

Responses to Referee # 1

We thank the reviewer for carefully reviewing our manuscript. The comments and suggestions are greatly appreciated. All the comments have been addressed. In the following, please find our responses to the comments one by one and corresponding revisions made to the manuscript. The original comments are shown in italics. The revised parts of the manuscript are highlighted.

General comments

The paper presents the results on multiphase reaction of SO₂ with NO₂ on individual CaCO₃ particles in N₂ at RH between 17 and 72% using Micro-Raman spectrometer with a flow reaction system. The reaction process was systematically investigated and found that CaCO₃ converts first to Ca(NO₃)₂ (by the reaction with NO₂) and its deliquescence to droplet, where further SO₂ oxidizes with NO₂ forming CaSO₄. The reactive uptake coefficient γ of SO₂ was determined on the basis of sulfate formation rate.

Although many studies concerning SO₂ oxidation in the atmosphere were performed in late 1980s and 1990s, mainly due to much higher pollution with SO₂ all over the world at that time, and various pathways of oxidation were identified, the questions concerning sulfate formation have not yet been fully resolved. As shown e.g., that high concentrations of sulfate during heavily polluted episodes under haze conditions in China could not be explained on the basis of known pathways only. In addition, due to the progress and development of techniques, nowadays there are more possibilities to study processes also on the micro level as shown in this paper.

Thus, I found the paper of sufficient atmospheric interest to merit publication after revision; in “specific comments” some questions and/or comments are listed which should be considered.

However, I would strongly recommend showing also the results for the system SO₂/NO₂/H₂O/O₂ together with those presented here and not in the next paper as said in line 80. Experimental conditions will be closer to atmospheric, and as mentioned on p.9 (lines 301-303) it is expected that the reactions under O₂ are faster and could be more important source of sulfate.

Response:

We thank the reviewer for the supporting remarks.

As to the recommendation “*showing also the results for the system SO₂/NO₂/H₂O/O₂ together with those presented here and not in the next paper as said in line 80*”, we realized that our phrasing in the some texts of the manuscript was not precise and clear enough to express our primary motivation. We have modified these texts (e.g. lines 80-83, lines 350-357) in the revised manuscript to clearly state our motivation, i.e., to address the multiphase reaction of SO₂ directly with NO₂ and evaluate the

importance of this reaction pathway in sulfate formation in the real atmosphere, which was proposed by a number of recent studies (Cheng et al., 2016; Wang et al., 2016; Xue et al., 2016) but remains unclear. In order to exclude potential confounding reactions from other compounds, we used inert N₂ as a carrier gas. For this motivation, the direct reaction of SO₂ with NO₂ has ambient relevance no matter whether O₂ is present or not.

The reason that we did not include the multiphase reaction of SO₂ with O₂/NO₂ in this paper is because we found that in this reaction SO₂ was actually oxidized by O₂, not by NO₂. It is distinct from the reaction of SO₂ directly with NO₂ with markedly different mechanisms, products, and atmospheric implications, as we will show (Yu et al., 2017). O₂ was the main oxidant of SO₂ and NO₂ only acted as an initiator of chain reactions. The atmospheric implications are significantly different from the direct reaction of SO₂ with NO₂ because not only the oxidation of SO₂ by O₂ leads to much faster sulfate oxidation but also the reaction is not linked to reactive nitrogen chemistry in the atmosphere. Therefore, we address this reaction in a separate companion manuscript (Yu et al., 2017).

In addition, in order to reflect the distinction of these two studies more precisely, we have revised the title of our manuscript as follows:

“Multiphase Reaction of SO₂ on CaCO₃ Particles. 1. Oxidation of SO₂ by NO₂”.

Accordingly, we plan to change the title of our companion manuscript to:

“Multiphase Reaction of SO₂ on CaCO₃ Particles. 2. NO₂-initiated Oxidation of SO₂ by O₂”.

Specific comments

Introduction: (1) P.3, lines 59-62: It would be worth to mention also the studies from 2001 (Turšič et al. 2001, Atmos. Environ.).

Response: Accepted.

In the revised manuscript, we have added Turšič et al. (2001) in our citation.

Experimental: (2) The experimental approach (Raman mapping analysis) where you can follow the changes during the reaction course (as can be seen in Fig. S2) is intriguing.

Response: We thank the reviewer for the supporting remark.

Results and discussion: (3) Fig. 2 nicely shows how the peak for CO₃²⁻ decreases and disappears after certain time of reaction; the change can be seen also in Fig. 3. What happens to it (releases as CO₂)? (4) It is not correct to explain its “disappearance” as “completely consumed” (line 171).

Response:

CO_3^{2-} was converted to CO_2 by the reaction with H^+ , which was released into the gas phase. In the revised manuscript, we have briefly discussed this process.

“The formation of $\text{Ca}(\text{NO}_3)_2$ started with the reaction of NO_2 with adsorbed or liquid water, forming HNO_3 and HNO_2 . Then HNO_3 reacted with CaCO_3 forming $\text{Ca}(\text{NO}_3)_2$ as well as CO_2 , which was released to the gas phase.”

