

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

Title: “Effects of NO₂ and C₃H₆ on the heterogeneous oxidation of SO₂ on TiO₂ 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

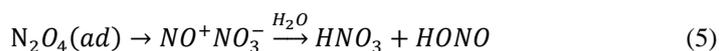
This manuscript describes a set of experiments looking at the effects of UV radiation, NO₂, and C₃H₆ on heterogeneous SO₂ oxidation. The authors demonstrate that on TiO₂ aerosols the presence of NO₂ alone or NO₂ and C₃H₆ can suppress sulfate formation when in the presence of UV light. The authors also 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 NO₂ 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 NO₂ 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 SO₂ to sulfite (S(IV)) on the surface. It has been demonstrated that coexisting NO₂ 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 N₂O₄, 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).

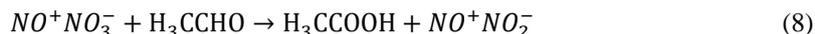
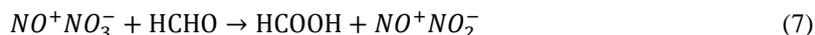
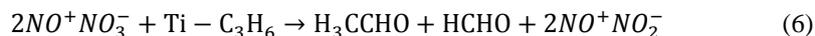


Besides N₂O₄, NO₂ may also react directly with surface OH and form HNO₃ on TiO₂ (Liu et al., 2017a). The HNO₃ generated through this pathway may also contribute to the oxidation of S(IV) to S(VI). It has also been proposed that aqueous oxidation of SO₂ by NO₂ (as an oxidizing agent) contributed to significant 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 C₃H₆ inhibited heterogeneous sulfate formation with NO₂ by competing with SO₂ for reactive oxygen species or active sites on the aerosol, we added the following discussions.

Page 10, Line 7-15:

“When C₃H₆ was introduced together with NO₂, sulfate formation was less than that in the reaction of SO₂+NO₂, probably due to the reaction between C₃H₆ and the reactive nitrogen species. The detailed mechanism was not explored in this study. The following reactions may take place in this process.



Heterogeneous reactions between NO₂ 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 TiO₂, 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, α -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 SiO₂ for the heterogeneous reaction of NO₂, while Fe₂O₃, with its unique Fe²⁺/Fe³⁺ redox chemistry, favors the formation of SO₄²⁻ and the heterogeneous conversion of NO₂. 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 SO₂ 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 NO₂ and C₃H₆ on the heterogeneous oxidation in the presence or absence of UV irradiation, we chose TiO₂ since it is a semiconductor material and a well-known photocatalyst, although it is less abundant than CaO, Fe₂O₃ or MgO in the atmosphere. TiO₂ 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 TiO₂ 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 NO_x enhance SO₂ oxidation on different mineral dusts (He et al., 2014), we anticipate the effects of coexisting of NO₂ and C₃H₆ might be ubiquitous; while for the UV experiments, we anticipate the effects of NO₂ and C₃H₆ 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 NO₂ and C₃H₆ on the heterogeneous oxidation in a relatively complex oxidation system (with coexistence of multiple gases, in both dark and illuminated conditions), we chose TiO₂ due to the fact that it is a semiconductor material and a well-known photocatalyst. TiO₂ has been widely reported to be present in airborne particulate matter (PM) (Chen et al., 2012), Although TiO₂ represents only a relatively small portion of the mass of PM and is less abundant than CaO, Fe₂O₃ or MgO, the TiO₂ 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 TiO₂ 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. NO₂ oxidized SO₂ as an oxidizing agent happened under specified conditions, such as in aqueous phase and in the presence of NH₃ that the pH is not very low. This reaction should not be significant since our experiments were carried out under dry condition. Since NO₂ also transformed to nitrate in the reaction itself and there was competition between NO₂ and SO₂ for surface active sites, it was not easy to demonstrate the role of NO₂ from how it changes.

Page 7, Line 21-24:

ADD “It has also been proposed that aqueous oxidation of SO₂ by NO₂ (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 SO₂ under various conditions, it is not fully understood how the heterogeneous oxidation of SO₂ is influenced by co-existing pollutants under dark or illumination conditions. Meanwhile, the interactions between organic and inorganic species in the heterogeneous oxidation of SO₂ at low concentrations have not been deeply researched yet. In this study, we focus on the effects of co-existing NO₂ and propene at low concentrations (200 ppb) on the heterogeneous oxidation of SO₂ on TiO₂ with *in situ* DRIFTS under both dark and illumination conditions.”

WERE CHANGED TO:

“Despite these studies involving the heterogeneous oxidation of SO₂ under various conditions, the effects of co-existing pollutants on the heterogeneous oxidation of SO₂ 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 NO₂ and propene (C₃H₆) on the heterogeneous oxidation of SO₂ on TiO₂ 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 SO₂, NO_x, and VOCs as well as mineral dust exist in the atmosphere at the same time.”

