**Response to reviewer #1**

We thank the reviewer for carefully reviewing our manuscript; the comments are greatly appreciated. We have addressed all the comments and made major changes to the manuscript. In particular, we have substantially revised the section of “Introduction”, “Experimental”, and “Reaction mechanism”. We believe that the revisions based on these comments have substantially improved our manuscript. In the following please find our responses to the comments one by one, and the corresponding changes made to the manuscript. The original comments are shown in italics. The changes made in the revised manuscript are highlighted.

***General comments***

*In this manuscript, the results on multiphase reaction of* $SO_2$ *on individual* $CaCO_3$ *particles in the presence of* $NO_2$ *and* $O_2$ *at RH 72% using Micro-Raman spectrometer with a flow reaction system are presented. The main conclusion is that* $CaCO_3$ *converts first to* $Ca(NO_3)_2$ *droplet (by the reaction with* $NO_2$*), where actually further aqueous* $SO_2$ *oxidation by* $O_2$ *takes place. The reactive uptake coefficient* $\gamma$ *of* $SO_2$ *determined on the basis of* $SO_4^{2-}$ *formation rate was ca. three orders of magnitude higher than that determined in the absence of* $O_2$*. On the basis of their results and mainly on literature data, they suggested that NO2 first initiates a free-radical chain mechanism via reaction of* $NO_2$ *with* $HSO_3^-/SO_3^{2-}$*, where* $SO_3^{\bullet-}$ *radical is formed, which reacts quickly with* $O_2$ *to form* $SO_5^{\bullet-}$*, etc…The presented mechanism is well known and confirmed by many authors, and as expected the reaction under* $O_2$ *conditions is relatively fast and can be important source of sulfate.*

*As I have already pointed out in the previous review (Zhao et al., ACPD), I support the topic, mainly due still unresolved questions concerning high sulfate formation shown during heavily polluted episodes under haze conditions in China. And also, I like the approach used for studying processes on the micro level.*

*However, I found many mistakes (not only English language, but in general); the article is not well readable and many times confusing, many sentences are repeated with no need through the manuscript; thus, I cannot recommend it in the present form for publication in ACP.*

*Further, I again strongly suggest presenting the results for both systems* $SO_2/NO_2/H_2O/N_2$ *and* $SO_2/NO_2/H_2O/O_2$ *together in one article, although the authors of the first manuscript gave their reasons (in the responses) why to present separately. I think it is reasonable to show both together, first due to easier comparison, further due to easier discussion on differences in the mechanisms, etc. Anyway, the authors compare the results with the* *previous one during the whole manuscript. In addition, the experimental part is practically the same.*

*I highlight some of the main comments, questions and mistakes below. I will not expose the language mistakes, they are too many. Many parts of the manuscript should be rewritten.*

**Response:**

In the revised manuscript, we have made major changes to the manuscript in order to make the text more clearly written with improved readability. Moreover, we have made a thorough language check of the text of this manuscript and corrected the errors in language.

Regarding the arrangement of the two manuscripts, although they have some parts in common, the scientific questions under investigation and the chemistry in these two studies are substantially different. We have decided to arrange the two manuscripts as independent papers instead of companion papers to highlight their distinct features. The reasons for this arrangement are as follows:

1. The question whether the multiphase reaction of $SO_2$ directly with $NO_2$ is an important pathway for sulfate formation in the real atmosphere, e.g., during haze episodes in China, requires investigating the "pure" reaction of $SO_2$ with $NO_2$ without confounding effects of other oxidants. In another manuscript (Zhao et al., 2017), we address this question. And in this manuscript, we address a different question, i.e., whether the multiphase reaction of $SO_2$ with $O_2$ in the presence of $NO_2$ is an important reaction pathway of $SO_2$ oxidation; obviously, this reaction is more relevant to real atmospheric conditions.

2. We found that the multiphase reaction of $SO_2$ with $NO_2$ and the reaction of $SO_2$ with $O_2$ in the presence of $NO_2$ have significantly different chemistry, with different reaction mechanisms, products, and atmospheric implications.

i. The multiphase reaction of $SO_2$ directly with $NO_2$ involves two reactants whereas the reaction of $SO_2$ with $O_2/NO_2$ involves three reactants. In the former reaction $NO_2$ is the main oxidant of $SO_2$ while in the latter reaction $O_2$ is the main oxidant of $SO_2$ and $NO_2$ only acts as an initiator of chain reactions.

ii. According to the reaction mechanism, the main products in the multiphase reaction of $SO_2$ with $NO_2$ are sulfate and nitrite with a stoichiometry of 1:1. In contrast, the main product in the multiphase reaction of $SO_2$ with $O_2$ in the presence of $NO_2$ is sulfate and the ratio of sulfate to nitrite is expected to be much higher than 1:1 according to the free-radical chain mechanism in the present study because nitrite is only formed in the chain initiation step.

iii. Due to the different reaction mechanism, the atmospheric implication of the reaction of $SO_2$ with $O_2$ in the presence of $NO_2$ is significantly different from the direct reaction of $SO_2$

with $NO_2$ because the former leads to much faster sulfate formation.

Based on these reasons, we have changed the title of this manuscript to "$NO_2$-initiated Multiphase Oxidation of $SO_2$ by $O_2$ on $CaCO_3$ Particles" in the revised manuscript. Accordingly, in the revised manuscript we have deleted the parts where we stated about the companionship of these two papers (lines 63-64, 80 in the manuscript). We have also adjusted the wording in the abstract and introduction to reflect this change.

***Specific comments***

*Introduction: It needs to be rewritten.*

*1. The authors should say something on well known and published mechanisms in the introduction. Discussion on the p.6/7 should partly be included here. Especially, the mechanism (R1-R6) does not fit on p.6, because it seems that is not important for their results.*

**Response:**

Agree. In the revised manuscript, we have made major changes to the introduction and added the published mechanism to the introduction.

As the reviewer suggested, in the introduction we have also included part of the discussion regarding the mechanism on the p.6-7. It now reads:

"Despite such a reaction mechanism for $SO_2$ oxidation being proposed, its role in $SO_2$ oxidation in the ambient atmosphere is not well established. Most previous studies have focused on the direct reaction of $SO_2$ with $NO_2$, including the determination of its rate constant (Lee and Schwartz, 1983; Clifton et al., 1988; Shen and Rochelle, 1998; Spindler et al., 2003; Nash, 1979; Huie and Neta, 1986). According to the reaction products and their reported yields (Lee and Schwartz, 1983; Clifton et al., 1988), the overall reaction equations of the direct reaction of $SO_2$ with $NO_2$ are as follows:

$$2NO_2(aq) + HSO_3^-(aq) + H_2O \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + 3H^+(aq), \quad \text{(R1)}$$

$$2NO_2(aq) + SO_3^{2-}(aq) + H_2O \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + 2H^+(aq), \quad \text{(R2)}$$

and the reactions are proposed to proceed via $NO_2$–S(IV) adduct complexes (Clifton et al., 1988).

$$NO_2(aq) + SO_3^{2-}(aq) \rightarrow [NO_2 - SO_3]^{2-}(aq). \quad \text{(R3)}$$

$$NO_2(aq) + [NO_2 - SO_3]^{2-}(aq) \rightarrow [NO_2 - SO_3 - NO_2]^{2-}(aq). \quad \text{(R4)}$$

$$[NO_2 - SO_3 - NO_2]^{2-}(aq) + OH^-(aq) \rightarrow [NO_2 - SO_4H - NO_2]^{3-}(aq). \quad \text{(R5)}$$

$[NO_2 - SO_4H - NO_2]^{3-}(aq) \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + H^+(aq).$ (R6)”

*2. P. 2, line 39 and p. 8, line 243: Dissolution/absorption of $SO_2$ in aqueous solution results in total dissolved S(IV), i.e. three species $SO_2$•$H_2O$, $HSO_3^-$ and $SO_3^{2-}$, which are in equilibrium; which species will prevail depends on pH! So, $H_2SO_3$ ($2H^+$+$SO_3^{2-}$) are the same species as you have already written. In addition, it is not “rapid interconversion” between the species.*

**Response:**

Agree. In the revised manuscript, we have changed “$H_2SO_3$” to “$SO_2$•$H_2O$”. And we have changed “rapid interconversion” to “fast dissociations of $SO_2$•$H_2O$ and $HSO_3^-$”.

Experimental:

*3. RH is not mentioned in the experimental part, only in figure captions (RH 72%) and Table 1 (RH 82%). Is this fine or wrong?*

**Response:**

The values for RH in figures and Table 1 are correct. The experiments were carried out at two RH, 72% and 82%. The experiments with varied concentrations of $O_2$ were done at 82 % RH. For the experiments at 72% RH, the reactive uptake coefficients were not quantified. Therefore, only the reactive uptake coefficients at 82% RH are shown in Table 1. In the revised manuscript, we have elaborated the experimental part and clarified this point as follows.

“The experiments were conducted under two RHs (72% and 82%) at 75 ppm $SO_2$ and 75 ppm $NO_2$.”

*4. Can you say something on pH of the formed aqueous layer of $Ca(NO_3)_2$? If you know the pH you can say something more on mechanism; i.e. if it is above 6, than $SO_3^{2-}$ species are the main species which are involved.*

**Response:**

The pH of the aqueous layer of $Ca(NO_3)_2$ may not be completely homogeneous within the aqueous layer and may change dynamically with time during the reaction. In the surface of the aqueous layer pH was supposed to be lower, which was mainly determined by the gas-aqueous equilibrium of $SO_2$, and estimated to be ~3. In the vicinity of the $CaCO_3$ core, pH was supposed to be higher due to carbonate hydrolysis, and was estimated to be ~7.6.

Additionally, in the beginning of the reaction the overall pH of the aqueous layer should be higher due to the larger $CaCO_3$ core and thinner aqueous layer while in the end of the reaction overall pH should be lower, which was mainly determined by the gas-aqueous equilibrium of $SO_2$. Therefore, it is likely that both $HSO_3^-$ and $SO_3^{2-}$ were present, and the dominant species depended on the reaction time and location within the aqueous droplet. In the revised manuscript, we have added short discussion on this point.

"The dominant S(IV) species depends on pH. Due to the fast dissociations of $SO_2•H_2O$ and $HSO_3^-$, reactions consuming one of these S(IV) species will result in instantaneous re-establishment of the equilibria between them (Seinfeld and Pandis, 2006). In this study, the pH of the aqueous layer of $Ca(NO_3)_2$ may change dynamically with time during the reaction and may not be completely homogeneous within the aqueous droplet. The pH values could vary between ~3 and ~7.6. In the surface of the aqueous layer, pH was mainly determined by the gas–aqueous equilibrium of $SO_2$, and was estimated to be ~3. In the vicinity of the $CaCO_3$ core, pH was mainly determined by the hydrolysis of carbonate and was estimated to be ~7.6. It is likely that both $HSO_3^-$ and $SO_3^{2-}$ were present, and the dominant species depended on the reaction time and location within the aqueous droplet. Nevertheless, to make the reaction mechanism clearer, $HSO_3^-$ was used in the reaction equations. Similar reaction equations are also applicable to $SO_3^{2-}$ because of the fast dissociations of $SO_2•H_2O$ and $HSO_3^-$."

*Results and discussion:*

*5. If you once define that you have a system $NO_2/H_2O/O_2$, where $O_2$ is from synthetic air, there is no need to repeat "in synthetic air" throughout the manuscript.*

**Response:**

Agree. In the revised manuscript, we do not use "in synthetic air" throughout the manuscript where it is not necessary.

*6. Paragraph 3.2 An explanation on increasing concentration of $NO_3^-$ during the reaction is needed.*

**Response:**

Agree. The concentration of $NO_3^-$ increased during the reaction because $NO_3^-$ was continuously formed by the reaction of $CaCO_3$ with $NO_2$ and $H_2O$. In the revised manuscript, we have briefly discussed this point.

"The decrease in the amount of carbonate and the increase in the amount of nitrate was because carbonate reacted continuously with $NO_2$ and $H_2O$, forming $Ca(NO_3)_2$. The detailed mechanism of the multiphase reaction of carbonate with $NO_2$ and $H_2O$ were discussed in our previous studies (Li et al., 2010; Zhao et al., 2017)."

*7. P.5, line 146: The reactive uptake coefficient γ of $SO_2$ was determined at three different $O_2$ concentrations, and not in the range 5-86%.*

**Response:**

Agree. In the revised manuscript, we have changed "with $NO_2$ in presence of $O_2$ (5%-86%)" to "with $O_2/NO_2$ at three $O_2$ concentrations (5, 20, and 86%)".

*8. P. 5, line 147: I can see that the increase in the reactive uptake coefficient γ of $SO_2$ is ca. three orders (and not two to three) of magnitude higher than that determined in the absence of $O_2$.*

**Response:**

The reactive uptake coefficient γ of $SO_2$ for the reaction with $O_2/NO_2$ in synthetic air ($1.2\times10^{-5}$) was around 370 times higher than that determined for the direct oxidation of $SO_2$ by $NO_2$ ($3.22\times10^{-8}$). Therefore, we described this difference as "two to three orders of magnitude".

