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Effects of NO_2 and C_3H_6 on the heterogeneous oxidation of SO_2 on TiO_2 in the presence or absence of UV irradiation

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Abstract. The heterogeneous reactions of SO_2 in the presence of NO_2 and C_3H_6 on TiO_2 were investigated with the aid of *in situ* DRIFTS under dark conditions or with UV irradiation. Sulfate formation with or without the coexistence of NO_2 and/or C_3H_6 was analyzed with IC. Under dark conditions, SO_2 reacting alone resulted in sulfite formation on TiO_2, while the presence of ppb levels of NO_2 promoted the oxidation of SO_2 to sulfate. The presence of C_3H_6 had little effect on sulfate formation in the heterogeneous reaction of SO_2 but suppressed sulfate formation in the heterogeneous reaction of SO_2 and NO_2. UV irradiation could significantly enhance the heterogeneous oxidation of SO_2 on TiO_2, leading to a copious generation of sulfate, while the coexistence of NO_2 and/or C_3H_6 significantly suppressed sulfate formation in experiments with UV lights. Step-by-step exposure experiments indicated that C_3H_6 mainly competes for reactive oxygen species (ROS), while NO_2 competes with SO_2 for both surface active sites and ROS. Meanwhile, the coexistence of NO_2 with C_3H_6 further resulted in less sulfate formation compared to introducing either one of them separately to the SO_2-TiO_2 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 SO_2.

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 SO_2, NO_x, 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_2O_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_2O_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_2O_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 an catalyst to activate O_2 in the oxidation, in which the intermediates observed in the spectra, i.e. nitrogen tetroxide (N_2O_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_2O_3, ZnO, MgO, α-Al_2O_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_3CHO was found to suppress the heterogeneous reaction of large amounts of SO_2 on the surface of α-Fe_2O_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_2O_3 was suppressed by the presence of acetaldehyde (CH_3CHO).

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 ($\lambda < 387$ nm), resulting in active species (primarily O_2^- and OH) that can participate in atmospheric photochemical

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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_2O 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_2O, 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_7H_{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_3H_6 (5.9 ppm in N_2, Beijing Huayuan) were used as reactant gases.

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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_2CO_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_3H_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_3H_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_3H_6 had no apparent effect with UV irradiation. The similar spectra obtained for the SO_2 reaction and SO_2+C_3H_6 reaction indicated that C_3H_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_3H_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_3H_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_3H_6 were all 200 ppb. The product species in the reaction of $SO_2/NO_2/C_3H_6$ 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_3H_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_3H_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_3H_6; (3) SO_2+NO_2; (4) SO_2+NO_2+C_3H_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_3H_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_3H_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_3H_6 for the ROS due to NO_2. In the UV irradiation experiments, on the contrary, both

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NO_2 and C_3H_6 had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO_2. The opposite effect of NO_2 on sulfate formation relative to dark experiments may be explained by the different influence of NO_2 on the oxidation capacity in the heterogeneous photooxidation, compared to dark experiments. In dark experiments, the contribution of NO_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_2 on the heterogeneous oxidation of SO_2 under dark conditions and the inhibiting effect of NO_2 and C_3H_6 on heterogeneous photooxidation of SO_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_2 was most significant for the individual reaction of SO_2, while it became less noticeable under more complex pollution, i.e. in the presence of NO_2 and some VOCs.

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

To further investigate the effects of NO_2 and C_3H_6 on the heterogeneous oxidation of SO_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_2, C_3H_6, or both for 2 h, then flushing with air for 1 h, and finally exposing them to SO_2 for 2 h. In the first step, the spectra for TiO_2 exposure to 200 ppm NO_2 are shown with the black lines in Fig. 5(a). The nitrate bands at 1611, 1586, 1507, and 1288, 1241 cm^{-1} increased in intensity. When the NO_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^{-1} shifted to 1637 cm^{-1} due to the absorption of water (Qingxin et al., 2010), indicating a relatively steady adsorption of nitrate species. Then the NO_2-preadsorbed TiO_2 particles were exposed to SO_2 in the third step, marked by red lines in Fig. 5(a). A new band at 1168 cm^{-1} assigned to sulfate appeared and the bands at 1350-1200 cm^{-1} became broader due to the formation of sulfate. Meanwhile, the nitrate bands at 1586 and 1507 cm^{-1} decreased in intensity and even disappeared. The possible reason might be either the replacement of nitrite with sulfate from SO_2 heterogeneous photooxidation (Park et al., 2017) or the photolysis of nitrate (Ye et al., 2017).

