Ms. Ref. No.: acp-2019-532

Title: "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"

We appreciate the comments from the reviewer's on this manuscript. We have answered them in the following paragraphs (the text in italics is the reviewer comments, followed by our response) point by point. The page and line numbers in the response are from the revised manuscript.

Response for Reviewer #1

This manuscript describes a set of experiments looking at the effects of UV radiation, NO2, and C3H6 on heterogeneous SO2 oxidation. The authors demonstrate that on TiO2 aerosols the presence of NO2 alone or NO2 and C3H6 can suppress sulfate formation when in the presence of UV light. The authors also show that in dark conditions NO2 alone or NO2 and C3H6 can increase heterogeneous sulfate formation, but that the presence of C3H6 decreases heterogeneous sulfate formation compared to heterogeneous sulfate formation with NO2 only. That the presence of VOCs may suppress sulfate formation is an interesting and little focused on point. The authors need to add a bit more of a discussion of why they interpret their experiments as supporting their proposed mechanism. For example, the authors suggest that the presence of C3H6 inhibited heterogeneous sulfate formation with NO2 by competing with SO2 for reactive oxygen species or active sites on the aerosol. It is not clear to readers how the authors reach this particular conclusion. The authors mention that the presence of NO2 induced the generation of reactive oxygen species, but the mechanism behind this is never satisfactorily explained. It is also unclear if the authors are saying that C3H6 competes with SO2 or with NO2 for active sites on the aerosol. A more detailed discussion of the mechanism behind the 'dark' oxidation of SO2 in the presence of NO2 and identifying the points in that mechanism in which C3H6 interferes could help clarify these issues. There are also some other outstanding issues listed below. Nevertheless, the key point that VOCs may suppress heterogeneous sulfate formation in dark conditions is a very important one. Altogether, the manuscript requires some important revisions before publication in ACP.

Response: Thanks for the reviewer's comments. The reviewer mentioned two main aspects about the mechanisms, one is related to that the presence of VOCs may suppress sulfate formation, and the other is for that NO_2 induced the generation of reactive oxygen species. In the revised manuscript, a discussion section about the proposed mechanisms on these effects are added.

For that NO_2 induced the generation of reactive oxygen species, we added the following discussions.

Page 9, Line 26 - Page 10, Line 6:

“These adsorption processes result in the conversion of SO_2 to sulfite (S(IV)) on the surface. It has been demonstrated that coexisting NO_2 can induce the generation of some ROS, which oxidize S(IV) to S(VI) on mineral oxides (Ma et al., 2008;Liu et al., 2012;Ma et al., 2017). There were several possible responsible ROS proposed in previous studies, although the detailed mechanism has not yet been fully explored. One possible ROS is N_2O_4, which can undergo hydrolysis to N(III) and N(V) species (Liu et al., 2012;Finlayson-Pitts et al., 2003;Li et al., 2018). These reactive nitrogen species can oxidize S(IV) to S(VI) (Wang et al., 2016b;Li et al., 2018).

$$2\mathrm{Ti}-NO_2 \rightarrow \mathrm{Ti}_2-\mathrm{N}_2O_4 \qquad (4)$$

$$\mathrm{N}_2O_4(ad) \rightarrow NO^+NO_3^- \xrightarrow{H_2O} HNO_3 + HONO \qquad (5)$$

Besides N_2O_4, NO_2 may also react directly with surface OH and form HNO_3 on TiO_2 (Liu et al., 2017a). The HNO_3 generated through this pathway may also contribute to the oxidation of S(IV) to S(VI). It has also been proposed that aqueous oxidation of SO_2 by NO_2 (as an oxidizing agent) contributed to significant sulfate formation in haze events (Wang et al., 2016b;Cheng et al., 2016). This aqueous reaction should not be significant in the reaction systems of this study due to the limited amount of water under low RH condition (<1% RH).”

For that the presence of VOCs may suppress sulfate formation, or that the presence of C_3H_6 inhibited heterogeneous sulfate formation with NO_2 by competing with SO_2 for reactive oxygen species or active sites on the aerosol, we added the following discussions.

Page 10, Line 7-15:

“When C_3H_6 was introduced together with NO_2, sulfate formation was less than that in the reaction of SO_2+NO_2, probably due to the reaction between C_3H_6 and the reactive nitrogen species. The detailed mechanism was not explored in this study. The following reactions may take place in this process.

$$2NO^+NO_3^- + \mathrm{Ti}-\mathrm{C_3H_6} \rightarrow \mathrm{H_3CCHO} + \mathrm{HCHO} + 2NO^+NO_2^- \qquad (6)$$

$$NO^+NO_3^- + \mathrm{HCHO} \rightarrow \mathrm{HCOOH} + NO^+NO_2^- \qquad (7)$$

$$NO^+NO_3^- + \mathrm{H_3CCHO} \rightarrow \mathrm{H_3CCOOH} + NO^+NO_2^- \qquad (8)$$

Heterogeneous reactions between NO_2 and organics can also lead to nitro-organics on hexane soot (Kwamena and Abbatt, 2008;Al-Abadleh and Grassian, 2000) , which may also occur on the surface of TiO_2, and these products blocked some reactive sites for sulfate formation.”

Similarly, we also added the mechanisms in the light experiments in the revised manuscript.

Other general comments:

1. *The authors need to better explain why TiO2 is a good compound for approximating the heterogeneous oxidation of SO2 on mineral dust aerosols. The authors mention 4 studies using different types of mineral oxides (line 21 page 2). What were*

the differences between these studies attributable to the different mineral oxide used? Why did the authors in this study choose TiO2 instead of CaO, a-Fe2O3 or MgO, when calcium, magnesium, and iron are usually a much larger portions of mineral dust? What do the authors anticipate the effect of using different mineral oxides would be on their experiments?

Response: We have the same concern as the reviewer and plan to investigate these processes on different mineral dust and authentic dust particles in the future. Actually, the heterogeneous reactivity depends greatly on the properties of mineral oxides, such as the acid–base nature, or the redox properties (Tang et al., 2016;Yang et al., 2016;Yang et al., 2019). For example, basic mineral oxides such as MgO and CaO were more active than acidic SiO_2 for the heterogeneous reaction of NO_2, while Fe_2O_3, with its unique Fe^{2+}/Fe^{3+} redox chemistry, favors the formation of SO_4^{2-} and the heterogeneous conversion of NO_2. There are many previous studies using different types of mineral oxides and some using authentic dust particles to study heterogeneous process. The uptake coefficient of SO_2 onto pure metal oxides is generally larger than authentic dust particles. Semiconductive metal oxides were known to be responsible for heterogeneous photo-oxidation of tracer gases. In this study, with the coexisting of multigas, the oxidation system is relatively complex, and both dark experiments and UV experiments were carried out. In order to better study the effects of NO_2 and C_3H_6 on the heterogeneous oxidation in the presence or absence of UV irradiation, we chose TiO_2 since it is a semiconductor material and a well-known photocatalyst, although it is less abundant than CaO, Fe_2O_3 or MgO in the atmosphere. TiO_2 particles are expected to provide important surfaces for heterogeneous photocatalysis of atmospheric gases due to their high photocatalytic activity, especially with the growing application of TiO_2 in human activities (Chen et al., 2012). We tried to anticipate the effect of choosing different mineral oxides, but it is difficult since very few previous studies compared heterogeneous reactions on different mineral dust, especially for heterogeneous reactivity in multigas coexisting system. For the dark experiments, since NOx enhance SO_2 oxidation on different mineral dusts (He et al., 2014), we anticipate the effects of coexisting of NO_2 and C_3H_6 might be ubiquitous; while for the UV experiments, we anticipate the effects of NO_2 and C_3H_6 might be applied to semiconductive metal oxides and authentic dust particles contain semiconductive metal oxides. In the revised manuscript, the following statement were added.

Page 3, Line 13-19:

ADD "In order to better study the effects of NO_2 and C_3H_6 on the heterogeneous oxidation in a relatively complex oxidation system (with coexistence of multiple gases, in both dark and illuminated conditions), we chose TiO_2 due to the fact that it is a semiconductor material and a well-known photocatalyst. TiO_2 has been widely reported to be present in airborne particulate matter (PM) (Chen et al., 2012), Although TiO_2 represents only a relatively small portion of the mass of PM and is less abundant than CaO, Fe_2O_3 or MgO, the TiO_2 particles are expected to provide important surfaces for heterogeneous photocatalysis of atmospheric gases due to their high photocatalytic activity, especially with the growing application of TiO_2 in human activities (Chen et al., 2012)."

Page 3, Line 22-25:

ADD "However, we must point out that the heterogeneous reactivity depends greatly on the properties of the mineral oxides, such as acid–base nature or redox properties (Tang et al., 2016;Yang et al., 2016;Yang et al., 2019), while different

VOCs may also have quite different heterogeneous and photochemical reactivity. Investigating these processes on different mineral dust and authentic dust particles with different types of VOCs is needed in future studies."

2. Similar to the point in comment 1, the authors should elaborate further why propene was selected as a representative VOC. What evidence is there that propene is representative of different VOCs? How might the type of VOC used affect results?

Response: Besides the revision as mentioned in the response to comment 1. We further elaborate why propene was selected in the revised manuscript as follows:

Page 3, Line 19-25:

ADD "Propene is selected as a representative VOC since it is the most abundant alkene compound in the atmosphere, and coexists with NO_x in vehicle exhaust emission (Wang et al., 2016a). Propene is widely used as an accelerator in photochemical reactions in some smog chamber studies (Jang and Kamens, 2001;Song et al., 2007). The relatively simple oxidation products and well understood oxidation mechanism of propene are also helpful in explaining our experimental results. Propene is selected also due to the high vapor pressure of its oxidation products, which normally do not generate condensed organic aerosol (Odum et al., 1996)."

3. As the authors are likely aware, it has also been proposed that a significant sulfate formation pathway for Chinese winter haze is heterogeneous oxidation of SO2 by NO2 (e.g. Wang et al., 2016; Cheng et al., 2016). The authors need to demonstrate that this reaction is not significant in their experiments. This could be done by showing how NO2 changes along with SO2 in their experiments. In the proposed mechanism of the authors, NO2 acts as a catalyst and therefore concentrations should not change. In the alternative mechanism NO2 is the oxidizing agent and therefore should be depleted along with SO2 as sulfate forms. If it turns out this other reaction is significant, this should be accounted for.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Zamora, M. L., Hu, M., et al. (2016). Persistent sulfate formation from London Fog to Chinese haze. Proceedings of the National Academy of Sciences, 113(48), 13630–13635. https://doi.org/10.1073/pnas.1616540113

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., et al. (2016). Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. Science Advances, 2(12), e1601530. https://doi.org/10.1126/sciadv.1601530

Response: Thanks for the reminding. NO_2 oxidized SO_2 as an oxidizing agent happened under specified conditions, such as in aqueous phase and in the presence of NH_3 that the pH is not very low. This reaction should not be significant since our experiments were carried out under dry condition. Since NO_2 also transformed to nitrate in the reaction itself and there was competition between NO_2 and SO_2 for surface active sites, it was not easy to demonstrate the role of NO_2 from how it changes.

Page 7, Line 21-24:

ADD “It has also been proposed that aqueous oxidation of SO_2 by NO_2 (as an oxidizing agent) contributed to significant sulfate formation in haze events (Wang et al., 2016b;Cheng et al., 2016). This reaction should not be the main pathway in the reaction systems in this study since the experiments were carried out under dry conditions (RH<1%), although water can still exist, as we mentioned earlier.”

4. The concluding paragraph of the introduction has multiple sentences that are oddly phrased.

Response: The paragraph were rewritten in the revised version. Besides the added sentences, some original sentence were modified:

Page 3, Line 9-13:

“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.”

WERE CHANGED TO:

“Despite these studies involving the heterogeneous oxidation of SO_2 under various conditions, the effects of co-existing pollutants on the heterogeneous oxidation of SO_2 under both dark and illuminated conditions need further investigation. Meanwhile, the interactions between organic and inorganic species in these heterogeneous processes at low concentrations are not fully understood. In this study, we focus on the effects of co-existing NO_2 and propene (C_3H_6) on the heterogeneous oxidation of SO_2 on TiO_2 under both dark and illuminated conditions with *in situ* DRIFTS.”

Page 3, Line 28-31:

“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.”

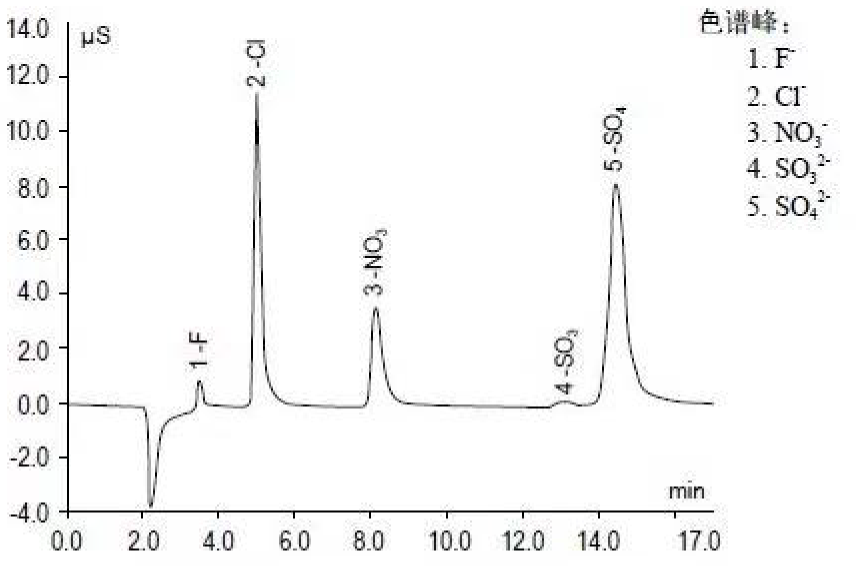
WERE CHANGED TO:

“Rather than UV lights, a xenon light is used in this study to better simulate the solar ultraviolet radiation on the earth’s surface. Generally, our study could be helpful for gaining a better understanding of the heterogeneous formation of sulfate under complex air pollution conditions, in which abundant SO_2, NO_x, VOCs, and mineral dust coexist in the atmosphere.”

5. In the IC section of the methods, what column type was used? Moch et al., 2018 found that certain IC column types could easily separate hydroxymethanesulfonate (HMS) and sulfate and others could not. Since the author’s method involves adding *a 1% formaldehyde solution to the samples, this would create HMS and possible an artifact in the IC measurements depending on the column type. Additionally, the authors mention that CH2O was observed when the surface was exposed to NO2 and C3H6, which might also indicate HMS formation*

Moch, J. M., Dovrou, E., Mickley, L. J., Keutsch, F. N., Cheng, Y., Jacob, D. J., et al. (2018). Contribution of Hydroxymethane Sulfonate to Ambient Particulate Matter: A Potential Explanation for High Particulate Sulfur During Severe Winter Haze in Beijing. Geophysical Research Letters, 45(21), 11,969-11,979. https://doi.org/10.1029/2018GL079309

Response: Thanks for the reminding. We used a Thermo AS14 Column in the IC, as we mentioned in the manuscript in the IC section. We read the paper of Moch and some references therein. But we had no clue if our column could separate HMS and sulfate or not, although in our IC measurements, we can see a peak of S(IV) a little earlier than S(VI). One good thing is that the IC measurements were only used to further compare the sulfate formation among different experimental systems in this study as the sulfate were also compared according to the *In situ* DRIFTS spectra and the K-M integrated area. The possible interferes of HMS on sulfate measurement in the IC doesn't change our conclusions. CH_2O was observed when the surface was exposed to NO_2 and C_3H_6, but its reaction with sulfite might not be significant on the surface since the RH is <1%. In the revised manuscript, the possible interferes of HMS on sulfate were added. The description related to the IC measurement results were modified.



Page 8, Line 2:

DELETE "quantitatively"

Page 8, Line 1:

“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.”

WERE CHANGED TO:

“Since formaldehyde was added to inhibit the oxidation of sulfite to sulfate in the solution, there is a possibility that HMS would be generated in the solution and be measured as sulfate (Moch et al., 2018). However, the possible interference by HMS in the measurement of sulfate by IC will not influence our conclusions on the effects of NO_2 and C_3H_6, since the K-M integrated area of sulfate in the *In situ* DRIFTS spectra were also compared.”

Title of Figure. 4:

ADD: “Since formaldehyde was added to inhibit the oxidation of sulfite to sulfate in the solution, there is a possibility that HMS would be generated in the solution and be measured as sulfate.”

6. Many parts of the Results and Discussion section are better suited for placement in the methods section (e.g. the first and third sentence of section 3.1.1, large parts of the first paragraph of 3.3, etc.). The authors should consider moving sentences that describe how the experiments were conducted to the methods section and focus only on the results in the results section.