WERE CHANGED TO:

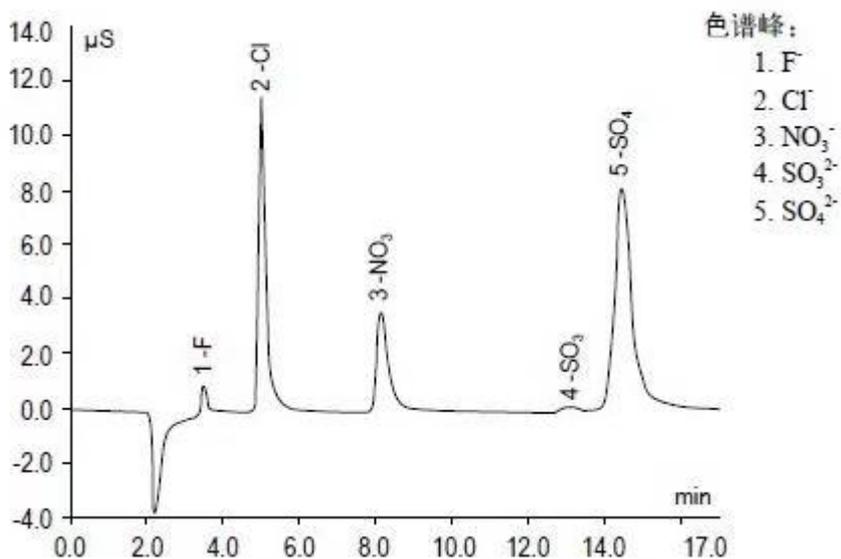
“Rather than UV lights, a xenon light is used in this study to better simulate the solar ultraviolet radiation on the earth’s surface. Generally, our study could be helpful for gaining a better understanding of the heterogeneous formation of sulfate under complex air pollution conditions, in which abundant SO₂, 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. CH₂O was observed when the surface was exposed to NO₂ and C₃H₆, 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 NO₂ on the heterogeneous oxidation of SO₂ under dark conditions and the inhibiting effect of NO₂ and C₃H₆ on heterogeneous photooxidation of SO₂.”

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 NO₂ and C₃H₆, 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 SO₂ under different gas conditions, the TiO₂ 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 SO₂, 200 ppb NO₂ and 200 ppb C₃H₆, 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 NO₂ and C₃H₆ on the heterogeneous oxidation of SO₂ 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 NO₂, C₃H₆, or both for 2 h, then flushing with air for 1 h, and finally exposing them to SO₂ 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 SO₂ and NO₂ 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 SO₂ and NO₂ being used in this study.”

Page 11, Line 28-29:

“It was found that the presence of NO₂ could enhance the heterogeneous formation of sulfate with pollutants at close to ambient concentrations”

WERE CHANGED TO:

“Coexisting NO₂ 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 SO₂ oxidized by O₂ and catalyzed by NO₂. To avoid confusing, we modified these sentences in the revised manuscript.

Page 2, Line 18:

“Therefore, NO₂ was proposed to act as an catalyst to activate O₂ in the oxidation”

WERE CHANGED TO:

“Therefore, NO₂ was proposed to act as a catalyst in the oxidation of SO₂ by O₂”

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 SO₃²⁻ and generate hydroxymethanesulfonate (HMS) in the northern China winter haze period (Moch et al., 2018; Song et al., 2019).”

Response for Reviewer #2

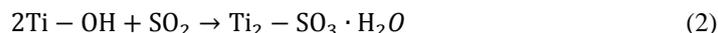
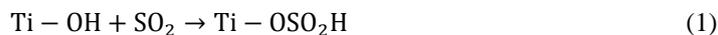
Chu et al. reported the effect of NO₂ and C₃H₆ on the heterogeneous oxidation of SO₂ into sulfate on TiO₂ particles. Under dark conditions, the presence of NO₂ generally enhanced the SO₂ oxidation, whereas C₃H₆ had little influence. In contrast, the presence of NO₂ and/or C₃H₆ suppressed the sulfate 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.

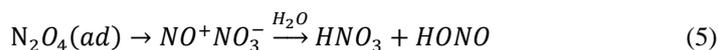
Page 9- Page 11:

“4.1 Dark reactions

The heterogeneous oxidation of SO₂ on TiO₂ has been investigated by many previous studies. The following mechanisms for SO₂ adsorption on TiO₂ surfaces have been proposed in previous studies (Nanayakkara et al., 2012):

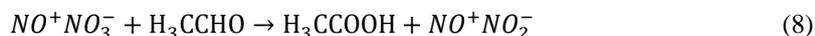
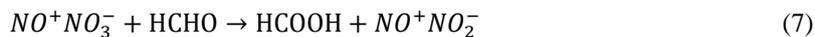
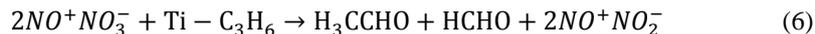


These adsorption processes result in the conversion of SO₂ to sulfite (S(IV)) on the surface. It has been demonstrated that coexisting NO₂ can induce the generation of some ROS, which oxidize S(IV) to S(VI) on mineral oxides (Ma et al., 2008;Liu et al., 2012;Ma et al., 2017). There were several possible responsible ROS proposed in previous studies, although the detailed mechanism has not yet been fully explored. One possible ROS is N₂O₄, 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).



Besides N₂O₄, NO₂ may also react directly with surface OH and form HNO₃ on TiO₂ (Liu et al., 2017a). The HNO₃ 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 SO₂ by NO₂ (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).

