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Multiphase Reaction of SO_2 with NO_2 on $CaCO_3$ Particles. 2. NO_2-initialized Oxidation of SO_2 by O_2

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Abstract. The reaction of SO_2 with NO_2 on the surface of aerosol particles has been suggested to be important in sulfate formation during severe air pollution in China. However, we found that the direct oxidation of SO_2 by NO_2 was slow and might not be the main reason for sulfate formation in ambient air. In this study, we investigated the multiphase reaction of SO_2 with NO_2 on single $CaCO_3$ particles in synthetic air, i.e., in the presence of O_2, using Micro-Raman spectroscopy. The reaction converted the $CaCO_3$ particle to the $Ca(NO_3)_2$ droplet containing $CaSO_4$•$2H_2O$ solid particles embedded in it, which constituted a large fraction of the droplet volume at the end of the reaction. Compared with the reaction in the absence of O_2, the morphology of the particle during the reaction in synthetic air was significantly different and the amount of sulfate formed at the end of the experiment was much higher. The reactive uptake coefficient of SO_2 for sulfate formation was on the order of 10^{-5}, which was two to three orders of magnitude higher than that in the absence of O_2. According to the difference between the reactive uptake coefficient of SO_2 in the absence of O_2 and that in the presence of O_2, we found that in the multiphase reaction of SO_2 with NO_2 in synthetic air, O_2 was the main oxidant of SO_2 and necessary for radical chain propagation. NO_2 acted as the initializer of the radical formation but not the main oxidant. Such synergy of NO_2 and O_2 resulted in much faster sulfate formation than when either of them was absent. We estimated that the multiphase oxidation of SO_2 by O_2 in the presence of NO_2 can be an important source of sulfate and sink of SO_2 based on the calculated lifetime of SO_2 regarding the loss by the multiphase reaction versus the lifetime regarding the loss by the gas phase reaction with OH radical. Parameterizing the reactive uptake coefficient of the reaction observed in our laboratory for further model simulation is needed, as well as an integrated assessment based on field observation, laboratory study results, and model simulation to evaluate the importance of the reaction in ambient air during the severe air pollution period, especially in China.

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1 Introduction

Multiphase or heterogeneous oxidation of SO_2 by NO_2 has been suggested to potentially play an important role in sulfate formation in the atmosphere (Seinfeld and Pandis, 2006). Recently the multiphase oxidation of SO_2 by NO_2 has been introduced in air quality model simulation to explain the discrepancy between the modeled and observed sulfate concentration during the heavily polluted episodes frequently occurring in China (Cheng et al., 2016; Gao et al., 2016; Wang et al., 2016; Xue et al., 2016), despite the different opinions about the pH value of aerosol particles in China (Wang et al., 2016; Cheng et al., 2016; Liu et al., 2017; Guo et al., 2017).

Quantitative and accurate assessment of the role of multiphase oxidation SO_2 by NO_2 on particle relies on determining reaction kinetic parameters and understanding the reaction mechanism. The aqueous oxidation of SO_2 (S(IV) species including H_2SO_3, SO_3^{2-}, and HSO_3^-) by NO_2 has been investigated by a number of laboratory studies (Nash, 1979; Lee and Schwartz, 1983; Clifton et al., 1988; Littlejohn et al., 1993; Santachiara et al., 1990, 1993; Shen and Rochelle, 1998; Spindler et al., 2003; Tursic et al., 2001; Huie and Neta, 1986) and valuable kinetic parameters and understanding on reaction products and process have been obtained. For example, Lee and Schwartz (1983) and Clifton et al. (1988) measured the second order rate constant of the reaction of NO_2 with bisulfate and sulfite solution. The reaction products observed include nitrite, sulfate, and dithionate (e.g., (Littlejohn et al., 1993; Lee and Schwartz, 1983)). Based on these studies, the reaction mechanism was deduced (Clifton et al., 1988; Spindler et al., 2003; Nash, 1979; Littlejohn et al., 1993; Shen and Rochelle, 1998).