*9. In the second paragraph of 3.3 you compare your results with the literature. Of course, that your results are different than that from Lee and Swartz (1983), due to many reasons, but probably the most important is their different approach. You can probably make some comparisons of your reaction rates with the rates got for the gas mixture $SO_2/NO_2$/air introduced into aqueous solution (Turšič et al., 2001).*

**Response:**

We thank the reviewer for the suggestion. Regarding the experimental approach, Turšič et al. (2001) studied the absorption of the $SO_2/NO_2$/air mixture into aqueous solution, which is indeed more similar to our study. However, due to the mass transfer limitations, it is difficult to directly compare the reaction rates in that study with ours and the rate constants in other studies. A rate constant of $2.4\times10^{3}$ mol$^{-1}$ L s$^{-1}$ (at pH 3) can be derived from the study of Turšič et al. (2001) , which is much lower than the values from the study of Lee and Schwartz (1983) and of Clifton et al. (1988). This is likely attributed to the limiting step by the aqueous phase mass transfer. The characteristic mixing time in the aqueous phase in the study of Turšič et al. (2001) is likely much longer than that of Lee and Schwartz (1983) (1.7-5.3 s) according to the time series of $HSO_3^-$ concentration in the study of Turšič et al. (2001), although it was not explicitly reported. Nevertheless, in the revised manuscript, we have added this comparison as follows.

"Only few studies have reported the S(IV) oxidation rate in the reaction of S(IV) with $O_2/NO_2$ mixtures (Turšič et al., 2001; Littlejohn et al., 1993). However, due to the limiting step by the aqueous phase mass transfer, it is difficult to quantitatively compare the reaction rates in those studies with the uptake coefficient in our study and the rate constants determined by Lee and Schwartz (1983) and Clifton et al. (1988). For example, a rate constant of $2.4 \times 10^3$ $mol^{-1}$ L $s^{-1}$ (at pH 3) can be derived from the results of Turšič et al. (2001), which is much lower than the values reported by Lee and Schwartz (1983) and Clifton et al. (1988). This can be attributed to the limiting step by the aqueous-phase mass transfer because the characteristic mixing time in the aqueous phase in Turšič et al. (2001) was likely much longer than that of Lee and Schwartz (1983) (1.7–5.3 s), according to the $HSO_3^-$ concentration time series reported by Turšič et al. (2001)."

*10. The mechanism shown on p.6 (from line 172 to 189) should be deleted here and just mentioned in the introduction. It is not important for the discussion, but can be written in one sentence why this mechanism is not possible.*

**Response:**

Agree. In the revised manuscript, we have deleted the mechanism from line 172 to 189 and only mentioned them in the introduction, as the reviewer suggested. Instead, we have briefly discussed why this mechanism is not possible as follows.

"According to the $NO_2$–S(IV) adduct mechanism, the presence of $O_2$ should not affect the $SO_2$ oxidation rate; however, in this study, a substantial enhancement in the $SO_2$ oxidation rate was observed in the presence of $O_2$ compared with that in the absence of $O_2$. Therefore, the $NO_2$–S(IV) adduct mechanism was not considered to have been important in this study."

*11. Check the reactions in the text and in the Table 2 (see R7-R8 in the text and those in the Table, R8–R10, R8a, R8b)! Anyway, it is no need to repeat; all important reactions in the Table are enough.*

*If you know the pH, you can write the reaction with only one species, $HSO_3^-$ or $SO_3^{2-}$.*

**Response:**

Agree. In the revised manuscript, we have changed R8 to R7. We have deleted R7-17 in the text and only shown them in the table. Moreover, as discussed above (the response to comment 4) we have only shown the reaction equations for $HSO_3^-$ for clarity, although these reaction equations are also applicable to $SO_3^{2-}$ because of the fast dissociations of $SO_2$•$H_2O$

and $HSO_3^-$.

*12. P.7, line 209-213: Nice study on $S_2O_6^{2-}$ species formation, although in a different system, can be found in Podkrajšek et al, Chemosphere 49 (2002). Whatever, the mechanism (and the reason) of its formation should be the same.*

**Response:**

We thank the reviewer for raising this study on $S_2O_6^{2-}$ formation. In the revised manuscript, we have added this paper in our citation and briefly discussed it as follows.

"In addition to $SO_4^{2-}$ and $NO_2^-$, $S_2O_6^{2-}$ was detected with an appreciable yield using Raman spectroscopy, following the reaction of $NO_2$ with aqueous sulfite (Littlejohn et al., 1993). $S_2O_6^{2-}$ was also observed in the aqueous oxidation of bisulfite in an $N_2$-saturated solution in the presence of Fe(III) using ion-interaction chromatography (Podkrajšek et al., 2002)."

*13. Better than "radical mechanism" is "a free-radical chain mechanism".*

**Response:**

Agree. In the revised manuscript, we have changed the "radical mechanism" to "a free-radical chain mechanism".

*14. P. 8, Line 239: I do not agree that there is a synergy between $NO_2$ and $O_2$ (definition of synergy!); $NO_2$ only initiates the free-radical chain mechanism, and after the induction period, the reaction is relatively fast; and according to the proposed mechanism does not have other role, except in the first step when $Ca(NO_3)_2$ is formed in the reaction between $CaCO_3$ and $NO_2$. This part is now explained well in the first manuscript (Zhao et al., ACPD).*

**Response:**

By synergy, we meant that the overall effect on the $SO_2$ oxidation rate when both $NO_2$ and $O_2$ were present was higher than the sum of the effect of $NO_2$ and of $O_2$, although the reactions of $SO_2$ with $O_2$ and with $NO_2$ were not always simultaneous. As we have shown, the $SO_2$ oxidation rates in the direct reaction of $SO_2$ with $NO_2$ and with $O_2$ were both very low.

In the revised manuscript, we have further elaborated this discussion as follows.

" In the experiment without $NO_2$, but with other reaction conditions the same, we found that no sulfate was formed after 5 h of reaction. This indicates that $O_2$ by itself cannot initiate the chain reactions (although it favors chain propagation), and that the oxidation of $SO_2$ by $O_2$ was slow. The effect on the $SO_2$ oxidation rate when both $NO_2$ and $O_2$ were present was much higher than the sum of the effect of $NO_2$ and $O_2$. We refer to this effect as the synergy of $NO_2$ and $O_2$, which resulted in the fast oxidation of $SO_2$ to form sulfate in this study. This effect is similar to a "ternary" reaction found with the reaction of $NO_2$–particles–$H_2O$ or $SO_2$–particles–$O_3$ (Zhu et al., 2011), where the reaction rate can be much faster than the sum of the reaction rates for the reaction of the second and third reactant with the first reactant."

*15. I also suggest excluding older references, and rather including only those after 1990.*

**Response:**

We thank the reviewer for the suggestion. However, some of the references earlier than 1990 are also important for the discussion of this study such as Lee and Schwartz (1983). Since ACP does not limit the number of references, we think it may be more reasonable to keep these references.

*16. The radicals throughout the manuscript are written incorrectly.*

**Response:**

Agree. In the revised manuscript, we have checked and corrected the writing of radicals throughout the manuscript wherever there were mistakes.

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**Response to reviewer #2**

We thank the reviewer for carefully reviewing our manuscript and providing helpful comments. All the comments have been addressed in the revised manuscript and we believe that the revisions based on these comments have substantially improved our manuscript. In the following please find our responses to the comments one by one, and the corresponding changes made to the manuscript. The original comments are shown in italics. The changes made in the revised manuscript are highlighted.

*I support the other referee's assessment, including the recommendation that Part 1 and Part 2 be combined into a single article. The articles don't stand on their own, and studying the reaction of* $SO_2$ *with* $NO_2$ *in the absence of* $O_2$*, as in Part 1 - since* $O_2$ *apparently plays a role in the reaction - is not relevant for atmospheric chemistry. I also agree that there are numerous English language errors in this manuscript.*

**Response:**

We appreciate the reviewer's opinion on how to better present our studies. However, these two studies are substantially different regarding the scientific questions under investigation and the chemistry involved, although they have some links. We have decided to arrange the two manuscripts as independent papers instead of companion papers to highlight their distinct features. The reasons for this arrangement are as follows:

1. The question whether the multiphase reaction of $SO_2$ directly with $NO_2$ is an important pathway for sulfate formation in the real atmosphere, e.g., during haze episodes in China, requires investigating the "pure" reaction of $SO_2$ with $NO_2$ without confounding effects of other oxidants. In another manuscript (Zhao et al., 2017), we address this question. And in this manuscript, we address a different question, i.e., whether the multiphase reaction of $SO_2$ with $O_2$ in the presence of $NO_2$ is an important reaction pathway of $SO_2$ oxidation. Both reactions have their own relevance to the atmosphere.

2. We found that the multiphase reaction of $SO_2$ with $NO_2$ and the reaction of $SO_2$ with $O_2$ in the presence of $NO_2$ have significantly different chemistry, with different reaction mechanisms, products, and atmospheric implications.

i. The multiphase reaction of $SO_2$ directly with $NO_2$ involves two reactants whereas the reaction of $SO_2$ with $O_2/NO_2$ involves three reactants. In the former reaction $NO_2$ is the main oxidant of $SO_2$ while in the latter reaction $O_2$ is the main oxidant of $SO_2$ and $NO_2$ only acts as an initiator of chain reactions.

ii. According to the reaction mechanism, the main products in the multiphase reaction of $SO_2$ with $NO_2$ are sulfate and nitrite with a stoichiometry of 1:1. In contrast, the main product in the multiphase reaction of $SO_2$ with $O_2$ in the presence of $NO_2$ is sulfate and the ratio of sulfate to nitrite is expected to be much higher than 1:1 according to the free-radical chain mechanism in the present study because nitrite is only formed in the chain initiation step.

iii. Due to the different reaction mechanism, the atmospheric implication of the reaction of $SO_2$ with $O_2$ in the presence of $NO_2$ is significantly different from the direct reaction of $SO_2$ with $NO_2$ because the former leads to much faster sulfate formation.

Based on these reasons, we have changed the title of this manuscript to "$NO_2$-initiated Multiphase Oxidation of $SO_2$ by $O_2$ on $CaCO_3$ Particles" in the revised manuscript. Accordingly, in the revised manuscript we have deleted the parts where we stated about the companionship of these two papers (lines 63-64, 80 in the manuscript). We have also adjusted the wording in the abstract and introduction to reflect this change.

Regarding the language errors, we have made a thorough language check of the text of this manuscript and corrected the errors in language.

*The study and the results presented are interesting. However, I have doubts about the technical soundness of the approach. For one thing, it's impossible to understand the experimental approach based on what is written in section 2 of this manuscript. Yes, the reactor was a flow reactor, but where were the particles? Were they part of the flow? Or were gases flowing past the particles which are stationary on a surface? What were the particles like (size, shape, porosity, etc.)? How were they prepared and dispersed? The manuscript is meaningless without these basic pieces of information. It is possible that they were mentioned in Part I of the manuscript, but I am being asked to review only this manuscript - and it must stand on its own at least to this extent.*

**Response:**

Agree. In the revised manuscript, we have elaborated the experimental part. The details of experiments including the details that the reviewer is concerned with have been added and explicitly described. The revision has also reflected the change from the companion paper of our last manuscript to a completely independent paper. The revised experimental part is as follows.

"The experiments were conducted using a flow reaction system and the setup is shown in Fig. S1. The experimental setup and procedure used have been described in detail in previous studies (Zhao et al., 2017; Zhao et al., 2011; Liu et al., 2008). A gas mixture of $NO_2$, $SO_2$, $O_2$, $N_2$, and water vapor reacted with particles deposited on a substrate in the flow reaction cell. The concentrations of $SO_2$ and $NO_2$ were controlled using mass flow controllers by varying the flow rates of $SO_2$ (2,000 ppm in high purity $N_2$, National Institute of Metrology P.R.

China), $NO_2$ (1,000 ppm in high purity $N_2$, Messer, Germany), and synthetic air [20% $O_2$ (high purity grade: 99.999%, Beijing Haikeyuanchang Practical Gas Co., Ltd.) and 80% $N_2$ (high purity grade: 99.999%, Beijing Haikeyuanchang Practical Gas Co., Ltd.)]. Relative humidity (RH) was controlled by regulating the flow rates of reactant gases, dry synthetic air, and humidified synthetic air. Humidified synthetic air was prepared by bubbling synthetic air through fritted glass in water. In some experiments, the $O_2$ concentrations were varied by regulating the mixing ratios of $O_2$ and $N_2$ to investigate the effect of $O_2$. $SO_2/O_2/NO_2/H_2O$ mixtures flew through the reaction cell and reacted with individual stationary $CaCO_3$ particles, which were deposited on a Teflon-FEP film substrate annealed to a silicon wafer. RH and temperature were measured using a hygrometer (HMT100, Vaisala, Vantaa, Finland) at the exit of the reaction cell. Additionally, temperature was measured using another small temperature sensor (Pt 100, 1/3 DIN B, Heraeus, Hanau, Germany) in the reaction cell. All the experiments were conducted at 298 ± 0.5 K. The experiments were conducted under two RHs (72% and 82%) at 75 ppm $SO_2$ and 75 ppm $NO_2$.