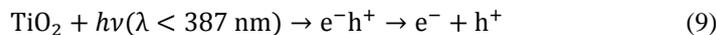
When C₃H₆ was introduced together with NO₂, sulfate formation was less than that in the reaction of SO₂+NO₂, probably due to the reaction between C₃H₆ and the reactive nitrogen species. The detailed mechanism was not explored in this study. The following reactions may take place in this process.



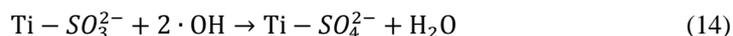
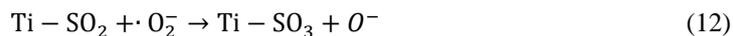
Heterogeneous reactions between NO₂ and organics can also lead to nitro-organics on hexane soot (Kwamena and Abbatt, 2008;Al-Abadleh and Grassian, 2000), which may also occur on the surface of TiO₂, and these products blocked some reactive sites for sulfate formation.

4.2 Light reactions

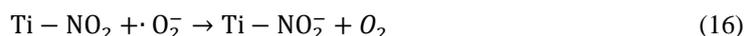
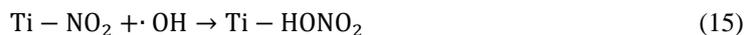
With UV illumination, TiO₂ can be excited by UV light ($\lambda < 387$ nm), then the photogenerated electrons and holes can react with H₂O and O₂ to produce additional ROS (primarily $\cdot O_2^-$ and $\cdot OH$), and oxidize more SO₂ to sulfate on TiO₂ than that produced under dark conditions (Shang et al., 2010a; Chen et al., 2012). The detailed mechanism was summarized by Chen et al. (Chen et al., 2012) and references therein:



Then the SO₂ can react with these ROS and promote the formation of sulfate (Shang et al., 2010b):

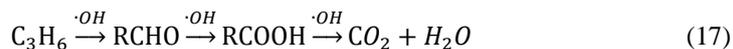


In the UV-Vis irradiation experiments, NO₂ had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO₂. Rather than resulting in ROS formation and oxidation of S(IV) to S(VI) in dark experiments, the main reaction of NO₂ with the surface ROS resulted in nitrate formation in experiments with UV-Vis irradiation (Ndour et al., 2008; Yu and Jang, 2018).



The nitrate or nitrite generated from the oxidation of NO₂ might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO₂ on TiO₂ also suppressed the formation of sulfate and resulted in similar sulfate formation to that in the experiment introducing NO₂ and SO₂ simultaneously. The competition between SO₂ and NO₂ for surface reactive sites might be the main reason for the fact that the coexistence of NO₂ with SO₂ 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 $\cdot O_2^-$ and $\cdot OH$ in the presence of UV-Vis irradiation rather than the photolysis of nitrate.

C₃H₆ also had a distinct suppressing effect on sulfate formation. Similar to NO₂, C₃H₆ will react with surface ROS.



where R represents H or an alkyl group. These gaseous products in the photo-oxidation of C₃H₆ do not seem to block surface reactive sites, which can explain why the pre-adsorption of C₃H₆ on TiO₂ did not show an obvious suppressing effect on the formation of sulfate in the step-by-step experiment.

When C₃H₆ + NO₂ were introduced simultaneously into the reaction system together with SO₂, both competed for ROS with SO₂ and therefore resulted in the lowest formation of sulfate among the heterogeneous reactions. Besides, in the step-by-step experiments, the pre-adsorption of C₃H₆+NO₂ on TiO₂ suppressed sulfate formation significantly, which

indicated that lots of reactive sites for SO₂ 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 NO₂ and C₃H₆ on the heterogeneous oxidation in the presence or absence of UV-Vis irradiation, we chose TiO₂ due to the fact that it is a semiconductor material and a well-known photocatalyst. The present study investigate the heterogeneous oxidation of SO₂ on TiO₂, 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 NO₂ and C₃H₆ on the heterogeneous oxidation in a relatively complex oxidation system (with coexistence of multiple gases, in both dark and illuminated conditions), we chose TiO₂ due to the fact that it is a semiconductor material and a well-known photocatalyst. TiO₂ has been widely reported to be present in airborne particulate matter (PM) (Chen et al., 2012), Although TiO₂ represents only a relatively small portion of the mass of PM and is less abundant than CaO, Fe₂O₃ or MgO, the TiO₂ 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 TiO₂ 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 SO₂ and NO₂ 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 SO₂ and NO₂ being used in this study.”

Page 11, Line 28-29:

“It was found that the presence of NO₂ could enhance the heterogeneous formation of sulfate with pollutants at close to ambient concentrations”

WERE CHANGED TO:

“Coexisting NO₂ 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 SO₂ under various conditions, it is not fully understood how the heterogeneous oxidation of SO₂ is influenced by co-existing pollutants under dark or illumination conditions. Meanwhile, the interactions between organic and inorganic species in the heterogeneous oxidation of SO₂ at low concentrations have not been deeply researched yet. In this study, we focus on the effects of co-existing NO₂ and propene at low concentrations (200 ppb) on the heterogeneous oxidation of SO₂ on TiO₂ with *in situ* DRIFTS under both dark and illumination conditions.”