Response: Thanks for the suggestions. Corresponding reorganization and revision were made in the revised manuscript. The description of experiments were moved to 2.2.1.

Page 4, Line 24- Page 5, Line 3:

“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. Two series of *in situ* DRIFTS experiments were carried out in this study. For the heterogeneous reaction of SO_2 under different gas conditions, the TiO_2 sample was initially flushed with the synthetic air at a total flow rate of 100 mL min^{-1} for 2 h. The temperature was 303 K and the relative humidity was less than 1% in all experiments. Then the background spectra were recorded when they showed little change with time. After that, gas reactants, such as 200 ppb SO_2, 200 ppb NO_2 and 200 ppb C_3H_6, were introduced to the gas flow and then passed through the reaction chamber for 12 h. These experiments were carried out under both dark and with UV-Vis irradiation conditions. The other series of experiments were step-by-step exposure experiments for further investigation of the effects of NO_2 and C_3H_6 on the heterogeneous oxidation of SO_2 with UV-Vis irradiation. 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.”

Other comments:

1. Line 12 on page 2 says that “SO2 can be irreversibly converted into sulfite, bisulfite or sulfate.” This is incorrect for sulfite and bisulfite. Even if the particular conditions of the particle mean that sulfite or bisulfite are stable, if conditions change the

SO2-HSO3–SO32- equilibrium can shift and the authors should therefore avoid the use of the word "irreversibly" as applied to HSO3- and SO32- formation.

Response: Thanks for the reminding. Yes, the word "irreversibly" is not correct.

Page 2, Line 12:

The word "irreversibly" was DELETED in the revised manuscript.

2. Line 14 on page 2 says the authors say "low concentrations (200 ppb)." Was this a typo and the authors meant to write ppt? If not and the authors may mean low for a laboratory setting, but this type of phrasing could be confusing to non-laboratory scientists who may be interested in the author's work since atmospheric propene concentrations are rarely more than a couple of ppb. Later the authors say they used pollutants are "close to ambient concentration" (line 28 page 8), but 200 ppb NO2 and SO2 is much higher than ambient concentrations of these pollutants even during the extremely severe winter haze in Beijing. The authors should either include reference values for the concentrations of these gases in the laboratory compared to the atmosphere, or drop the use of "low concentrations" or "ambient" all together.

Response: Yes, the so called "low concentrations (200 ppb)" only means low for laboratory *In situ* DRIFTS study. To avoid confusing, we dropped the use of "low concentrations" and "ambient" in the revised manuscript.

Page 3, Line 14:

DELETE "at low concentrations (200 ppb)"

Page 6, Line 15-17:

"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."

WERE CHANGED TO:

"which is consistent with previous studies (Ma et al., 2008;Liu et al., 2012), in spite of much lower concentration levels of SO_2 and NO_2 being used in this study."

Page 11, Line 28-29:

"It was found that the presence of NO_2 could enhance the heterogeneous formation of sulfate with pollutants at close to ambient concentrations"

WERE CHANGED TO:

"Coexisting NO_2 could enhance the heterogeneous formation of sulfate with much lower concentrations (200 ppb) relative to previous studies (~100 ppm) (Ma et al., 2008;Liu et al., 2012;Zhao et al., 2018)."

3. Line 18 on page 2 regarding states "NO2 was proposed to act as a catalyst to activate O2 in the oxidation." This was a bit confusing, but I assume this means that the authors mean NO2 catalyzed the oxidation of SO2 by O2. If that is correct the *authors should change the sentence. Since there is also the heterogeneous oxidation of SO2 by NO2, the author be sure to clarify when the mechanisms involving NO2 they are referring to have SO2 oxidized by O2 and catalyzed by NO2 or have SO2 oxidized by NO2. I believe in most instances the authors are referring to the former reaction (i.e. catalyzed by NO2 and oxidized by O2).*

Response: Yes, we mean that SO_2 oxidized by O_2 and catalyzed by NO_2. To avoid confusing, we modified these sentences in the revised manuscript.

Page 2, Line 18:

"Therefore, NO_2 was proposed to act as an catalyst to activate O_2 in the oxidation"

WERE CHANGED TO:

"Therefore, NO_2 was proposed to act as a catalyst in the oxidation of SO_2 by O_2"

4. With regards to the formation of hydroxymethanesulfonate (line 26-27 page 2), it would be appropriate for authors to also cite Moch et al., 2018 (referenced above) which also proposed the reaction of CH2O and sulfite/bisulfite in northern China winter haze.

Response: This reference was ADDED accordingly.

Page 2, Line 27:

"HCHO was proposed to react with SO_3^{2-} and generate hydroxymethanesulfonate (HMS) in the northern China winter haze period (Moch et al., 2018;Song et al., 2019)."

Response for Reviewer #2

Chu et al. reported the effect of NO2 and C3H6 on the heterogeneous oxidation of SO2 into sulfate on TiO2 particles. Under dark conditions, the presence of NO2 generally enhanced the SO2 oxidation, whereas C3H6 had little influence. In contrast, the presence of NO2 and/or C3H6 suppressed the sulfate formation in the presence of UV irradiation. The authors attributed these results to the competitions between NO2 and SO2 for surface reactive sites on TiO2 and reactive oxygen species, and between C2H6 and SO2 for reactive oxygen species. However, their arguments on the underlying mechanisms are not satisfactorily explained based on the experimental results and the mechanistic insight is lacking. The impact of this study would be incremental to the understanding of heterogeneous oxidation of SO2 in the atmosphere. The manuscript requires major revisions before publication in ACP.

Response: Thanks for the reviewer's comments. As mentioned in the response to the first reviewer, a discussion section about the proposed mechanisms on these effects are added in the revised manuscript.

Page 9- Page 11:

"4.1 Dark reactions

The heterogeneous oxidation of SO_2 on TiO_2 has been investigated by many previous studies. The following mechanisms for SO_2 adsorption on TiO_2 surfaces have been proposed in previous studies (Nanayakkara et al., 2012):

$$\mathrm{Ti-OH+SO_2 \rightarrow Ti-OSO_2H} \qquad (1)$$

$$\mathrm{2Ti-OH+SO_2 \rightarrow Ti_2-SO_3 \cdot H_2}O \qquad (2)$$

$$\mathrm{Ti-O^{2-}+SO_2 \rightarrow Ti-}SO_3^{2-} \qquad (3)$$

These adsorption processes result in the conversion of SO_2 to sulfite (S(IV)) on the surface. It has been demonstrated that coexisting NO_2 can induce the generation of some ROS, which oxidize S(IV) to S(VI) on mineral oxides (Ma et al., 2008;Liu et al., 2012;Ma et al., 2017). There were several possible responsible ROS proposed in previous studies, although the detailed mechanism has not yet been fully explored. One possible ROS is N_2O_4, which can undergo hydrolysis to N(III) and N(V) species (Liu et al., 2012;Finlayson-Pitts et al., 2003;Li et al., 2018). These reactive nitrogen species can oxidize S(IV) to S(VI) (Wang et al., 2016b;Li et al., 2018).

$$\mathrm{2Ti-}NO_2 \rightarrow \mathrm{Ti_2-N_2}O_4 \qquad (4)$$

$$\mathrm{N_2}O_4(ad) \rightarrow NO^+NO_3^- \xrightarrow{H_2O} HNO_3+HONO \qquad (5)$$

Besides N_2O_4, NO_2 may also react directly with surface OH and form HNO_3 on TiO_2 (Liu et al., 2017a). The HNO_3 generated through this pathway may also contribute to the oxidation of S(IV) to S(VI). It has also been proposed that aqueous oxidation of SO_2 by NO_2 (as an oxidizing agent) contributed to significant sulfate formation in haze events (Wang et al., 2016b;Cheng et al., 2016). This aqueous reaction should not be significant in the reaction systems of this study due to the limited amount of water under low RH condition (<1% RH).

When C_3H_6 was introduced together with NO_2, sulfate formation was less than that in the reaction of SO_2+NO_2, probably due to the reaction between C_3H_6 and the reactive nitrogen species. The detailed mechanism was not explored in this study. The following reactions may take place in this process.

$$2NO^+NO_3^- + \mathrm{Ti-C_3H_6 \rightarrow H_3CCHO+HCHO+}2NO^+NO_2^- \qquad (6)$$

$$NO^+NO_3^- + \mathrm{HCHO \rightarrow HCOOH+}NO^+NO_2^- \qquad (7)$$

$$NO^+NO_3^- + \mathrm{H_3CCHO \rightarrow H_3CCOOH+}NO^+NO_2^- \qquad (8)$$

Heterogeneous reactions between NO_2 and organics can also lead to nitro-organics on hexane soot (Kwamena and Abbatt, 2008;Al-Abadleh and Grassian, 2000) , which may also occur on the surface of TiO_2, and these products blocked some reactive sites for sulfate formation.

4.2 Light reactions

With UV illumination, TiO_2 can be excited by UV light ($\lambda < 387$ nm), then the photogenerated electrons and holes can react with H_2O and O_2 to produce additional ROS (primarily $\cdot \mathrm{O_2^-}$ and $\cdot \mathrm{OH}$), and oxidize more SO_2 to sulfate on TiO_2 than that produced under dark conditions (Shang et al., 2010a;Chen et al., 2012).The detailed mechanism was summarized by Chen et al. (Chen et al., 2012) and references therein:

$$\mathrm{TiO_2} + h\nu(\lambda < 387\ \mathrm{nm}) \rightarrow \mathrm{e^-h^+} \rightarrow \mathrm{e^-} + \mathrm{h^+} \tag{9}$$

$$\mathrm{O_2} + \mathrm{e^-} \rightarrow \cdot\, \mathrm{O_2^-} \tag{10}$$

$$\mathrm{H_2O} + \mathrm{h^+} \rightarrow \cdot\, \mathrm{OH} + \mathrm{H^+} \tag{11}$$

Then the SO_2 can react with these ROS and promote the formation of sulfate (Shang et al., 2010b):

$$\mathrm{Ti} - \mathrm{SO_2} + \cdot\, \mathrm{O_2^-} \rightarrow \mathrm{Ti} - \mathrm{SO_3} + O^- \tag{12}$$

$$\mathrm{Ti} - \mathrm{SO_3} + \mathrm{H_2O} \rightarrow \mathrm{Ti} - \mathrm{H_2SO_4} \tag{13}$$

$$\mathrm{Ti} - SO_3^{2-} + 2 \cdot \mathrm{OH} \rightarrow \mathrm{Ti} - SO_4^{2-} + \mathrm{H_2O} \tag{14}$$

In the UV-Vis irradiation experiments, NO_2 had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO_2. Rather than resulting in ROS formation and oxidation of S(IV) to S (VI) in dark experiments, the main reaction of NO_2 with the surface ROS resulted in nitrate formation in experiments with UV-Vis irradiation (Ndour et al., 2008;Yu and Jang, 2018).

$$\mathrm{Ti} - \mathrm{NO_2} + \cdot\, \mathrm{OH} \rightarrow \mathrm{Ti} - \mathrm{HONO_2} \tag{15}$$

$$\mathrm{Ti} - \mathrm{NO_2} + \cdot\, \mathrm{O_2^-} \rightarrow \mathrm{Ti} - \mathrm{NO_2^-} + O_2 \tag{16}$$

The nitrate or nitrite generated from the oxidation of NO_2 might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO_2 on TiO_2 also suppressed the formation of sulfate and resulted in similar sulfate formation to that in the experiment introducing NO_2 and SO_2 simultaneously. The competition between SO_2 and NO_2 for surface reactive sites might be the main reason for the fact that the coexistence of NO_2 with SO_2 resulted in decreased sulfate formation with UV-Vis irradiation in this study. Although Gen et al. (Gen et al., 2019) found that photolysis of nitrate enhanced sulfate formation in wet aerosols, this mechanism may not be applied in this study since the reaction system is quite different from their study. The ROS which oxidize S(IV) to S(VI) are mainly $\cdot \mathrm{O_2^-}$ and $\cdot \mathrm{OH}$ in the presence of UV-Vis irradiation rather than the photolysis of nitrate.

C_3H_6 also had a distinct suppressing effect on sulfate formation. Similar to NO_2, C_3H_6 will react with surface ROS.

$$\mathrm{C_3H_6} \xrightarrow{\cdot OH} \mathrm{RCHO} \xrightarrow{\cdot OH} \mathrm{RCOOH} \xrightarrow{\cdot OH} \mathrm{C}O_2 + H_2O \tag{17}$$

where R represents H or an alkyl group. These gaseous products in the photo-oxidation of C_3H_6 do not seem to block surface reactive sites, which can explain why the pre-adsorption of C_3H_6 on TiO_2 did not show an obvious suppressing effect on the formation of sulfate in the step-by-step experiment.

When C_3H_6 + NO_2 were introduced simultaneously into the reaction system together with SO_2, both competed for ROS with SO_2 and therefore resulted in the lowest formation of sulfate among the heterogeneous reactions. Besides, in the step-by-step experiments, the pre-adsorption of C_3H_6+NO_2 on TiO_2 suppressed sulfate formation significantly, which indicated that lots of reactive sites for SO_2 oxidation might be blocked by these oxidation products in pre-adsorption with UV-Vis irradiation. Karagulian et al. (Karagulian et al., 2009) found that nitrite can induce the photo-oxidation of VOCs on airborne particles and produce organic nitrates and carbonyl compounds. Thus, the formation of organic nitrates may be an important factor to suppress the formation of sulfate due to the blocking effect."

Specific comments:

The authors need to specify why TiO2 was chosen as the target material to put this work in a more appropriate context. For instance, the line 32 on page mention "TiO2, …., has been widely used for studying heterogeneous photochemical reactions. What is the novelty in the present study?

Response: Semiconductive metal oxides were known to be responsible for heterogeneous photo-oxidation of tracer gases. In this study, with the coexisting of multiple gases, the oxidation system is relatively complex, and both dark experiments and UV-Vis experiments were carried out. In order to better study the effects of NO_2 and C_3H_6 on the heterogeneous oxidation in the presence or absence of UV-Vis irradiation, we chose TiO_2 due to the fact that it is a semiconductor material and a well-known photocatalyst. The present study investigate the heterogeneous oxidation of SO_2 on TiO_2, but with quite different conditions in the gas phase in both dark and UV-Vis irradiation conditions, i.e. the coexisting of multiple gases including one VOC. Besides, compare the previous studies, relative low concentrations (200 ppb) are used for laboratory *In situ* DRIFTS study. In the revised manuscript, the following statement were added or modified:

Page 3, Line 13-19:

ADD "In order to better study the effects of NO_2 and C_3H_6 on the heterogeneous oxidation in a relatively complex oxidation system (with coexistence of multiple gases, in both dark and illuminated conditions), we chose TiO_2 due to the fact that it is a semiconductor material and a well-known photocatalyst. TiO_2 has been widely reported to be present in airborne particulate matter (PM) (Chen et al., 2012), Although TiO_2 represents only a relatively small portion of the mass of PM and is less abundant than CaO, Fe_2O_3 or MgO, the TiO_2 particles are expected to provide important surfaces for heterogeneous photocatalysis of atmospheric gases due to their high photocatalytic activity, especially with the growing application of TiO_2 in human activities (Chen et al., 2012)."

Page 3, Line 25-28:

ADD "However, we must point out that the heterogeneous reactivity depends greatly on the properties of the mineral oxides, such as acid−base nature or redox properties (Tang et al., 2016;Yang et al., 2016;Yang et al., 2019), while different VOCs may also have quite different heterogeneous and photochemical reactivity. Investigating these processes on different mineral dust and authentic dust particles with different types of VOCs is needed in future studies."

Page 6, Line 15-17:

"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."

WERE CHANGED TO:

"which is consistent with previous studies (Ma et al., 2008;Liu et al., 2012), in spite of much lower concentration levels of SO_2 and NO_2 being used in this study."

Page 11, Line 28-29:

"It was found that the presence of NO_2 could enhance the heterogeneous formation of sulfate with pollutants at close to ambient concentrations"

WERE CHANGED TO:

"Coexisting NO_2 could enhance the heterogeneous formation of sulfate with much lower concentrations (200 ppb) relative to previous studies (~100 ppm) (Ma et al., 2008;Liu et al., 2012;Zhao et al., 2018)."

Page 3, Line 9-13:

"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."

WERE CHANGED TO:

"Despite these studies involving the heterogeneous oxidation of SO_2 under various conditions, the effects of co-existing pollutants on the heterogeneous oxidation of SO_2 under both dark and illuminated conditions need further investigation. Meanwhile, the interactions between organic and inorganic species in these heterogeneous processes at low concentrations are not fully understood. In this study, we focus on the effects of co-existing NO_2 and propene (C_3H_6) on the heterogeneous oxidation of SO_2 on TiO_2 under both dark and illuminated conditions with *in situ* DRIFTS."

