the TiO$_2$ sample as a function of time at 303K in a flow of 20% O$_2$ + 80% N$_2$ with 200 ppb SO$_2$ under dark conditions (a) and with UV light (b); with 200 ppb SO$_2$ + 200 ppb NO$_2$ under dark conditions (c) or with UV light (d); with 200 ppb SO$_2$ + 200 ppb C$_3$H$_6$ under dark conditions (e) or with UV light (f); with 200 ppb SO$_2$ + 200 ppb NO$_2$ + 200 ppb C$_3$H$_6$ under dark conditions (g) or with UV light (h).
Figure 2: Peak fit of DRIFTS spectrum in the range of 1000-1400 cm⁻¹ for the last spectrum in Figure 1(b).
Figure 3: Integrated absorbance of the sulfate band (1198-1135 cm$^{-1}$) observed during the reaction of 200 ppb SO$_2$, 200 ppb SO$_2$+200 ppb NO$_2$, 200 ppb SO$_2$+200 ppb C$_3$H$_6$, 200 ppb SO$_2$+200 ppb NO$_2$+200 ppb C$_3$H$_6$ in dark experiments (a) and experiments with UV light (b).
Figure 4: Ion chromatography results of the amounts of sulfate (product per unit mass/surface area of sample) formed on the surface of TiO$_2$ after reaction with SO$_2$, SO$_2$+NO$_2$, SO$_2$+C$_3$H$_6$ and SO$_2$+C$_3$H$_6$+NO$_2$ in experiments under dark conditions or with UV light.

Figure 4: Ion chromatography results of the amounts of sulfate (product per unit mass/surface area of sample) formed on the surface of TiO$_2$ after reaction with SO$_2$, SO$_2$+NO$_2$, SO$_2$+C$_3$H$_6$ and SO$_2$+C$_3$H$_6$+NO$_2$ in experiments under dark conditions or with UV light.
Figure 5: In situ DRIFTS spectra of surface products on TiO$_2$ in the step-by-step exposure experiments with irradiation: (a) exposure to 200 ppm NO$_2$ for 2 h (black lines), after purging 1 h (blue line), and then to 200 ppm SO$_2$ for 2 h (red lines); (b) exposure to 200 ppm C$_3$H$_6$ for 2 h (black lines), after purging 1 h (blue line), and then to 200 ppm SO$_2$ for 2 h (red lines); (c) exposure to 200 ppm NO$_2$+200 ppm C$_3$H$_6$ for 2 h (black lines), after purging 1 h (blue line), and then to 200 ppm SO$_2$ for 2 h (red lines).
Figure 6: Integrated absorbance of the sulfate band (1168 cm\(^{-1}\)) for the illuminated reactions with UV lights of 200 ppm SO\(_2\) (black, solid), 200 ppm SO\(_2\) on a 200 ppm C\(_3\)H\(_6\)-presaturated surface (blue, dashed), 200 ppm SO\(_2\)+200 ppm NO\(_2\) (red, solid), 200 ppm SO\(_2\) on a 200 ppm NO\(_2\)-presaturated surface (green, dashed), 200 ppm SO\(_2\)+200 ppm C\(_3\)H\(_6\) (blue, solid), 200 ppm SO\(_2\)+200 ppm NO\(_2\)+200 ppm C\(_3\)H\(_6\) (pink, solid), and 200 ppm SO\(_2\) on a 200 ppm NO\(_2\)+200 ppm C\(_3\)H\(_6\)-presaturated surface (purple, dashed).
Table 1: Vibrational frequencies of chemisorbed species formed on TiO₂.

<table>
<thead>
<tr>
<th>surface species</th>
<th>frequencies(cm⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>S⁰³⁻/HSO⁻⁴</td>
<td>1098, 1078, 1052</td>
<td>(Liu et al., 2012; Nanayakkara et al., 2012b)</td>
</tr>
<tr>
<td>S⁰⁴⁻</td>
<td>1344</td>
<td>(Nanayakkara et al., 2012b)</td>
</tr>
<tr>
<td></td>
<td>bidentate</td>
<td>1290                                          (Yang et al., 2005)</td>
</tr>
<tr>
<td></td>
<td>bridging</td>
<td>1177, 1141                                    (Chen et al., 2007)</td>
</tr>
<tr>
<td>N⁰³⁻</td>
<td>1611, 1246</td>
<td>(Goodman et al., 2001a; Underwood et al., 1999; Hadjiivanov and Knözinger, 2000)</td>
</tr>
<tr>
<td></td>
<td>bidentate</td>
<td>1584, 1284                                    (Hadjiivanov and Knözinger, 2000)</td>
</tr>
<tr>
<td></td>
<td>monodentate</td>
<td>1503, 1453                                    (Piazzesi et al., 2006)</td>
</tr>
<tr>
<td>HNO₃</td>
<td>1682</td>
<td>(Goodman et al., 2001b)</td>
</tr>
<tr>
<td>COO⁻</td>
<td>1585, 1541</td>
<td>(Busca et al., 1987; Idriss et al., 1995; Rachmady and Vannice, 2002a; Mattsson and Österlund, 2010)</td>
</tr>
<tr>
<td>-CH₃</td>
<td>1452, 1379</td>
<td>(Busca et al., 1987)</td>
</tr>
<tr>
<td>-CH</td>
<td>1361</td>
<td>(Rachmady and Vannice, 2002b)</td>
</tr>
<tr>
<td>-CHO</td>
<td>1745</td>
<td>(Liao et al., 2001)</td>
</tr>
<tr>
<td>H₂O</td>
<td>1626</td>
<td>(Goodman et al., 1999)</td>
</tr>
<tr>
<td>OH</td>
<td>3690</td>
<td>(Primet et al., 1971)</td>
</tr>
<tr>
<td>H-bonded</td>
<td>3631</td>
<td>(Tsyganenko and Filimonov, 1973; Ferretto and Glisenti, 2003)</td>
</tr>
<tr>
<td>OH</td>
<td>3456, 3310, 3190</td>
<td>(Tarbuck and Richmond, 2006)</td>
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