WERE CHANGED TO:

“Despite these studies involving the heterogeneous oxidation of SO₂ under various conditions, the effects of co-existing pollutants on the heterogeneous oxidation of SO₂ 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 NO₂ and propene (C₃H₆) on the heterogeneous oxidation of SO₂ on TiO₂ 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 SO₂, 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 SO₂, 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:

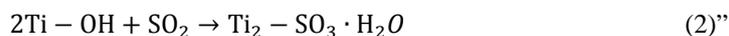
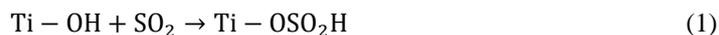
“These negative peaks indicated that some SO_2 was absorbed on the surface hydroxyls, and were observed in all the reaction systems in this study, as shown in Fig. 1.”

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:

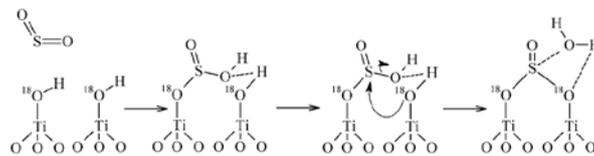
ADD: “The heterogeneous oxidation of SO_2 on TiO_2 has been investigated by many previous studies. The following mechanisms for SO_2 adsorption on TiO_2 surfaces have been proposed in previous studies (Nanayakkara et al., 2012):



For the comparison of experiments with SO_2 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, $\text{HSO}_3^- + \text{O}^- + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + \text{e}^-$, as proposed by Zhang et al. (Zhang et al., 2006).



Scheme 1 Reaction of SO₂ 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:

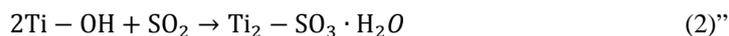
“Surface water may be formed in the photochemical reaction or via enhanced adsorption of water due to the increased hygroscopicity induced by sulfate (Ma et al., 2019).”

WERE CHANGED TO:

“Surface water can be formed in the heterogeneous reaction of SO₂ (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 SO₂ on TiO₂ has been investigated by many previous studies. The following mechanisms for SO₂ adsorption on TiO₂ surfaces have been proposed in previous studies (Nanayakkara et al., 2012):



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 SO₂ into sulfate. With UV illumination, TiO₂ can be excited by UV light ($\lambda < 387$ nm), resulting in additional ROS (primarily O₂⁻ and OH), and oxidize more SO₂ to sulfate on TiO₂ 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:

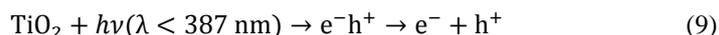
ADD: “With UV-Vis illumination, TiO₂ can be excited by UV light ($\lambda < 387$ nm), then the photogenerated electrons and holes can react with H₂O and O₂ to produce additional ROS (primarily $\cdot O_2^-$ and $\cdot OH$), and oxidize more SO₂ to sulfate on TiO₂ than that produced under dark conditions (Shang et al., 2010a;Chen et al., 2012).”

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

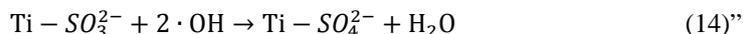
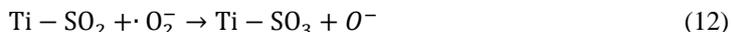
DELETE “Compared with the reaction under dark conditions, i.e. Fig.1 (a), sulfate species rather than sulfite species were generated, indicating a different mechanism for the formation of sulfate with UV irradiation.”

Page 10, Line 18-28:

ADD: “With UV illumination, TiO₂ can be excited by UV light ($\lambda < 387$ nm), then the photogenerated electrons and holes can react with H₂O and O₂ to produce additional ROS (primarily $\cdot O_2^-$ and $\cdot OH$), and oxidize more SO₂ to sulfate on TiO₂ 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:



Then the SO₂ can react with these ROS and promote the formation of sulfate (Shang et al., 2010b):



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 NO₂, 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 SO₂+NO₂ system is less than that of SO₂ 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:

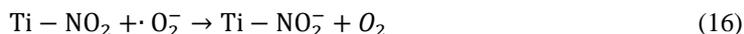
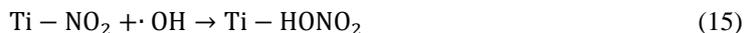
“Compared to the dark experiment of SO₂ and NO₂ in Fig 1(c), more sulfate species were generated with UV irradiation, which is consistent with the fact that UV irradiation significantly promotes sulfate formation in the reaction of SO₂ alone. Also, compared with the spectra of TiO₂ exposed to only SO₂ with UV irradiation, the bands of sulfate species decreased in intensity in the presence of NO₂. The effect of NO₂ on sulfate formation with UV irradiation was opposite to that under dark conditions.”

WERE CHANGED TO:

“Compared to the dark experiment of SO₂ and NO₂ 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 SO₂ alone.”

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

ADD: “In the UV-Vis irradiation experiments, NO₂ had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO₂. Rather than resulting in ROS formation and oxidation of S(IV) to S(VI) in dark experiments, the main reaction of NO₂ with the surface ROS resulted in nitrate formation in experiments with UV-Vis irradiation (Ndour et al., 2008;Yu and Jang, 2018).