Page 3, Line 28-31:

"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."

WERE CHANGED TO:

"Rather than UV lights, a xenon light is used in this study to better simulate the solar ultraviolet radiation on the earth's surface. Generally, our study could be helpful for gaining a better understanding of the heterogeneous formation of sulfate under complex air pollution conditions, in which abundant SO_2, NO_x, VOCs, and mineral dust coexist in the atmosphere."

In the line 2 on page 5, I don't understand the correlation between the negative peaks (consumption) of the surface hydroxyls and the SO2 adsorption. Can you elaborate how the SO2 adsorption causes the negative peaks?

Response: The two negative peaks at 3691 and 3630 cm^{-1} were attributed to the vibration of hydroxyl on Ti atoms (Primet et al., 1971;Nanayakkara et al., 2012). The loss of surface hydroxyl groups from the surface upon adsorption of SO_2 implies that surface OH groups were involved in the reaction of SO_2 on TiO_2 in both dark reactions and UV-Vis irradiation conditions. This result is consistent with previous studies on TiO_2 (Nanayakkara et al., 2012;Ma et al., 2019). We made the following revision in the revised manuscript.

Page 5, Line 19-22:

“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.”

WERE CHANGED TO:

“These negative peaks were observed in all the reaction systems in this study, as shown in Fig. 1, which is consistent with previous studies (Nanayakkara et al., 2012;Ma et al., 2019). The loss of surface hydroxyl groups from the surface upon adsorption of SO_2 implies that surface OH groups were involved in the reaction of SO_2 on TiO_2 under both dark and UV-Vis irradiation conditions.”

Page 9, Line 21-24:

ADD: “The heterogeneous oxidation of SO_2 on TiO_2 has been investigated by many previous studies. The following mechanisms for SO_2 adsorption on TiO_2 surfaces have been proposed in previous studies (Nanayakkara et al., 2012):

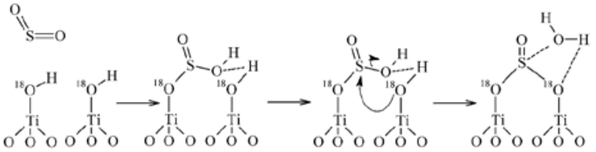
$$\mathrm{Ti-OH+SO_2\rightarrow Ti-OSO_2H} \qquad (1)$$

$$\mathrm{2Ti-OH+SO_2\rightarrow Ti_2-SO_3\cdot H_2}O \qquad (2)$$”

For the comparison of experiments with SO2 alone in the presence and the absence of UV illumination, the authors suggested the potential formation of molecularly adsorbed water, but the connection of this formation to the sulfate production is lacking. What is the role of molecularly adsorbed water in the reactions studied? The formation of adsorbed water is closely related to relative humidity (e.g., Romakkaniemi et al., 2001), but no information on relative humidity has been articulated in this work.

Romakkaniemi, S., Hämeri, K., Väkevä, M., and Laaksonen, A., J. Phys. Chem. A, 105, 8183−8188, 2001.

Response: There are two sources of the molecularly adsorbed water related to sulfate formation. One is water formation during the heterogeneous reaction. For example, SO_2 reacted with two neighboring OH groups will result in sulfite and water formation, as shown in the following scheme (Nanayakkara et al., 2012). Meanwhile, a sulfate formation mechanism that involves both surface OH and O can also generate water, $HSO_3^- + O^- + OH^- \rightarrow SO_4^{2-} + H_2O + e^-$, as proposed by Zhang et al. (Zhang et al., 2006).


Scheme 1 Reaction of SO_2 and surface hydroxyl groups to form adsorbed sulfite and water.

The other possible source of water is that water absorption from the introduced gas to the generated sulfate (Ma et al., 2019). In our experiments, no extra water flow was introduced to the reaction system (RH<1%), but still water cannot be entirely avoided in the introduced gas flows. In Fig.1, we can see the signal strength of the adsorbed water have good positive correlation with the amount of sulfite/sulfate formation in different experimental systems. In the revised manuscript, additional experimental information was added, and the discussion about the source of the adsorption water was extended.

Page 4, Line 27-28:

ADD: “The temperature was 303 K and the relative humidity was less than 1% in all experiments.”

Page 5, Line 31 -Page 6, Line 4:

“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).”

WERE CHANGED TO:

“Surface water can be formed in the heterogeneous reaction of SO_2 (Nanayakkara et al., 2012;Zhang et al., 2006), or via enhanced adsorption of water due to the increased hygroscopicity induced by sulfate (Ma et al., 2019). Although the RH was controlled at less than 1% in our experiments, water cannot be entirely removed in the introduced gas flows. In Fig.1, there is a positive correlation between the signal intensities of the adsorbed water and sulfite/sulfate among different experimental systems.”

Page 9, Line 21-24:

ADD: “The heterogeneous oxidation of SO_2 on TiO_2 has been investigated by many previous studies. The following mechanisms for SO_2 adsorption on TiO_2 surfaces have been proposed in previous studies (Nanayakkara et al., 2012):

$$\mathrm{Ti-OH+SO_2 \rightarrow Ti-OSO_2H} \qquad (1)$$

$$\mathrm{2Ti-OH+SO_2 \rightarrow Ti_2-SO_3 \cdot H_2}O \qquad (2)”$$

The UV illumination (Fig. 1b) significantly enhanced the sulfate formation relative to the dark experiment. The authors need to discuss what is the role of UV illumination in the enhanced sulfate formation in the paragraph starting from the line 4 on page 5. Because of the lacking discussion, the argument in the lines 11-12 on page 5 does not seem correct. High sulfate formation rates under UV illumination might also cause the disappearance of sulfite peaks in the spectra due to rapid conversion of SO2 into sulfate.

Response: We agree that UV illumination may also cause high sulfate formation rates and the disappearance of sulfite peaks in the spectra due to rapid conversion of SO_2 into sulfate. With UV illumination, TiO_2 can be excited by UV light (λ< 387 nm), resulting in additional ROS (primarily O_2^- and OH), and oxidize more SO_2 to sulfate on TiO_2 than that under dark condition (Shang et al., 2010;Chen et al., 2012). We added some discussion on Page 5 as well as in the new discussion section.

Page 5, Line 26-29:

ADD: "With UV-Vis illumination, TiO_2 can be excited by UV light (λ< 387 nm), then the photogenerated electrons and holes can react with H_2O and O_2 to produce additional ROS (primarily $\cdot O_2^-$ and $\cdot OH$), and oxidize more SO_2 to sulfate on TiO_2 than that produced under dark conditions (Shang et al., 2010a;Chen et al., 2012)."

Page 5, Line 11-12 (Old version):

DELETE "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."

Page 10, Line 18-28:

ADD: "With UV illumination, TiO_2 can be excited by UV light (λ< 387 nm), then the photogenerated electrons and holes can react with H_2O and O_2 to produce additional ROS (primarily $\cdot O_2^-$ and $\cdot OH$), and oxidize more SO_2 to sulfate on TiO_2 than that produced under dark conditions (Shang et al., 2010a;Chen et al., 2012).The detailed mechanism was summarized by Chen et al. (Chen et al., 2012) and references therein:

$$\mathrm{TiO_2} + h\nu(\lambda < 387\ \mathrm{nm}) \rightarrow \mathrm{e^-h^+} \rightarrow \mathrm{e^-} + \mathrm{h^+} \qquad (9)$$

$$\mathrm{O_2} + \mathrm{e^-} \rightarrow \cdot\,\mathrm{O_2^-} \qquad (10)$$

$$\mathrm{H_2O} + \mathrm{h^+} \rightarrow \cdot\,\mathrm{OH} + \mathrm{H^+} \qquad (11)$$

Then the SO_2 can react with these ROS and promote the formation of sulfate (Shang et al., 2010b):

$$\mathrm{Ti-SO_2} + \cdot\,\mathrm{O_2^-} \rightarrow \mathrm{Ti-SO_3} + O^- \qquad (12)$$

$$\mathrm{Ti-SO_3} + \mathrm{H_2O} \rightarrow \mathrm{Ti-H_2SO_4} \qquad (13)$$

$$\mathrm{Ti} - SO_3^{2-} + 2\cdot\mathrm{OH} \rightarrow \mathrm{Ti} - SO_4^{2-} + \mathrm{H_2O} \qquad (14)$$"

In the lines 28-30 on page 5, the authors described that more sulfate with UV irradiation in the SO2 + NO2 system than without UV irradiation was consistent with the results in the SO2 alone system. However, the mechanism might be different between the two systems. For instance, nitrate formed is subjected to photolysis under UV irradiation (> 300 nm). Recent work has found that nitrate photolysis can enhance the conversion of SO2 into sulfate in wet aerosols (Gen et al., 2019). It would be useful if the authors provide more discussion from a perspective of the mechanisms.

Gen, M., Zhang, R., Huang, D., Li, Y., and Chan, C. K., Heterogeneous Oxidation of SO2 in Sulfate Production During Nitrate Photolysis at 300 nm: Effect of pH, Relative Humidity, Irradiation Intensity, and the Presence of Organic Compounds. Environ. Sci. Technol., 2019.

In the line 31 on page 5, it is not clear about what is the opposing effect. The authors need to clarify this effect.

Response: Thanks for the reminding. Since nitrate were generated in the presence of NO_2, there is a possibility that photolysis of the nitrate would enhance sulfate formation. The RH is very low (RH<1%) in our experiments. It seems the enhancing effect of nitrate on sulfate formation is not very significant since sulfate formation in SO_2+NO_2 system is less than that of SO_2 alone system with the presence of UV irradiation. We added the discussion about this effect and modified the related description in the revised manuscript.

Page 6, Line 20-23:

"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."

WERE CHANGED TO:

"Compared to the dark experiment of SO_2 and NO_2 in Fig 1(c), more sulfate species were generated with UV-Vis irradiation, which might be due to the fact that UV-Vis irradiation significantly promotes sulfate formation by generating additional active species (Shang et al., 2010a;Chen et al., 2012) as in the reaction of SO_2 alone."

Page 10, Line 21-Page 11, Line 2:

ADD: "In the UV-Vis irradiation experiments, NO_2 had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO_2. Rather than resulting in ROS formation and oxidation of S(IV) to S (VI) in dark experiments, the main reaction of NO_2 with the surface ROS resulted in nitrate formation in experiments with UV-Vis irradiation (Ndour et al., 2008;Yu and Jang, 2018).

$$\mathrm{Ti-NO_2+\cdot OH \rightarrow Ti-HONO_2} \qquad (15)$$

$$\mathrm{Ti-NO_2+\cdot O_2^- \rightarrow Ti-NO_2^-} + O_2 \qquad (16)$$

The nitrate or nitrite generated from the oxidation of NO_2 might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO_2 on TiO_2 also suppressed the formation of sulfate and resulted in similar sulfate formation to that in the experiment introducing NO_2 and SO_2 simultaneously. The competition between SO_2 and NO_2 for surface reactive sites might be the main reason for the fact that the coexistence of NO_2 with SO_2 resulted in decreased sulfate formation with UV-Vis irradiation in this study. Although Gen et al. (Gen et al., 2019) found that photolysis of nitrate enhanced sulfate formation in wet aerosols, this mechanism may not be applied in this study since the reaction system is quite different from their study. The ROS which oxidize S(IV) to S(VI) are mainly $\cdot \mathrm{O_2^-}$ and $\cdot \mathrm{OH}$ in the presence of UV-Vis irradiation rather than the photolysis of nitrate."

The discussion in the lines 3-5 on page 7 cannot explain the suppressing effect of NO2 on the sulfate formation under UV irradiation, relative to the SO2 alone system. How the presence of NO2 suppresses sulfate formation on TiO2 under UV irradiation.

Response: Thanks for your reminding. We added the possible blocking of surface reactive sites by nitrate here.

Page 7, Line 31-Page 8, Line 1:

Add "What's more, the nitrate formation from oxidation of NO_2 might block some surface reactive sites, and therefore, resulted in less sulfate formation in the reaction of SO_2+NO_2 than that of SO_2 alone with UV-Vis irradiation."

Reactive oxygen species (ROS) are seemingly responsible for the oxidation of SO2 into sulfate. However, the lacking information here is what ROS are generated on TiO2. The authors need to explain what are formed on TiO2 and how the formed ROS oxide SO2 in the earlier part of the manuscript.

Response: More discussion about the formation and their roles in oxidation of SO_2 were added in the revised manuscript.

Page 5, Line 26-29:

"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., 2012)."

WERE CHANGED TO:

"With UV-Vis illumination, TiO_2 can be excited by UV light (λ< 387 nm), then the photogenerated electrons and holes can react with H_2O and O_2 to produce additional ROS (primarily $\cdot O_2^-$ and $\cdot OH$), and oxidize more SO_2 to sulfate on TiO_2 than that produced under dark conditions (Shang et al., 2010a;Chen et al., 2012)."

Page 7, Line 19-24:

ADD: "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). The detailed mechanism for this effect has not been fully explored and will be discussed later. It has also been proposed that aqueous oxidation of SO_2 by NO_2 (as an oxidizing agent) contributed to significant sulfate formation in haze events (Wang et al., 2016b;Cheng et al., 2016). This reaction should not be the main pathway in the reaction systems in this study since the experiments were carried out under dry conditions (RH<1%), although water can still exist, as we mentioned earlier."

Page 9, Line 26-Page 10, Line 6:

ADD: "It has been demonstrated that coexisting NO_2 can induce the generation of some ROS, which oxidize S(IV) to S(VI) on mineral oxides (Ma et al., 2008;Liu et al., 2012;Ma et al., 2017). There were several possible responsible ROS proposed in previous studies, although the detailed mechanism has not yet been fully explored. One possible ROS is N_2O_4, which can undergo hydrolysis to N(III) and N(V) species (Liu et al., 2012;Finlayson-Pitts et al., 2003;Li et al., 2018). These reactive nitrogen species can oxidize S(IV) to S(VI) (Wang et al., 2016b;Li et al., 2018).

$$2\mathrm{Ti}-NO_2 \rightarrow \mathrm{Ti}_2-\mathrm{N}_2O_4 \qquad (4)$$

$$\mathrm{N}_2O_4(ad) \rightarrow NO^+NO_3^- \xrightarrow{H_2O} HNO_3 + HONO \qquad (5)$$

Besides N_2O_4, NO_2 may also react directly with surface OH and form HNO_3 on TiO_2 (Liu et al., 2017a). The HNO_3 generated through this pathway may also contribute to the oxidation of S(IV) to S(VI). It has also been proposed that aqueous oxidation of SO_2 by NO_2 (as an oxidizing agent) contributed to significant sulfate formation in haze events (Wang et al., 2016b;Cheng et al., 2016). This aqueous reaction should not be significant in the reaction systems of this study due to the limited amount of water under low RH condition (<1% RH)."

In the lines 19−21 on page 8, this discussion is purely a simple guess. What are potential products blocking the surface reactive sites? Do you have any experimental evidence to support the presence of products (e.g., in DRIFTS spectra)?

Response: In the step-to-step experiments, since the NO_2 and C_3H_6 was cut off after pre-adsorption, and ROS was expected to be generated on TiO_2 with UV, it is quite possible that some products blocked surface reactive sites and decreased sulfate formation. The potential products would be nitrate, aldehydes and carboxylic acids from the oxidation of NO_2 and propene. Besides the abundant nitrate, the bands at 1750 and 1524 cm^{-1} in DRIFTS spectra, which could be assigned to CH_2O (Liao et al., 2001) and COO groups (Mattsson and Österlund, 2010), respectively. We add some additional discussion in the revised manuscript.

Page 9, Line 14-18:

"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."

WERE CHANGED TO:

"Although the detailed reason for this phenomenon was not discovered in this study, a possible reason might be that the oxidation products from NO_2 and C_3H_6 blocked some reactive sites on TiO_2 and suppress sulfate formation in heterogeneous photooxidation, since NO_2 and C_3H_6 was cut off after pre-adsorption and ROS was expected to be generated on TiO_2 with UV-Vis irradiation. According to the DRIFTS spectra in Fig. 4(c), besides nitrate, aldehydes (1750 cm^{-1}) and carboxylic acids (1524 cm^{-1}) were also observed on TiO_2 after the pre-adsorption with of NO_2 + C_3H_6."

In the line 26 on page 8, what was saturated with?

Response: It is sulfite.

Page 11, Line 26-27:

"With reaction time increasing, the surface became saturated and prevented SO_2 from adsorbing on the particles further"

WERE CHANGED TO:

"With reaction time increasing, the adsorption sites on the surface became saturated with sulfite and prevented SO_2 from adsorbing on the particles further."