Similarly, the spectra in the 200 ppm C_3H_6 pre-saturated experiment are shown in Fig. 5(b). After C_3H_6 was introduced into the reaction cell for 2 h, intense bands at 1582, 1541, 1452, 1379, and 1361 cm^{-1} were observed. These principal bands are assigned to carboxylate (-COO, 1582, 1541 cm^{-1}) methyl (-CH_3, 1452, 1379 cm^{-1}), and methyne (-CH, 1361 cm^{-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_3H_6 and flushing the cell with synthetic air for 1 h, the surface products were reduced, indicating that these species from C_3H_6 were not stable and could be removed easily from the surface. The subsequent introduction of SO_2 into the system resulted in sulfate formation, as seen by the bands in the 1380-1050 cm^{-1}

region. Introducing NO_2 and C_3H_6 together before SO_2 resulted in both nitrate and organic species on TiO_2, as shown in Fig. 5(c). It is interesting that some distinct new bands were observed when the surface was exposed to NO_2+C_3H_6, such as the bands at 1750, 1682, and 1524 cm^{-1}, which could be assigned to CH_2O (Liao et al., 2001), HNO_3 (Goodman et al., 2001b) and COO groups (Mattsson and Österlund, 2010) respectively. This may indicate some interaction between NO_2 and C_3H_6 and a possible influence of C_3H_6 on nitrate formation, as well as NO_2 on C_3H_6 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 SO_2 alone, the pre-adsorption of C_3H_6 on TiO_2 did not have any apparent influence. This is consistent with the supposition that the formate, and acetate species from heterogeneous oxidation of C_3H_6 might be easily removed from the surface. Since introducing C_3H_6 with SO_2 together suppressed sulfate formation in the heterogeneous photooxidation while pre-adsorption of C_3H_6 had little influence, C_3H_6 is proposed to compete with SO_2 for ROS rather than surface reactive sites in the heterogeneous photooxidation. Instead, the pre-adsorption of NO_2 on TiO_2 suppressed the formation of sulfate, which might have resulted from the different absorption status of the oxidation products of NO_2 and C_3H_6. Compared to the experiment introducing NO_2 and SO_2 simultaneously, sulfate formation was more inhibited with pre-adsorption of NO_2 in the first hour, while sulfate formation in these two cases became similar after 1.5 h duration. Compared to the individual reaction of SO_2, both pre-adsorption of NO_2 and introducing NO_2 simultaneously suppressed sulfate formation from the beginning of the heterogeneous photooxidation. This indicated competition between SO_2 and NO_2 for both surface reactive sites and ROS. It is interesting that pre-adsorption with of NO_2 + C_3H_6 resulted in much less sulfate formation compared to the pre-adsorption of NO_2 or C_3H_6, as well as the reaction of SO_2+NO_2+C_3H_6. 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 NO_2 and C_3H_6 at the same time, and these species seemed to block some reactive sites on TiO_2 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 SO_2 in the presence of NO_2 and C_3H_6. Under dark conditions at 303K, only a few monodentate sulfite species formed. SO_2 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 SO_2 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 NO_2 could enhance the heterogeneous formation of sulfate with pollutants at close to ambient concentrations. The presence of C_3H_6 had little effect on sulfate formation in the heterogeneous reaction of SO_2 but suppressed sulfate formation in the heterogeneous reaction of SO_2 and NO_2, indicating that heterogeneous oxidation of C_3H_6 competes with SO_2 for ROS or surface active sites on TiO_2 with the coexistence of NO_2.

https://doi.org/10.5194/acp-2019-532
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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_3H_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_3H_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_3H_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_3H_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

QM, BC and HH designed the study. YW, WY and BC carried out the experiments. BC, WY, JM, and QM analysed the data with input from all co-authors. BC and YW wrote the paper with contribution from YL, JM, WY, and PZ on the editing of the paper.