In the revised manuscript, we have rephrased the “completely consumed” to “completely reacted”.

(5) Line 186: “the consumption of CaCO_3 ” is not appropriate

Response: Accepted.

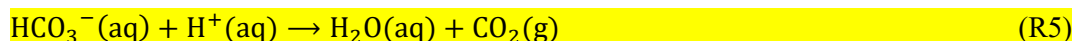
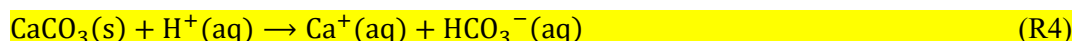
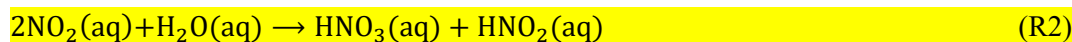
In the revised manuscript, we have changed it to “the decline of CaCO_3 ”.

(6) Lines 186-187: If $\text{Ca}(\text{NO}_3)_2$ is formed in the reaction between CaCO_3 and NO_2 , NO_2 should first disproportionate to NO_3^- and NO_2^- , which is possible in the presence of water. How is then $\text{Ca}(\text{NO}_3)_2$ first formed from CaCO_3 , and only then converts into droplet in the presence of water? The authors should explain the reactions also for the first step, i.e. the conversion of CaCO_3 to $\text{Ca}(\text{NO}_3)_2$ although the reference is given (line 188). I suggest that the complete mechanism is written.

Response:

The details of the mechanism of the reaction of CaCO_3 with NO_2 are reported in our previous paper (Li et al., 2010). In the revised manuscript, we have added the following texts and reaction equations:

$\text{Ca}(\text{NO}_3)_2$ has been observed in the reaction of CaCO_3 with NO_2 in previous studies (Li et al., 2010; Tan et al., 2017). The formation of $\text{Ca}(\text{NO}_3)_2$ started with the reaction of NO_2 with adsorbed or liquid water, forming HNO_3 and HNO_2 . Then HNO_3 reacted with CaCO_3 forming $\text{Ca}(\text{NO}_3)_2$ as well as CO_2 , which was released to the gas phase. The reaction equations are as follows:



(7) The authors may want to add a reference of Tan et al., 2016, ACP.

Response: Accepted.

In the revised manuscript, we have added Tan et al. (2016) as a reference.

(8) It is concluded that aqueous phase plays a key role in SO₂ oxidation by NO₂, which is also known from previous studies. Line 219: pH is estimated to be around 3. What would be the concentrations of reactive species in Ca(NO₃)₂ droplet?

Response:

We suppose that the reviewer referred to the concentrations of S(IV) species. The concentrations of HSO₃⁻, H₂SO₃, and SO₃²⁻ were estimated to be $\sim 1.1 \times 10^{-3}$, 9.2×10^{-5} , and 6.6×10^{-8} mol L⁻¹, respectively, using the equilibrium constants in Seinfeld and Pandis (2006).

We have added these values in the revised manuscript.

“The concentrations of HSO₃⁻, H₂SO₃, and SO₃²⁻ were estimate to be $\sim 1.1 \times 10^{-3}$, 9.2×10^{-5} , and 6.6×10^{-8} mol L⁻¹, respectively, using the equilibrium constants in Seinfeld and Pandis (2006) and thus the main S(IV) species was HSO₃⁻.”

(9) Lines 236-241: This part is not well understandable. It is concluded that precipitation of CaSO₄ formed in/on Ca(NO₃)₂ droplet promotes sulfate formation. On the other hand, when NaNO₃ or NH₄NO₃ droplet is used instead of Ca(NO₃)₂, no sulfate was formed after 300 min. If aqueous phase is a key factor for the oxidation of SO₂ with NO₂, then this should happen also in these droplets, although the reaction is most probably much slower. Why the reaction was not carried out at longer times?

Response:

The purpose of the comparison between the reaction of NaNO₃ and NH₄NO₃ and the reaction of Ca(NO₃)₂ was to qualitatively examine the effect of cations on sulfate formation rate. At 300 min, sulfate was readily detectable in the reaction of Ca(NO₃)₂ while it was below the detection limit in the reaction of NaNO₃ and NH₄NO₃ (Fig. 5, Fig. 6). Although sulfate may have been formed, the absence of sulfate at 300 min shows that the sulfate production was extremely slow. The difference by 300 min has clearly indicated that the sulfate formation in the reaction of Ca(NO₃)₂ was much faster than that in the reaction the NaNO₃ and NH₄NO₃ and Ca²⁺ promoted sulfate formation, which likely resulted from CaSO₄ precipitation. Therefore, the reaction was not continued for longer times.