During the reaction, particles were monitored *in-situ* via a glass window on the top of the reaction cell using a Micro-Raman spectrometer (LabRam HR800, HORIBA Jobin Yvon, Kyoto, Japan) to obtain microscopic images and Raman spectra. A 514-nm excitation laser was used, and back scattering Raman signals were detected. The details of the instrument are described elsewhere (Liu et al., 2008; Zhao et al., 2011). Because the particles were larger than the laser spot in this study (~1.5 μm), confocal Raman mapping was used to measure the spectra at different locations on a particle to obtain the chemical information of the entire particle. The mapping area was rectangular and was slightly larger than the particle, with mapping steps of 1 × 1 μm. Raman spectra in the range of 800–3,900 $cm^{-1}$ were acquired with an exposure time of 1 s for each mapping point. Raman spectra were analyzed using Labspec 5 software (HORIBA Jobin Yvon). Raman peaks were fitted to Gaussian–Lorentzian functions to obtain peak positions and peak areas at different locations on the particle. The peak areas were then added together to obtain the peak area for the entire particle.

Particles of $CaCO_3$ (98%, Sigma-Aldrich, USA), with average diameters of about 7–10 μm as specified by the manufacturer, were used in the experiments. The $CaCO_3$ particles were rhombohedron crystals; X-ray diffraction analysis indicated that they were calcite (Fig. S2). Individual particles were prepared by dripping a dilute $CaCO_3$ suspended solution onto Teflon-FEP film using a pipette and then drying the sample in an oven at 80ºC for 10 h.

The amount of $CaSO_4$ as a reaction product was quantified based on Raman peak areas and particle sizes. The details of the method are described in our previous study (Zhao et al., 2017). Briefly, the amount of reaction product $CaSO_4$ formed was determined as a function of time using Raman peak areas. Raman peak areas were converted to the amount of compound formed using a calibration curve obtained from pure $CaSO_4$ particles of different sizes, which were determined according to microscopic images. The reaction rate, i.e., the sulfate production rate, was derived from the amount of sulfate formed as a function of time. The reactive uptake coefficient of $SO_2$ for sulfate formation (γ) was further determined from the reaction rate and collision rate of $SO_2$ on the surface of a single particle.

$$\gamma = \frac{\frac{d\{SO_4^{2-}\}}{dt}}{Z} \quad . \tag{1}$$

$$Z = \frac{1}{4} c A_s [SO_2], \tag{2}$$

$$c = \sqrt{\frac{8RT}{\pi M_{SO_2}}} \quad , \tag{3}$$

where R is the gas constant, T is temperature, $M_{SO_2}$ is the molecular weight of $SO_2$, c is the mean molecular velocity of $SO_2$, $A_s$ is the surface area of an individual particle, and Z is the collision rate of $SO_2$ on the surface of a particle. $\{SO_4^{2-}\}$ indicates the amount of sulfate in the particle phase in moles. The average reaction rate and surface area of particles during the multiphase reaction period were used to derive the reactive uptake coefficient. The period was chosen to start after the induction period when ~10% of the final sulfate was formed. $[SO_2]$ indicates the concentration of $SO_2$ in the gas phase.

The influence of gas phase diffusion on reactive uptake was evaluated using the resistor model described by Davidovits et al. (2006) and references therein, as well as using the gas phase diffusion correction factor for a reactive uptake coefficient according to the method described by Pöschl et al. (2007). The reactive uptake of $SO_2$ was found to not be limited by gas phase diffusion (see details in the Supplement S1).

In addition, we conducted experiments of the reaction $SO_2$ with only $O_2$ on both $CaCO_3$ solid particles and internally mixed $CaCO_3/Ca(NO_3)_2$ particles (with $CaCO_3$ embedded in $Ca(NO_3)_2$ droplets), while keeping other conditions the same as the reaction of $SO_2$ with an $O_2/NO_2$ mixture. These experiments of the multiphase oxidation of $SO_2$ by $O_2$ can help determine the role of $NO_2$ in the reaction of $SO_2$ with an $O_2/NO_2$ mixture."

*I suspect that the particles were not part of the flow. In which case, did the authors consider the issue of gas phase diffusion limitations in their data analysis?*

**Response:**

Particles were deposited on a Teflon-FEP film in this study. Please refer the description about the experimental setup.

We evaluated the influence of gas phase diffusion on the reactive uptake coefficient using the resistor model described by Davidovits et al. (2006) and references therein (see details in the

Supplement S1 below, which has been added in the revised manuscript). The contribution of the resistance ($1/\Gamma_{diff}$) due to gas phase diffusion to the reactive uptake coefficient in this study was less than 0.1%. Therefore we conclude that the reactive uptake of $SO_2$ was not limited by gas phase diffusion. The same conclusion can also be drawn by calculating the gas phase diffusion correction factor for a reactive uptake coefficient according to the method in Pöschl et al. (2007) (Equation 20 in their study).

In the revised manuscript, we have briefly discussed this point.

"The influence of gas phase diffusion on reactive uptake was evaluated using the resistor model described by Davidovits et al. (2006) and references therein, as well as using the gas phase diffusion correction factor for a reactive uptake coefficient according to the method described by Pöschl et al. (2007). The reactive uptake of $SO_2$ was found to not be limited by gas phase diffusion (see details in the Supplement S1)."

The Supplement S1 that has been added in the revised manuscript is as follows.

"**S1. Influence of gas phase diffusion on reactive uptake coefficients**

The Influence of the gas phase diffusion on reactive uptake coefficients was analyzed using the resistor model described by Davidovits et al. (2006) and the references therein.

$$\frac{1}{\gamma} = \frac{1}{\Gamma_{diff}} + \frac{1}{\alpha} + \frac{1}{\Gamma_{sat}+\Gamma_{rxn}} \qquad (1)$$

where $\Gamma_{diff}$ is the transport coefficient in the gas phase, $1/\Gamma_{diff}$ is the resistance due to the diffusion in the gas phase. Similarly, $1/\Gamma_{sat}$ and $1/\Gamma_{rxn}$ are the resistance due to liquid phase saturation and liquid phase reaction, respectively. $\alpha$ is the mass accommodation coefficient of $SO_2$.

$1/\Gamma_{diff}$ can be determined using the following equation:

$$\frac{1}{\Gamma_{diff}} = \frac{0.75+0.238\mathrm{Kn}}{\mathrm{Kn}(1+\mathrm{Kn})} \ . \qquad (2)$$

where Kn is Knudsen number. Knudsen number is defined as

$$\mathrm{Kn} = \frac{\lambda}{a} \ , \qquad (3)$$

where $\lambda$ is the mean free path of a molecule in the gas phase and a is the radius of the particle. $\lambda$ can be derived from

$$\lambda = \frac{3D_g}{c}, \qquad (4)$$

where $D_g$ is the diffusion coefficient in the gas phase and c is the mean molecular velocity. c is determined by

$$c = \sqrt{\frac{8RT}{\pi M}} \qquad (5)$$

where R is the gas constant, T is temperature, and M is the molecular mass of $SO_2$.

$1/\Gamma_{diff}$ was calculated to be 78 and $1/\gamma$ was calculated to be ~$8.3\times10^4$. $1/\Gamma_{diff}$ only accounted for <0.1% of $1/\gamma$. Therefore, the reactive uptake of $SO_2$ in this study was not limited by gas phase diffusion.

The same conclusion can also be drawn by calculating the gas phase diffusion correction factor for a reactive uptake coefficient according to the method in Pöschl et al. (2007) (Equation 20 in their study, also shown as equation 6 below).

$$C_g = \frac{1}{1+\gamma\frac{0.75}{Kn}} \qquad (6)$$

where $C_g$ is the gas phase diffusion correction factor for a reactive uptake coefficient."

*Was relative humidity actually measured or only inferred from mixing ratios of humid and dry air? RH is well know to be unpredictable in experiments, it should be measured directly.*

**Response:**

Relative humidity was measured directly in our study using a hygrometer (HMT100, Vaisala). In the revised manuscript, we have clearly described this as follows.

"RH and temperature were measured using a hygrometer (HMT100, Vaisala, Vantaa, Finland) at the exit of the reaction cell. Additionally, temperature was measured using another small temperature sensor (Pt 100, 1/3 DIN B, Heraeus, Hanau, Germany) in the reaction cell."

*Line 36: This may be a language issue but it is not appropriate to refer to a point of disagreement in the literature which has prompted detailed analysis and publications as "different opinions." Replace with "uncertainties in the pH value..." or something similar.*

**Response:**

Agree. In the revised manuscript, we have changed "different opinions" to "uncertainties in the pH value".

*Line 56: Delete "$O_2$ is abundant in the atmosphere," this is an atmospheric chemistry journal.*

**Response:**

Agree. In the revised manuscript, we have deleted this sentence.

## References

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# ~~Multiphase Reaction of $SO_2$ with~~ $NO_2$ ~~on $CaCO_3$ Particles. 2. $NO_2$-initialized~~-initiated multiphase oxidation of $SO_2$ by $O_2$ on $CaCO_3$ particles

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**Abstract.** The reaction of $SO_2$ with $NO_2$ on the surface of aerosol particles has been suggested to be important in sulfate formation during severe air pollution episodes in China. However, we found that the direct oxidation of $SO_2$ by $NO_2$ was slow and might not be the main reason for sulfate formation in ambient air. In this study, we investigated the multiphase reaction of $SO_2$ with an $O_2$/$NO_2$ mixture on single $CaCO_3$ particles ~~in synthetic air, i.e., in the presence of $O_2$,~~ using Micro-Raman spectroscopy. The reaction converted the $CaCO_3$ particle to ~~the~~a $Ca(NO_3)_2$ droplet ~~containing~~, with $CaSO_4•2H_2O$ solid particles embedded in it, which constituted a ~~large~~significant fraction of the droplet volume at the end of the reaction. ~~Compared with the reaction in the absence of $O_2$, the morphology of the particle during the reaction in synthetic air was significantly different and the amount of sulfate formed at the end of the experiment was much higher.~~ The reactive uptake coefficient of $SO_2$ for sulfate formation was on the order of $10^{-5}$, which was ~~two to three~~higher than that for the multiphase reaction of $SO_2$ directly with $NO_2$ by 2–3 orders of magnitude~~ higher than that in the absence of $O_2$.~~. According to ~~the difference between the reactive uptake coefficient of $SO_2$ in the absence of $O_2$ and that in the presence of $O_2$~~our observations and the literature, we found that in the multiphase reaction of $SO_2$ with the $O_2$/$NO_2$ ~~in synthetic air~~mixture, $O_2$ was the main oxidant of $SO_2$ and was necessary for radical chain propagation. $NO_2$ acted as the initia~~lize~~tor of ~~the~~ radical formation, but not as the main oxidant. ~~Such~~The synergy of $NO_2$ and $O_2$ resulted in much faster sulfate formation than ~~when either of them was absent.~~the sum of the reaction rates with $NO_2$ and with $O_2$ alone. We estimated that the multiphase oxidation of $SO_2$ by $O_2$ ~~in the presence of~~initiated by $NO_2$ ~~can~~could be an important source of sulfate and a sink of $SO_2$, based on the calculated lifetime of $SO_2$ regarding the loss ~~by~~through the multiphase reaction versus the ~~lifetime regarding the~~ loss ~~by~~through the gas-phase reaction with OH radical. Parameterizing the reactive uptake coefficient of the reaction observed in our laboratory for further model simulation is needed, as well as an integrated assessment based on field observations, laboratory study results, and model simulations to evaluate the importance of the reaction in ambient air during ~~the~~ severe air pollution ~~p~~e~~r~~pisodes, especially in China.

## 1 Introduction

It has been suggested that multiphase or heterogeneous oxidation of $SO_2$ ~~by $NO_2$ has been suggested to~~ potentially plays an important role in sulfate formation in the atmosphere (Seinfeld and Pandis, 2006). During the severe pollution episodes that occur frequently in China, high sulfate concentrations cannot be explained by the gas phase oxidation of $SO_2$ and its well-known aqueous chemistry (Zheng et al., 2015a; Cheng et al., 2016), highlighting the role of under-appreciated heterogeneous oxidation or multiphase pathways.

Recently, the multiphase oxidation of $SO_2$ by $NO_2$ has been introduced in air quality model simulations to explain the discrepancy between the modeled and observed sulfate concentration during ~~the heavily polluted~~severe pollution episodes~~ frequently occurring~~ in China (Cheng et al., 2016; Gao et al., 2016; Wang et al., 2016; Xue et al., 2016), despite the ~~different opinions about~~uncertainties in the kinetic parameters for $SO_2$ oxidation and in the pH value of aerosol particles in China (Wang et al., 2016; Cheng et al., 2016; Liu et al., 2017; Guo et al., 2017). However, according to our recently published results (Zhao et al., 2017)~~.~~, the direct oxidation of $SO_2$ by $NO_2$ could not contribute significantly to sulfate formation in the atmosphere because the reactive uptake coefficient of $SO_2$ for sulfate formation due to direct oxidation by $NO_2$ is very low ($\sim10^{-8}$).

Although the contribution of the direct oxidation of $SO_2$ by $NO_2$ to sulfate formation is not significant, $NO_2$ may be involved in other oxidation pathways of $SO_2$. It has been reported that the reaction of $NO_2$ with $SO_3^{2-}$ and $HSO_3^-$ in the bulk aqueous phase can form the $SO_3^{\bullet-}$ radical, which can further react with $O_2$ and produce a series of radicals that oxidize S(IV) species (Littlejohn et al., 1993). The reaction pathway may result in a fast $SO_2$ oxidation due to the potential synergy of $NO_2$ and $O_2$.