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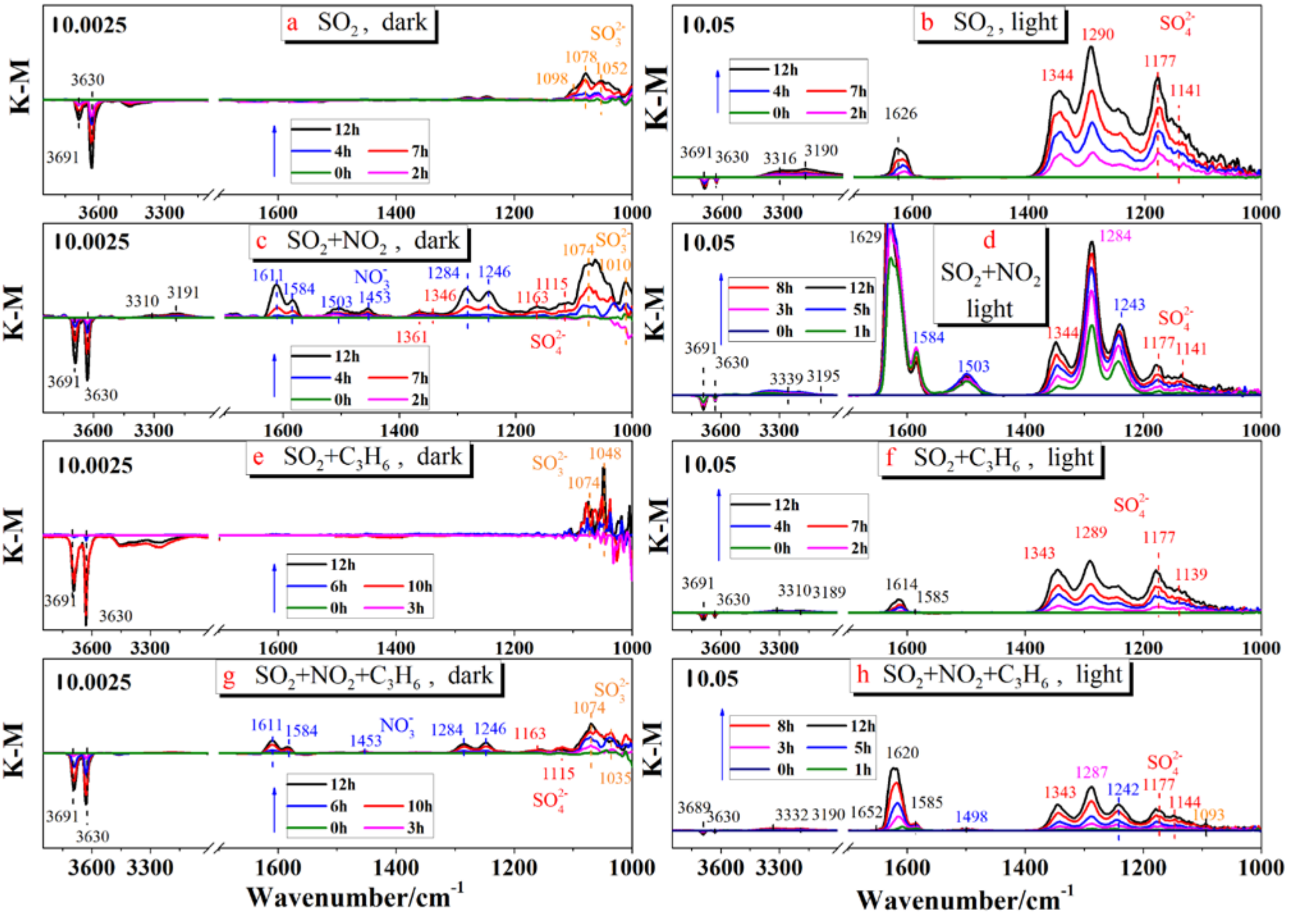

