

Interactive comment on “Multiphase Reaction of SO₂ with NO₂ on CaCO₃ Particles. 1. Oxidation of SO₂ by NO₂” by Defeng Zhao et al.

Anonymous Referee #1

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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

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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.

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.).

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.

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).

(5) Line 186: “the consumption of CaCO₃” is not appropriate

(6) Lines 186-187: If Ca(NO₃)₂ is formed in the reaction between CaCO₃ and NO₂, NO₂ should first disproportionate to NO₃⁻ and NO₂⁻, which is possible in the presence of water. How is then Ca(NO₃)₂ first formed from CaCO₃, and only then converts into

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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.

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

(8) It is concluded that aqueous phase plays a key role in SO_2 oxidation by NO_2 , 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 $\text{Ca}(\text{NO}_3)_2$ droplet?

(9) Lines 236-241: This part is not well understandable. It is concluded that precipitation of CaSO_4 formed in/on $\text{Ca}(\text{NO}_3)_2$ droplet promotes sulfate formation. On the other hand, when NaNO_3 or NH_4NO_3 droplet is used instead of $\text{Ca}(\text{NO}_3)_2$, no sulfate was formed after 300 min. If aqueous phase is a key factor for the oxidation of SO_2 with NO_2 , 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?

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

(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?

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

(13) Line 206: ATD particles?

(14) Lines 273-275: Is this statement correct? Higher concentrations of aqueous sulfate may suppress the reaction between SO_2 and NO_2 , while CaSO_4 precipitation can promote it.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2017-610/acp-2017-610-RC1-supplement.pdf>

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-610>, 2017.

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