Despite such a reaction mechanism for $SO_2$ oxidation being proposed, its role in $SO_2$ oxidation in the ambient atmosphere is not well established. Most previous studies have focused on the direct reaction of $SO_2$ with $NO_2$, including the determination of its rate constant (Lee and Schwartz, 1983; Clifton et al., 1988; Shen and Rochelle, 1998; Spindler et al., 2003; Nash, 1979; Huie and Neta, 1986). According to the reaction products and their reported yields (Lee and Schwartz, 1983; Clifton et al., 1988), the overall reaction equations of the direct reaction of $SO_2$ with $NO_2$ are as follows:

$$2NO_2(aq) + HSO_3^-(aq) + H_2O \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + 3H^+(aq), \tag{R1}$$

$$2NO_2(aq) + SO_3^{2-}(aq) + H_2O \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + 2H^+(aq), \tag{R2}$$

and the reactions are proposed to proceed via $NO_2$–S(IV) adduct complexes (Clifton et al., 1988).

$$NO_2(aq) + SO_3^{2-}(aq) \rightarrow [NO_2 - SO_3]^{2-}(aq). \tag{R3}$$

$$NO_2(aq) + [NO_2 - SO_3]^{2-}(aq) \rightarrow [NO_2 - SO_3 - NO_2]^{2-}(aq). \tag{R4}$$

$$[NO_2 - SO_3 - NO_2]^{2-}(aq) + OH^-(aq) \rightarrow [NO_2 - SO_4H - NO_2]^{3-}(aq). \tag{R5}$$

$$[NO_2 - SO_4H - NO_2]^{3-}(aq) \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + H^+(aq). \tag{R6}$$

However, studies of the oxidation rate of $SO_2$ at the $O_2$ concentrations relevant to the ambient atmosphere and the potential influence of the synergy of $NO_2$ and $O_2$ on the oxidation rate are very limited (Turšič et al., 2001; He et al., 2014), except a few studies investigated $SO_2$ oxidation in the presence of $NO_2$ as well as $O_2$ (Littlejohn et al., 1993; Shen and Rochelle, 1998; Santachiara et al., 1990)~~Quantitative and accurate assessment of the role of multiphase oxidation $SO_2$ by $NO_2$ on particle relies on determining reaction kinetic parameters and understanding the reaction mechanism. The aqueous oxidation of $SO_2$ (S(IV) species including $H_2SO_3$, $SO_3^{2-}$, and $HSO_3^-$) by~~

~~$NO_2$ has been investigated by a number of laboratory studies and valuable kinetic parameters and understanding on reaction products and process have been obtained. For example, and measured the second order rate constant of the reaction of $NO_2$ with bisulfate and sulfite solution. The reaction products observed include nitrite, sulfate, and dithionate (e.g., ). Based on these studies, the reaction mechanism was deduced .~~

~~Previous studies~~ . Moreover, previous studies have mainly focused on the reaction in bulk solution~~.~~ and only few studies ~~on~~have investigated the oxidation of $SO_2$ by $NO_2$ on aerosol particles (Santachiara et al., 1990, 1993)~~have been conducted .~~. On aerosol particles, water activity ~~of aerosol water~~, pH, ionic strength, the presence of other compounds or ions, and the role of particle surface are different from in dilute bulk solution and may affect the reaction process and reaction rate. ~~Moreover, many previous studies conducted the experiments either in the absence of $O_2$ or with low $O_2$ concentrations. Studies on the potential role of $O_2$ especially at the concentration levels in ambient air and the potential synergy of $NO_2$ and $O_2$ in the reaction are very limited. $O_2$ is abundant in the atmosphere and may affect the multiphase reaction of $SO_2$ with $NO_2$. For example, found that the oxidation rate of sulfite in the aqueous reaction with $NO_2$ increases with $O_2$ concentration (0-5% by volume). The enhancement of $SO_2$ oxidation rate in the reaction with $NO_2$ have been also found in the heterogeneous reaction on mineral particle surface when $O_2$ is present .~~ Therefore, further studies of the multiphase reaction of $SO_2$ with $O_2$/$NO_2$ mixtures on aerosol particles ~~in air~~ are ~~needed in order~~required to determine the kinetic parameters and ~~elucidate~~ the mechanism of the reaction.

In ~~a companion manuscript , we reported the results of the~~ this study ~~on~~, we investigated the multiphase ~~oxid~~reaction of $SO_2$ ~~directly by $NO_2$~~with $O_2$ in ~~$N_2$~~the presence of $NO_2$ on $CaCO_3$ particles. ~~We found that the reactive uptake coefficient of $SO_2$ for sulfate formation due to the oxidation by $NO_2$ is on the order of $10^{-8}$, and concluded that the oxidation of $SO_2$ by $NO_2$ alone could not contribute significantly to sulfate formation in the atmosphere. In this manuscript, we present the results of our study on the multiphase reaction of $SO_2$ with $NO_2$ in synthetic air, i.e., in the presence of $O_2$, on $CaCO_3$ particles.~~ We quantified the reactive uptake coefficient of $SO_2$ due to the reaction with an $O_2$/$NO_2$~~/$O_2$~~/$H_2O$ mixture ~~in synthetic air.~~. Based on ~~the~~our observations and the existing literature, we further discussed the reaction mechanism. ~~By comparing with the~~ Furthermore, we estimated the role of the multiphase oxidation of $SO_2$ by ~~$NO_2$ in $N_2$, we highlight the role of~~ $O_2$ in the ~~multiphase oxidation~~presence of ~~$SO_2$~~$NO_2$ in the atmosphere.

## 2 Experimental

~~The~~ The experiments were conducted using a flow reaction system and the setup is shown in Fig. S1. The experimental setup and procedure used ~~in this study~~ have been described in detail~~s~~ in previous studies (Zhao et al., 2017; Zhao et al., 2011; Liu et al., 2008). ~~Here we only provide a brief description. The reaction~~ A gas mixture of ~~$SO_2$ with~~ $NO_2$ ~~on $CaCO_3$~~, $SO_2$, $O_2$, $N_2$, and water vapor reacted with particles ~~was investigated using~~ deposited on a ~~flow reactor. $SO_2$ (2000 ppm~~substrate in ~~high purity $N_2$)~~ the flow reaction cell. The concentrations of $SO_2$ and $NO_2$ ~~(1000~~were controlled using mass flow controllers by varying the flow rates of $SO_2$ (2,000 ppm in high purity $N_2$, National Institute of Metrology P.R. China), $NO_2$ (1,000 ppm in high purity $N_2$~~) were diluted with~~, Messer, Germany), and synthetic air [20% $O_2$ (high purity grade: 99.999%, Beijing Haikeyuanchang Practical Gas Co., Ltd~~.),~~.) and 80% $N_2$ (high purity grade: 99.999%, Beijing Haikeyuanchang Practical Gas Co., Ltd~~.)] to 75 ppm.~~.)].

Relative humidity (RH) was controlled by regulating the flow rates of reactant gases, dry synthetic air, and humidified synthetic air. ~~More details about the experiment conditions can be found in the companion paper .~~ ~~$SO_2$/$NO_2$/$H_2O$ reaction mixture in~~ Humidified synthetic air was prepared by bubbling synthetic air through fritted glass in water. In some experiments, the $O_2$ concentrations were varied by regulating the mixing ratios of $O_2$ and $N_2$ to investigate the effect of $O_2$. $SO_2$/$O_2$/$NO_2$/$H_2O$ mixtures flew through the reaction cell and reacted with individual stationary $CaCO_3$ particles, which were deposited on a Teflon-FEP film~~.~~ – substrate annealed to a silicon wafer. RH and temperature were measured using a hygrometer (HMT100, Vaisala, Vantaa, Finland) at the exit of the reaction cell. Additionally, temperature was measured using another small temperature sensor (Pt 100, 1/3 DIN B, Heraeus, Hanau, Germany) in the reaction cell. All the experiments were conducted at 298 ± 0.5 K. The experiments were conducted under two RHs (72% and 82%) at 75 ppm $SO_2$ and 75 ppm $NO_2$.

During the reaction, ~~the~~ particles were ~~*in-situ*~~ monitored *in-situ* via a glass window on the top of the ~~flow reactor~~reaction cell using a Micro-Raman spectrometer (LabRam HR800, HORIBA Jobin Yvon, Kyoto, Japan) to obtain microscopic images and Raman spectra. A 514-nm excitation laser was used, and back scattering Raman signals were detected. The details of the instrument are described elsewhere (Liu et al., 2008; Zhao et al., 2011)~~All the experiments were conducted at 298±0.5 K~~. Because the particles were larger than the laser spot in this study (~1.5 μm), confocal Raman mapping was used to measure the spectra at different locations on a particle to obtain the chemical information of the entire particle. The mapping area was rectangular and was slightly larger than the particle, with mapping steps of 1 × 1 μm. Raman spectra in the range of 800–3,900 $cm^{-1}$ were acquired with an exposure time of 1 s for each mapping point. Raman spectra were analyzed using Labspec 5 software (HORIBA Jobin Yvon). Raman peaks were fitted to Gaussian–Lorentzian functions to obtain peak positions and peak areas at different locations on the particle. The peak areas were then added together to obtain the peak area for the entire particle.

Particles of $CaCO_3$ (98%, Sigma-Aldrich, USA), with average diameters of about 7–10 μm as specified by the supplier, were used in the experiments. The $CaCO_3$ particles were rhombohedron crystals; X-ray diffraction analysis indicated that they were calcite (Fig. S2). Individual particles were prepared by dripping a dilute $CaCO_3$ suspended solution onto Teflon-FEP film using a pipette and then drying the sample in an oven at 80°C for 10 h.

The amount of ~~the~~$CaSO_4$ as a reaction product~~ $CaSO_4$~~ was quantified based on Raman peak areas and particle sizes. The details of the method are described in our previous study (Zhao et al., 2017). Briefly, the amount of reaction product $CaSO_4$ formed was ~~followed~~determined as a function of time using Raman peak areas. Raman peak areas were converted to the amount of compound formed using a calibration curve obtained from pure $CaSO_4$ particles of different sizes, which were determined according to microscopic images. The reaction rate, ~~that is,~~i.e., the sulfate production rate, was derived from the amount of sulfate formed as a function of time. The reactive uptake coefficient of $SO_2$ for sulfate formation (γ) was further determined from the reaction rate and collision rate of $SO_2$ on the surface of a single particle.

$$\gamma = \frac{\frac{d\{SO_4^{2-}\}}{dt}}{Z} \ . \tag{1}$$

$$Z = \frac{1}{4} c A_s [SO_2], \tag{2}$$

$$c = \sqrt{\frac{8RT}{\pi M_{SO_2}}} \ , \tag{3}$$

where R is the gas constant, T is temperature, Mso$_2$ is the molecular weight of $SO_2$, ~~and~~ c is the mean molecular velocity of $SO_2$, $A_s$ is the surface area of an individual particle, and Z is the collision rate of $SO_2$ on the surface of a particle. $\{SO_4^{2-}$~~}~~$\}$ indicates the amount of sulfate ~~on~~in the particle phase in moles. The average reaction rate and surface area of particles during the multiphase reaction period were used to derive the reactive uptake coefficient. The period was chosen to start after the induction period when ~10% of the final sulfate was formed. $[SO_2]$ indicates the concentration of $SO_2$ in the gas phase.

~~Besides~~The influence of gas phase diffusion on reactive uptake was evaluated using the resistor model described by Davidovits et al. (2006)~~reaction of $SO_2$ with $NO_2/O_2/H_2O$ on $CaCO_3$ particles in synthetic air, in some experiments, we varied~~ and references therein, as well as using the ~~concentrations of $O_2$ in~~ gas phase diffusion correction factor for a reactive uptake coefficient according to the method described by Pöschl et al. (2007)~~carrier gas in order to investigate~~. The reactive uptake of $SO_2$ was found to not be limited by gas phase diffusion (see details in the ~~effect of $O_2$ concentration on the reaction.~~ Supplement S1).

In addition, we ~~carried out~~conducted experiments ~~without $NO_2$,~~of the reaction $SO_2$ with only $O_2$ on ~~either~~both $CaCO_3$ solid ~~particle, or $CaCO_3/Ca(NO_3)_2$~~ particles and internally mixed ~~particle~~ $CaCO_3/Ca(NO_3)_2$ particles (with $CaCO_3$ embedded in $Ca(NO_3)_2$ ~~droplet in order to elucidate~~droplets), while keeping other conditions the same as the reaction of $SO_2$ with an $O_2/NO_2$ mixture. These experiments of the multiphase oxidation of $SO_2$ by $O_2$ can help determine the role of $NO_2$ in the reaction of $SO_2$ with an $O_2/NO_2$ mixture.