Previous studies mainly focused on the reaction in bulk solution. Few studies on the oxidation of SO_2 by NO_2 on aerosol particles have been conducted (Santachiara et al., 1990, 1993). On aerosol particles, water activity of aerosol water, pH, ion strength, presence of other compounds or ions, and the role of particle surface are different from dilute bulk solution and may affect the reaction process and reaction rate. Moreover, many previous studies conducted the experiments either in the absence of O_2 or with low O_2 concentrations. Studies on the potential role of O_2 especially at the concentration levels in ambient air and the potential synergy of NO_2 and O_2 in the reaction are very limited.

O_2 is abundant in the atmosphere and may affect the multiphase reaction of SO_2 with NO_2. For example, Littlejohn et al. (1993) found that the oxidation rate of sulfite in the aqueous reaction with NO_2 increases with O_2 concentration (0-5% by volume). The enhancement of SO_2 oxidation rate in the reaction with NO_2 have been also found in the heterogeneous reaction on mineral particle surface when O_2 is present (He et al., 2014). Therefore, further studies of the multiphase reaction of SO_2 with NO_2 on aerosol particles in air are needed in order to determine kinetic parameters and elucidate the mechanism of the reaction.

In a companion manuscript (Zhao et al., 2017), we reported the results of the study on the multiphase oxidation of SO_2 directly by NO_2 in N_2 on $CaCO_3$ particles. We found that the reactive

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Atmospheric Chemistry and Physics Discussions

uptake coefficient of SO_2 for sulfate formation due to the oxidation by NO_2 is on the order of 10^{-8}, and concluded that the oxidation of SO_2 by NO_2 alone could not contribute significantly to sulfate formation in the atmosphere. In this manuscript, we present the results of our study on the multiphase reaction of SO_2 with NO_2 in synthetic air, i.e., in the presence of O_2, on $CaCO_3$ particles. We quantified the reactive uptake coefficient of SO_2 due to the reaction with $NO_2/O_2/H_2O$ mixture in synthetic air. Based on the observations and literature, we further discussed the reaction mechanism. By comparing with the oxidation of SO_2 by NO_2 in N_2, we highlight the role of O_2 in the multiphase oxidation of SO_2.

2 Experimental

The experimental setup and procedure used in this study have been described in details in previous studies (Zhao et al., 2017; Zhao et al., 2011; Liu et al., 2008). Here we only provide a brief description. The reaction of SO_2 with NO_2 on $CaCO_3$ particles was investigated using a flow reactor. SO_2 (2000 ppm in high purity N_2) and NO_2 (1000 ppm in high purity N_2) were diluted with synthetic air [20% O_2 (high purity grade: 99.999%, Beijing Haikeyuanchang Practical Gas Co., Ltd.), 80% N_2 (high purity grade: 99.999%, Beijing Haikeyuanchang Practical Gas Co., Ltd.)] to 75 ppm. Relative humidity was controlled by regulating the flow rates of reactant gases, dry synthetic air, and humidified synthetic air. More details about the experiment conditions can be found in the companion paper (Zhao et al., 2017). $SO_2/NO_2/H_2O$ reaction mixture in synthetic air reacted with individual $CaCO_3$ particles deposited on Teflon-FEP film. During the reaction, the particles were *in-situ* monitored via a glass window of the flow reactor using a Micro-Raman spectrometer to obtain microscopic images and Raman spectra. All the experiments were conducted at 298±0.5 K.