In the line 11 on page 9, how can we know that NO2 may compete with SO2 for both surface active sites and ROS? Based on the results (Fig. 6), NO2 appears to compete with SO2 for the surface active sites, but not for ROS since the sulfate formation rate (increasing rate of the K-M integrated area) with the step-by-step gas (NO2 first and then SO2) injection in the later reaction time becomes comparable to that with both gases together.

Response: We agree with the reviewer that NO_2 mainly compete with SO_2 for the surface active sites according to the experiments result. In the step-by-step (NO_2 first and then SO_2) reaction, sulfate formation was less than that in the reaction of NO_2+SO_2, while in the later reaction time becomes comparable to that in the reaction of NO_2+SO_2, indicating that NO_2 maily compete with SO_2 for the surface active sites and resulted in less sulfate formation compare to the reaction of SO_2 alone with the presence of UV-Vis irradiation which resulted in continuous production of ROS on TiO_2 surface. We deleted the related description in the Conclusion section, and discussed this in the discussion part in the revised manuscript.

Page 11, Line 27 (Page 9, Line 8-13 in the Old version):

DELETE: "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."

Page 10, Line 29-Page 11, Line 7:

ADD: "In the UV-Vis irradiation experiments, NO_2 had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO_2. Rather than resulting in ROS formation and oxidation of S(IV) to S (VI) in dark experiments, the main reaction of NO_2 with the surface ROS resulted in nitrate formation in experiments with UV-Vis irradiation (Ndour et al., 2008;Yu and Jang, 2018).

$$\mathrm{Ti-NO_2+\cdot OH\rightarrow Ti-HONO_2} \qquad (15)$$

$$\mathrm{Ti-NO_2+\cdot O_2^-\rightarrow Ti-NO_2^-}+O_2 \qquad (16)$$

The nitrate or nitrite generated from the oxidation of NO_2 might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO_2 on TiO_2 also suppressed the formation of sulfate and resulted in similar sulfate formation to that in the experiment introducing NO_2 and SO_2 simultaneously. The competition between SO_2 and NO_2 for surface reactive sites might be the main reason for the fact that the coexistence of NO_2 with SO_2 resulted in decreased sulfate formation with UV-Vis irradiation in this study."

The statement in the line 14 on page 9 is too general. Need to rewrite.

Response: This statement was rewritten.

Page 12, Line 3-4:

"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."

WERE CHANGED TO

"These results indicated that heterogeneous oxidation of SO_2 might be influenced by the co-existing inorganic and organic gas pollutants under complex pollution conditions due the competition for ROS and active surface sites among them."

Page 12, Line 5:

DELETE "Besides inorganic species, organics could also significantly change the heterogeneous oxidation of SO_2."

Minor comments:

In the line 30 on page 2, please specify what type of illumination the authors refer to.

Response: It is UV illumination.

Page 2, Line 29:

"Illumination"

WERE CHANGED TO

"UV illumination"

Line 9 on page 4: what are the wavelengths of the UV irradiation?

Response: The information about the wavelengths was added in the revised manuscript.

Page 4, Line 19-21:

ADD "The wavelengths of the UV-Vis irradiation were measured to be in the range of 250-850 nm by a fiber optic spectrometer (BLUE-Wave-UVNb, Stellar Net Inc., USA), as shown in Fig. S1 in the Supplemental Information."

Please state gas concentrations in the experimental.

Response: The information about the concentrations was added in the revised manuscript.

Page 4, Line 29-30:

ADD “After that, gas reactants, such as 200 ppb SO_2, 200 ppb NO_2 and 200 ppb C_3H_6, were introduced to the gas flow and then passed through the reaction chamber for 12 h.”

Page 5, Line 14; Page 6, Line 8 & Line 18:

ADD “DRIFTS spectra for heterogeneous reaction of 200 ppb SO_2 on TiO_2”

ADD” 200 ppb SO_2 and 200 ppb NO_2”

ADD” 200 ppb SO_2 and 200 ppb NO_2”

I believe that the title of sub-section 3.1.3 is typo.

Response: Thanks for pointing out. “NO_2” was REVISED to “C_3H_6”.

Line 17 on page 8: “with of” is typo.

Response: Thanks for pointing out. The word “of” was DELETED.

Response for Reviewer #3

This manuscript presents an experimental study on the influence of NO2 and a specific VOC (propene) on the heterogeneous production of sulfate on TiO2 particles. The study argues for the complexity in the situation of multiple precursors. The topic fits well in the journal. However, there are significant issues within the manuscript. Below are the major, minor and technical comments. They should be satisfactorily addressed before consideration for publication in the final ACP.

Major:

A major question that I have is on the set up of the experiments in which many details are missing in the current manuscript. Specifically, (1) is relative humidity controlled? A lot of previous studies show the importance of RH in heterogeneous reactions. RH (or the abundance of water vapor) also impacts gas phase reactions through HOx cycle. (2) about UV light illumination. What is the amplitude and the range of wavelength? Is it represent of the real atmosphere? (3) the detection of ion chromatography. Is it interfered by HMS hydroxymethanesulfonate? (4) Rational of the choice of materials: TiO2 and propene. How well do they represent the aerosol particles and VOCs? These above questions should be clearly answered in the manuscript.

Response: Thanks for the reviewer’s comments. More details were added in the revised manuscript as the reviewer suggested.

(1) RH.

In our experiments, no water flow was introduced to the reaction system (RH<1%). In the revised manuscript, additional experimental information was added, and the discussion about the source of the adsorption water was extended.

Page 4, Line 27-28:

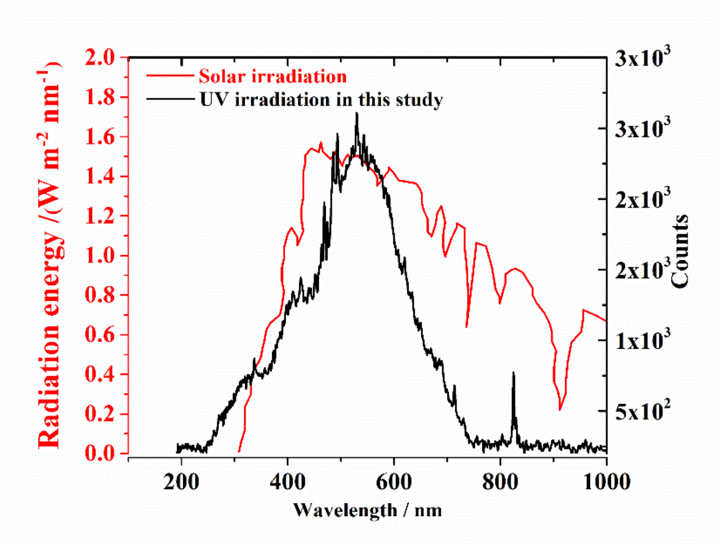
ADD: “The temperature was 303 K and the relative humidity was less than 1% in all experiments.”

(2) UV.

In the manuscript, we mentioned that “The intensity of UV irradiation was measured as 478 μW cm^{-2}”, while the information about the wavelengths was added in the revised manuscript. We also compared the spectrum of the UV irradiation with solar irradiation on the earth surface, as shown in the below picture, which was also added in the Supplemental Information. The spectrum of the UV-Vis irradiation seems to be comparable with the spectrum of solar irradiation on the earth surface, and therefore we think the UV-Vis irradiation used in this study may represent the real atmosphere.

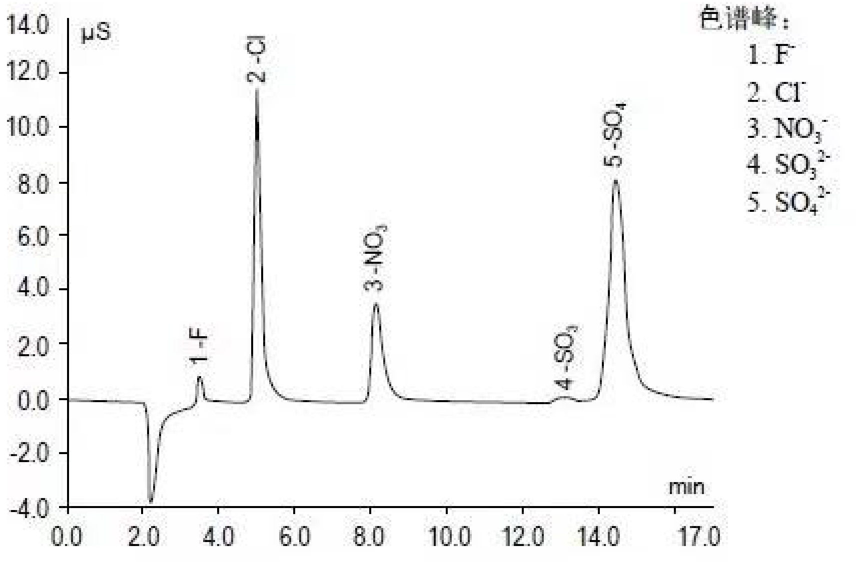
Page 4, Line 19-21:

ADD “The wavelengths of the UV-Vis irradiation were measured to be in the range of 250-850 nm by a fiber optic spectrometer (BLUE-Wave-UVNb, Stellar Net Inc., USA), as shown in Fig. S1 in the Supplemental Information. The spectrum of the UV-Vis irradiation is comparable to the spectrum of solar irradiation on the earth surface, and therefore we think the UV-Vis irradiation used in this study may represent the conditions in the real atmosphere.”



(3) IC.

Thanks for the reminding. We used a Thermo AS14 Column in the IC, which was mentioned in the manuscript in the IC section. We read the paper of Moch and some references therein. But we had no clue if our column could separate HMS and sulfate or not, although in our IC measurements, we can see a peak of S(IV) a little earlier than S(VI). One good thing is that the IC measurements were only used to further compare the sulfate formation among different experimental systems in this study as the sulfate were also compared according to the *In situ* DRIFTS spectra and the K-M integrated area. The possible interferes of HMS on sulfate measurement in the IC doesn't change our conclusions. CH_2O was observed when the surface was exposed to NO_2 and C_3H_6, but its reaction with sulfite might not be significant on the surface since the RH is <1%. In the revised manuscript, the possible interferes of HMS on sulfate were added. The description related to the IC measurement results were modified.



Page 8, Line 2:

DELETE "quantitatively"

Page 8, Line 1:

"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."

WERE CHANGED TO:

"Since formaldehyde was added to inhibit the oxidation of sulfite to sulfate in the solution, there is a possibility that HMS would be generated in the solution and be measured as sulfate (Moch et al., 2018). However, the possible interference by HMS in the measurement of sulfate by IC will not influence our conclusions on the effects of NO_2 and C_3H_6, since the K-M integrated area of sulfate in the *In situ* DRIFTS spectra were also compared."

Title of Figure. 4:

ADD: "Since formaldehyde was added to inhibit the oxidation of sulfite to sulfate in the solution, there is a possibility that HMS would be generated in the solution and be measured as sulfate."

(4) TiO_2 and C_3H_6

We have the same concern as the reviewer and plan to investigate these process on different mineral dust and authentic dust particles in the future. Actually, the heterogeneous reactivity depends greatly on the properties of mineral oxides, such as the acid−base nature, or the redox properties (Tang et al., 2016;Yang et al., 2016;Yang et al., 2019). For example, basic mineral oxides such as MgO and CaO were more active than acidic SiO_2 for the heterogeneous reaction of NO_2, while Fe_2O_3, with its unique Fe^{2+}/Fe^{3+} redox chemistry, favors the formation of SO_4^{2-} and the heterogeneous conversion of NO_2. There are many previous studies using different types of mineral oxides and also some using authentic dust particles to study heterogeneous process. The uptake coefficient of SO_2 onto pure metal oxides is generally larger than authentic dust particles. Semiconductive metal oxides were known to be responsible for heterogeneous photo-oxidation of tracer gases. In this study, with the coexisting of multigas, the oxidation system is relatively complex, and both dark experiments and UV experiments were carried out. In order to better study the effects of NO_2 and C_3H_6 on the heterogeneous oxidation in the presence or absence of UV irradiation, we chose TiO_2 due to the fact that it is a semiconductor material and a well-known photocatalyst, although it is less abundant than CaO, Fe_2O_3 or MgO in the atmosphere. We tried to anticipate the effect of choosing different mineral oxides, but it is difficult since very few previous studies compared heterogeneous reactions on different mineral dust, especially for heterogeneous reactivity in multigas coexisting system. For the dark experiments, since NOx enhance SO_2 oxidation on different mineral dusts (He et al., 2014), we anticipate the effects of coexisting of NO_2 and C_3H_6 might be ubiquitous; while for the UV experiments, we anticipate the effects of NO_2 and C_3H_6 might be applied to semiconductive metal oxides and authentic dust particles contain semiconductive metal oxides. In the revised manuscript, the following statement were added.

Page 3, Line 13-19:

ADD "In order to better study the effects of NO_2 and C_3H_6 on the heterogeneous oxidation in a relatively complex oxidation system (with coexistence of multiple gases, in both dark and illuminated conditions), we chose TiO_2 due to the fact that it is a semiconductor material and a well-known photocatalyst. TiO_2 has been widely reported to be present in airborne particulate matter (PM) (Chen et al., 2012), Although TiO_2 represents only a relatively small portion of the mass of PM and is less abundant than CaO, Fe_2O_3 or MgO, the TiO_2 particles are expected to provide important surfaces for heterogeneous photocatalysis of atmospheric gases due to their high photocatalytic activity, especially with the growing application of TiO_2 in human activities (Chen et al., 2012)."

Page 3, Line 22-25:

ADD "However, we must point out that the heterogeneous reactivity depends greatly on the properties of the mineral oxides, such as acid−base nature or redox properties (Tang et al., 2016;Yang et al., 2016;Yang et al., 2019), while different VOCs may also have quite different heterogeneous and photochemical reactivity. Investigating these processes on different mineral dust and authentic dust particles with different types of VOCs is needed in future studies."

Page 3, Line 19-25:

ADD "Propene is selected as a representative VOC since it is the most abundant alkene compound in the atmosphere, and coexists with NO_x in vehicle exhaust emission (Wang et al., 2016a). Propene is widely used as an accelerator in photochemical reactions in some smog chamber studies (Jang and Kamens, 2001;Song et al., 2007). The relatively simple oxidation products and well understood oxidation mechanism of propene are also helpful in explaining our experimental results. Propene is selected also due to the high vapor pressure of its oxidation products, which normally do not generate condensed organic aerosol (Odum et al., 1996)."

The second one is on the structure of the manuscript. Currently, a big chunk of the method description resides in the results and discussion. I suggest that the authors should re-organize the structure and separate method, results, and discussion (three sections). The experiments conducted in this study should be summarized at first in the method section. In the discussion section, a more thorough and clear discussion on the influencing factors of SO2 oxidation should be provided.

Response: Thanks for the suggestions. Corresponding reorganization and revision were made in the revised manuscript. The description of experiments were moved to 2.2.1. A separate discussion part was also added after the results section.

Page 4, Line 24- Page 5, Line 3:

"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. Two series of *in situ* DRIFTS experiments were carried out in this study. For the heterogeneous reaction of SO_2 under different gas conditions, the TiO_2 sample was initially flushed with the synthetic air at a total flow rate of 100 mL min^{-1} for 2 h. The temperature was 303 K and the relative humidity was less than 1% in all experiments. Then the background spectra were recorded when they showed little change with time. After that, gas reactants, such as 200 ppb SO_2, 200 ppb NO_2 and 200 ppb C_3H_6, were introduced to the gas flow and then passed through the reaction chamber for 12 h. These experiments were carried out under both dark and with UV-Vis irradiation conditions. The other series of experiments were step-by-step exposure experiments for further investigation of the effects of NO_2 and C_3H_6 on the heterogeneous oxidation of SO_2 with UV-Vis irradiation. 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."