In the revised manuscript, we have made some changes to improve the clarity of the discussion. Now it reads:

“Based on Raman spectra, we found that in the reaction of a NaNO_3 or a NH_4NO_3 droplet with NO_2/SO_2 sulfate was below the detection limit after 300 min in the same reaction conditions as $\text{Ca}(\text{NO}_3)_2$ and CaCO_3 (Fig. 6 and Table 1). Accordingly, no sulfate solid particles were observed in these droplets. Clearly, the sulfate production rate was larger in the presence of Ca^{2+} compared to those in the presence of Na^+ or NH_4^+ . The difference can be explained by the change of Gibbs energy.”

“ $\Delta_r G$ increases with increasing sulfate concentration. According to the different results between the reaction on $\text{Ca}(\text{NO}_3)_2$ droplet and the reaction on NaNO_3 and NH_4NO_3 droplet, there might be a backward reaction of SO_2 oxidation which consumed sulfate, although the detailed mechanism of the backward reaction is unknown at the moment. For NaNO_3 and NH_4NO_3 droplet, once sulfate concentration reached certain level, the reaction may stop due to the increase of $\Delta_r G$. For $\text{Ca}(\text{NO}_3)_2$ droplet, the precipitation of CaSO_4 can substantially decrease the activity of SO_4^{2-} , and thus decrease $\Delta_r G$ and promote the oxidation of SO_2 and sulfate formation.”

(10) Line 240: In droplets of NaNO_3 or NH_4NO_3 , CaSO_4 cannot be formed.

Response:

Accepted. In the revised manuscript, we have changed “ CaSO_4 ” to “sulfate”.

(11) Line 250: Is it correct that at RH of 46% the conditions for a complete conversion into a $\text{Ca}(\text{NO}_3)_2$ droplet are achieved?

Response:

Yes. We observed that a complete conversion from CaCO_3 particle to $\text{Ca}(\text{NO}_3)_2$ droplet occurred at 46% RH and then sulfate was observed.

(12) Line 259: Write what is DRIFTS technique (it was not mentioned before).

Response:

Accepted. In the revised manuscript, we have provided the full name of DRIFTS as “Diffuse Reflectance Infrared Fourier Transform Spectroscopy”.

(13) Line 206: ATD particles?

Response:

In the revised manuscript, we have provided the full name of ATD as “Arizona Test Dust”.

(14) Lines 273-275: Is this statement correct? Higher concentrations of aqueous sulfate may suppress the reaction between SO₂ and NO₂, while CaSO₄ precipitation can promote it.

Response:

As we found on the effect of cations (Section 3.3.2), reduced sulfate concentration by CaSO₄ precipitation likely led to the enhanced sulfate production rate in the reaction of SO₂ on Ca(NO₃)₂. According to Eq. 5, higher sulfate concentration could increase the reaction Gibbs energy $\Delta_r G$ and thus suppress the reaction of SO₂ and NO₂.

In the revised manuscript, we have further explained this statement.

“According to the effect of cations (Section 3.3.2), while reduced sulfate concentration by CaSO₄ precipitation likely led to the enhanced sulfate production rate in the reaction of SO₂ on Ca(NO₃)₂, higher sulfate concentration could increase the reaction Gibbs energy $\Delta_r G$ (as shown in Eq. 5) and thus suppress the reaction of SO₂ and NO₂. This can reduce the uptake coefficient of SO₂.”

References

- Cheng, Y. F., Zheng, G. J., Wei, C., Mu, Q., Zheng, B., Wang, Z. B., Gao, M., Zhang, Q., He, K. B., Carmichael, G., Poschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, *Sci. Adv.*, 2, 10.1126/sciadv.1601530, 2016.
- Li, H. J., Zhu, T., Zhao, D. F., Zhang, Z. F., and Chen, Z. M.: Kinetics and mechanisms of heterogeneous reaction of NO₂ on CaCO₃ surfaces under dry and wet conditions, *Atmos. Chem. Phys.*, 10, 463-474, 2010.
- Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, 2nd ed., John Wiley & Sons. Inc., 2006.
- Tan, F., Jing, B., Tong, S. R., and Ge, M. F.: The effects of coexisting Na₂SO₄ on heterogeneous uptake of NO₂ on CaCO₃ particles at various RHs, *Sci. Total Environ.*, 586, 930-938, 10.1016/j.scitotenv.2017.02.072, 2017.
- Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, *Proc. Nat. Acad. Sci. U.S.A.*, 113, 13630-13635, 10.1073/pnas.1616540113, 2016.
- Xue, J., Yuan, Z. B., Griffith, S. M., Yu, X., Lau, A. K. H., and Yu, J. Z.: Sulfate Formation Enhanced by a Cocktail of High NO_x, SO₂, Particulate Matter, and Droplet pH during Haze-Fog Events in Megacities in China: An Observation-Based Modeling Investigation, *Environ. Sci. Technol.*, 50, 7325-7334, 10.1021/acs.est.6b00768, 2016.
- Yu, T., Zhao, D., Song, X., and Zhu, T.: Multiphase Reaction of SO₂ with NO₂ on CaCO₃ Particles. 2. NO₂-initialized Oxidation of SO₂ by O₂, *Atmos. Chem. Phys. Discuss.*, 2017, 1-20, 10.5194/acp-2017-900, 2017.