The amount of the reaction product $CaSO_4$ was quantified based on Raman peak areas and particle sizes. The details of the method are described in our previous study (Zhao et al., 2017). Briefly, the amount of reaction product $CaSO_4$ formed was followed as a function of time using Raman peak areas. Raman peak areas were converted to the amount of compound using a calibration curve obtained from pure $CaSO_4$ particles of different sizes, which were determined according to microscopic image. The reaction rate, that is, sulfate production rate, was derived from the amount of sulfate as a function of time. The reactive uptake coefficient of SO_2 for sulfate formation (γ) was further determined from the reaction rate and collision rate of SO_2 on surface of a single particle.

$$\gamma = \frac{\frac{d\{SO_4^{2-}\}}{dt}}{Z} . \quad (1)$$

$$Z = \frac{1}{4} c A_s [SO_2], \quad (2)$$

$$c = \sqrt{\frac{8RT}{\pi M_{SO_2}}} , \quad (3)$$

where R is the gas constant, T is temperature, Mso_2 is the molecular weight of SO_2, and c is the mean molecular velocity of SO_2, A_s is the surface area of an individual particle, and Z is the collision rate of SO_2 on surface of a particle. $\{SO_4^{2-}\}$ indicates the amount of sulfate on the particle phase in mole. The average reaction rate and surface area of particles during the multiphase reaction period were used to derive the reactive uptake coefficient. The period was chosen to start after the induction period when ~10 % of final sulfate was formed. $[SO_2]$ indicates the concentration of SO_2 in the gas phase.

Besides the reaction of SO_2 with $NO_2/O_2/H_2O$ on $CaCO_3$ particles in synthetic air, in some experiments, we varied the concentrations of O_2 in the carrier gas in order to investigate the effect of O_2 concentration on the reaction. In addition, we carried out experiments without NO_2, on either $CaCO_3$ solid particle, or $CaCO_3/Ca(NO_3)_2$ internally mixed particle with $CaCO_3$ embedded in $Ca(NO_3)_2$ droplet in order to elucidate the role of NO_2 in the reaction.

3 Results and discussion

3.1 Reaction products and particle morphology change

Figure 1 shows the Raman spectra of a $CaCO_3$ particle during the multiphase reaction of SO_2 with $NO_2/O_2/H_2O$ on it in synthetic air. The peak at 1087 cm^{-1} is assigned to the symetric stretching of carbonate ($\nu_s(CO_3^{2-})$) (Nakamoto, 1997). During the reaction, the peak at 1087 cm^{-1} decreased continously and finally disappeared and some new peaks were observed. The peak at 1050 cm^{-1} is assigned to the symmetric stretching of nitrate ($\nu_s(NO_3^-)$). The peak at 1010 cm^{-1} and 1136 cm^{-1} are assigned to the symmetric stretching ($\nu_s(SO_4^{2-})$) and asymetric stretching($\nu_{as}(SO_4^{2-})$) of sulfate in gypsum ($CaSO_4 \cdot 2H_2O$), respectively (Sarma et al., 1998). In addition, after the reaction, a broad envelop in the range of 2800-3800 cm^{-1} assigned to OH stretching of water was observed. On the top of this envelope, there are two peaks at 3408 cm^{-1} and 3497 cm^{-1}, which are assigned to the OH stretching in crystallization water of $CaSO_4 \cdot 2H_2O$ (Sarma et al., 1998; Ma et al., 2013).

During the multiphase reaction with $SO_2/NO_2/O_2/H_2O$ mixture, the $CaCO_3$ particle showed a remarkable change in morphology. The original $CaCO_3$ particle was a rhombohedron crystal (Fig. 2, panel i, a). As reaction proceeded, its edge became smoother and later a transparent droplet layer formed, which had a newly-formed solid phase embed in it (Fig. 2, panel i, d). The size of the new solid grew during the reaction (Fig. 2, panel i, d-f) and it seemed to contain a number of micro-crystals. Raman mapping reveals that the new solid phase consisted of $CaSO_4 \cdot 2H_2O$ (Fig. 2, panel iv), and the surrounding aqueous layer consisted of $Ca(NO_3)_2$ (Fig. 2, panel iii).

The particle morphology change shown in Fig. 2 is significantly different from the morphology change in the absence of O_2 (Zhao et al., 2017), where the $CaCO_3$ particle was first converted to a spherical $Ca(NO_3)_2$ droplet and then needle-shaped $CaSO_4$ crystals formed inside the droplet (Zhao et al., 2017). Moreover, the amount of $CaSO_4$ formed in the presence of O_2 was much higher than that in

the absence of O_2. $CaSO_4$ solid particle constituted most of the volume droplet here while in the absence of O_2 the few needle-shaped $CaSO_4$ crystals formed only constituted a small fraction of the droplet volume.

