

Interactive comment on »Multiphase Reaction of SO₂ with NO₂ on CaCO₃ Particles. 2. NO₂-Initialized Oxidation of SO₂ by O₂»

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.

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.

2. P. 2, line 39 and p. 8, line 243: Dissolution/absorption of SO_2 in aqueous solution results in total dissolved S(IV), i.e. three species $\text{SO}_2 \times \text{H}_2\text{O}$, HSO_3^- and SO_3^{2-} , which are in equilibrium; which species will prevail depends on pH! So, H_2SO_3 ($2\text{H}^+ + \text{SO}_3^{2-}$) are the same species as you have already written. In addition, it is not “rapid inter-conversion” between the species.

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?
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.

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.
6. Paragraph 3.2 An explanation on increasing concentration of NO_3^- during the reaction is needed.
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%.
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 .
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).
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.
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-} .

12. P.7, line 209-213: Nice study on $S_2O_6^{2-}$ 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.
13. Better than “radical mechanism” is “a free-radical chain mechanism”
14. P. 8, Line 239: I do not agree that there is a synergy between NO_2 and O_2 (definition of synergy!); NO_2 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 $Ca(NO_3)_2$ is formed in the reaction between $CaCO_3$ and NO_2 . This part is now explained well in the first manuscript (Zhao et al., ACPD).
15. I also suggest excluding older references, and rather including only those after 1990.
16. The radicals throughout the manuscript are written incorrectly.