

Response to reviewer #1

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

General comments

In this manuscript, the results on multiphase reaction of SO₂ on individual CaCO₃ particles in the presence of NO₂ and O₂ at RH 72% using Micro-Raman spectrometer with a flow reaction system are presented. The main conclusion is that CaCO₃ converts first to Ca(NO₃)₂ droplet (by the reaction with NO₂), where actually further aqueous SO₂ oxidation by O₂ takes place. The reactive uptake coefficient γ of SO₂ determined on the basis of SO₄²⁻ formation rate was ca. three orders of magnitude higher than that determined in the absence of O₂. 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 NO₂ with HSO₃⁻/SO₃²⁻, where SO₃⁻ radical is formed, which reacts quickly with O₂ to form SO₅⁻, etc...The presented mechanism is well known and confirmed by many authors, and as expected the reaction under O₂ 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 SO₂/NO₂/H₂O/N₂ and SO₂/NO₂/H₂O/O₂ 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 will make major changes to the manuscript in order to make the text more clear and improve readability. Moreover, we will have a thorough language check of the text of

this manuscript and correct 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 SO₂ directly with NO₂ is an important pathway for sulfate formation in the real atmosphere, e.g., during haze episodes in China, requires investigating the “pure” reaction of SO₂ with NO₂ 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 SO₂ with O₂ in the presence of NO₂ is an important reaction pathway of SO₂ oxidation; obviously, this reaction is more relevant to real atmospheric conditions.

2. We found that the multiphase reaction of SO₂ with NO₂ and the reaction of SO₂ with O₂ in the presence of NO₂ have significantly different chemistry, with different reaction mechanisms, products, and atmospheric implications.

i. The multiphase reaction of SO₂ directly with NO₂ involves two reactants whereas the reaction of SO₂ with O₂/NO₂ involves three reactants. In the former reaction NO₂ is the main oxidant of SO₂ while in the latter reaction O₂ is the main oxidant of SO₂ and NO₂ only acts as an initiator of chain reactions.

ii. According to the reaction mechanism, the main products in the multiphase reaction of SO₂ with NO₂ are sulfate and nitrite with a stoichiometry of 1:1. In contrast, the main product in the multiphase reaction of SO₂ with O₂ in the presence of NO₂ is sulfate and the ratio of sulfate to nitrite is much higher than 1:1 because nitrite is only formed in the chain initiation step.

iii. Due to the different reaction mechanism, the atmospheric implication of the reaction of SO₂ with O₂ in the presence of NO₂ is significantly different from the direct reaction of SO₂ with NO₂ because the former leads to much faster sulfate formation and has much less influence on reactive nitrogen chemistry in the atmosphere.

Based on these reasons, we will change the title of this manuscript to “NO₂-initiated Multiphase Oxidation of SO₂ by O₂ on CaCO₃ Particles” in the revised manuscript. Accordingly, in the revised manuscript we will delete the parts where we stated about the companionship of these two papers (lines 63-64, 80 in the manuscript). We will also adjust 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.

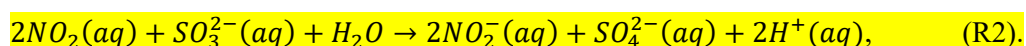
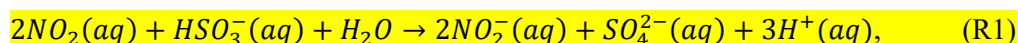
Discussion on the p.6/7 should partly be included here. Especially, the mechanism (R1-R6) does not fit on p.6, because it seems that is not important for their results.

Response:

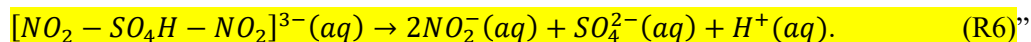
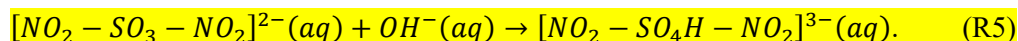
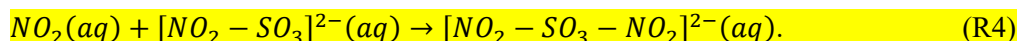
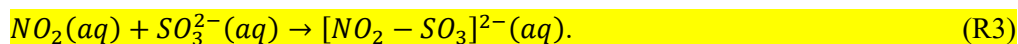
Agree. In the revised manuscript, we will make major changes to the introduction and add the published mechanism to the introduction.

As the reviewer suggested, in the introduction we will also include part of the discussion regarding the mechanism on the p.6-7. It will read:

“Despite such a reaction mechanism of SO₂ oxidation has been proposed, its role in the SO₂ oxidation in the ambient atmosphere is not well established. Most previous studies focus on the direct reaction of SO₂ with NO₂, including determining 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 yields (Lee and Schwartz, 1983; Clifton et al., 1988), the overall reaction equation of the direct reaction of NO₂ with SO₂ is as follows:



which were proposed to proceed via NO₂-S(IV) adduct complexes (Clifton et al., 1988).