## 3 Results and discussion

### 3.1 Reaction products and changes in particle morphology ~~change~~

Figure 1 shows the Raman spectra of a $CaCO_3$ particle during the multiphase reaction of $SO_2$ with $O_2$/$NO_2$/~~$O_2$/~~$H_2O$ on ~~it in synthetic air.~~its surface. The peak at ~~1087~~1,087 cm$^{-1}$ ~~is~~was assigned to the symmetric stretching of carbonate ($\nu_s(CO_3^{2-}$~~))~~)) (Nakamoto, 1997). During the reaction, the peak at ~~1087~~1,087 cm$^{-1}$ decreased continuously and finally disappeared ~~and some~~as new peaks were observed. The peak at ~~1050~~1,050 cm$^{-1}$ ~~is~~was assigned to the symmetric stretching of nitrate ($\nu_s(NO_3^-$~~)).~~)). The peaks at ~~1010~~1,010 cm$^{-1}$ and ~~1136~~1,136 cm$^{-1}$ ~~a~~were assigned to the symmetric stretching ($\nu_s(SO_4^{2-}$~~))~~)) and asymmetric stretching($\nu_{as}(SO_4^{2-}$~~))~~)) of sulfate in gypsum ($CaSO_4\cdot 2H_2O$), respectively (Sarma et al., 1998). In addition, after the reaction, a broad envelope in the range of ~~2800-3800~~2,800–3,800 cm$^{-1}$ assigned to ~~OH~~the stretching of the OH bond in water molecules was observed. ~~On the top of~~Above this envelope, there ~~a~~were two peaks at ~~3408~~3,408 cm$^{-1}$ and ~~3497~~3,497 cm$^{-1}$, which ~~a~~were assigned to ~~the~~ OH bond stretching in crystallization water of $CaSO_4\cdot 2H_2O$ (Sarma et al., 1998; Ma et al., 2013).

During the multiphase reaction with the $SO_2$/$O_2$/$NO_2$/~~$O_2$/~~$H_2O$ mixture, the $CaCO_3$ ~~particle showed~~particles displayed a remarkable change in morphology. The original $CaCO_3$ particle was a rhombohedron crystal (Fig. 2, panel i, a). As the reaction proceeded, its edges became smoother and later a transparent droplet layer formed, which had a newly ~~-~~formed solid phase embed in it (Fig. 2, panel i, d). The size of the new solid phase grew during the reaction (Fig. 2, panel i, d~~-~~–f) and it seemed to contain ~~a number of~~many micro-crystals. Raman mapping reveal~~s~~ed that the new solid phase consisted of $CaSO_4\cdot 2H_2O$ (Fig. 2, panel iv), and the surrounding aqueous layer consisted of $Ca(NO_3)_2$ (Fig. 2, panel iii).

The particle morphology change shown in Fig. 2 ~~is~~was significantly different from the morphology change in the ~~absence~~direct reaction of ~~$O_2$~~$SO_2$ with $NO_2$ (Zhao et al., 2017), where the $CaCO_3$ particle was first converted to a spherical $Ca(NO_3)_2$ droplet and then needle-shaped $CaSO_4$ crystals formed inside the droplet (Zhao et al., 2017). Moreover, the amount of $CaSO_4$ formed in ~~the presence of $O_2$~~this study was much higher than that in the ~~absence of $O_2$.~~direct reaction of $SO_2$ with $NO_2$. The $CaSO_4$ solid particle constituted ~~most~~ a significant fraction of the volume of the ~~volume~~ droplet~~ here~~, while in the ~~absence~~direct reaction of ~~$O_2$~~$SO_2$ with $NO_2$ the few needle-shaped $CaSO_4$ crystals that formed only constituted a small fraction of the droplet volume (Zhao et al., 2017).

## 3.2 Reaction process

During the reaction, the amounts of carbonate, nitrate, and sulfate were ~~followed~~determined as a function of time, as shown in Fig. 3. ~~In~~At the beginning of the reaction, the amount of carbonate decreased slowly~~ and~~, while the amount of nitrate and sulfate increased slowly. After a period of induction of around 50 min, the reaction accelerated significantly, leading to a ~~fast~~rapid consumption of carbonate and production of nitrate and sulfate. The decrease in the amount of carbonate and the increase in the amount of nitrate was because carbonate reacted continuously with $NO_2$ and $H_2O$, forming $Ca(NO_3)_2$. The detailed mechanism of the multiphase reaction of carbonate with $NO_2$ and $H_2O$ were discussed in our previous studies (Li et al., 2010; Zhao et al., 2017). The mechanism of sulfate formation is discussed in detail in Section 3.4 of the present study. Finally, the carbonate was completely consumed, and the amounts of nitrate and sulfate levelled off.

Figure 3 shows that nitrate and sulfate were formed simultaneously during the reaction. This ~~finding is in contrast to~~contrasts with the ~~finding in the absence~~observations made during the direct reaction of ~~$O_2$~~$SO_2$ with $NO_2$, where nitrate was formed first, and sulfate was essentially formed after the complete conversion of $CaCO_3$ particles to $Ca(NO_3)_2$ droplets (Zhao et al., 2017)~~droplet.~~. Moreover, the time taken for carbonate to be completely consumed was longer ~~here~~in this study than ~~that~~ in the ~~absence~~direct reaction of ~~$O_2$~~$SO_2$ with $NO_2$ (~120 ~~min~~ vs. ~40 min) when other conditions were kept the same (Zhao et al., 2017).

## 3.3 Reactive uptake coefficient of $SO_2$

The reactive uptake coefficients of $SO_2$ for sulfate formation (γ) in the reaction of $SO_2$ with the $O_2$/$NO_2$/~~$O_2$~~/$H_2O$/$N_2$ mixture on $CaCO_3$ ~~in synthetic air and in $O_2/N_2$ carrier gas~~ with vari~~ed~~ous $O_2$ concentrations ~~is~~are shown in Table 1. The value of γ for the reaction of $SO_2$ with $O_2$/$NO_2$ ~~in presence of~~at three $O_2$ concentrations (5~~%-~~, 20, and 86%) ~~is~~was in the range of (0.35~~ to ~~–1.7~~×~~) × $10^{-5}$, and ~~is~~was 1.2~~×~~ × $10^{-5}$ in synthetic air. Th~~e~~is latter ~~is two to three~~ value was 2–3 orders of magnitude higher than that for the reaction ~~in $N_2$~~of $SO_2$ directly with $NO_2$ under similar conditions (Zhao et al., 2017). When other conditions were kept constant, γ increased with the $O_2$ concentration. This indicates that $O_2$ played a key role in enhancing the oxidation rate of $SO_2$.

The role of $O_2$ in enhancing the reactive uptake of $SO_2$ reported here is consistent with the findings in some ~~of~~ previous studies. For example, Littlejohn et al. (1993)'s data showed that sulfite oxidation rate increases with the $O_2$ concentration (0~~-~~–5% by volume). Shen and Rochelle (1998) also found that in the presence of $O_2$, the aqueous sulfite oxidation ~~was~~rate is enhanced. By investigating the oxidation of $SO_2$ by $NO_2$ in ~~mono-dispersed~~monodispersed water droplets growing on carbon nuclei, Santachiara et al. (1990) found that sulfate formation rate with 2% $O_2$ is much higher than that without $O_2$. Yet, our ~~finding is~~findings, as well as those in the studies referred to above, are in contrast to ~~the study~~those reported by Lee and Schwartz (1983), who found that changing from $N_2$ to air as a carrier gas only increases ~~$SO_2$~~bisulfite oxidation rate by no more than 10%. The difference between our study and Lee and Schwartz (1983)~~the study by~~ could be due to the difference in $O_2$ diffusion from gas to the condensed phase and the different mechanisms between the multiphase reaction on particles and the aqueous reaction.

Only few studies have reported the S(IV) oxidation rate in the reaction of S(IV) with $O_2$/$NO_2$ mixtures (Turšič et al., 2001; Littlejohn et al., 1993). However, due to the limiting step by the aqueous phase mass transfer, it is difficult to quantitatively compare the reaction rates in those studies with the uptake coefficient in our study and the rate constants determined by Lee and Schwartz (1983) and Clifton et al. (1988). For example, a rate constant of $2.4 \times 10^3$ $mol^{-1}$ L $s^{-1}$ (at pH 3) can be derived from the results of Turšič et al. (2001), which is much lower than the values reported by Lee and Schwartz (1983) and Clifton et al. (1988). This can be attributed to the limiting step by the aqueous-phase mass transfer because the characteristic mixing time in the aqueous phase in Turšič et al. (2001) was likely much longer than that of Lee and Schwartz (1983) (1.7–5.3 s), according to the $HSO_3^-$ concentration time series reported by Turšič et al. (2001).

## 3.4 Reaction mechanism

In the multiphase reaction of $SO_2$ with $O_2$/$NO_2$/~~$O_2$~~/$H_2O$ on $CaCO_3$ particles~~in synthetic air~~, we found that $CaCO_3$ ~~could react~~reacted with $NO_2$ and $H_2O$ and produced $Ca(NO_3)_2$, which ~~could deliquesce~~deliquesced, forming liquid water, and provided a site for the aqueous oxidation of $SO_2$. This ~~processs was~~process is similar to the direct reaction ~~in $N_2$~~of $SO_2$ with $NO_2$ on $CaCO_3$ particles. The details of this part of the reaction mechanism ~~have been~~were discussed in our previous study (Zhao et al., 2017).

Once the aqueous phase was formed, $SO_2$ ~~can~~could undergo multiphase reactions with $O_2$/$NO_2$~~/$O_2$~~. The ~~detailed~~ mechanism of the direct aqueous reaction of S(IV) with $NO_2$ in the absence of $O_2$ is complex. Previous studies have proposed two different ~~kinds of meechanism.~~mechanisms for the reaction. One involves ~~the~~ $SO_3$~~.~~$^{-\bullet}$ radical formation (Littlejohn et al., 1993; Shen and Rochelle, 1998; Turšič et al., 2001)~~and~~, while the other ~~one~~ involves the formation of ~~adduct~~$NO_2$–S(IV) complexes (Clifton et al., 1988), but no~~t~~ radical formation.

~~In the absence of $O_2$, suggest the following reaction equation,~~ According to the ~~reaction products and their yields,~~

~~$2NO_2(aq) + HSO_3^-(aq) + H_2O \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + 3H^+(aq)$ (R1)~~

~~The yields of $SO_4^{2-}$,~~ $NO_2^-$~~, and $H^+$ relative to the $HSO_3^-$ consumed are 1.0±0.05, 1.5±0.4, and 2.5±0.4, respectively, and the $NO_2^-$ formed relative to $NO_2$ consumed is 1.0±0.18.~~

~~proposed that the reaction proceeds via $NO_2$-S(IV) adduct complexes:~~

~~$NO_2(aq) + SO_3^{2-}(aq) \rightarrow [NO_2 - SO_3]^{2-}(aq)$ (R2)~~

~~$NO_2(aq) + [NO_2 - SO_3]^{2-}(aq) \rightarrow [NO_2 - SO_3 - NO_2]^{2-}(aq)$ (R3)~~

~~$[NO_2 - SO_3 - NO_2]^{2-}(aq) + OH^-(aq) \rightarrow [NO_2 - SO_4H - NO_2]^{3-}(aq)$ (R4)~~

~~$[NO_2 - SO_4H - NO_2]^{3-}(aq) \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + H^+(aq).$ (R5)~~

~~By combing reactions R2-R5, the overall reaction equation can be obtained as follows:~~

~~$2NO_2(aq) + SO_3^{2-}(aq) + H_2O \rightarrow 2NO_2^{-}(aq) + SO_4^{2-}(aq) + 2H^{+}(aq)$.~~ ~~(R6).~~

~~The reaction R6 is similar to R1.~~

~~If the $NO_2$-~~S(IV) adduct mechanism~~ were the main mechanism in this study, there should be no significant difference in the $SO_2$ oxidation rate between the reaction in~~ , the presence of $O_2$ ~~and in the absence of $O_2$. In fact, in the presence of $O_2$ we observed~~ should not affect the $SO_2$ oxidation rate; however, in this study, a substantial enhancement in the $SO_2$ oxidation rate was observed in the presence of $O_2$ compared ~~to the reaction~~with that in the absence of $O_2$. Therefore, the $NO_2$~~-~~–S(IV) adduct mechanism ~~is unlikely~~was not considered to have been important in this study.