Page 9- Page 11:

"4 Discussion

4.1 Dark reactions

The heterogeneous oxidation of SO_2 on TiO_2 has been investigated by many previous studies. The following mechanisms for SO_2 adsorption on TiO_2 surfaces have been proposed in previous studies (Nanayakkara et al., 2012):

$$\mathrm{Ti-OH+SO_2\rightarrow Ti-OSO_2H} \qquad (1)$$

$$\mathrm{2Ti-OH+SO_2\rightarrow Ti_2-SO_3\cdot H_2}O \qquad (2)$$

$$\mathrm{Ti} - \mathrm{O}^{2-} + \mathrm{SO}_2 \rightarrow \mathrm{Ti} - SO_3^{2-} \qquad (3)$$

These adsorption processes result in the conversion of SO_2 to sulfite (S(IV)) on the surface. It has been demonstrated that coexisting NO_2 can induce the generation of some ROS, which oxidize S(IV) to S(VI) on mineral oxides (Ma et al., 2008;Liu et al., 2012;Ma et al., 2017). There were several possible responsible ROS proposed in previous studies, although the detailed mechanism has not yet been fully explored. One possible ROS is N_2O_4, which can undergo hydrolysis to N(III) and N(V) species (Liu et al., 2012;Finlayson-Pitts et al., 2003;Li et al., 2018). These reactive nitrogen species can oxidize S(IV) to S(VI) (Wang et al., 2016b;Li et al., 2018).

$$2\mathrm{Ti} - NO_2 \rightarrow \mathrm{Ti}_2 - \mathrm{N}_2O_4 \qquad (4)$$

$$\mathrm{N}_2O_4(ad) \rightarrow NO^+NO_3^- \xrightarrow{H_2O} HNO_3 + HONO \qquad (5)$$

Besides N_2O_4, NO_2 may also react directly with surface OH and form HNO_3 on TiO_2 (Liu et al., 2017a). The HNO_3 generated through this pathway may also contribute to the oxidation of S(IV) to S(VI). It has also been proposed that aqueous oxidation of SO_2 by NO_2 (as an oxidizing agent) contributed to significant sulfate formation in haze events (Wang et al., 2016b;Cheng et al., 2016). This aqueous reaction should not be significant in the reaction systems of this study due to the limited amount of water under low RH condition (<1% RH).

When C_3H_6 was introduced together with NO_2, sulfate formation was less than that in the reaction of SO_2+NO_2, probably due to the reaction between C_3H_6 and the reactive nitrogen species. The detailed mechanism was not explored in this study. The following reactions may take place in this process.

$$2NO^+NO_3^- + \mathrm{Ti} - \mathrm{C}_3\mathrm{H}_6 \rightarrow \mathrm{H}_3\mathrm{CCHO} + \mathrm{HCHO} + 2NO^+NO_2^- \qquad (6)$$

$$NO^+NO_3^- + \mathrm{HCHO} \rightarrow \mathrm{HCOOH} + NO^+NO_2^- \qquad (7)$$

$$NO^+NO_3^- + \mathrm{H}_3\mathrm{CCHO} \rightarrow \mathrm{H}_3\mathrm{CCOOH} + NO^+NO_2^- \qquad (8)$$

Heterogeneous reactions between NO_2 and organics can also lead to nitro-organics on hexane soot (Kwamena and Abbatt, 2008;Al-Abadleh and Grassian, 2000) , which may also occur on the surface of TiO_2, and these products blocked some reactive sites for sulfate formation.

4.2 Light reactions

With UV illumination, TiO_2 can be excited by UV light (λ< 387 nm), then the photogenerated electrons and holes can react with H_2O and O_2 to produce additional ROS (primarily $\cdot \mathrm{O}_2^-$ and $\cdot \mathrm{OH}$), and oxidize more SO_2 to sulfate on TiO_2 than that produced under dark conditions (Shang et al., 2010a;Chen et al., 2012).The detailed mechanism was summarized by Chen et al. (Chen et al., 2012) and references therein:

$$\mathrm{TiO}_2 + h\nu(\lambda < 387\ \mathrm{nm}) \rightarrow \mathrm{e}^-\mathrm{h}^+ \rightarrow \mathrm{e}^- + \mathrm{h}^+ \qquad (9)$$

$$\mathrm{O}_2 + \mathrm{e}^- \rightarrow \cdot\, \mathrm{O}_2^- \qquad (10)$$

$$\mathrm{H}_2\mathrm{O} + \mathrm{h}^+ \rightarrow \cdot\, \mathrm{OH} + \mathrm{H}^+ \qquad (11)$$

Then the SO_2 can react with these ROS and promote the formation of sulfate (Shang et al., 2010b):

$$\mathrm{Ti-SO_2+\cdot O_2^- \rightarrow Ti-SO_3} + O^- \quad (12)$$

$$\mathrm{Ti-SO_3+H_2O \rightarrow Ti-H_2SO_4} \quad (13)$$

$$\mathrm{Ti}-SO_3^{2-}+2\cdot \mathrm{OH} \rightarrow \mathrm{Ti}-SO_4^{2-}+\mathrm{H_2O} \quad (14)$$

In the UV-Vis irradiation experiments, NO_2 had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO_2. Rather than resulting in ROS formation and oxidation of S(IV) to S (VI) in dark experiments, the main reaction of NO_2 with the surface ROS resulted in nitrate formation in experiments with UV-Vis irradiation (Ndour et al., 2008;Yu and Jang, 2018).

$$\mathrm{Ti-NO_2+\cdot OH \rightarrow Ti-HONO_2} \quad (15)$$

$$\mathrm{Ti-NO_2+\cdot O_2^- \rightarrow Ti-NO_2^-} + O_2 \quad (16)$$

The nitrate or nitrite generated from the oxidation of NO_2 might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO_2 on TiO_2 also suppressed the formation of sulfate and resulted in similar sulfate formation to that in the experiment introducing NO_2 and SO_2 simultaneously. The competition between SO_2 and NO_2 for surface reactive sites might be the main reason for the fact that the coexistence of NO_2 with SO_2 resulted in decreased sulfate formation with UV-Vis irradiation in this study. Although Gen et al. (Gen et al., 2019) found that photolysis of nitrate enhanced sulfate formation in wet aerosols, this mechanism may not be applied in this study since the reaction system is quite different from their study. The ROS which oxidize S(IV) to S(VI) are mainly $\cdot \mathrm{O_2^-}$ and $\cdot \mathrm{OH}$ in the presence of UV-Vis irradiation rather than the photolysis of nitrate.

C_3H_6 also had a distinct suppressing effect on sulfate formation. Similar to NO_2, C_3H_6 will react with surface ROS.

$$\mathrm{C_3H_6} \xrightarrow{\cdot OH} \mathrm{RCHO} \xrightarrow{\cdot OH} \mathrm{RCOOH} \xrightarrow{\cdot OH} \mathrm{C}O_2 + H_2O \quad (17)$$

where R represents H or an alkyl group. These gaseous products in the photo-oxidation of C_3H_6 do not seem to block surface reactive sites, which can explain why the pre-adsorption of C_3H_6 on TiO_2 did not show an obvious suppressing effect on the formation of sulfate in the step-by-step experiment.

When C_3H_6 + NO_2 were introduced simultaneously into the reaction system together with SO_2, both competed for ROS with SO_2 and therefore resulted in the lowest formation of sulfate among the heterogeneous reactions. Besides, in the step-by-step experiments, the pre-adsorption of C_3H_6+NO_2 on TiO_2 suppressed sulfate formation significantly, which indicated that lots of reactive sites for SO_2 oxidation might be blocked by these oxidation products in pre-adsorption with UV-Vis irradiation. Karagulian et al. (Karagulian et al., 2009) found that nitrite can induce the photo-oxidation of VOCs on airborne particles and produce organic nitrates and carbonyl compounds. Thus, the formation of organic nitrates may be an important factor to suppress the formation of sulfate due to the blocking effect."

The third one is on the proposed mechanisms which in my opinion are not well justified. The study intends to explore the underlying mechanisms through different combinations of chemical precursors. The proposed mechanisms are specifically related to the production and/or competition for ROS and surface reactive sites. But the study does not provide a good way in *the experiments to argue for the importance of ROS and reactive sites. What are differences in terms of production and fate of ROS under dark and illumination conditions? Is there a way to detecting the saturation of surface reactive sites?*

Response: As mentioned in the response of the second major comment, we added a separate discussion section to discuss the proposed mechanisms of sulfate formation and the competition for ROS and surface reactive sites. Some of the related discussion are listed below. Although we carried our step-to-step experiments and trying to better understand the competition for ROS and surface reactive sites, there is still uncertainty about these process. Take NO_2 as an example, in the step-by-step (NO_2 first and then SO_2) reaction, sulfate formation was less than that in the reaction of NO_2+SO_2, while in the later reaction time becomes comparable to that in the reaction of NO_2+SO_2, indicating that NO_2 maily compete with SO_2 for the surface active sites and resulted in less sulfate formation compare to the reaction of SO_2 alone with the presence of UV-Vis irradiation which resulted in continuous production of ROS on TiO_2 surface. We deleted the related description in the conclusion section, and discussed this in the discussion part in the revised manuscript. As the reviewer pointed out, detecting the saturation of surface reactive sites, as well as the ROS should be greatly helpful, but unfortunately, we don't have a good method for these measurement yet in our group.

Page 12, Line 2 (Page 9, Line 8-13 in the Old version):

DELETE: “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.”

Page 10, Line 29-Page 11 Line 10:

ADD: “In the UV-Vis irradiation experiments, NO_2 had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO_2. Rather than resulting in ROS formation and oxidation of S(IV) to S (VI) in dark experiments, the main reaction of NO_2 with the surface ROS resulted in nitrate formation in experiments with UV-Vis irradiation (Ndour et al., 2008;Yu and Jang, 2018).

$$\mathrm{Ti-NO_2+\cdot OH \rightarrow Ti-HONO_2} \qquad (15)$$

$$\mathrm{Ti-NO_2+\cdot O_2^- \rightarrow Ti-NO_2^-} + O_2 \qquad (16)$$

The nitrate or nitrite generated from the oxidation of NO_2 might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO_2 on TiO_2 also suppressed the formation of sulfate and resulted in similar sulfate formation to that in the experiment introducing NO_2 and SO_2 simultaneously. The competition between SO_2 and NO_2 for surface reactive sites might be the main reason for the fact that the coexistence of NO_2 with SO_2 resulted in decreased sulfate formation with UV-Vis irradiation in this study. Although Gen et al. (Gen et al., 2019) found that photolysis of nitrate enhanced sulfate formation in wet aerosols, this mechanism may not be applied in this study since the reaction system is quite different from their study. The ROS which oxidize S(IV) to S(VI) are mainly $\cdot \mathrm{O}_2^-$ and $\cdot \mathrm{OH}$ in the presence of UV-Vis irradiation rather than the photolysis of nitrate."

Page 9, Line 26-Page 10, Line 6:

ADD: "These adsorption processes result in the conversion of SO_2 to sulfite (S(IV)) on the surface. It has been demonstrated that coexisting NO_2 can induce the generation of some ROS, which oxidize S(IV) to S(VI) on mineral oxides (Ma et al., 2008;Liu et al., 2012;Ma et al., 2017). There were several possible responsible ROS proposed in previous studies, although the detailed mechanism has not yet been fully explored. One possible ROS is N_2O_4, which can undergo hydrolysis to N(III) and N(V) species (Liu et al., 2012;Finlayson-Pitts et al., 2003;Li et al., 2018). These reactive nitrogen species can oxidize S(IV) to S(VI) (Wang et al., 2016b;Li et al., 2018).

$$2\mathrm{Ti}-NO_2 \rightarrow \mathrm{Ti}_2-\mathrm{N}_2O_4 \qquad (4)$$

$$\mathrm{N}_2O_4(ad) \rightarrow NO^+NO_3^- \xrightarrow{H_2O} HNO_3 + HONO \qquad (5)$$

Besides N_2O_4, NO_2 may also react directly with surface OH and form HNO_3 on TiO_2 (Liu et al., 2017a). The HNO_3 generated through this pathway may also contribute to the oxidation of S(IV) to S(VI). It has also been proposed that aqueous oxidation of SO_2 by NO_2 (as an oxidizing agent) contributed to significant sulfate formation in haze events (Wang et al., 2016b;Cheng et al., 2016). This aqueous reaction should not be significant in the reaction systems of this study due to the limited amount of water under low RH condition (<1% RH)."

For that the presence of VOCs may suppress sulfate formation, or that the presence of C_3H_6 inhibited heterogeneous sulfate formation with NO_2 by competing with SO_2 for reactive oxygen species or active sites on the aerosol, we added the following discussions.

Page 10, Line 7-15:

"When C_3H_6 was introduced together with NO_2, sulfate formation was less than that in the reaction of SO_2+NO_2, probably due to the reaction between C_3H_6 and the reactive nitrogen species. The detailed mechanism was not explored in this study. The following reactions may take place in this process.

$$2NO^+NO_3^- + \mathrm{Ti}-\mathrm{C}_3\mathrm{H}_6 \rightarrow \mathrm{H}_3\mathrm{CCHO} + \mathrm{HCHO} + 2NO^+NO_2^- \qquad (6)$$

$$NO^+NO_3^- + \mathrm{HCHO} \rightarrow \mathrm{HCOOH} + NO^+NO_2^- \qquad (7)$$

$$NO^+NO_3^- + \mathrm{H}_3\mathrm{CCHO} \rightarrow \mathrm{H}_3\mathrm{CCOOH} + NO^+NO_2^- \qquad (8)$$

Heterogeneous reactions between NO_2 and organics can also lead to nitro-organics on hexane soot (Kwamena and Abbatt, 2008;Al-Abadleh and Grassian, 2000) , which may also occur on the surface of TiO_2, and these products blocked some reactive sites for sulfate formation."

Page 11, Line 11-22:

ADD: "C_3H_6 also had a distinct suppressing effect on sulfate formation. Similar to NO_2, C_3H_6 will react with surface ROS.

$$\mathrm{C}_3\mathrm{H}_6 \xrightarrow{\cdot OH} \mathrm{RCHO} \xrightarrow{\cdot OH} \mathrm{RCOOH} \xrightarrow{\cdot OH} CO_2 + H_2O \qquad (17)$$

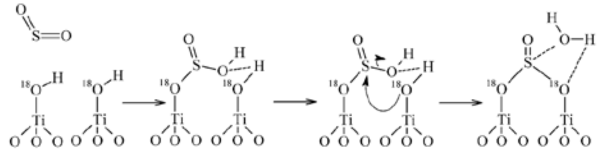
where R represents H or an alkyl group. These gaseous products in the photo-oxidation of C_3H_6 do not seem to block surface reactive sites, which can explain why the pre-adsorption of C_3H_6 on TiO_2 did not show an obvious suppressing effect on the formation of sulfate in the step-by-step experiment.

When C_3H_6 + NO_2 were introduced simultaneously into the reaction system together with SO_2, both competed for ROS with SO_2 and therefore resulted in the lowest formation of sulfate among the heterogeneous reactions. Besides, in the step-by-step experiments, the pre-adsorption of C_3H_6+NO_2 on TiO_2 suppressed sulfate formation significantly, which indicated that lots of reactive sites for SO_2 oxidation might be blocked by these oxidation products in pre-adsorption with UV-Vis irradiation. Karagulian et al. (Karagulian et al., 2009) found that nitrite can induce the photo-oxidation of VOCs on airborne particles and produce organic nitrates and carbonyl compounds. Thus, the formation of organic nitrates may be an important factor to suppress the formation of sulfate due to the blocking effect."

Minor:

Page 5, Line 9-10: Elaborate on the processes leading to surface water formation.

Response: There are two sources of the molecularly adsorbed water related to sulfate formation. One is water formation during the heterogeneous reaction. For example, SO_2 reacted with two neighboring OH groups will resulted in sulfite and water formation, as shown in the following scheme (Nanayakkara et al., 2012). Meanwhile, a sulfate formation mechanism that involves both surface OH and O can also generate water, $HSO_3^- + O^- + OH^- \rightarrow SO_4^{2-} + H_2O + e^-$, as proposed by Zhang et al. (Zhang et al., 2006).



Scheme 1 Reaction of SO_2 and surface hydroxyl groups to form adsorbed sulfite and water.

The other possible source of water is that water absorption from the introduced gas to the generated sulfate (Ma et al., 2019). In our experiments, no water flow was introduced to the reaction system (RH<1%), but still water cannot be entirely avoided in the introduced gas flows. In Fig.1, we can see the signal strength of the adsorbed water have good positive correlation with the amount of sulfite/sulfate formation in different experimental systems. In the revised manuscript, additional experimental information was added, and the discussion about the source of the adsorption water was extended.

Page 9, Line 21-24:

ADD: "The heterogeneous oxidation of SO_2 on TiO_2 has been investigated by many previous studies. The following mechanisms for SO_2 adsorption on TiO_2 surfaces have been proposed in previous studies (Nanayakkara et al., 2012):

$$\mathrm{Ti-OH+SO_2\rightarrow Ti-OSO_2H} \qquad (1)$$

$$\mathrm{2Ti-OH+SO_2\rightarrow Ti_2-SO_3\cdot H_2}O \qquad (2)"$$

Page 5, Line 31 -Page 6, Line 4:

"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)."

WERE CHANGED TO:

"Surface water can be formed in the heterogeneous reaction of SO_2 (Nanayakkara et al., 2012;Zhang et al., 2006), or via enhanced adsorption of water due to the increased hygroscopicity induced by sulfate (Ma et al., 2019). Although the RH was controlled at less than 1% in our experiments, water cannot be entirely removed in the introduced gas flows. In Fig.1, there is a positive correlation between the signal intensities of the adsorbed water and sulfite/sulfate among different experimental systems."