Figure 1: Dynamic changes in the *in situ* DRIFTS spectra of the TiO_2 sample as a function of time at 303K in a flow of 20% O_2 + 80% N_2 with 200 ppb SO_2 under dark conditions (a) and with UV light (b); with 200 ppb SO_2 + 200 ppb NO_2 under dark conditions (c) or with UV light (d); with 200 ppb SO_2 + 200 ppb C_3H_6 under dark conditions (e) or with UV light (f); with 200 ppb SO_2 + 200
5 **ppb NO_2+ 200 ppb C_3H_6 + under dark conditions (g) or with UV light (h).**

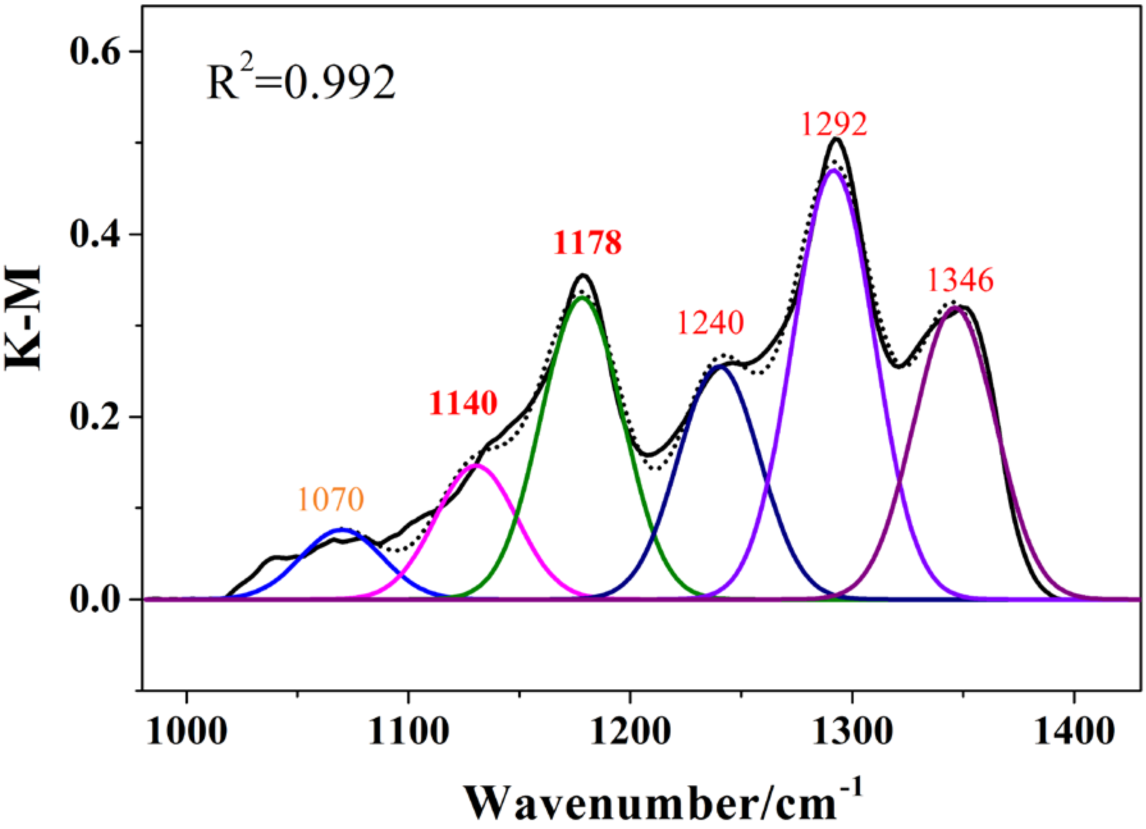

Figure 2: Peak fit of DRIFTS spectrum in the range of 1000-1400 cm^{-1} for the last spectrum in Figure 1(b).