~~In contrast to the adduct complex mechanism, suggested a~~ In the free-radical mechanism, the $SO_3^{\bullet-}$ radical is proposed to be formed (R7, Table 2), which is based on the observation of $S_2O_6^{2-}$ formation, with $S_2O_6^{2-}$ known to be the combination reaction product of $SO_3^{\bullet-}$ (Eriksen, 1974; Hayon et al., 1972; Deister and Warneck, 1990; Brandt et al., 1994; Waygood and McElroy, 1992)~~. In~~ . In addition to $SO_4^{2-}$ and $NO_2^{-}$, $S_2O_6^{2-}$ was detected with an appreciable yield using Raman spectroscopy, following the reaction of $NO_2$ with aqueous sulfite (Littlejohn et al., 1993). $S_2O_6^{2-}$ was also observed in the aqueous oxidation of bisulfite in an $N_2$-saturated solution in the presence of Fe(III) using ion-interaction chromatography (Podkrajšek et al., 2002)~~, besides $SO_4^{2-}$ and $NO_2^{-}$, they detected $S_2O_6^{2-}$ with an appreciable yield using Raman spectroscopy. Since $S_2O_6^{2-}$ is known to be the combination reaction product of $SO_3^{\bullet-}$, $SO_3^{\bullet-}$ radical is proposed to be formed:~~

~~$NO_2(aq) + SO_3^{2-}(aq) \rightarrow NO_2^{-}(aq) + SO_3^{\bullet-}(aq)$.~~ ~~(R7)~~

. The $SO_3^{\bullet-}$ radical can react via two pathways, forming either $S_2O_6^{2-}$ or $SO_4^{2-}$~~:~~

~~$SO_3^{\bullet-}(aq) + SO_3^{\bullet-}(aq) \rightarrow S_2O_6^{2-}(aq)$~~ (R8~~)~~

~~$SO_3^{\bullet-}(aq) + SO_3^{\bullet-}(aq) \rightarrow SO_3^{2-}(aq) + SO_3$~~ ~~(R9)~~

~~$SO_3(aq) + H_2O \rightarrow SO_4^{2-}(aq) + 2H^{+}(aq)$.~~ (R10~~)~~

, Table 2). The reactions R8~~-~~–R10 have been well established in ~~the study~~studies of~~ the~~ S(IV) oxidation by other pathways, including ~~the~~ OH oxidation, photo-oxidation, and transition~~al~~ metal catalyzed oxidation (Eriksen, 1974; Hayon et al., 1972; Deister and Warneck, 1990; Brandt et al., 1994; Brandt and Vaneldik, 1995; Waygood and McElroy, 1992). In addition, although previous studies have not reported the direct observation of the $SO_3^{\bullet-}$ radical in the aqueous reaction of S(IV) with $NO_2$, $SO_3^{\bullet-}$ was ~~directly~~ observed in the reaction of $NO_2^{-}$ with $SO_3^{2-}$ in an acidic buffer solution (pH~~=~~ = 4.0) using electron spin resonance (ESR) (Shi, 1994). ~~Since~~Because $NO_2^{-}$ is formed in the aqueous reaction of $SO_2$ with $NO_2$, and $S_2O_6^{2-}$ as the combination reaction product of $SO_3^{\bullet-}$ is observed (Littlejohn et al., 1993), $SO_3^{\bullet-}$ formation is plausible.

In the presence of $O_2$, the $SO_3^{\bullet-}$ radical can react rapidly with $O_2$, forming the $SO_5^{\bullet-}$ radical (R11, Table 2). Following this reaction, a number of chain reactions can occur to ultimately form sulfate (Littlejohn et al., 1993; Seinfeld and Pandis, 2006; Shen and Rochelle, 1998) (R12–R15, Table 2). Littlejohn et al. (1993) observed that the ~~relative~~ amount of $S_2O_6^{2-}$ relative to $SO_4^{2-}$ formed in the aqueous reaction of $NO_2$ with sulfite decreases ~~and $S_2O_6^{2-}$ is undetectable~~in the presence of $O_2$ compared with the reaction in the absence of $O_2$. At low $NO_2$ concentrations (< 5 ppm~~)~~), $S_2O_6^{2-}$ is undetectable in the ~~aqueous reaction~~presence of ~~$NO_2$ with sulfite~~$O_2$. This indicates that $O_2$ suppresses the reaction pathway of $S_2O_6^{2-}$ formation (R8, Table 2). Because the $SO_3^{\bullet-}$ radical can react rapidly with $O_2$, forming the $SO_5^{\bullet-}$ radical, and ~~thus~~would therefore be consumed, the suppression of $S_2O_6^{2-}$ ~~is readily~~ formation can be attributed to the reac~~i~~tion of $SO_3^{\bullet-}$ with $O_2$~~.~~

~~$SO_3^{\bullet-}(aq) + O_2(aq) \rightarrow SO_5^{\bullet-}(aq)$ (R11)~~

~~Following this reaction, a number of chain reactions can occur and form sulfate :~~

~~$SO_5^{\bullet-}(aq) + SO_3^{2-}(aq) + H^+(aq) \rightarrow HSO_5^-(aq) + SO_3^{\bullet-}(aq)$ (R12)~~

~~$HSO_5^-(aq) + SO_3^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + H^+(aq)$ (R13)~~

~~$SO_5^{\bullet-}(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + SO_4^{\bullet-}(aq)$ (R14)~~

~~$SO_4^{\bullet-}(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + SO_3^{\bullet-}(aq).$ (R15)~~

~~The reactions~~ (R11~~-~~, Table 2). The reactions R11–R15 have been well established by ~~the study on~~studies of the oxidation of S(IV) by OH or photo-oxidation, and all the radicals have been observed (Hayon et al., 1972; Huie et al., 1989; Huie and Neta, 1987; Chameides and Davis, 1982; Seinfeld and Pandis, 2006).

The free-radical chain mechanism is consistent with the findings of this study and is therefore more plausible ~~here~~. The enhancement of ~~$SO_2$ oxidation rate in the reaction of~~the $SO_2$ oxidation rate in the reaction of $SO_2$ with $O_2$/$NO_2$~~/$O_2$~~/$H_2O$ ~~with~~ on $CaCO_3$ particles ~~in synthetic air~~ compared ~~to~~with that in ~~$N_2$ can be~~the direct reaction of $SO_2$ with $NO_2$/$H_2O$ was attributed to~~ the role of~~ $O_2$. Although during the reaction in the absence of $O_2$~~, that is,~~—i.e., the direct oxidation of $SO_2$ by $NO_2$~~,~~—the $SO_3^{\bullet-}$ radical can be formed (R7), the reaction chain cannot propagate (R11~~-~~–R15). Therefore, the S(IV) oxidation rate and the reactive uptake coefficient of $SO_2$ were much lower than that in the presence of $O_2$. According to the difference between the reactive uptake coefficient in ~~the absence of $O_2$~~this study and in the direct reaction of $SO_2$ with $NO_2$ (Zhao et al., 2017)~~presence of $O_2$,~~, the sulfate production rate via chain reactions due to the presence of $O_2$ (20%) was ~~two to three~~2–3 orders of magnitude faster than the direct oxidation of $SO_2$ by $NO_2$. This indicates that sulfate production in the reaction of $SO_2$ with $O_2$/$NO_2$ was largely ~~contributed by~~due to $O_2$ oxidation via the chain reaction pathway, i.e., ~~“auto-~~“autoxidation” of S(IV), rather than the direct oxidation~~”~~ of ~~S(IV)~~$SO_2$ by $NO_2$ and thus $O_2$ was the main oxidant of $SO_2$.

Although the direct ~~re~~oxida~~e~~tion of $SO_2$ by $NO_2$ ~~with $SO_2$~~ only ~~contributed~~ accounted for a very small fraction ~~to~~of sulfate formation, $NO_2$ played an important role in the $SO_2$ oxidation by initia~~l~~ti~~zi~~ng the chain reactions via ~~producing~~the production of the $SO_3^{\bullet-}$ radical (R7). In the experiment without $NO_2$ ~~while keeping~~, but with other reaction conditions the same, we ~~found that no~~were unable to detect sulfate ~~was formed~~ after 5 h of reaction. This indicates that $O_2$ by itself cannot initia~~liz~~te the chain reaction~~,~~s (although it favors chain propagation~~. Therefore, $NO_2$ initiated~~), and that the oxida~~i~~tion of $SO_2$ by $O_2$ ~~and it is the syngergy~~was slow. The effect on the $SO_2$ oxidation rate when both $NO_2$ and $O_2$ were present was much higher than the sum of the effect of $NO_2$ and $O_2$ ~~that~~. We refer to this effect as the synergy of $NO_2$ and $O_2$, which resulted in the fast oxidation of $SO_2$ ~~forming~~to form sulfate in this study. ~~Without either $NO_2$~~ This effect is similar to a “ternary” reaction found with the reaction of $NO_2$–particles–$H_2O$ or $SO_2$–particles–$O_3$ (Zhu et al., 2011)~~$O_2$,~~, where the reaction ~~proceeded much slower~~rate can be much faster than the sum of the reaction rates for the reaction of the second and third reactant with the first reactant. In addition to acting as the initiator of chain reactions, $NO_2$ also contributed to the formation of the aqueous phase through the reaction with $CaCO_3$, forming $Ca(NO_3)_2$ as discussed above, which provided a site for S(IV) oxidation.

Based on the discussion above, we summarize the reaction mechanism ~~of~~that occurred in this study in Table 2. The reactions are classified as chain initiation, chain propagation, and chain termination. The dominant S(IV) species depends on pH. Due to the ~~rapid inter-conversion between $H_2SO_3$,~~fast dissociations of $SO_2$•$H_2O$ and $HSO_3^-$~~, and $SO_3^{2-}$~~;~~,~~ reactions consuming one of these S(IV) species will result in instantaneous re-establishment of the equilibria between them (Seinfeld and Pandis, 2006)~~.~~. In this study, the pH of the aqueous layer of $Ca(NO_3)_2$ may change dynamically with time during the reaction and may not be completely homogeneous within the aqueous droplet. The pH values could vary between ~3 and ~7.6. In the surface of the aqueous layer, pH was mainly determined by the gas–aqueous equilibrium of $SO_2$, and was estimated to be ~3. In the vicinity of the $CaCO_3$ core, pH was mainly determined by the hydrolysis of carbonate and was estimated to be ~7.6. It is likely that both $HSO_3^-$ and $SO_3^{2-}$ were present, and the dominant species depended on the reaction time and location within the aqueous droplet. Nevertheless, to make the reaction mechanism clearer, $HSO_3^-$ was used in the reaction equations. Similar reaction equations are also applicable to $SO_3^{2-}$ because of the fast dissociations of $SO_2$•$H_2O$ and $HSO_3^-$. Overall, the reaction can be written as follows, which ~~shows~~ clearly shows that $O_2$ was the main oxidant for sulfate formation:

$$2NO_2(aq) \cancel{+ 2SO_3^{2-}(aq) + (0-1)O_2} + 2HSO_3^-(aq) + (0/1)O_2 \rightarrow 2NO_2^-(aq) + S_2\cancel{O_{6-8}^{2-}}O_{6/8}^{2-}(aq) + 2H^+(aq), \qquad (R18)$$

$$\cancel{2SO_3^{2-}(aq) + O_2 \rightarrow 2S}nO_2 + 2nHSO_3^-(aq) \rightarrow 2nSO_4^{2-}\cancel{(aq)}(aq) + 2nH^+(aq), \qquad (R19)$$

$$\cancel{2HSO_3^-(aq) + O_2 \rightarrow 2SO_4^{2-}(aq) + 2H^+(aq). \qquad (R20)}$$

where n >> 1. Once sulfuric acid was formed, it ~~can further react~~reacted with $CaCO_3$, forming $CaSO_4$:

$$CaCO_3(s) + SO_4^{2-}(aq) + 2H^+(aq) + H_2O(aq) \rightarrow CaSO_4 \bullet 2H_2O(s) + CO_2(g). \qquad (R20)$$

~~Overall, besides acting as the initializer of the chain reaction, $NO_2$ contributed to the formation of aqueous phase by the reaction with $CaCO_3$ forming $Ca(NO_3)_2$ as discussed above. The aqueous phase provided the site for S(IV) oxidation.~~

As mentioned above, compared with the direct reaction ~~in $N_2$~~of $SO_2$ with $NO_2$, $CaCO_3$ was consumed ~~slower~~more slowly in the reaction ~~in synthetic air. This difference can be attributed to~~with $O_2$/$NO_2$. There were two possible reasons~~. Firstly~~ for this. First, the $CaSO_4$~~·~~•$2H_2O$ formed in the reaction ~~can~~could cover the $CaCO_3$ surface and partly suppress the diffusion of aqueous ions, such as protons, and also limit the contact of reactants with ~~$CaCO_3$~~the surface of the $CaCO_3$ particles, thus reducing the $CaCO_3$ consumption rate. Second~~ly~~, compared with the direct reaction ~~in $N_2$~~of $SO_2$ with $NO_2$, a much higher fraction of $CaCO_3$ was converted to $CaSO_4$~~·~~•$2H_2O$ instead of $Ca(NO_3)_2$ due to the fast production of $CaSO_4$~~·~~•$2H_2O$. Therefore, the volume of a $Ca(NO_3)_2$ droplet was much smaller than that ~~for~~in the direct reaction ~~in $N_2$~~of $SO_2$ with $NO_2$ for a given $CaCO_3$ particle. ~~Since~~Because the uptake rate of $NO_2$ was proportional to the droplet surface area and the $NO_2$ hydrolysis rate ~~is~~was proportional to the droplet volume, the ~~production~~ rate of nitric acid production from $NO_2$ hydrolysis and its reaction rate with $CaCO_3$ were reduced. Therefore, the $CaCO_3$ ~~particle was~~ particles were consumed ~~slower~~more slowly in the reaction with $O_2$/$NO_2$.