The nitrate or nitrite generated from the oxidation of NO₂ might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO₂ on TiO₂ also suppressed the formation of sulfate and resulted in similar sulfate formation to that in the experiment introducing NO₂ and SO₂ simultaneously. The competition between SO₂ and NO₂ for surface reactive sites might be the main reason for the fact that the coexistence of NO₂ with SO₂ 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 $\cdot \text{O}_2^-$ and $\cdot \text{OH}$ 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 NO₂ might block some surface reactive sites, and therefore, resulted in less sulfate formation in the reaction of SO₂+NO₂ than that of SO₂ 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 oxidize SO₂ in the earlier part of the manuscript.

Response: More discussion about the formation and their roles in oxidation of SO₂ were added in the revised manuscript.

Page 5, Line 26-29:

“TiO₂ can be excited by UV light ($\lambda < 387$ nm), resulting in active species (primarily O₂⁻ and OH) that can participate in atmospheric photochemical reactions (Chen et al., 2012).”

WERE CHANGED TO:

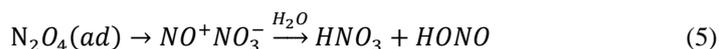
“With UV-Vis illumination, TiO₂ can be excited by UV light ($\lambda < 387$ nm), then the photogenerated electrons and holes can react with H₂O and O₂ to produce additional ROS (primarily \cdot O₂⁻ and \cdot OH), and oxidize more SO₂ to sulfate on TiO₂ than that produced under dark conditions (Shang et al., 2010a;Chen et al., 2012).”

Page 7, Line 19-24:

ADD: “The presence of NO₂ seemed to induce the generation of some ROS, which oxidize S(IV) to S(VI) on TiO₂ (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 SO₂ by NO₂ (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 NO₂ 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 N₂O₄, 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).



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 $\text{NO}_2 + \text{C}_3\text{H}_6$.”

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 SO₂ 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 SO₂ 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.

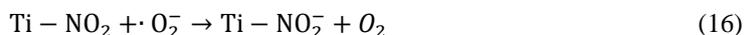
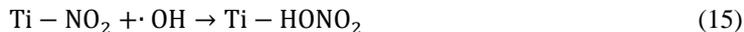
Response: We agree with the reviewer that NO₂ mainly compete with SO₂ for the surface active sites according to the experiments result. In the step-by-step (NO₂ first and then SO₂) reaction, sulfate formation was less than that in the reaction of NO₂+SO₂, while in the later reaction time becomes comparable to that in the reaction of NO₂+SO₂, indicating that NO₂ mainly compete with SO₂ for the surface active sites and resulted in less sulfate formation compare to the reaction of SO₂ alone with the presence of UV-Vis irradiation which resulted in continuous production of ROS on TiO₂ 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 C₃H₆ and then flushing had no significant influence on sulfate formation in the heterogeneous photooxidation of SO₂, while presaturation with NO₂ and then flushing suppressed sulfate formation. These results indicated that C₃H₆ mainly competes with SO₂ for ROS on the surface, while NO₂ competes with SO₂ for both surface active sites and ROS. The coexistence of NO₂ and C₃H₆ seemed to lead to more organics formation on the surface of TiO₂ 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, NO₂ had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO₂. Rather than resulting in ROS formation and oxidation of S(IV) to S(VI) in dark experiments, the main reaction of NO₂ with the surface ROS resulted in nitrate formation in experiments with UV-Vis irradiation (Ndour et al., 2008; Yu and Jang, 2018).



The nitrate or nitrite generated from the oxidation of NO₂ might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO₂ on TiO₂ also suppressed the formation of sulfate and resulted in similar sulfate formation to that in the experiment introducing NO₂ and SO₂ simultaneously. The competition between SO₂ and NO₂ for

surface reactive sites might be the main reason for the fact that the coexistence of NO₂ with SO₂ 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 SO₂ 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 SO₂ 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 SO₂.”

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 SO₂, 200 ppb NO₂ and 200 ppb C₃H₆, 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 SO₂ on TiO₂”

ADD” 200 ppb SO₂ and 200 ppb NO₂”

ADD” 200 ppb SO₂ and 200 ppb NO₂”

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

Response: Thanks for pointing out. “NO₂” was REVISED to “C₃H₆”.

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 HO_x 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:

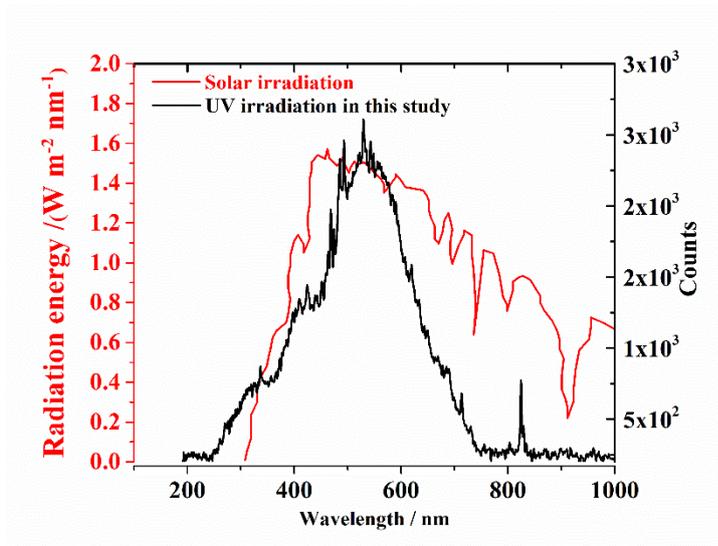
ADD: “The temperature was 303 K and the relative humidity was less than 1% in all experiments.”