3.2 Reaction process

During the reaction, the amounts of carbonate, nitrate, and sulfate were followed as a function of time as shown in Fig. 3. In the beginning of the reaction, carbonate decreased slowly and nitrate and sulfate increased slowly. After a period of induction of around 50 min, the reaction accelerated significantly, leading to a fast consumption of carbonate and production of nitrate and sulfate. Finally, carbonate was completely consumed and nitrate and sulfate leveled off.

Figure 3 shows nitrate and sulfate were formed simultaneously during the reaction. This finding is in contrast to the finding in the absence of O_2, where nitrate was formed first and sulfate was essentially formed after the complete conversion of $CaCO_3$ particle to $Ca(NO_3)_2$ droplet. Moreover, the time for carbonate to be completely consumed was longer here than that in the absence of O_2 (~120 min vs. ~40 min) when other conditions were kept the same.

3.3 Reactive uptake coefficient of SO_2

The reactive uptake coefficient of SO_2 for sulfate formation (γ) in the reaction of SO_2 with $NO_2/O_2/H_2O$ on $CaCO_3$ in synthetic air and in O_2/N_2 carrier gas with varied O_2 concentrations is shown in Table 1. γ for the reaction of SO_2 with NO_2 in presence of O_2 (5%-86%) is in the range of 0.35 to 1.7×10^{-5}, and is 1.2×10^{-5} in synthetic air. The latter is two to three orders of magnitude higher than that for the reaction in N_2 under similar conditions (Zhao et al., 2017). When other conditions were kept constant, γ increased with O_2 concentration. This indicates that O_2 played a key role in enhancing the oxidation of SO_2.

The role of O_2 in enhancing the reactive uptake of SO_2 is consistent with the findings in some of previous studies. For example, Littlejohn et al. (1993)'s data show that sulfite oxidation rate increases with O_2 concentration (0-5% by volume). Shen and Rochelle (1998) also found that in the presence of O_2, aqueous sulfite oxidation was enhanced. By investigating the oxidation of SO_2 by NO_2 in mono-dispersed water droplets growing on carbon nuclei, Santachiara et al. (1990) found that sulfate formation rate with 2% O_2 is much higher than that without O_2. Yet, our finding is in contrast to the study by Lee and Schwartz (1983), who found that changing from N_2 to air as carrier gas only increases SO_2 oxidation rate by no more than 10%. The difference between our study and the study by Lee and Schwartz (1983) could be due to the difference in O_2 diffusion from gas to condensed phase and different mechanisms between multiphase reaction on particles and aqueous reaction.

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3.4 Reaction mechanism

In the multiphase reaction of SO_2 with $NO_2/O_2/H_2O$ on $CaCO_3$ particles in synthetic air, we found $CaCO_3$ could react with NO_2 and H_2O and produce $Ca(NO_3)_2$, which could deliquesce, forming liquid water, and provide a site for aqueous oxidation of SO_2. This processs was similar to the reaction in N_2. The details of this part of the reaction mechanism have been discussed in our previous study (Zhao et al., 2017).

Once aqueous phase was formed, SO_2 can undergo multiphase reactions with NO_2/O_2. The detailed mechanism of the aqueous reaction of S(IV) with NO_2 is complex. Previous studies have proposed two different kinds of mecchanism. One involves the $SO_3^{\bullet-}$ radical formation (Littlejohn et al., 1993; Shen and Rochelle, 1998; Tursic et al., 2001; Spindler et al., 2003) and the other one involves the formation of adduct complexes (Clifton et al., 1988), but not radical formation.