## 4 Conclusion and implications

We investigated the multiphase reaction of $SO_2$ with $O_2$/$NO_2$/~~$O_2$/~~$H_2O$ on $CaCO_3$ ~~particle in synthetic air.~~particles. The reaction converted $CaCO_3$ particles to $Ca(NO_3)_2$ ~~droplet with~~droplets, in which $CaSO_4$~~·~~•$2H_2O$

~~particle~~was embedded ~~in it. $CaSO_4 \cdot 2H_2O$ constituted~~ and accounted for a ~~large~~significant fraction of the droplet volume ~~in~~by the end of the reaction~~, in contrast to the small fraction of the droplet volume in the absence of $O_2$.~~. The $Ca(NO_3)_2$ droplet formed by the reaction of $CaCO_3$ with $NO_2$ provided a site for the multiphase oxidation of $SO_2$. Generally, nitrate and sulfate were formed simultaneously. The reactive uptake coefficient of $SO_2$ for sulfate formation in the reaction of $SO_2$ with $NO_2$/~~$O_2$~~$H_2O$ in synthetic air was determined to be around $10^{-5}$. Compared with the reaction of $SO_2$ with $NO_2$ on a $CaCO_3$ particle in ~~$N_2$, that is,~~the absence of $O_2$, i.e., the direct oxidation of $SO_2$ by $NO_2$ in $N_2$, sulfate production rate in the reaction of $SO_2$ with $O_2$/$NO_2$ was enhanced by ~~around two to three~~2–3 orders of magnitude~~ in the presence of $O_2$.~~. According to the findings of this study and the existing literature, $SO_2$ oxidation likely proceeded via a free-radical chain reaction mechanism~~ according to the findings of this study and literature.~~. $O_2$ was the main oxidant of $SO_2$, and $NO_2$ mainly acted as an initia~~lize~~tor of the chain reactions. The synergy of $NO_2$ and $O_2$ resulted in the fast oxidation of $SO_2$. The absence of either $NO_2$ or $O_2$ led to much slower $SO_2$ oxidation.

Using a method ~~used~~developed in our previous study (Zhao et al., 2017), we assessed the importance of the multiphase ~~re~~oxida~~c~~tion of $SO_2$ ~~with~~by $O_2$ in the presence of $NO_2$~~/$O_2$/$H_2O$~~ by estimating the lifetime of $SO_2$ due to multiphase reactions and the lifetime due to the gas phase reaction (with the OH radical). The lifetime of $SO_2$ due to the multiphase reaction of $SO_2$ with $O_2$/$NO_2$~~/$O_2$ is~~ was estimated to be around 20 days using the reactive uptake coefficient of $SO_2$ ~~of~~ (1.2~~×~~ × $10^{-5}$) and ~~a~~the typical particle surface area concentration for mineral aerosols in winter in Beijing (6.3~~×~~ × $10^{-6}$ $cm^2$ $cm^{-3}$) (Huang et al., 2015). This lifetime is ~~substantially shorter than the lifetime regarding the direct oxidation of $SO_2$ by $NO_2$ (~7000 days), and~~ comparable to the lifetime of $SO_2$ due to the gas phase reaction with OH~~ (~~, which is ~12 days assuming that the daytime OH concentration is 1~~×~~ × $10^6$ molecules $cm^{-3}$~~)~~ (Lelieveld et al., 2016; Prinn et al., 2005). Therefore, we conclude that the multiphase oxidation of $SO_2$ by $O_2$ in the presence of $NO_2$ is likely to be an important source of sulfate and a sink of $SO_2$ in the ambient atmosphere, and can play a significant role in the sulfate formation ~~in the heavily polluted~~during severe haze episodes, such as those that frequently occur~~ring~~ in China. ~~High sulfate concentrations are observed during these~~ During haze episodes, ~~but the mechanism of sulfate formation is still not clear. Model simulation often substantially underestimate sulfate . During the haze episodes, the~~ there are high concentrations of $SO_2$ and $NO_2$~~ co-exist~~ and relative humidity is often high (Zhang et al., 2014; Wang et al., 2016; Zheng et al., 2015b). Under these conditions, the multiphase oxidation of $SO_2$ by $O_2$ in the presence of $NO_2$ could proceed rapidly, forming sulfate. The enhanced sulfate concentration due to multiphase reactions and result~~ed~~ing aerosol water content can further promote the multiphase oxidation of $SO_2$. The reaction thus proceeds in a self-accelerat~~ed~~ing way. Therefore, it can contribute significantly to sulfate formation during haze episodes, which could explain the discrepancies between the observed and modelled sulfate concentrations (Cheng et al., 2016; Gao et al., 2016; Wang et al., 2016; Zheng et al., 2015a)~~.~~.

~~Further understanding~~In addition, elucidating the mechanism of the multiphase reaction of $SO_2$ with $O_2$/$NO_2$/$H_2O$~~/$O_2$~~ in ~~air~~ the atmosphere is important ~~to understand~~ for the other atmospheric implications of the reaction besides sulfate formation. According to the reaction mechanism, the direct oxidation of $SO_2$ by $NO_2$ forms ~~$NO_2^-$~~sulfate and nitrite, with a stoichiometry of 1:1, and nitrite can further form HONO under acidic conditions. The HONO ~~can~~could then evaporate into the atmosphere~~ and is~~, where it would be an important source of OH radical. If $NO_2$ were the main oxidant of $SO_2$ in the multiphase reaction, the reaction would form one HONO molecule for every sulfate formed. Thus, the oxidation of $SO_2$ by $NO_2$ can simultaneously be an important source of HONO and OH radical, and ~~the~~ $SO_2$ oxidation would be strongly coupled with reactive nitrogen chemistry. ~~Yet~~However, according to the mechanism of this study, $NO_2$ only acted as an initia~~lize~~tor of the chain reactions in $SO_2$ oxidation and essentially all the ~~entire~~ $SO_2$ was oxidized by $O_2$. Therefore, the amount of HONO formation per sulfate formed was trivial. The oxidation of $SO_2$ by $O_2$/$NO_2$ is expected to be neither ~~be~~ an important source of HONO and OH in the atmosphere nor ~~significantly~~to have a significant influence on reactive nitrogen chemistry.

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**Table 1.** Reactive uptake coefficient of $SO_2$ for sulfate formation ~~under~~at 82% RH and at different $O_2$ con~~di~~centrations.

| **$SO_2$/$NO_2$/~~$SO_2$/~~$O_2$ concentration** | **γ** |
|---|---|
| 75 ppm/ 75 ppm/ 86 % | $1.7\times10^{-5}$ |
| 75 ppm/ 75 ppm/ 20 % | $1.2\times10^{-5}$ |
| 75 ppm/ 75 ppm/ 5 % | $3.5\times10^{-6}$ |

**Table 2.** Summary of the mechanism of the reaction S(IV) with $O_2$/$NO_2$~~/$O_2$~~

| Step | Reactions |
|---|---|
| Initiation | ~~$NO_2(aq) + SO_3^{2-}(aq) \rightarrow NO_2^-(aq) + SO_3^{\bullet-}(aq)$ (R8a)~~<br>~~$NO_2(aq) + HSO_3^-(aq) \rightarrow NO_2^-(aq) + SO_3^{\bullet-}(aq) + H^+(aq)$ (R8b)~~ $NO_2(aq) + HSO_3^-(aq) \rightarrow NO_2^-(aq) + SO_3^{\bullet-}(aq) + H^+(aq)$ (R7) |
| Propagation | ~~$SO_3^{\bullet-}(aq) + O_2(aq) \rightarrow SO_5^{\bullet-}(aq)$~~ $SO_3^{\bullet-}(aq) + O_2(aq) \rightarrow SO_5^{\bullet-}(aq)$ (R11)<br>~~$SO_5^{\bullet-}(aq) + SO_3^{2-}(aq) + H^+(aq) \rightarrow HSO_5^-(aq) + SO_3^{\bullet-}(aq)$ (R12)~~<br>~~$SO_5^{\bullet-}(aq) + HSO_3^-(aq) \rightarrow HSO_5^-(aq) + SO_3^{\bullet-}(aq)$ (R12b)~~<br>~~$HSO_5^-(aq) + SO_3^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + H^+(aq)$ (R13)~~<br>~~$HSO_5^-(aq) + HSO_3^-(aq) \rightarrow 2SO_4^{2-}(aq) + 2H^+(aq)$ (R13b)~~<br>~~$SO_5^{\bullet-}(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + SO_4^{\bullet-}(aq)$ (R14)~~<br>~~$SO_5^{\bullet-}(aq) + HSO_3^-(aq) \rightarrow SO_4^{2-}(aq) + SO_4^{\bullet-}(aq) + H^+(aq)$ (R14b)~~<br>~~$SO_4^{\bullet-}(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + SO_3^{\bullet-}(aq)$ (R15)~~<br>~~$SO_4^{\bullet-}(aq) + HSO_3^-(aq) \rightarrow SO_4^{2-}(aq) + SO_3^{\bullet-}(aq) + H^+(aq)$ (R15b)~~ $SO_5^{\bullet-}(aq) + HSO_3^-(aq) \rightarrow HSO_5^-(aq) + SO_3^{\bullet-}(aq)$ (R12)<br>$HSO_5^-(aq) + HSO_3^-(aq) \rightarrow 2SO_4^{2-}(aq) + 2H^+(aq)$ (R13)<br>$SO_5^{\bullet-}(aq) + HSO_3^-(aq) \rightarrow SO_4^{2-}(aq) + SO_4^{\bullet-}(aq) + H^+(aq)$ (R14)<br>$SO_4^{\bullet-}(aq) + HSO_3^-(aq) \rightarrow SO_4^{2-}(aq) + SO_3^{\bullet-}(aq) + H^+(aq)$ (R15) |
| Termination | ~~$SO_3^{\bullet-}(aq) + SO_3^{\bullet-}(aq) \rightarrow S_2O_6^{2-}(aq)$~~ $SO_3^{\bullet-}(aq) + SO_3^{\bullet-}(aq) \rightarrow S_2O_6^{2-}(aq)$ (R8)<br>~~$SO_3^{\bullet-}(aq) + SO_3^{\bullet-}(aq) \rightarrow SO_3^{2-}(aq) + SO_3$ (R9~~<br>~~$SO_3(aq) + H_2O \rightarrow SO_4^{2-}(aq)$~~ $SO_3^{\bullet-}(aq) + SO_3^{\bullet-}(aq) \rightarrow SO_3^{2-}(aq) + SO_3$ (R9)<br>$SO_3(aq) + H_2O \rightarrow SO_4^{2-}(aq) + 2$~~$H^+(aq)$~~ $H^+(aq)$ (R10)<br>~~$SO_4^{\bullet-}(aq) + SO_4^{\bullet-}(aq) \rightarrow S_2O_8^{2-}(aq)$~~ $SO_4^{\bullet-}(aq) + SO_4^{\bullet-}(aq) \rightarrow S_2O_8^{2-}(aq)$ (R16)<br>~~$SO_5^{\bullet-}(aq) + SO_5^{\bullet-}(aq) \rightarrow S_2O_8^{2-}(aq) + O_2(aq)$ (R17)~~ $SO_5^{\bullet-}(aq) + SO_5^{\bullet-}(aq) \rightarrow S_2O_8^{2-}(aq) + O_2(aq)$ (R17) |

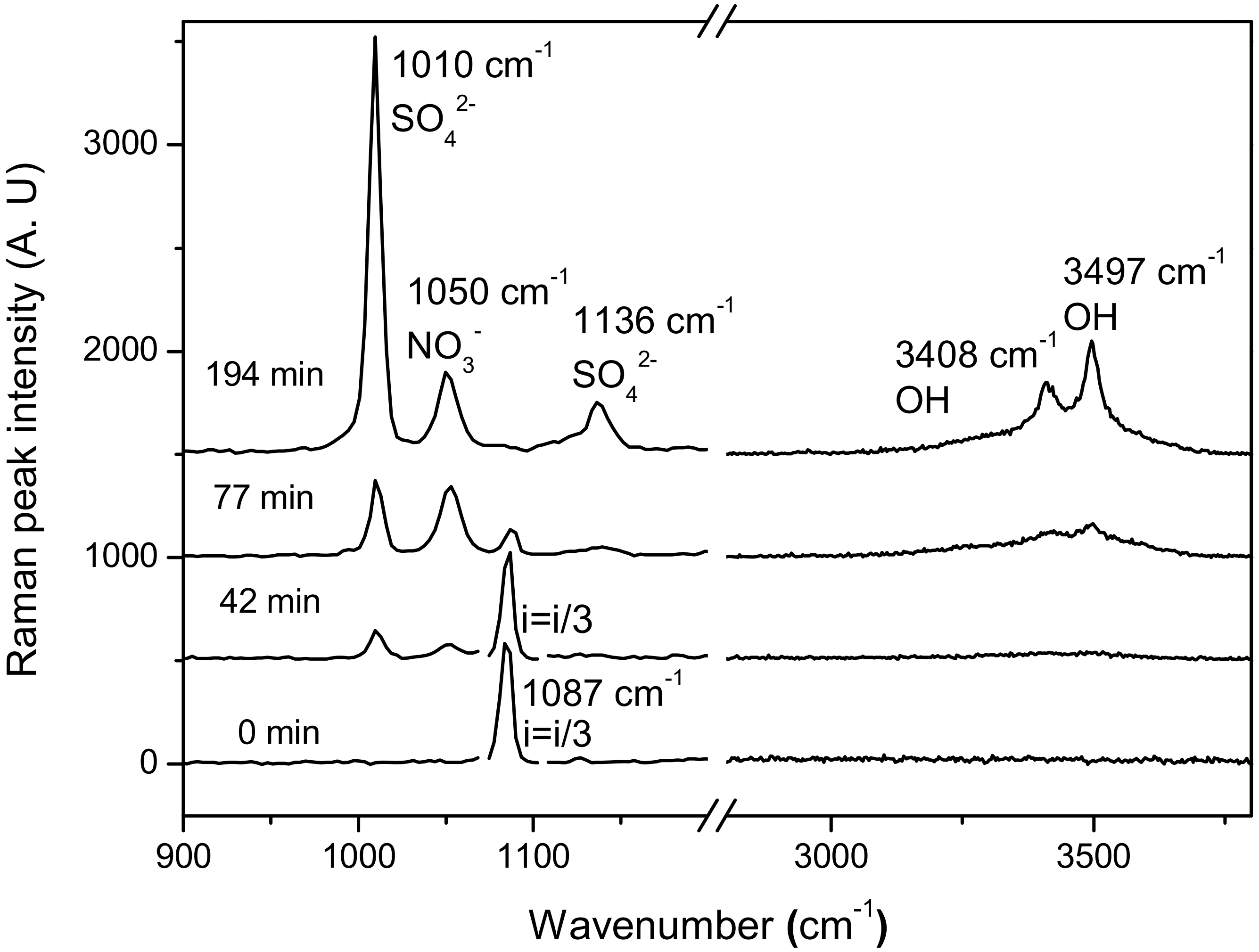
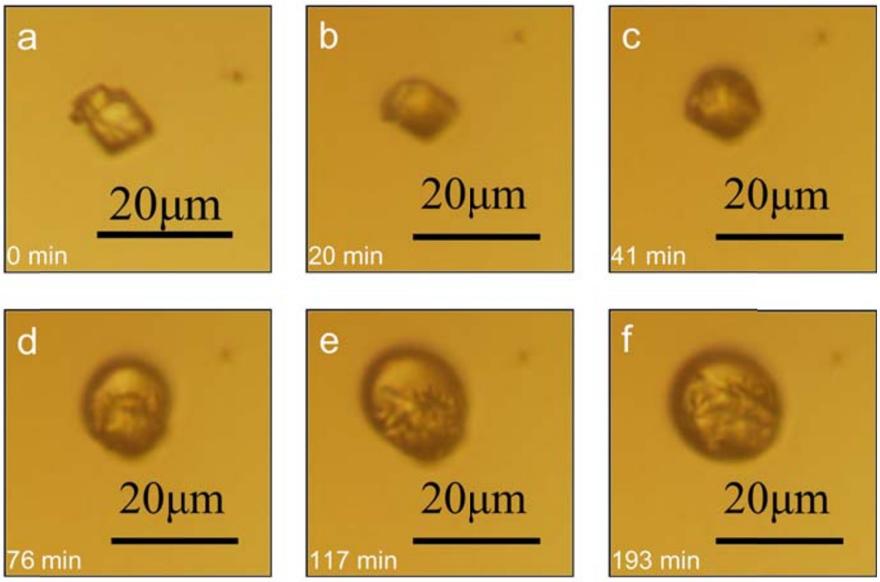