(2) UV.

In the manuscript, we mentioned that “The intensity of UV irradiation was measured as $478 \mu\text{W cm}^{-2}$ ”, 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:

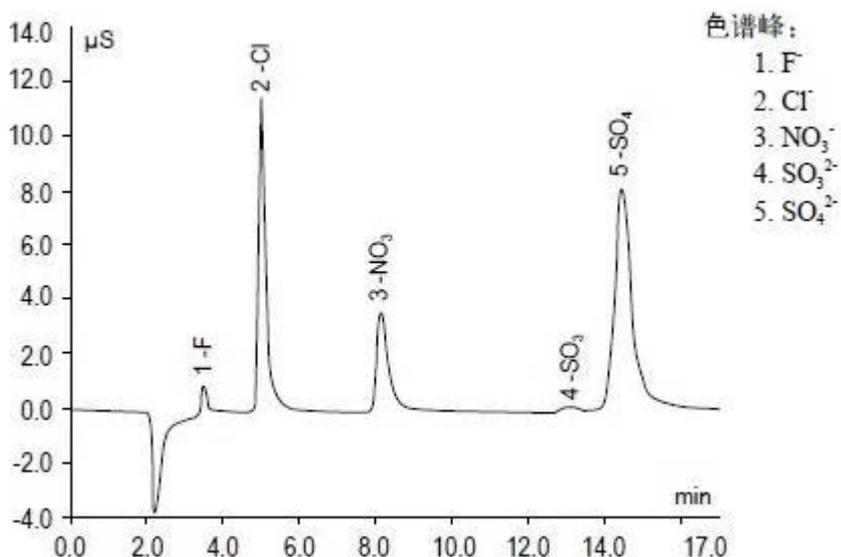
ADD “The wavelengths of the UV-Vis irradiation were measured to be in the range of 250-850 nm by a fiber optic spectrometer (BLUE-Wave-UVNb, Stellar Net Inc., USA), as shown in Fig. S1 in the Supplemental Information. The spectrum of the UV-Vis irradiation is comparable to the spectrum of solar irradiation 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. CH₂O was observed when the surface was exposed to NO₂ and C₃H₆, 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 NO₂ on the heterogeneous oxidation of SO₂ under dark conditions and the inhibiting effect of NO₂ and C₃H₆ on heterogeneous photooxidation of SO₂.”

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 NO₂ and C₃H₆, 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) TiO₂ and C₃H₆

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 SiO₂ for the heterogeneous reaction of NO₂, while Fe₂O₃, with its unique Fe²⁺/Fe³⁺ redox chemistry, favors the formation of SO₄²⁻ and the heterogeneous conversion of NO₂. 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 SO₂ 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 NO₂ and C₃H₆ on the heterogeneous oxidation in the presence or absence of UV irradiation, we chose TiO₂ due to the fact that it is a semiconductor material and a well-known photocatalyst, although it is less abundant than CaO, Fe₂O₃ 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 NO_x enhance SO₂ oxidation on different mineral dusts (He et al., 2014), we anticipate the effects of coexisting of NO₂ and C₃H₆ might be ubiquitous; while for the UV experiments, we anticipate the effects of NO₂ and C₃H₆ 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 NO₂ and C₃H₆ on the heterogeneous oxidation in a relatively complex oxidation system (with coexistence of multiple gases, in both dark and illuminated conditions), we chose TiO₂ due to the fact that it is a semiconductor material and a well-known photocatalyst. TiO₂ has been widely reported to be present in airborne particulate matter (PM) (Chen et al., 2012), Although TiO₂ represents only a relatively small portion of the mass of PM and is less abundant than CaO, Fe₂O₃ or MgO, the TiO₂ 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 TiO₂ 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:

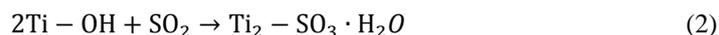
“To investigate heterogeneous sulfate formation in complex atmospheric pollution, *in situ* DRIFTS was used to analyze the products on particle surfaces in the reactions under different conditions. Two series of *in situ* DRIFTS experiments were carried out in this study. For the heterogeneous reaction of SO₂ under different gas conditions, the TiO₂ 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 SO₂, 200 ppb NO₂ and 200 ppb C₃H₆, 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 NO₂ and C₃H₆ on the heterogeneous oxidation of SO₂ 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 NO₂, C₃H₆, or both for 2 h, then flushing with air for 1 h, and finally exposing them to SO₂ for 2 h.”