In the absence of O_2, Lee and Schwartz (1983) suggest the following reaction equation, according to the reaction products and their yields,

$$2NO_2(aq) + HSO_3^-(aq) + H_2O \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + 3H^+(aq) \quad \text{(R1)}$$

The yields of SO_4^{2-}, NO_2^-, and H^+ relative to the HSO_3^- consumed are 1.0±0.05, 1.5±0.4, and 2.5±0.4, respectively, and the NO_2^- formed relative to NO_2 consumed is 1.0±0.18.

Clifton et al. (1988) proposed that the reaction proceeds via NO_2-S(IV) adduct complexes:

$$NO_2(aq) + SO_3^{2-}(aq) \rightarrow [NO_2 - SO_3]^{2-}(aq) \quad \text{(R2)}$$

$$NO_2(aq) + [NO_2 - SO_3]^{2-}(aq) \rightarrow [NO_2 - SO_3 - NO_2]^{2-}(aq) \quad \text{(R3)}$$

$$[NO_2 - SO_3 - NO_2]^{2-}(aq) + OH^-(aq) \rightarrow [NO_2 - SO_4H - NO_2]^{3-}(aq) \quad \text{(R4)}$$

$$[NO_2 - SO_4H - NO_2]^{3-}(aq) \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + H^+(aq). \quad \text{(R5)}$$

By combing reactions R2-R5, the overall reaction equation can be obtained as follows:

$$2NO_2(aq) + SO_3^{2-}(aq) + H_2O \rightarrow 2NO_2^-(aq) + SO_4^{2-}(aq) + 2H^+(aq). \quad \text{(R6)}.$$

The reaction R6 is similar to R1.

If the NO_2-S(IV) adduct mechanism were the main mechanism in this study, there should be no significant difference in the SO_2 oxidation rate between the reaction in the presence of O_2 and in the absence of O_2. In fact, in the presence of O_2 we observed a substantial enhancement in the SO_2 oxidation rate compared to the reaction in the absence of O_2. Therefore, the NO_2-S(IV) adduct mechanism is unlikely in this study.

In contrast to the adduct complex mechanism, Littlejohn et al. (1993) suggested a radical mechanism. In the reaction of NO_2 with aqueous sulfite, besides SO_4^{2-} and NO_2^-, they detected $S_2O_6^{2-}$ with an appreciable yield using Raman spectroscopy. Since $S_2O_6^{2-}$ is known to be the combination reaction product of $SO_3^{\bullet-}$ (Eriksen, 1974; Hayon et al., 1972; Deister and Warneck, 1990; Brandt et al., 1994; Waygood and McElroy, 1992), $SO_3^{\bullet-}$ radical is proposed to be formed:

$$NO_2(aq) + SO_3^{2-}(aq) \rightarrow NO_2^-(aq) + SO_3^{\bullet-}(aq). \quad \text{(R7)}$$

$SO_3^{\bullet-}$ can react via two pathways, forming either $S_2O_6^{2-}$ or SO_4^{2-}:

$$SO_3^{\bullet-}(aq) + SO_3^{\bullet-}(aq) \rightarrow S_2O_6^{2-}(aq) \quad \text{(R8)}$$

$$SO_3^{\bullet-}(aq) + SO_3^{\bullet-}(aq) \rightarrow SO_3^{2-}(aq) + SO_3 \quad \text{(R9)}$$

$$SO_3(aq) + H_2O \rightarrow SO_4^{2-}(aq) + 2H^+(aq). \quad \text{(R10)}$$

The reactions R8-R10 have been well established in the study of the S(IV) oxidation by other pathways, including the OH oxidation, photo-oxidation, and transitional metal catalyzed oxidation (Eriksen, 1974; Hayon et al., 1972; Deister and Warneck, 1990; Brandt et al., 1994; Brandt and Vaneldik, 1995; Waygood and McElroy, 1992). In addition, although previous studies have not reported the direct observation of $SO_3^{\bullet-}$ radical in the aqueous reaction of S(IV) with NO_2, $SO_3^{\bullet-}$ was directly observed in the reaction of NO_2^- with SO_3^{2-} in an acidic buffer solution (pH=4.0) using electron spin resonance (ESR) (Shi, 1994). Since NO_2^- is formed in the aqueous reaction of SO_2 with NO_2 and S_2O_6 as the combination reaction product of $SO_3^{\bullet-}$ is observed (Littlejohn et al., 1993), $SO_3^{\bullet-}$ formation is plausible.