Page 9, Paragraph 2: Elaborate on the different effects of different VOCs from previous studies.

Response: More discussion about the effects of different VOCs on sulfate formation was added to the paragraph.

Page 12, Line 3-12:

"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."

WERE CHANGED TO:

"These results indicated that heterogeneous oxidation of SO_2 might be influenced by the co-existing inorganic and organic gas pollutants under complex pollution conditions due the competition for ROS and active surface sites among them. 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). When a VOC and SO_2 coexist, the competition for ROS and surface reactive sites between the VOC and SO_2 is likely to suppress sulfate formation in the heterogeneous reactions, such as that observed for the presence of CH_3CHO on α-Fe_2O_3 in dark experiments (Zhao et al., 2015), the presence of C_7H_{16} on TiO_2 with UV-Vis irradiation (Du et al., 2000), and the presence of C_3H_6 on TiO_2 under dark condition or with UV-Vis irradiation in this study. Due to the different properties of the oxidation products, the influence of coexisting VOCs might be different for different VOC species and on different mineral dusts. Some coexisting VOCs, such as HCOOH on α-Fe_2O_3 (Wu et al., 2013), and HCHO in aerosol water (Moch et al., 2018;Song et al., 2019) might enhance sulfate formation."

The authors may consider move Figure 2 to the supplemental.

Response: Fig.2 was REMOVED to the Supplemental Information.

Technical:

Page 1, Line 17: full expression for "DRIFTS"

Response: The full expression for FRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) was ADDED in the abstract. There was also a full expression in the third paragraph in the introduction.

Page 2, Line 5: "the mechanisms of heterogeneous reaction processes as well as their"

Response: Thanks! It was REVISED accordingly.

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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~~UV-Vis 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* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)~~DRIFTS~~ under dark conditions or with ~~UV~~UV-Vis 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~~UV-Vis 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~~UV-Vis 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~~ need 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., 2017b) 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., 2006;Ma et al., 2018). However, the mechanism of the heterogeneous reaction process as well as ~~its their~~ its contribution to sulfate formation in “complex atmospheric pollution” remain uncertain (Yang et al., 2018;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., 2006), 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 a~~n~~ catalyst ~~to activate O_2~~ in the oxidation of SO_2 by O_2, 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 acetaldehyde (CH_3CHO)~~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., 2015), while HCHO was proposed to react with SO_3^{2-} and generate hydroxymethanesulfonate (HMS) in the northern China winter haze period (Moch et al., 2018;Song et al., 2019). Wu et al. (~~Wu et al.,~~ 2013) found that the synergistic effects between formic acid (HCOOH) and SO_2 in the heterogeneous reaction on hematite provide a new source of sulfate~~, while Zhao et al. (Zhao et al., 2015) found that sulfate formation on α-Fe_2O_3 was suppressed by the presence of acetaldehyde (CH_3CHO)~~.

~~Illumination~~ UV illumination can affect both the properties of particles and heterogeneous reactions on them (Nanayakkara et al., 2012;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., 2012). TiO_2 can be excited by UV light (λ< 387 nm), resulting in electrons and holes, which could react with O_2 and H_2O and produce $\cdot O_2^-$ and $\cdot OH$, respectively. These reactive oxygen species (ROS)~~active species (,~~ primarily $\cdot O_2^-$ and $\cdot OH$~~OH,) that~~ can participate in the heterogeneous oxidation of SO_2 on TiO_2 ~~atmospheric photochemical reactions~~ (Chen et al., 2012). Shang et al. (~~Shang et al.,~~ 2010a) 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., 2012) 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~~Despite these studies involving the heterogeneous oxidation of SO_2 under various conditions, the effects of co-existing pollutants on the heterogeneous oxidation of SO_2 ~~it is not fully understood how the heterogeneous oxidation of SO_2 is influenced by co-existing pollutants~~ under both dark ~~or~~ and ~~illumination~~ illuminated conditions need further investigation. Meanwhile, the interactions between organic and inorganic species in these heterogeneous ~~oxidation of SO_2~~processes at low concentrations ~~have not been deeply researched yet~~ are not fully understood. In this study, we focus on the effects of co-existing NO_2 and propene (C_3H_6) on the heterogeneous oxidation of SO_2 on TiO_2 ~~at low concentrations (200 ppb) on the heterogeneous oxidation of SO_2 on TiO_2 with *in situ* DRIFTS~~ under both dark and ~~illumination~~ illuminated conditions with *in situ* DRIFTS. In order to better study the effects of NO_2 and C_3H_6 on the heterogeneous oxidation in a relatively complex oxidation system (with coexist~~ing~~ence of multiple gases, in both dark and illuminat~~ion~~ed conditions), we chose TiO_2 due to the fact that it is a semiconductor material and a well-known photocatalyst. TiO_2 has been widely reported to be present in airborne particulate matter (PM) (Chen et al., 2012)~~,~~. Although TiO_2 represents only a relatively small portion of the mass of PM and is less abundant than CaO, Fe_2O_3 or MgO, the TiO_2 particles are expected to provide important surfaces for heterogeneous photocatalysis of atmospheric gases due to their high photocatalytic activity, especially with the growing application of TiO_2 in human activities (Chen et al., 2012). Propene is selected as a representative VOC since it is the most abundant alkene compound~~s of alkenes~~~~a ubiquitous VOC~~ in the atmosphere, and coexisted~~s~~ with NO_x in vehicle exhaust emission (Wang et al., 2016a)~~,~~. Propene~~and~~ is widely used as an accelerator in photochemical reactions in some smog chamber studies (Jang and Kamens, 2001;Song et al., 2007). The relatively simple oxidation products and well understood oxidation mechanism of propene ~~is~~are also helpful ~~to~~in explaining our experimental results. Propene is selected also due to the high vapor pressure of its oxidation products, which normally ~~don't~~do not generate condensed organic aerosol (Odum et al., 1996). However, we ~~have to~~must point out that the heterogeneous reactivity depends greatly on the properties of the mineral oxides, such as ~~the~~ acid−base nature~~,~~ or ~~the~~ redox properties (Tang et al., 2016;Yang et al., 2016;Yang et al., 2019), while different

VOCs may also have quite different heterogeneous and photochemical reactivity. Investigat~~e~~ing these processes on different mineral dust and authentic dust particles with different types of VOCs ~~are~~is needed in future studies. Rather than UV lights, a xenon light is used in this study ~~for a better simulation of to~~to better simulate the solar ultraviolet radiation~~UV irradiation from the sun~~ on the earth's surface~~ in this study~~. Generally, our study could be helpful for gaining a better understanding of the heterogeneous formation of sulfate ~~formation~~ under complex air pollution conditions, in which abundant SO_2, NO_x, ~~and~~ VOCs, and~~ as well as~~ mineral dust coexist 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.

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~~UV-Vis 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~~UV-Vis irradiation was measured as 478 μW cm^{-2} by a UV Meter (Photoelectric Instrument Factory of Beijing Normal University). The wavelengths of the UV-Vis irradiation were measured to be in the range of 300-800 nm by a fiber optic spectrometer (BLUE-Wave-UVNb, Stellar Net Inc., USA), as shown in Fig. S1 in the Supplemental Information. The spectrum of the UV-Vis irradiation ~~seems to be~~is comparable ~~with~~to the spectrum of solar irradiation on the earth surface, and therefore we think the UV-Vis irradiation used in this study may represent the conditions in the real atmosphere.

To investigate heterogeneous sulfate formation in complex atmospheric pollution, *in situ* DRIFTS was used to analy~~z~~sze the products on particle surfaces in the reactions under different conditions. Two series of ~~*I*~~*in situ* DRIFTS experiments were carried out in this study. For the heterogeneous reaction of SO_2 under different gas conditions, ~~Initially,~~ the TiO_2 sample was initially flushed with the synthetic air at a total flow rate of 100 mL min^{-1} ~~at 303K~~ for 2 h. The temperature was 303 K and the relative humidity was less than 1% in all ~~of our~~ experiments. Then the background spectra were recorded when they showed little change with time. After that, gas reactants, such as 200 ppb SO_2, 200 ppb NO_2 and 200 ppb C_3H_6, wa~~s~~ere introduced to the gas flow and then passed through the reaction chamber for 12 h. These experiments were carried out under both dark and with ~~UV~~UV-Vis irradiation conditions. The other series of experiments ~~are~~ were ~~three~~ step-by-step exposure experiments for ~~a~~~~To~~ further investigat~~e~~ion ~~on~~of the effects of NO_2 and C_3H_6 on the heterogeneous oxidation of SO_2 with ~~UV~~UV-Vis 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.

2.2.~~1~~ 2 IC

Sulfate products on the powders after the ~~*In*~~ *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~~ analysszed using a Wayee IC-6200 ion chromatograph equipped with a Thermo AS14~~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.~~ DRIFTS spectra for heterogeneous reaction of 200 ppb SO_2 on TiO_2~~The experiments were carried out~~ under dark conditions or with ~~UV~~UV-Vis 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, which is consistent with previous studies (Nanayakkara et al., 2012;Ma et al., 2019). The loss of surface hydroxyl groups from the surface upon adsorption of SO_2 implies that surface OH groups were involved in the reaction of SO_2 on TiO_2 under both dark and UV-Vis irradiation conditions.

With ~~UV~~UV-Vis 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} (Hug, 1997;Peak et al., 1999;Fu et al., 2007). With UV-Vis illumination, TiO_2 can be excited by UV light ($\lambda < 387$ nm), then the photogenerated electrons and holes can react with H_2O and O_2 to produce additional ROS (primarily $\cdot O_2^-$ and $\cdot OH$), and oxidize more SO_2 to sulfate on TiO_2 than that produced under dark conditions (Shang et al., 2010a;Chen et al., 2012). 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~~ can be formed in the ~~photochemical~~ heterogeneous reaction of SO_2 (Nanayakkara et al., 2012;Zhang et al., 2006)~~, such as Equation (2),~~ or via enhanced adsorption of water due to the increased hygroscopicity induced by sulfate (Ma et al., 2019). Although ~~that~~ the RH was controlled ~~to be~~at less than 1% in our experiments, water cannot be entirely removed in the introduced gas flows. In Fig.1, there is a positive correlation between the signal ~~strengths~~intensities of the adsorbed water and sulfite/sulfate among different experimental systems. ~~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 200 ppb SO_2 and 200 ppb 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., 2018). 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;Ma 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~~ much lower concentration levels of SO_2 and NO_2 being used in this study.

The spectra of TiO_2 exposed to 200 ppb SO_2 and 200 ppb NO_2~~SO_2 and NO_2~~ simultaneously with ~~UV~~UV-Vis 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~~UV-Vis irradiation, which ~~is consistent with~~might be due to the fact that ~~UV~~UV-Vis irradiation significantly promotes sulfate formation by generating additional active species (Shang et al., 2010a;Chen et al., 2012) as in the reaction of SO_2 alone. ~~(Gen et al., 2019)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 C_3H_6~~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~~UV-Vis 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~~UV-Vis irradiation~~.~~, ~~The~~ similar spectra were obtained for the ~~SO_2 reaction and~~ SO_2+C_3H_6 reaction, but the intensities decreased~~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~~UV-Vis irradiation~~ 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~~included both ~~of~~ the SO_2/NO_2 reaction (Fig. 1(c) and 1(d)) ~~reaction~~ and the SO_2/C_3H_6 reaction (Fig. 1(e) and 1(f))~~, regardless of whether irradiated or not~~ under dark conditions and with UV-Vis irradiation, respectively. Thus, the products included sulfite, nitrate, and some sulfate under dark ~~dark~~ conditions, while mainly sulfate and nitrate with UV-Vis irradiation.

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~~S2 in the Supplemental Information. 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~~UV-Vis light are shown in Fig. ~~3~~2(a) and Fig. ~~3~~2(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~~ discernible 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). The detailed mechanism for this effect ~~is~~has not been fully explored and will be discussed later. It has also been proposed that aqueous oxidation of SO_2 by NO_2 (as an oxidizing agent) contributed to significant sulfate formation in haze events (Wang et al., 2016b;Cheng et al., 2016). This reaction should not be ~~significant~~the main pathway in the reaction systems ~~of~~in this study since the experiments were carried out ~~at~~under dry conditions (RH<1%), although water can still exist~~ed~~, as we mentioned earlier. 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~~UV-Vis irradiation experiments, on the contrary, both 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~~UV-Vis irradiation. What's more, the nitrate formation from oxidation of NO_2 might block some surface reactive sites, and therefore, resulted in less sulfate formation in the reaction of SO_2+NO_2 than that of SO_2 alone with UV-Vis irradiation. To further probe and analyze the total amounts of sulfate in different systems ~~quantitatively~~, ~~sulfate~~ the samples after reaction in the different ~~reaction systems~~experiments were also analyzed by IC. The results, which are shown in Fig. ~~4~~3, are consistent with the results derived from integrated peak areas in Fig. ~~3~~2. ~~These results confirmed the enhancing effect of NO_2 on the heterogeneous oxidation reaction of SO_2 under dark conditions and the inhibiting effect of NO_2 and C_3H_6 on heterogeneous photooxidation of SO_2.~~Since formaldehyde was added to inhibit the oxidation of sulfite to sulfate in the solution, there is a possibility that HMS would be generated in the solution and be measured as sulfate (Moch et al., 2018). However, the possible interfere~~s~~nce ~~of~~by HMS ~~on~~in the measurement of sulfate ~~measurement in the~~by IC will not influence our conclusions on the effects of NO_2

and C_3H_6, since the K-M integrated area of sulfate in the *In situ* DRIFTS spectra were also compared. Despite the different yields of sulfate under different atmospheres, the presence of ~~UV~~UV-Vis irradiation always increased sulfate formation significantly. We also observed that the promotion effect of ~~UV~~UV-Vis 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~~UV-Vis 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 step-by-step experiments ~~the first step~~, the spectra for TiO_2 exposure to 200 ppm NO_2 after the first step are shown ~~with~~ by the black lines in Fig. ~~5~~4(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~~ was recorded as the blue line in Fig. ~~5~~4(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 (Ma 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~~4(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~~ by sulfate from SO_2 heterogeneous photooxidation (Park et al., 2017) or the photolysis of nitrate (Ye et al., 2017).

~~Similarly, the spectra i~~In the 200 ppm C_3H_6 pre-saturated experiment ~~are~~, which is shown in Fig. ~~5~~4(b)~~. A~~, 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 band areas of 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~~4(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~~ 5 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. This may indicate~~d~~ that NO_2 suppressed sulfate formation, mainly due to the competition between SO_2 and NO_2 for surface reactive sites. 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. Although ~~T~~the detailed reason for this phenomenon was not discovered in this study,~~.~~ a~~One~~ possible reason might be that ~~some~~the oxidation products ~~were generated when the particles were exposed to~~from NO_2 and C_3H_6 ~~at the same time, and these species seemed to~~ blocked some reactive sites on TiO_2 and suppressed sulfate formation in heterogeneous photooxidation, since NO_2 and C_3H_6 ~~was~~were cut off after pre-adsorption and ROS ~~was~~were expected to be generated on TiO_2 with UV-Vis irradiation. According to the DRIFTS spectra in Fig. ~~5~~4(c), besides nitrate, aldehydes (1750 cm^{-1}) and carboxylic acids (1524 cm^{-1}) were also observed on TiO_2 after ~~the~~ pre-adsorption with ~~of~~ NO_2 + C_3H_6.

4 Discussion~~s~~

4.1 Dark reactions

The heterogeneous oxidation of SO_2 on TiO_2 has been investigated by many previous studies. The following mechanisms for SO_2 adsorption on TiO_2 surfaces have been proposed in previous studies (Nanayakkara et al., 2012):

$$\mathrm{Ti-OH+SO_2\rightarrow Ti-OSO_2H} \tag{1}$$

$$\mathrm{2Ti-OH+SO_2\rightarrow Ti_2-SO_3\cdot H_2}O \tag{2}$$

$$\mathrm{Ti-O^{2-}+SO_2\rightarrow Ti-}SO_3^{2-} \tag{3}$$

These adsorption processes result in the conversion of SO_2 to sulfite (S(IV)) on the surface. It has been demonstrated that coexisting NO_2 can induce the generation of some ROS, which oxidize S(IV) to S(VI) on mineral oxides (Ma et al., 2008;Liu et al., 2012;Ma et al., 2017). There were several possible responsible ROS proposed in previous studies, ~~in spite~~although the detailed mechanism ~~is~~has not yet been fully explored ~~yet~~. One possible ROS is N_2O_4, which can undergo hydrolysis to N(III) and N(V) species (Liu et al., 2012;Finlayson-Pitts et al., 2003;Li et al., 2018). These reactive nitrogen species can oxidize S(IV) to S(VI) (Wang et al., 2016b;Li et al., 2018).

$$2\mathrm{Ti}-NO_2 \rightarrow \mathrm{Ti}_2-\mathrm{N}_2O_4 \qquad (4)$$

$$\mathrm{N}_2O_4(ad) \rightarrow NO^+NO_3^- \xrightarrow{H_2O} HNO_3 + HONO \qquad (5)$$

Besides N_2O_4, NO_2 may also react directly with surface OH and form HNO_3 on TiO_2 (Liu et al., 2017a). The ~~generated~~ HNO_3 generated through this pathway may also contribute to the oxidation of S(IV) to S(VI).