Page 9- Page 11:

“4 Discussion

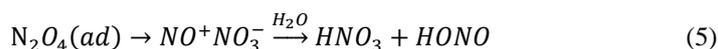
4.1 Dark reactions

The heterogeneous oxidation of SO₂ on TiO₂ has been investigated by many previous studies. The following mechanisms for SO₂ adsorption on TiO₂ surfaces have been proposed in previous studies (Nanayakkara et al., 2012):



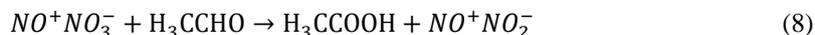
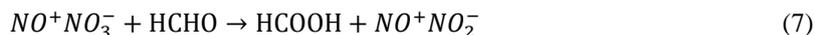
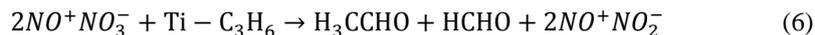


These adsorption processes result in the conversion of SO₂ to sulfite (S(IV)) on the surface. It has been demonstrated that coexisting NO₂ can induce the generation of some ROS, which oxidize S(IV) to S(VI) on mineral oxides (Ma et al., 2008;Liu et al., 2012;Ma et al., 2017). There were several possible responsible ROS proposed in previous studies, although the detailed mechanism has not yet been fully explored. One possible ROS is N₂O₄, 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).



Besides N₂O₄, NO₂ may also react directly with surface OH and form HNO₃ on TiO₂ (Liu et al., 2017a). The HNO₃ 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 SO₂ by NO₂ (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).

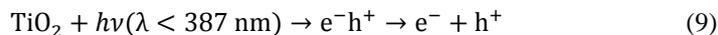
When C₃H₆ was introduced together with NO₂, sulfate formation was less than that in the reaction of SO₂+NO₂, probably due to the reaction between C₃H₆ and the reactive nitrogen species. The detailed mechanism was not explored in this study. The following reactions may take place in this process.



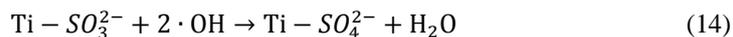
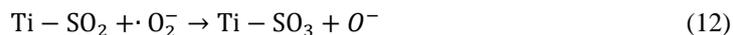
Heterogeneous reactions between NO₂ and organics can also lead to nitro-organics on hexane soot (Kwamena and Abbatt, 2008;Al-Abadleh and Grassian, 2000), which may also occur on the surface of TiO₂, and these products blocked some reactive sites for sulfate formation.

4.2 Light reactions

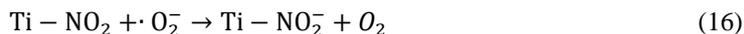
With UV illumination, TiO₂ can be excited by UV light ($\lambda < 387$ nm), then the photogenerated electrons and holes can react with H₂O and O₂ to produce additional ROS (primarily $\cdot\text{O}_2^-$ and $\cdot\text{OH}$), and oxidize more SO₂ to sulfate on TiO₂ than that produced under dark conditions (Shang et al., 2010a;Chen et al., 2012).The detailed mechanism was summarized by Chen et al. (Chen et al., 2012) and references therein:



Then the SO₂ can react with these ROS and promote the formation of sulfate (Shang et al., 2010b):

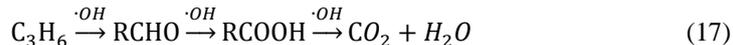


In the UV-Vis irradiation experiments, NO₂ had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO₂. Rather than resulting in ROS formation and oxidation of S(IV) to S(VI) in dark experiments, the main reaction of NO₂ with the surface ROS resulted in nitrate formation in experiments with UV-Vis irradiation (Ndour et al., 2008; Yu and Jang, 2018).



The nitrate or nitrite generated from the oxidation of NO₂ might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO₂ on TiO₂ also suppressed the formation of sulfate and resulted in similar sulfate formation to that in the experiment introducing NO₂ and SO₂ simultaneously. The competition between SO₂ and NO₂ for surface reactive sites might be the main reason for the fact that the coexistence of NO₂ with SO₂ 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 $\cdot \text{O}_2^-$ and $\cdot \text{OH}$ in the presence of UV-Vis irradiation rather than the photolysis of nitrate.

C₃H₆ also had a distinct suppressing effect on sulfate formation. Similar to NO₂, C₃H₆ will react with surface ROS.



where R represents H or an alkyl group. These gaseous products in the photo-oxidation of C₃H₆ do not seem to block surface reactive sites, which can explain why the pre-adsorption of C₃H₆ on TiO₂ did not show an obvious suppressing effect on the formation of sulfate in the step-by-step experiment.

When C₃H₆ + NO₂ were introduced simultaneously into the reaction system together with SO₂, both competed for ROS with SO₂ and therefore resulted in the lowest formation of sulfate among the heterogeneous reactions. Besides, in the step-by-step experiments, the pre-adsorption of C₃H₆+NO₂ on TiO₂ suppressed sulfate formation significantly, which indicated that lots of reactive sites for SO₂ 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?