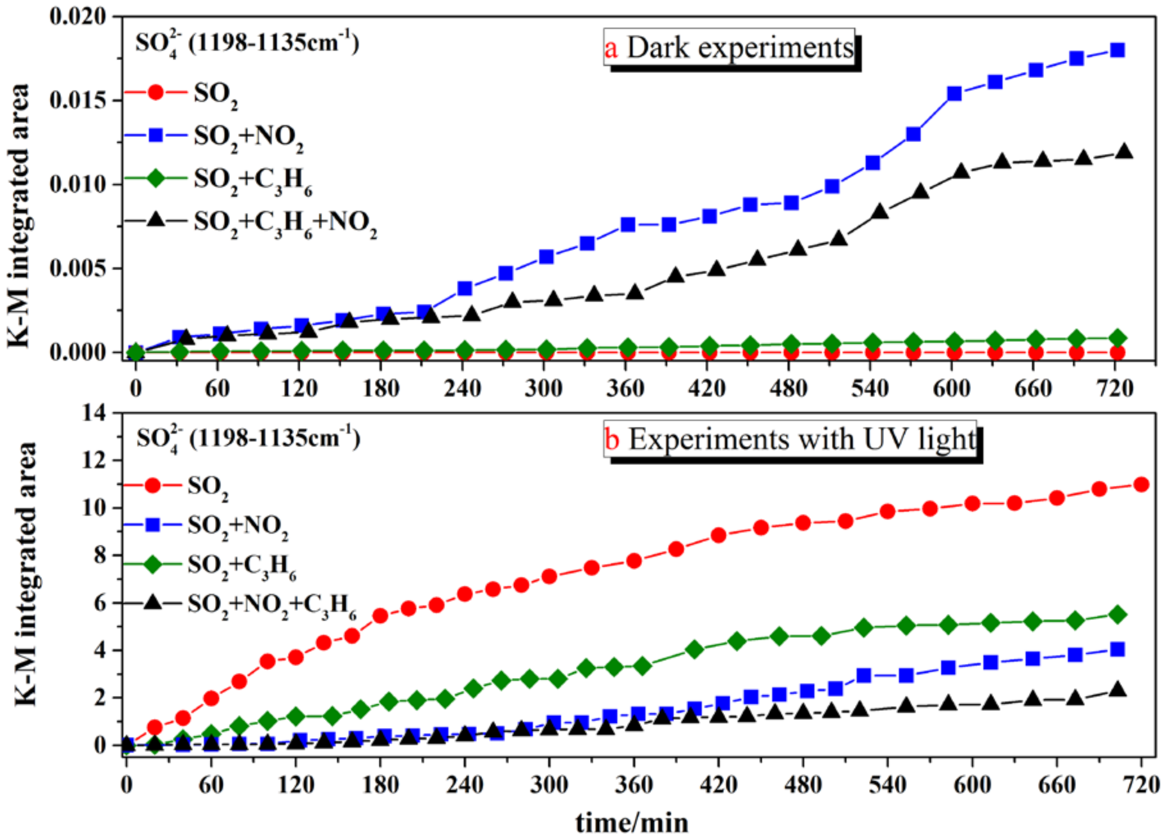

Figure 3: Integrated absorbance of the sulfate band (1198-1135 cm^{-1}) observed during the reaction of 200 ppb SO_2, 200 ppb SO_2+200 ppb NO_2, 200 ppb SO_2+200 ppb C_3H_6, 200 ppb SO_2+200 ppb NO_2+200 ppb C_3H_6 in dark experiments (a) and experiments with UV light (b).