It has also been proposed that aqueous oxidation of SO_2 by NO_2 (as an oxidizing agent) contributed to significant sulfate formation in haze events (Wang et al., 2016b;Cheng et al., 2016). This aqueous reaction should not be significant in the reaction systems of this study due to the limited amount of water under low RH condition (<1% RH).

When C_3H_6 was introduced together with NO_2 ~~together~~, sulfate formation was less than that in the reaction of SO_2+NO_2, probably due to the reaction between C_3H_6 and the reactive nitrogen species. ~~D~~The detailed mechanism was not explored in this study. The following reactions may ~~happen~~take place in this process.

$$2NO^+NO_3^- + \mathrm{Ti}-\mathrm{C_3H_6} \rightarrow \mathrm{H_3CCHO} + \mathrm{HCHO} + 2NO^+NO_2^- \qquad (6)$$

$$NO^+NO_3^- + \mathrm{HCHO} \rightarrow \mathrm{HCOOH} + NO^+NO_2^- \qquad (7)$$

$$NO^+NO_3^- + \mathrm{H_3CCHO} \rightarrow \mathrm{H_3CCOOH} + NO^+NO_2^- \qquad (8)$$

Heterogeneous reaction~~s~~s between NO_2 and organics can also lead to nitro-organics on hexane soot (Kwamena and Abbatt, 2008;Al-Abadleh and Grassian, 2000) , which may also ~~happen~~occur on the surface of TiO_2, and these products blocked some reactive sites for sulfate formation.

4.2 Light reactions

With UV illumination, TiO_2 can be excited by UV light (λ< 387 nm), then the photogenerated electrons and holes can react with H_2O and O_2 to produce additional ROS (primarily $\cdot O_2^-$ and $\cdot OH$), and oxidize more SO_2 to sulfate on TiO_2 than that produced under dark conditions (Shang et al., 2010a;Chen et al., 2012).The detailed mechanism ~~were~~was summarized by Chen et al. (Chen et al., 2012) and references therein:

$$\mathrm{TiO_2} + h\nu(\lambda < 387\ \mathrm{nm}) \rightarrow \mathrm{e^-h^+} \rightarrow \mathrm{e^-} + \mathrm{h^+} \qquad (9)$$

$$\mathrm{O_2} + \mathrm{e^-} \rightarrow \cdot \mathrm{O_2^-} \qquad (10)$$

$$\mathrm{H_2O} + \mathrm{h^+} \rightarrow \cdot \mathrm{OH} + \mathrm{H^+} \qquad (11)$$

Then the SO_2 can react with these ROS and promote the formation of sulfate (Shang et al., 2010b):

$$\mathrm{Ti}-\mathrm{SO_2} + \cdot \mathrm{O_2^-} \rightarrow \mathrm{Ti}-\mathrm{SO_3} + O^- \qquad (12)$$

$$\mathrm{Ti}-\mathrm{SO_3} + \mathrm{H_2O} \rightarrow \mathrm{Ti}-\mathrm{H_2SO_4} \qquad (13)$$

$$\mathrm{Ti}-SO_3^{2-} + 2\cdot\mathrm{OH} \rightarrow \mathrm{Ti}-SO_4^{2-} + \mathrm{H_2O} \qquad (14)$$

In the UV-Vis irradiation experiments, NO_2 had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO_2. Rather than result~~ed~~ing in ROS formation and oxid~~ized~~ation of S(IV) to S (VI) in dark experiments, the main reaction ~~for~~of NO_2 with the surface ROS result~~ing~~ed in nitrate and nitrite formation in experiments with UV-Vis irradiation (Ndour et al., 2008;Yu and Jang, 2018).

$$\mathrm{Ti-NO_2+\cdot OH \rightarrow Ti-HONO_2} \qquad (15)$$

$$\mathrm{Ti-NO_2+\cdot O_2^- \rightarrow Ti-NO_2^-}+O_2 \qquad (16)$$

The nitrate or nitrite generated from the oxidation of NO_2 might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO_2 on TiO_2 also suppressed the formation of sulfate and resulted in similar sulfate formation ~~as~~to that in the experiment introducing NO_2 and SO_2 simultaneously. The competition between SO_2 and NO_2 for surface reactive sites might be the main reason for the fact that the coexistence of NO_2 with SO_2 resulted in decreased sulfate formation with UV-Vis irradiation in this study. Although Gen et al. (Gen et al., 2019) found that photolysis of ~~the~~ nitrate ~~was found to~~ enhanced sulfate formation in wet aerosols, this mechanism may not be applied in this study since the reaction system is quite different from their study. The ROS, which oxidize S(IV) to S(VI), are mainly $\cdot \mathrm{O_2^-}$ and $\cdot \mathrm{OH}$ in the presence of UV-Vis irradiation rather than the photolysis of nitrate.

C_3H_6 also had a distinct suppressing effect on ~~the~~ sulfate formation. Similar ~~as~~to NO_2, C_3H_6 will react with ~~the~~ surface ROS.

$$\mathrm{C_3H_6} \xrightarrow{\cdot OH} \mathrm{RCHO} \xrightarrow{\cdot OH} \mathrm{RCOOH} \xrightarrow{\cdot OH} CO_2 + H_2O \qquad (17)$$

where R represents H or an alkyl group. These gaseous products in the photo-oxidation of C_3H_6 ~~seems not~~do not seem to block surface reactive sites, which can explain why the pre-adsorption of C_3H_6 on TiO_2 did not show an obvious suppressing effect on the formation of sulfate in the step-by-step experiment.

When C_3H_6 + NO_2 were introduced simultaneously into the reaction system together with SO_2, both ~~will~~ competed for ROS with SO_2 and therefore resulted in the ~~least amount~~lowest formation of sulfate ~~in~~among the heterogeneous reactions. Besides, in the step-by-step experiments, the pre-adsorption of C_3H_6+NO_2 on TiO_2 suppressed sulfate formation significantly, which indicated that lots of reactive sites for SO_2 oxidation might be blocked by these oxidation products in ~~the~~ pre-adsorption with UV-Vis irradiation. Karagulian et al. (Karagulian et al., 2009) found that nitrite can induce the photo-oxidation of VOCs on airborne particles and produce organic nitrates and carbonyl compounds. Thus, the formation of organic nitrates may be an important factor to suppress the formation of sulfate due to the blocking effect.

~~4~~ 5 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 conditions close to those in the real atmosphere. Under dark conditions at 303 K, ~~only a few monodentate sulfite species formed.~~ SO_2 could hardly react on the particle surface and only a few ~~except for weak adsorption as~~ sulfite-like species formed. With reaction time increasing, the adsorption sites on the surface became saturated with sulfite 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~~Coexisting NO_2 ~~canould~~could enhance the heterogeneous formation of sulfate with ~~pollutants at close to ambient~~much lower concentrations (200 ppb) relative to previous studies (~100 ppm) (Ma et al., 2008;Liu et al., 2012;Zhao et al., 2018). 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~~because C_3H_6 could react ~~ompetes with SO_2 for~~ ROS generated ~~or surface active sites on TiO_2 with the coexistence of~~in the adsorption of NO_2.

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~~ the ROS such as $\cdot OH$~~OH~~ and $\cdot O_2^-$ ~~can~~ could ~~then~~ initiate photocatalytic ~~reactions,~~ oxidation~~ize~~ of S(IV) species ~~and result in much more~~to sulfate ~~formation~~. Sulfate formation was suppressed significantly with the coexistence of NO_2 and/or C_3H_6 in ~~experiments with~~the presence of ~~UV~~UV-Vis light~~, although individual C_3H_6 has little effect on sulfate formation~~. The formation of nitrate, carbonyl compounds, and organic nitrate consumed both~~due to the competition~~ available ROS ~~for~~ and 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. However, after about 2 hours of reaction, sulfate formation on TiO_2 pre-saturated with NO_2 became comparable with the experiment with SO_2 and NO_2 together. These results indicated that C_3H_6 mainly competes with SO_2 for ROS on the surface, while NO_2 mainly 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~~the co-exist~~ed~~ing inorganic and organic gas pollutants under complex pollution conditions due to the competition for ROS and active surface sites among them ~~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). When a VOC and SO_2 coexist~~ed~~, ~~The~~ the competition for ROS and surface reactive sites between the~~se~~ VOC~~s~~ and SO_2 is likely to suppress sulfate formation in the heterogeneous reactions~~.~~, such as that observed for the presence of CH_3CHO on α-Fe_2O_3 in dark experiments (Zhao et al., 2015), the presence of C_7H_{16} on TiO_2 with UV-Vis irradiation (Du et al., 2000), and the presence of C_3H_6 on TiO_2 under dark condition or with UV-Vis irradiation in this study. Due to the different properties of the oxidation products, the influence of coexisting VOCs might be different for different VOC species and on different ~~the~~ mineral dusts. Some coexist~~ed~~ing VOCs, such as HCOOH on α-Fe_2O_3 (Wu et al., 2013), and HCHO in aerosol water (Moch et al., 2018;Song et al., 2019) might enhance sulfate formation. These 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, the kinetics of the heterogeneous oxidation of SO_2 must be developed with consideration of the influence of coexisting VOCs and other inorganic gases.

Author contributions

QM, BC and HH designed the study. YW, WY and BC carried out the experiments. BC, WY, JM, and QM ~~analysed~~ analyzed 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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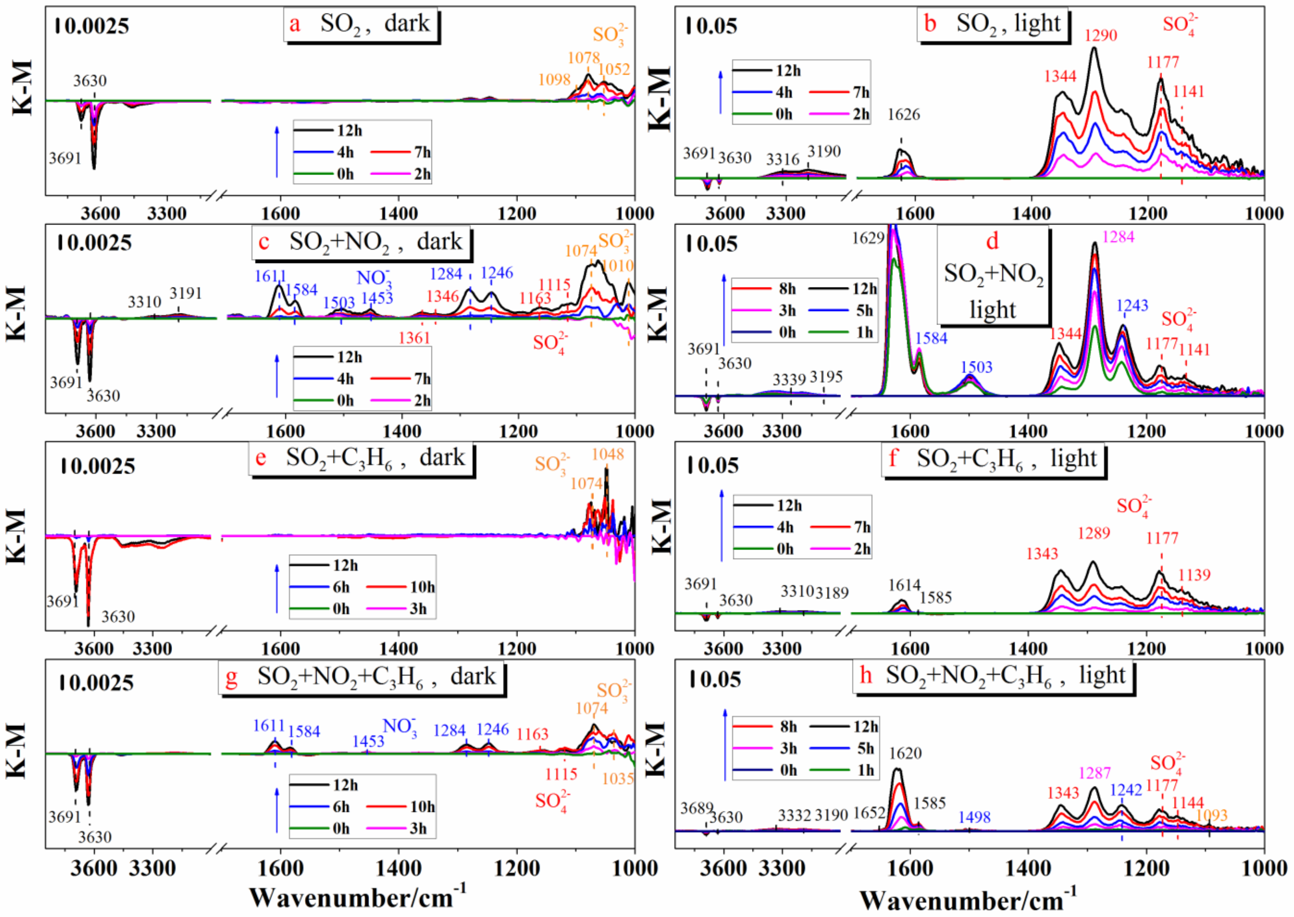
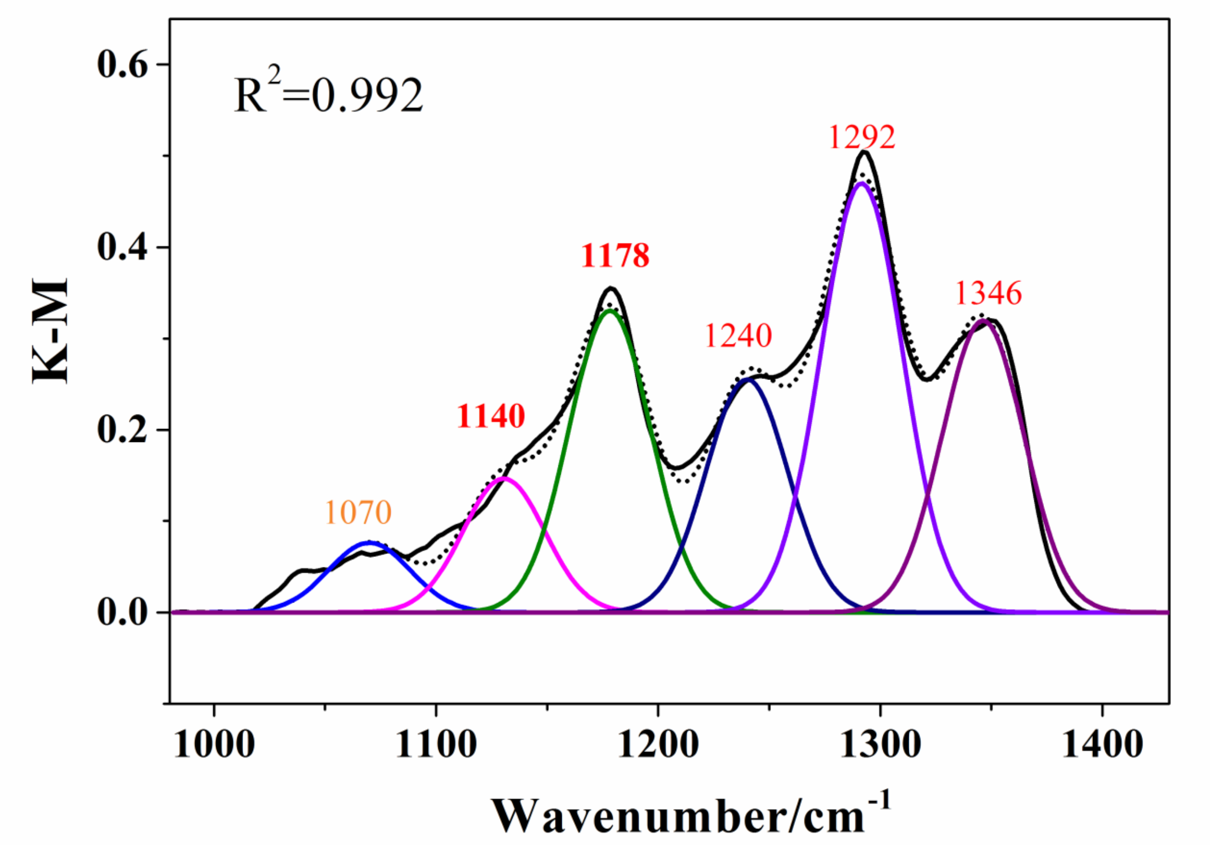