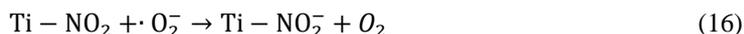
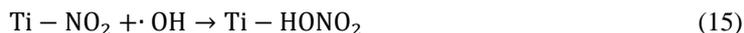
Response: As mentioned in the response of the second major comment, we added a separate discussion section to discuss the proposed mechanisms of sulfate formation and the competition for ROS and surface reactive sites. Some of the related discussion are listed below. Although we carried our step-to-step experiments and trying to better understand the competition for ROS and surface reactive sites, there is still uncertainty about these process. Take NO₂ as an example, in the step-by-step (NO₂ first and then SO₂) reaction, sulfate formation was less than that in the reaction of NO₂+SO₂, while in the later reaction time becomes comparable to that in the reaction of NO₂+SO₂, indicating that NO₂ maily compete with SO₂ for the surface active sites and resulted in less sulfate formation compare to the reaction of SO₂ alone with the presence of UV-Vis irradiation which resulted in continuous production of ROS on TiO₂ 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 C₃H₆ and then flushing had no significant influence on sulfate formation in the heterogeneous photooxidation of SO₂, while presaturation with NO₂ and then flushing suppressed sulfate formation. These results indicated that C₃H₆ mainly competes with SO₂ for ROS on the surface, while NO₂ competes with SO₂ for both surface active sites and ROS. The coexistence of NO₂ and C₃H₆ seemed to lead to more organics formation on the surface of TiO₂ 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, NO₂ had a distinct suppressing effect on the sulfate formation compared to the individual reaction of SO₂. Rather than resulting in ROS formation and oxidation of S(IV) to S(VI) in dark experiments, the main reaction of NO₂ with the surface ROS resulted in nitrate formation in experiments with UV-Vis irradiation (Ndour et al., 2008; Yu and Jang, 2018).

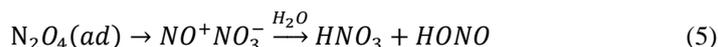


The nitrate or nitrite generated from the oxidation of NO₂ might block some surface reactive sites, since in the step-to-step experiments, the pre-adsorption of NO₂ on TiO₂ also suppressed the formation of sulfate and resulted in similar sulfate formation to that in the experiment introducing NO₂ and SO₂ simultaneously. The competition between SO₂ and NO₂ for surface reactive sites might be the main reason for the fact that the coexistence of NO₂ with SO₂ 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 $\cdot O_2^-$ and $\cdot OH$ 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).

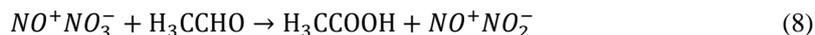
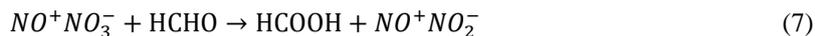
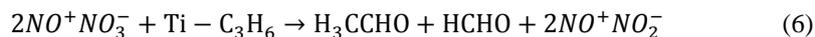


Besides N_2O_4 , NO_2 may also react directly with surface OH and form HNO_3 on TiO_2 (Liu et al., 2017a). The HNO_3 generated through this pathway may also contribute to the oxidation of S(IV) to S(VI). It has also been proposed that aqueous oxidation of SO_2 by NO_2 (as an oxidizing agent) contributed 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:

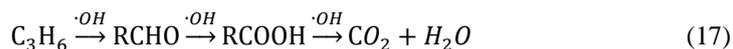
“When C_3H_6 was introduced together with NO_2 , sulfate formation was less than that in the reaction of SO_2+NO_2 , probably due to the reaction between C_3H_6 and the reactive nitrogen species. The detailed mechanism was not explored in this study. The following reactions may take place in this process.



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.



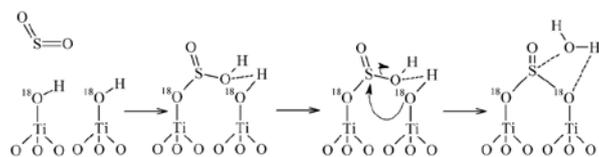
where R represents H or an alkyl group. These gaseous products in the photo-oxidation of C₃H₆ do not seem to block surface reactive sites, which can explain why the pre-adsorption of C₃H₆ on TiO₂ did not show an obvious suppressing effect on the formation of sulfate in the step-by-step experiment.

When C₃H₆ + NO₂ were introduced simultaneously into the reaction system together with SO₂, both competed for ROS with SO₂ and therefore resulted in the lowest formation of sulfate among the heterogeneous reactions. Besides, in the step-by-step experiments, the pre-adsorption of C₃H₆+NO₂ on TiO₂ suppressed sulfate formation significantly, which indicated that lots of reactive sites for SO₂ 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, SO₂ 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, $\text{HSO}_3^- + \text{O}^- + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + \text{e}^-$, as proposed by Zhang et al. (Zhang et al., 2006).

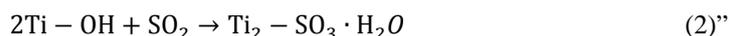


Scheme 1 Reaction of SO₂ and surface hydroxyl groups to form adsorbed sulfite and water.

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 SO₂ on TiO₂ has been investigated by many previous studies. The following mechanisms for SO₂ adsorption on TiO₂ surfaces have been proposed in previous studies (Nanayakkara et al., 2012):



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 SO₂ (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 SO₂ 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 SO₂. 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 SO₂ 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 SO₂ 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 SO₂ coexist, the competition for ROS and surface reactive sites between the VOC and SO₂ is likely to suppress sulfate formation in the heterogeneous reactions, such as that observed for the presence of CH₃CHO on α -Fe₂O₃ in dark experiments (Zhao et al., 2015), the presence of C₇H₁₆ on TiO₂ with UV-Vis irradiation (Du et al., 2000), and the presence of C₃H₆ on TiO₂ 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 -Fe₂O₃ (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 DRIFTS (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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