Figure 1. Raman spectra of a $CaCO_3$ particle during the multiphase reaction of $SO_2$ with $O_2$/$NO_2$/~~$O_2$/~~$H_2O$ on the particle~~ in synthetic air.~~. $SO_2$: 75 ppm, $NO_2$: 75 ppm, RH: 72%, $O_2$: 20%. The peak intensity of carbonate (1087 cm$^{-1}$) at 0 and 42 min was divided by three for ~~clearness.~~ clarity.


a
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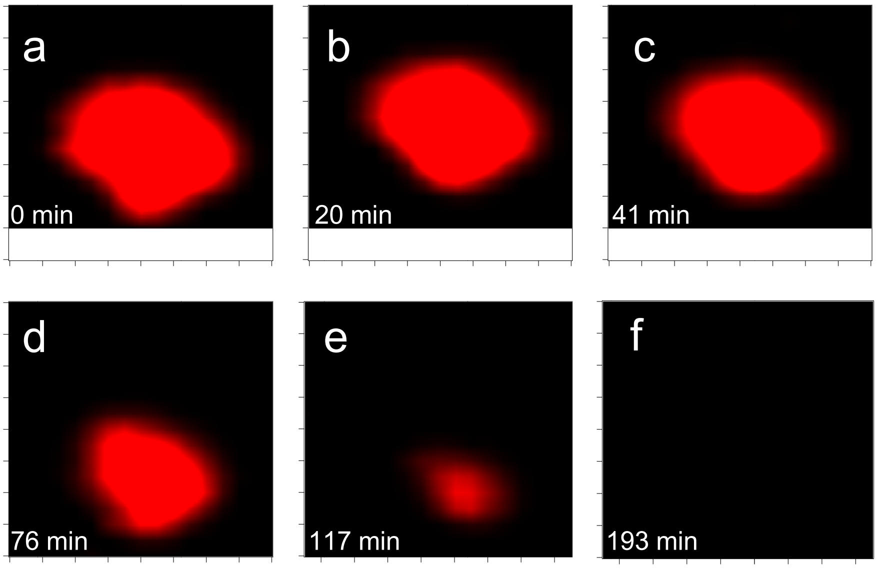
193 min

(i)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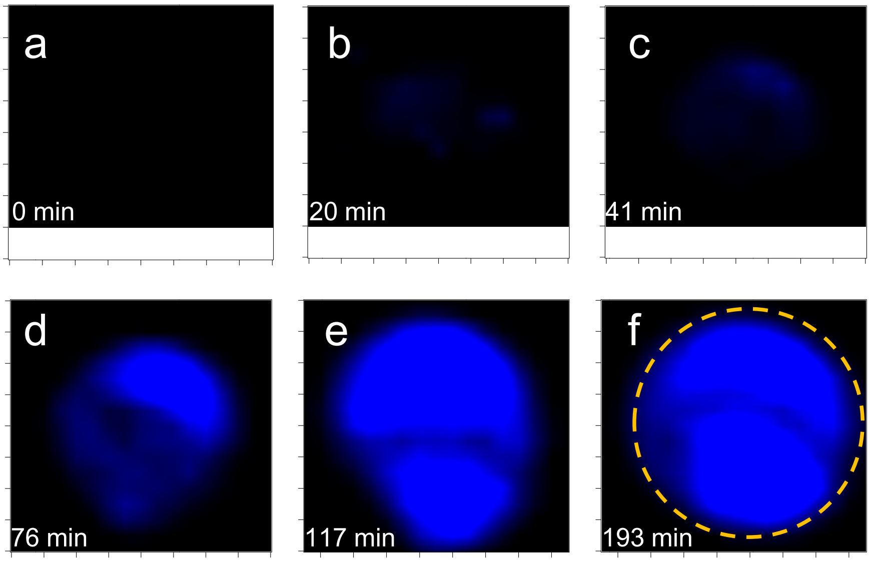
(ii)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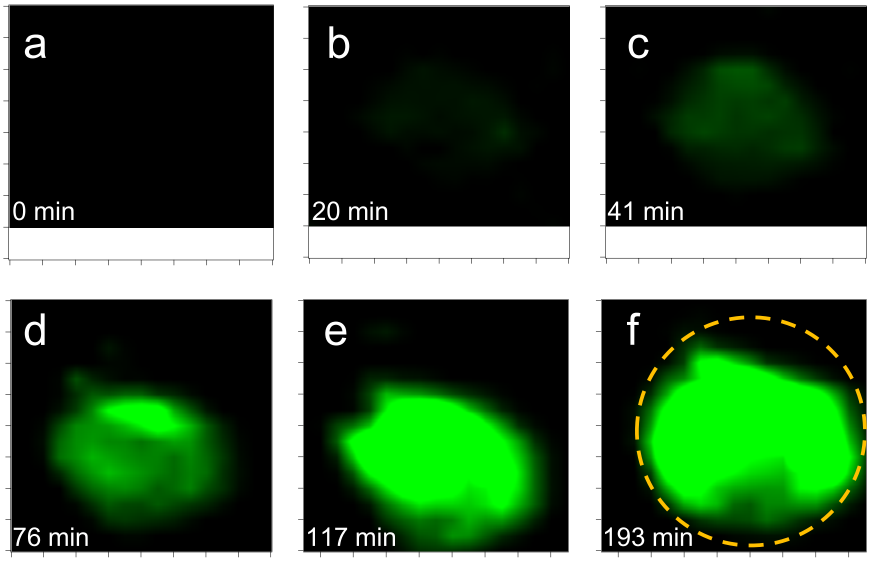
(iii)



(iv)

Figure 2. Microscopic image (i) and Raman mapping image of carbonate (ii), nitrate (iii), and sulfate (iv) on the CaCO$_3$ particle during the multiphase reaction SO$_2$ with O$_2$/NO$_2$/~~O$_2$/~~H$_2$O on the particle~~ in synthetic air.~~. A-f corresponds to the reaction time of 0, 20, 41, 76, 117, and 193 min. SO$_2$: 75 ppm, NO$_2$: 75 ppm, RH: 72%, O$_2$: 20%. The mapping image of carbonate, nitrate, and sulfate are made using the peak area at 1050, 1010, and 1087 cm$^{-1}$, respectively. The red, blue, and green colors indicate the peak intensity of carbonate, nitrate, and sulfate, respectively. The dashed lines in panel iii-f and iv-f indicate the shape of the droplet at the end of the reaction.

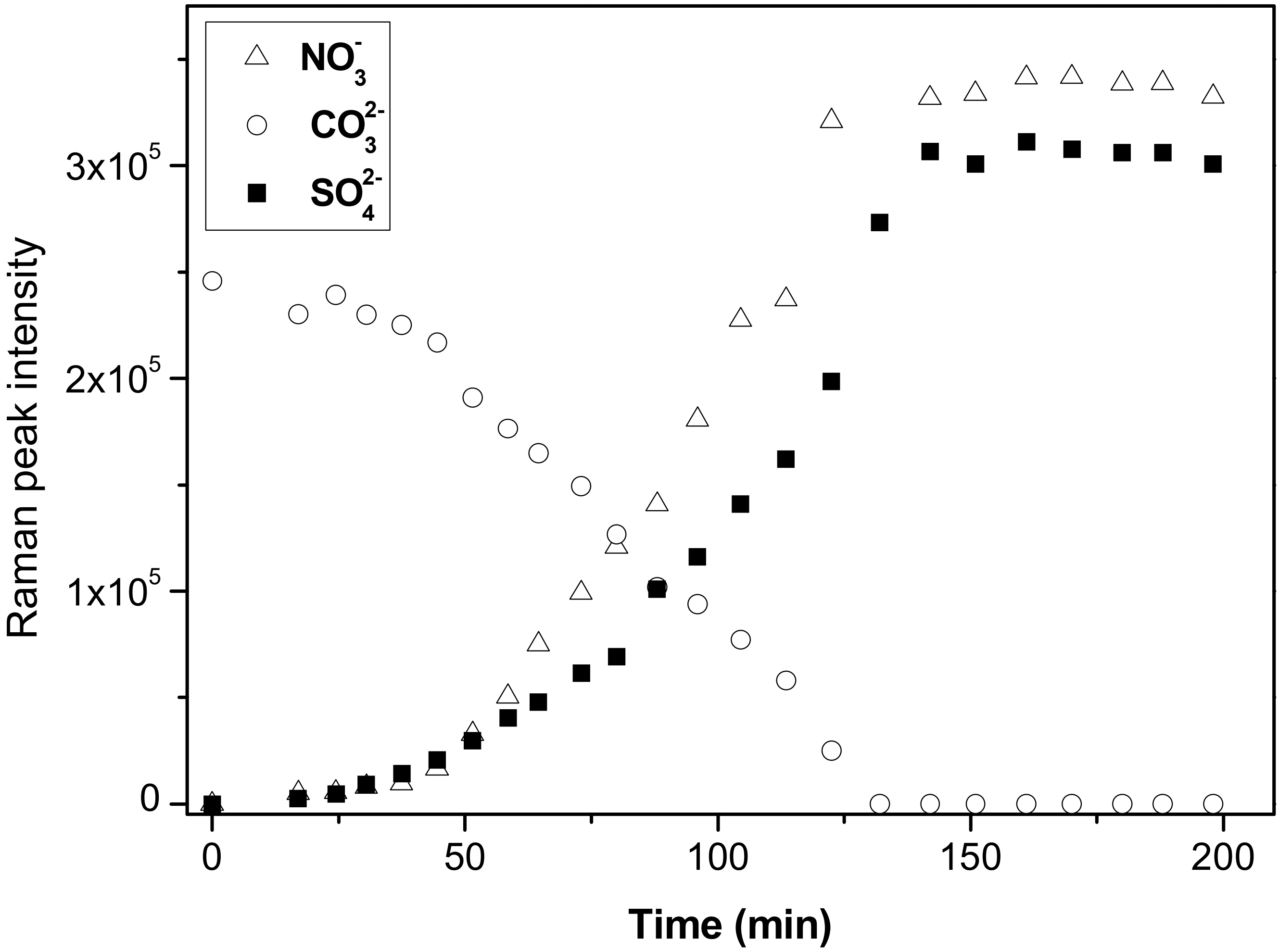


Figure 3. Time series of the Raman peak intensity of ~~the carbonate, nitrate,~~ $NO_3^-$, $SO_4^{2-}$, and ~~sulfate~~ $CO_3^{2-}$ during the reaction of $SO_2$ with $O_2$/$NO_2$/~~$O_2$~~/$H_2O$ on $CaCO_3$ particles~~ in synthetic air.~~. $SO_2$: 75 ppm, $NO_2$: 75 ppm, RH: 72%, $O_2$: 20%. The intensity of $NO_3^-$, $SO_4^{2-}$, and $CO_3^{2-}$ show the peak area at 1050, 1010, and 1087 $cm^{-1}$, respectively, in Raman spectra obtained by Raman mapping.