2. P. 2, line 39 and p. 8, line 243: Dissolution/absorption of SO₂ in aqueous solution results in total dissolved S(IV), i.e. three species SO₂x H₂O, HSO₃⁻ and SO₃²⁻, which are in equilibrium; which species will prevail depends on pH! So, H₂SO₃ (2H⁺+SO₃²⁻) 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 will change “H₂SO₃” to “SO₂•H₂O”. And we will change “rapid interconversion” to “fast dissociations of SO₂•H₂O and HSO₃⁻”.

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 O₂ 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 will elaborate the experimental part and clarified this point as follows.

“The experiments of this study were conducted under two RH (72% and 82%) at 75 ppm SO₂ and 75

ppm NO_2 .”

4. Can you say something on pH of the formed aqueous layer of $\text{Ca}(\text{NO}_3)_2$? 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 $\text{Ca}(\text{NO}_3)_2$ 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 will add short discussion on this point.

“The dominant S(IV) species depends on pH. Due to the fast dissociations of $\text{SO}_2 \cdot \text{H}_2\text{O}$ 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 $\text{Ca}(\text{NO}_3)_2$ may change dynamically with time during the reaction and may not 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 estimated to be ~ 3 . In the vicinity of the CaCO_3 core, pH was mainly determined by the hydrolysis of carbonate and 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, in order to make the reaction mechanism more clear, HSO_3^- is used in the reaction equations. Similar reaction equations are also applicable to SO_3^{2-} because of the fast dissociations of $\text{SO}_2 \cdot \text{H}_2\text{O}$ and HSO_3^- .”

Results and discussion:

5. If you once define that you have a system $\text{NO}_2/\text{H}_2\text{O}/\text{O}_2$, 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 will 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 will briefly

discuss this point.

“The decrease of carbonate and the increase of nitrate is because carbonate continuously reacted with NO_2 and H_2O forming $\text{Ca}(\text{NO}_3)_2$. The detailed mechanism of the multiphase reaction of carbonate with NO_2 and H_2O are 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 will change “in presence of O_2 (5%-86%)” to “in the presence of O_2 with three 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 (1.2×10^{-5}) was around 370 times higher than that determined for the direct oxidation of SO_2 by NO_2 (3.22×10^{-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 $\text{SO}_2/\text{NO}_2/\text{air}$ 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 $\text{SO}_2/\text{NO}_2/\text{air}$ 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 $2.4 \times 10^3 \text{ mol}^{-1} \text{ L s}^{-1}$ (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 will add this comparison as follows.

“Only few studies have reported the S(IV) oxidation rate in the reaction of S(IV) and 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 to 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 $2.4 \times 10^3 \text{ mol}^{-1} \text{ L s}^{-1}$ (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 because 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).”

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 will delete the mechanism from line 172 to 189 and only mention them in the introduction, as the reviewer suggested. Instead, we will briefly discuss why this mechanism is not possible as follows.

“According to the $\text{NO}_2\text{-S(IV)}$ adduct mechanism, the presence of O_2 should not affect the SO_2 oxidation rate, which is opposite to the substantial enhancement in the SO_2 oxidation rate observed in the presence of O_2 compared to that in the absence of O_2 . Therefore, $\text{NO}_2\text{-S(IV)}$ adduct mechanism is likely not 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 will change R8 to R7. We will delete R7-17 in the text and only show them in the table. Moreover, as discussed above (the response to comment 4) we will only show 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 $\text{SO}_2 \cdot \text{H}_2\text{O}$ and HSO_3^- .

12. *P.7, line 209-213: Nice study on $\text{S}_2\text{O}_6^{2-}$ 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 $\text{S}_2\text{O}_6^{2-}$ formation. In the revised manuscript, we will add this paper in our citation and briefly discussed it as follows.

“ $\text{S}_2\text{O}_6^{2-}$ was detected with an appreciable yield besides SO_4^{2-} and NO_2^- using Raman spectroscopy in the reaction of NO_2 with aqueous sulfite (Littlejohn et al., 1993). It was also observed in the aqueous oxidation of bisulfite in 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 will change the “radical mechanism” to “a free-radical chain mechanism”.

14. P. 8, Line 239: I do not agree that there is a synergy between NO₂ and O₂ (definition of synergy!); NO₂ 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(NO₃)₂ is formed in the reaction between CaCO₃ and NO₂. 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 SO₂ oxidation rate when both NO₂ and O₂ were present was higher than the sum of the effect of NO₂ and of O₂, although the reactions of SO₂ with O₂ and with NO₂ were not always simultaneous. As we have shown, the SO₂ oxidation rates in the direct reaction of SO₂ with NO₂ and with O₂ were both very low.

In the revised manuscript, we will further elaborate this discussion as follows.

“In the experiment without NO₂ while keeping other reaction conditions the same, we found that no sulfate was formed after 5 h of reaction. This indicates that O₂ by itself cannot initialize the chain reaction, although it favors chain propagation, and the oxidation of SO₂ by O₂ was slow. The effect on the SO₂ oxidation rate when both NO₂ and O₂ were present was much higher than the sum of the effect of NO₂ and of O₂. We refer to this effect as the synergy of NO₂ and O₂, which resulted in the fast oxidation of SO₂ forming sulfate in this study. Without either NO₂ or O₂, the reaction proceeded much slower.”

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 will check and correct the writing of radicals throughout the manuscript wherever there were mistakes.

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