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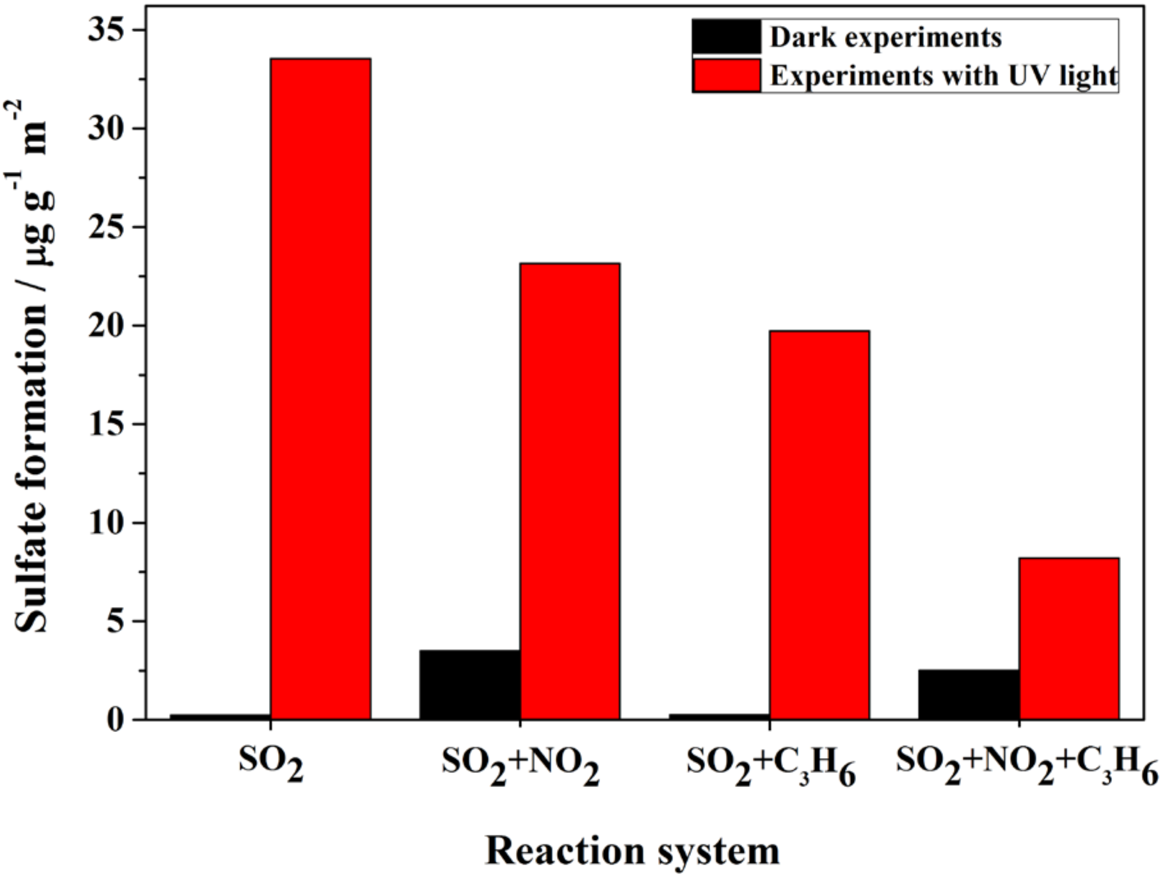

Figure 4: Ion chromatography results of the amounts of sulfate (product per unit mass/surface area of sample) formed on the surface of TiO_2 after reaction with SO_2, SO_2+NO_2, SO_2+C_3H_6 and SO_2+C_3H_6+NO_2 in experiments under dark conditions or with UV light.

