

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 #2

Received and published: 17 August 2017

This study investigated the heterogeneous reaction of SO₂ with NO₂ on individual CaCO₃ particles in N₂ using Micro-Raman spectroscopy. The results show that CaCO₃ was first converted to Ca(NO₃)₂ forming a droplet and promoting the oxidation of SO₂ by NO₂. The precipitation of CaSO₄ was suggested as a key step accelerating the sulfate formation. Based on the uptake coefficient determined, the authors concluded that the SO₂ + NO₂ reaction was not important compared to the oxidation of SO₂ by OH radicals. The experiment was well designed and the paper was well written. But I do have concerns about the role of CaSO₄ precipitation and I would also suggest the authors to compare their results with literature data before making strong statement on the role of NO₂+SO₂ chemistry.

Major concern:

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1. The authors generalized the results of their CaCO₃ experiments to assess the role of NO₂+SO₂ chemistry. I am not sure if such generalization is correct because according to early studies of Lee and Schwartz, 1983 and Clifton et al., 1988, this reaction can be important under polluted and less acidic conditions in contrary to the authors' statement. The authors used deposited super-micro particles in their experiments. But I don't expect much difference between such a system and bulk experiments because large particles are not subject to strong Kelvin effect and particles contacted with substrates would not become supersaturated solution of high ionic strength due to nucleation. Thus before generalizing results for ambient aerosols, I would suggest the authors to discuss their difference with those early studies.

2. Based on Equation (5), the authors concluded that the precipitation-induced reduction of sulfate will promote the oxidation of SO₂ by NO₂ (reaction 2). I don't know if it is correct to use Eq. (5) in this way. Because Equation (5) is valid for reversible reactions and removing/adding products of non-reversible reactions will not change the reaction rate much.

Other comments:

Page 5 line 133, half sentence?

Page 6 line 187, I would suggest to briefly describe the mechanism of Ca(NO₃)₂ formation. Will the presence of SO₂ influence the uptake of NO₂?

Fig. 4, no data for nitrate and carbonate after 120 min, why?

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

C2