In the presence of O_2, Littlejohn et al. (1993) observed that the relative amount of $S_2O_6^{2-}$ to SO_4^{2-} decreases and $S_2O_6^{2-}$ is undetectable at low NO_2 concentrations (<5 ppm) in the aqueous reaction of NO_2 with sulfite. This indicates that O_2 suppresses the reaction pathway of $S_2O_6^{2-}$ formation (R8). Because $SO_3^{\bullet-}$ radical can react rapidly with O_2, forming $SO_5^{\bullet-}$ radical, and thus be consumed, the suppression of $S_2O_6^{2-}$ is readily attributed to the reaciton of $SO_3^{\bullet-}$ with O_2.

$$SO_3^{\bullet-}(aq) + O_2(aq) \rightarrow SO_5^{\bullet-}(aq) \quad \text{(R11)}$$

Following this reaction, a number of chain reactions can occur and form sulfate (Littlejohn et al., 1993; Seinfeld and Pandis, 2006; Shen and Rochelle, 1998):

$$SO_5^{\bullet-}(aq) + SO_3^{2-}(aq) + H^+(aq) \rightarrow HSO_5^-(aq) + SO_3^{\bullet-}(aq) \quad \text{(R12)}$$

$$HSO_5^-(aq) + SO_3^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + H^+(aq) \quad \text{(R13)}$$

$$SO_5^{\bullet-}(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + SO_4^{\bullet-}(aq) \quad \text{(R14)}$$

$$SO_4^{\bullet-}(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + SO_3^{\bullet-}(aq). \quad \text{(R15)}$$

The reactions R11-R15 have been well established by the study on the oxidation of S(IV) by OH or photo-oxidation and all the radicals have been observed (Hayon et al., 1972; Huie et al., 1989; Huie and Neta, 1987; Chameides and Davis, 1982; Seinfeld and Pandis, 2006).

The radical mechanism is consistent with the findings of this study and more plausible here. The enhancement of SO_2 oxidation rate in the reaction of SO_2 with $NO_2/O_2/H_2O$ with on $CaCO_3$ particles in synthetic air compared to that in N_2 can be attributed to the role of O_2. Although during the reaction in the absence of O_2, that is, the direct oxidation of SO_2 by NO_2, $SO_3^{\bullet-}$ radical can be formed (R7), the reaction chain cannot propagate (R11-15). Therefore, the S(IV) oxidation rate and the reactive uptake coefficient of SO_2 were much lower than that in the presence of O_2. According to the difference between the reactive uptake coefficient in the absence of O_2 and in presence of O_2, the sulfate production rate via chain reactions due to O_2 (20%) was two to three orders of magnitude faster than the direct oxidation of

233 SO_2 by NO_2. This indicates that sulfate production was largely contributed by O_2 oxidation via the chain
234 reaction pathway, i.e., "auto-oxidation" of S(IV) and O_2 was the main oxidant of SO_2.

235 Although the direct reaction of NO_2 with SO_2 only contributed a very small fraction to sulfate
236 formation, NO_2 played an important role in SO_2 oxidation by initializing the chain reactions via
237 producing $SO_3^{\bullet-}$ radical (R7). In the experiment without NO_2 while keeping other reaction conditions
238 the same, we found that no sulfate was formed after 5 h of reaction. This indicates that O_2 by itself
239 cannot intialize the chain reaction, although it favors chain propagation. Therefore, NO_2 initiated the
240 oxidaiton of SO_2 by O_2 and it is the syngergy of NO_2 and O_2 that resulted in the fast oxidation of SO_2
241 forming sulfate in this study. Without either NO_2 or O_2, the reaction proceeded much slower.