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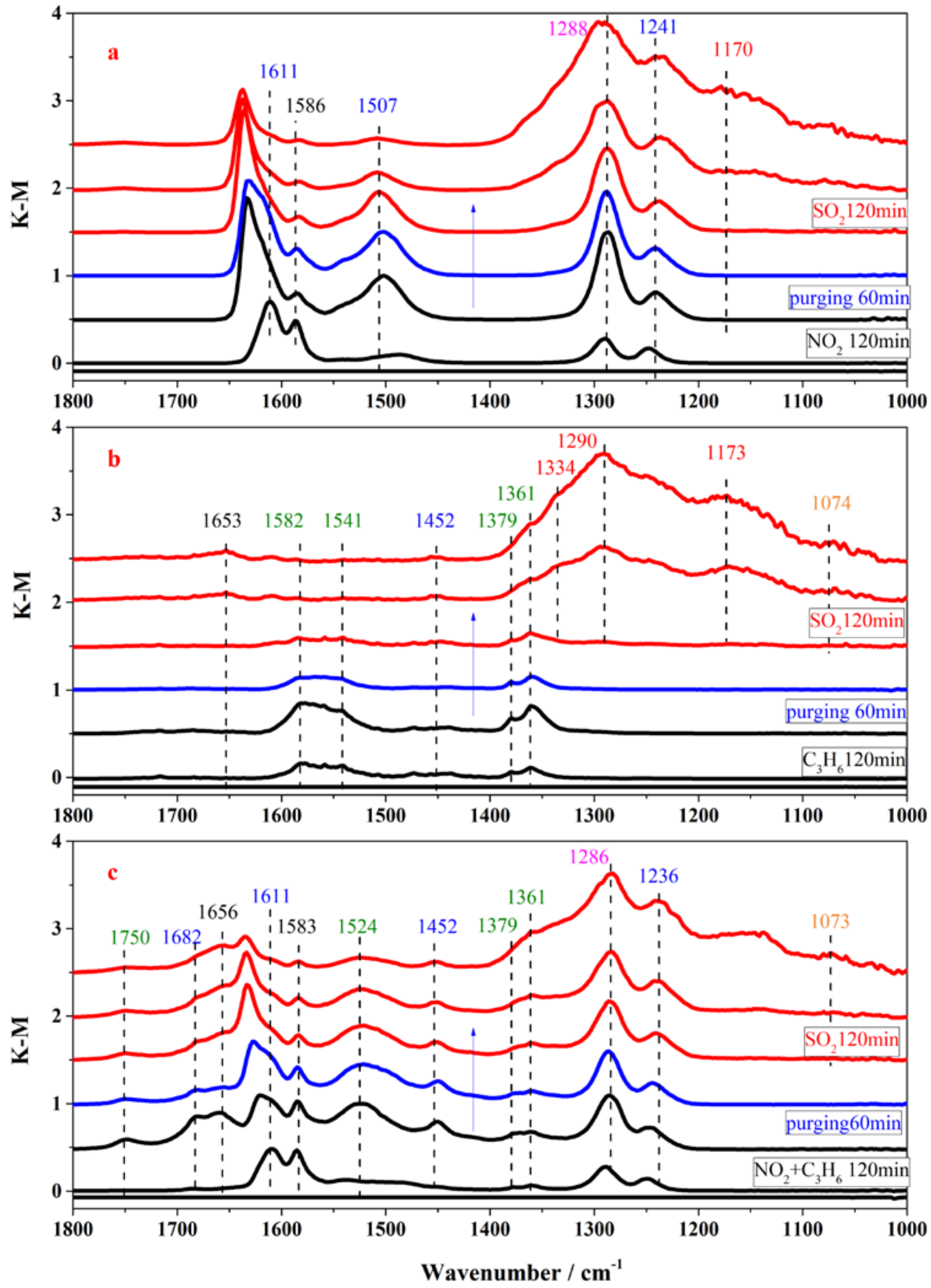

Figure 5: ***In situ*** **DRIFTS spectra of surface products on TiO_2 in the step-by-step exposure experiments with irradiation: (a) exposure to 200 ppm NO_2 for 2 h (black lines), after purging 1 h (blue line), and then to 200 ppm SO_2 for 2 h (red lines); (b) exposure to 200 ppm C_3H_6 for 2 h (black 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_3H_6 for 2 h (black lines), after purging 1 h (blue line), and then to 200 ppm SO_2 for 2 h (red lines).**