Figure 1: Dynamic changes in the *in situ* DRIFTS spectra of the TiO$_2$ sample as a function of time at 303K in a flow of 20% O$_2$ + 80% N$_2$ with 200 ppb SO$_2$ under dark conditions (a) and with ~~UV~~UV-Vis light (b); with 200 ppb SO$_2$ + 200 ppb NO$_2$ under dark conditions (c) or with ~~UV~~UV-Vis light (d); with 200 ppb SO$_2$ + 200 ppb C$_3$H$_6$ under dark conditions (e) or with ~~UV~~UV-Vis light (f); with 200 ppb SO$_2$ + 200 ppb NO$_2$+ 200 ppb C$_3$H$_6$ + under dark conditions (g) or with ~~UV~~UV-Vis 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).~~

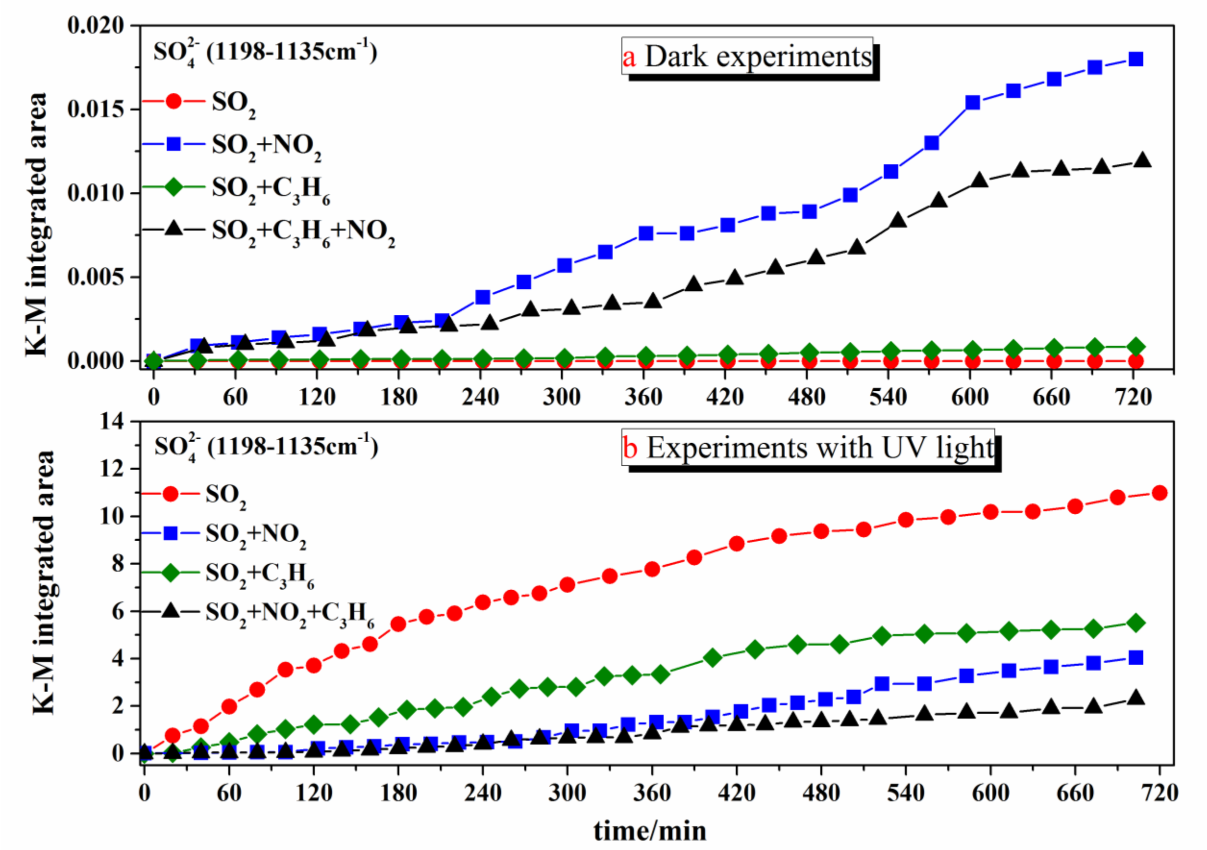


Figure 2~~3~~: Integrated absorbance of the sulfate band (1198-1135 cm^{-1}) observed during the reaction of 200 ppb SO_2, 200 ppb SO_2+200 ppb NO_2, 200 ppb SO_2+200 ppb C_3H_6, 200 ppb SO_2+200 ppb NO_2+200 ppb C_3H_6 in dark experiments (a) and experiments with ~~UV~~UV-Vis light (b).

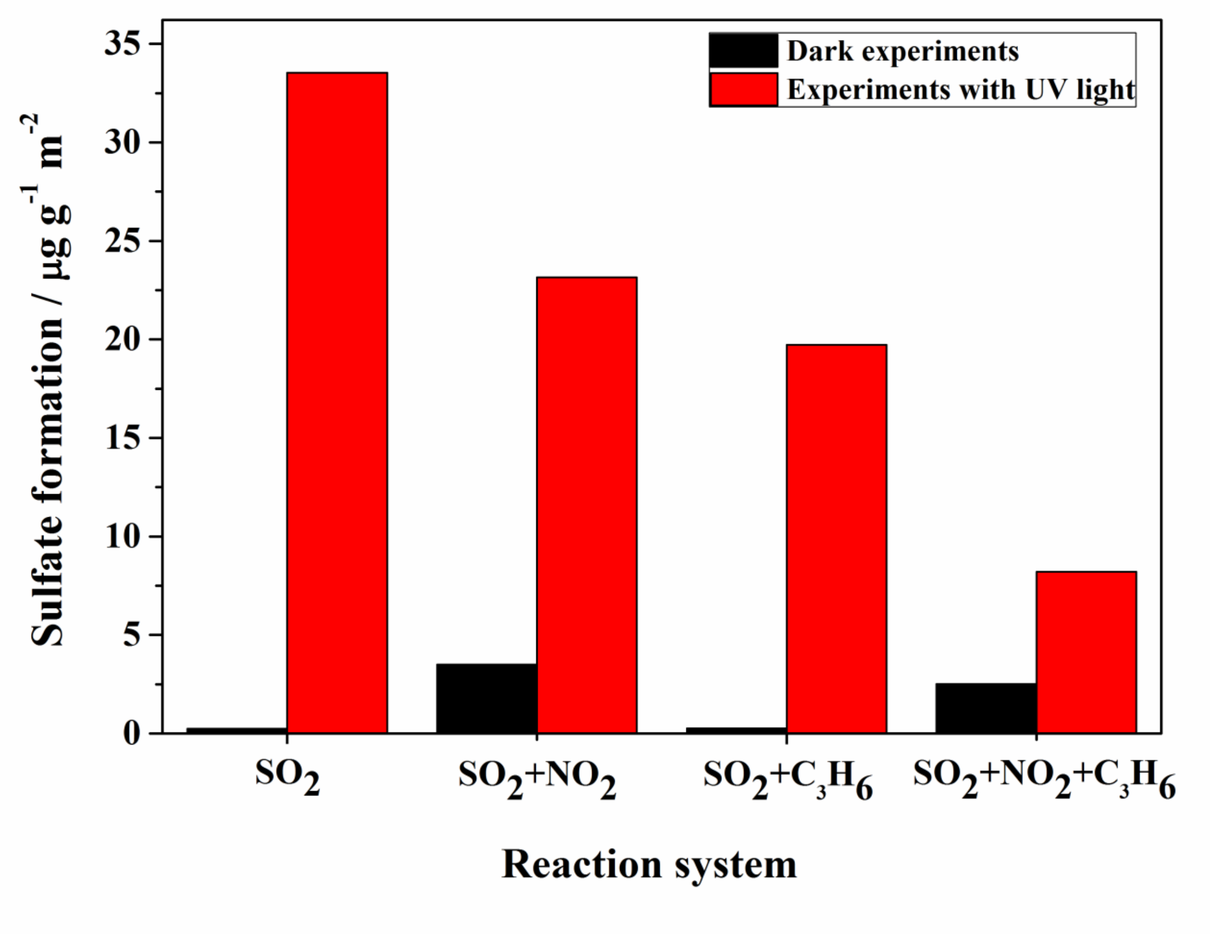


Figure 3~~4~~: Ion chromatography results of the amounts of sulfate (product per unit mass/surface area of sample) formed on the surface of TiO_2 after reaction with SO_2, SO_2+NO_2, SO_2+C_3H_6 and SO_2+C_3H_6+NO_2 in experiments under dark conditions or with ~~UV~~UV-Vis light. Since formaldehyde was added to inhibit the oxidation of sulfite to sulfate in the solution, there is a possibility that HMS would be generated in the solution and be measured as sulfate.

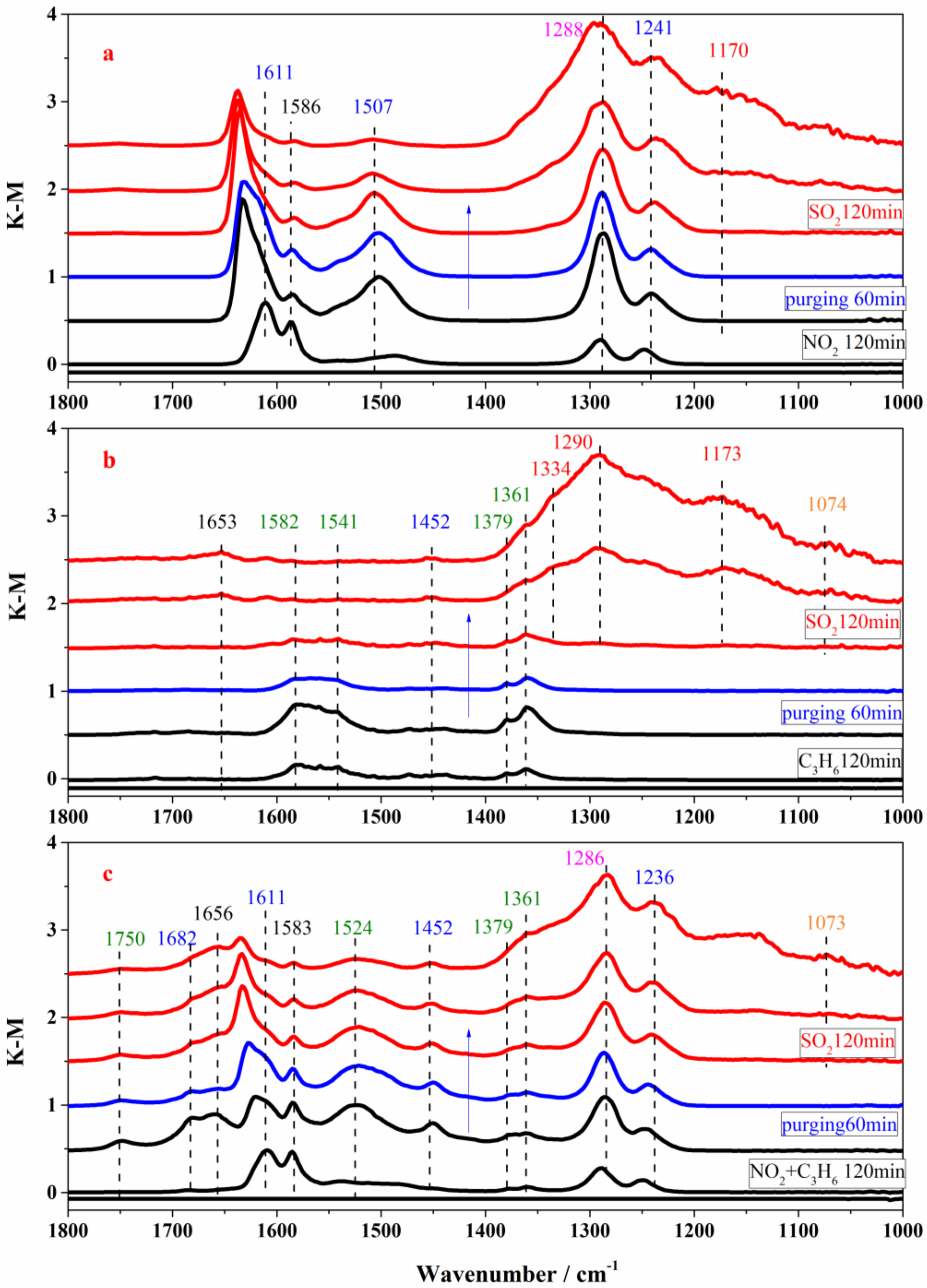


Figure 4~~5~~: ***In situ*** **DRIFTS spectra of surface products on TiO_2 in the step-by-step exposure experiments with irradiation: (a) exposure to 200 ppm NO_2 for 2 h (black lines), after purging 1 h (blue line), and then to 200 ppm SO_2 for 2 h (red lines); (b) exposure to 200 ppm C_3H_6 for 2 h (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).**

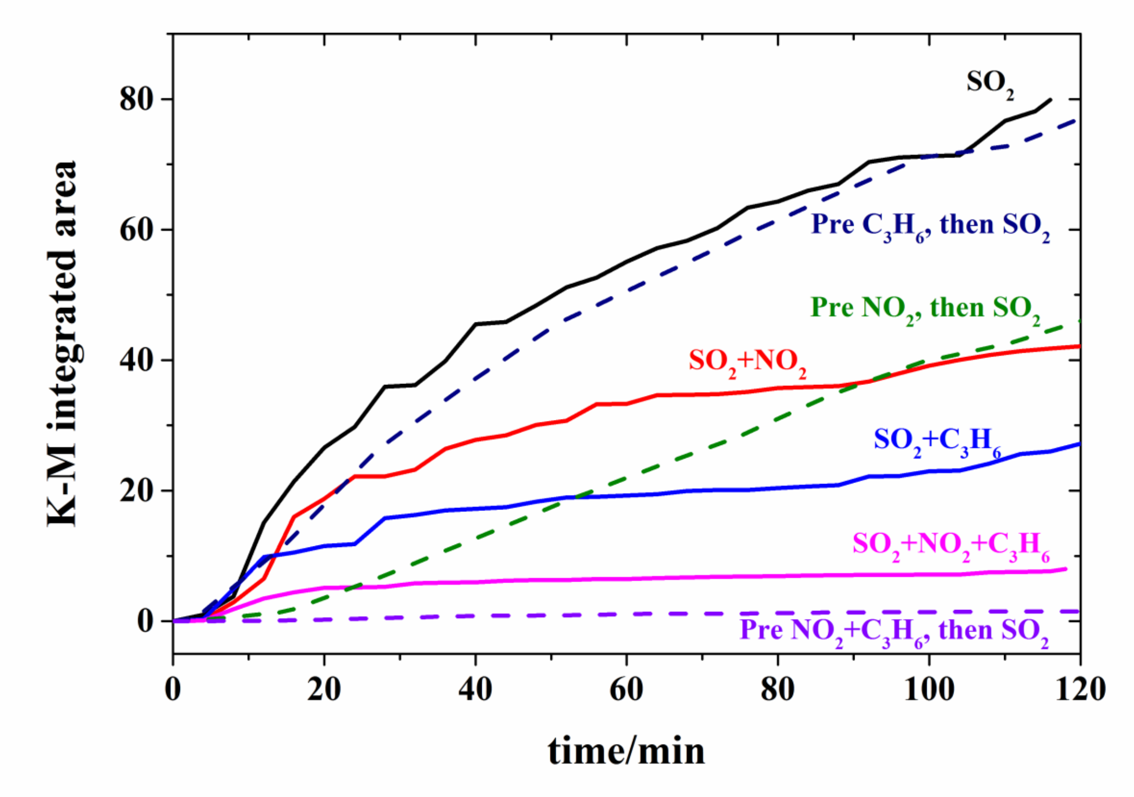


Figure 5~~6~~: Integrated absorbance of the sulfate band (1168 cm^{-1}) for the illuminated reactions with ~~UV~~UV-Vis lights of 200 ppm SO_2 (black, solid), 200 ppm SO_2 on a 200 ppm C_3H_6-presaturated surface (blue, dashed), 200 ppm SO_2+200 ppm NO_2 (red, solid), 200 ppm SO_2 on a 200 ppm NO_2-presaturated surface (green, dashed), 200 ppm SO_2+200 ppm C_3H_6 (blue, solid), 200 ppm SO_2+200 ppm NO_2+200 ppm C_3H_6 (pink, solid), and 200 ppm SO_2 on a 200 ppm NO_2+200 ppm C_3H_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., 2012)
$S0_4^{2-}$	state of aggregation	1344	(Nanayakkara et al., 2012)
	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)