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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Multiphase Reaction of SO_2 with NO_2 on $CaCO_3$ Particles. 1. Oxidation of SO_2 by NO_2" *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 CaCO3 to Ca(NO3)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 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?

(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?

(10) Line 240: In droplets of NaNO3 or NH4NO3, CaSO4 cannot be formed.

(11) Line 250: Is it correct that at RH of 46% the conditions for a complete conversion into a Ca(NO3)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 SO2 and NO2, while CaSO4 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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