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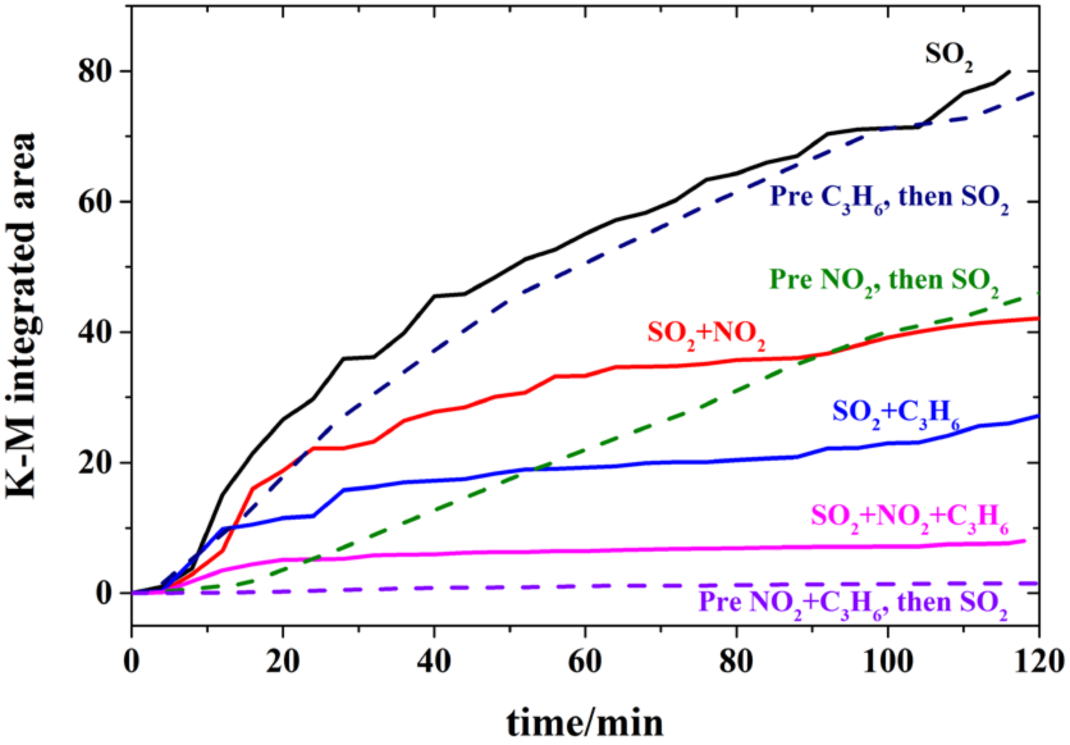

Figure 6: Integrated absorbance of the sulfate band (1168 cm^{-1}) for the illuminated reactions with UV lights of 200 ppm SO$_2$ (black, solid), 200 ppm SO$_2$ on a 200 ppm C$_3$H$_6$-presaturated surface (blue, dashed), 200 ppm SO$_2$+200 ppm NO$_2$ (red, solid), 200 ppm SO$_2$ on a 200 ppm NO$_2$-presaturated surface (green, dashed), 200 ppm SO$_2$+200 ppm C$_3$H$_6$ (blue, solid), 200 ppm SO$_2$+200 ppm
5 **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 TiO_2.

surface species		frequencies(cm^{-1})	References
$S0_3^{2-}/HS0_3^-$	monodentate sulfite	1098 1078 1052	(Liu et al., 2012; Nanayakkara et al., 2012b)
$S0_4^{2-}$	state of aggregation	1344	(Nanayakkara et al., 2012b)
	bidentate	1290	(Yang et al., 2005)
	bridging	1177 1141	(Chen et al., 2007)
$N0_3^-$	bridging	1611 1246	(Goodman et al., 2001a; Underwood et al., 1999; Hadjiivanov and Knözinger, 2000)
	bidentate	1584 1284	(Hadjiivanov and Knözinger, 2000)
	monodentate	1503 1453	(Piazzesi et al., 2006)
HNO_3		1682	(Goodman et al., 2001b)
COO^-		1585 1541	(Busca et al., 1987; Idriss et al., 1995; Rachmady and Vannice, 2002a; Mattsson and Österlund, 2010)
$-CH_3$		1452 1379	(Busca et al., 1987)
-CH		1361	(Rachmady and Vannice, 2002b)
-CHO		1745	(Liao et al., 2001)
H_2O	bending vibration	1626	(Goodman et al., 1999)
OH	isolated bicoordinated (on Ti atoms)	3690	(Primet et al., 1971)
	H-bonded	3631	(Tsyganenko and Filimonov, 1973; Ferretto and Glisenti, 2003)
OH	adsorbed water	3456 3310 3190	(Tarbuck and Richmond, 2006)