

## ***Interactive comment on »Multiphase Reaction of SO<sub>2</sub> with NO<sub>2</sub> on CaCO<sub>3</sub> Particles. 1. Oxidation of SO<sub>2</sub> by NO<sub>2</sub>»***

### **General comments**

The paper presents the results on multiphase reaction of SO<sub>2</sub> with NO<sub>2</sub> on individual CaCO<sub>3</sub> particles in N<sub>2</sub> at RH between 17 and 72% using Micro-Raman spectrometer with a flow reaction system. The reaction process was systematically investigated and found that CaCO<sub>3</sub> converts first to Ca(NO<sub>3</sub>)<sub>2</sub> (by the reaction with NO<sub>2</sub>) and its deliquescence to droplet, where further SO<sub>2</sub> oxidizes with NO<sub>2</sub> forming CaSO<sub>4</sub>. The reactive uptake coefficient  $\gamma$  of SO<sub>2</sub> was determined on the basis of sulfate formation rate.

Although many studies concerning SO<sub>2</sub> oxidation in the atmosphere were performed in late 1980s and 1990s, mainly due to much higher pollution with SO<sub>2</sub> 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 SO<sub>2</sub>/NO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub> 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 O<sub>2</sub> 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 CO<sub>3</sub><sup>2-</sup> decreases and disappears after certain time of reaction; the change can be seen also in Fig. 3. What happens to it (releases as CO<sub>2</sub>)?
- (4) It is not correct to explain its “disappearance” as “completely consumed” (line 171).

- (5) Line 186: “the consumption of  $\text{CaCO}_3$ ” is not appropriate
- (6) Lines 186-187: If  $\text{Ca}(\text{NO}_3)_2$  is formed in the reaction between  $\text{CaCO}_3$  and  $\text{NO}_2$ ,  $\text{NO}_2$  should first disproportionate to  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , which is possible in the presence of water. How is then  $\text{Ca}(\text{NO}_3)_2$  first formed from  $\text{CaCO}_3$ , 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  $\text{CaCO}_3$  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  $\text{SO}_2$  oxidation by  $\text{NO}_2$ , 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  $\text{CaSO}_4$  formed in/on  $\text{Ca}(\text{NO}_3)_2$  droplet promotes sulfate formation. On the other hand, when  $\text{NaNO}_3$  or  $\text{NH}_4\text{NO}_3$  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  $\text{SO}_2$  with  $\text{NO}_2$ , 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  $\text{NaNO}_3$  or  $\text{NH}_4\text{NO}_3$ ,  $\text{CaSO}_4$  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  $\text{SO}_2$  and  $\text{NO}_2$ , while  $\text{CaSO}_4$  precipitation can promote it.