242 Based on the discussion above, we summarize the reaction mechanism of this study in Table 2. The
243 reactions are classfied as chain initiation, chain propagation, and chain termination. Due to the rapid
244 inter-conversion between H_2SO_3, HSO_3^-, and SO_3^{2-}, reactions consuming one of these species will result
245 in instantaneous re-establishment of the equilibria between them (Seinfeld and Pandis, 2006). Overall,
246 the reaction can be written as follows, which shows clearly that O_2 was the main oxidant for sulfate
247 formation:

248 $$2NO_2(aq) + 2SO_3^{2-}(aq) + (0-1)O_2 \rightarrow 2NO_2^-(aq) + S_2O_{6-8}^{2-}(aq) \quad \text{(R18)}$$

249 $$2SO_3^{2-}(aq) + O_2 \rightarrow 2SO_4^{2-}(aq) \quad \text{(R19)}$$

250 $$2HSO_3^-(aq) + O_2 \rightarrow 2SO_4^{2-}(aq) + 2H^+(aq). \quad \text{(R20)}$$

251 Once sulfuric acid was formed, it can further react with $CaCO_3$, forming $CaSO_4$:

252 $$CaCO_3(s) + SO_4^{2-}(aq) + 2H^+(aq) + H_2O(aq) \rightarrow CaSO_4 \bullet 2H_2O(s) + CO_2(g).$$

253 Overall, besides acting as the initializer of the chain reaction, NO_2 contributed to the formation of
254 aqueous phase by the reaction with $CaCO_3$ forming $Ca(NO_3)_2$ as discussed above. The aqueous phase
255 provided the site for S(IV) oxidation.

256 As mentioned above, compared with the reaction in N_2, $CaCO_3$ was consumed slower in the
257 reaction in synthetic air. This difference can be attributed to two reasons. Firstly, the $CaSO_4 \cdot 2H_2O$
258 formed in the reaction can cover $CaCO_3$ surface and partly suppress the diffusion of aqueous ions such
259 as proton and the contact of reactants with $CaCO_3$ surface, thus reducing $CaCO_3$ consumption rate.
260 Secondly, compared with the reaction in N_2, a much higher fraction of $CaCO_3$ was converted to
261 $CaSO_4 \cdot 2H_2O$ instead of $Ca(NO_3)_2$ due to the fast production of $CaSO_4 \cdot 2H_2O$. Therefore, the volume of
262 $Ca(NO_3)_2$ droplet was much smaller than that for the reaction in N_2 for a given $CaCO_3$ particle. Since
263 the uptake rate of NO_2 was proportional to droplet surface and the NO_2 hydrolysis rate is proportional to
264 droplet volume, the production rate of nitric acid from NO_2 hydrolysis and its reaction rate with $CaCO_3$
265 were reduced. Therefore, the $CaCO_3$ particle was consumed slower.

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Atmospheric Chemistry and Physics Discussions

4 Conclusion and implications

We investigated the multiphase reaction of SO_2 with $NO_2/O_2/H_2O$ on $CaCO_3$ particle in synthetic air. The reaction converted $CaCO_3$ particle to $Ca(NO_3)_2$ droplet with $CaSO_4 \cdot 2H_2O$ particle embedded in it. $CaSO_4 \cdot 2H_2O$ constituted a large fraction of the droplet volume in the end of the reaction, in contrast to the small fraction of the droplet volume in the absence of O_2. The $Ca(NO_3)_2$ droplet formed by the reaction of $CaCO_3$ with NO_2 provided a site for multiphase oxidation of SO_2. Generally, nitrate and sulfate were formed simultaneously. The reactive uptake coefficient of SO_2 for sulfate formation in the reaction of SO_2 with NO_2/O_2 in synthetic air was determined to be around 10^{-5}. Compared with the reaction of SO_2 with NO_2 on $CaCO_3$ particle in N_2, that is, the direct oxidation of SO_2 by NO_2, sulfate production rate was enhanced by around two to three orders of magnitude in the presence of O_2. SO_2 oxidation likely proceeded via a chain reaction mechanism according to the findings of this study and literature. O_2 was the main oxidant of SO_2 and NO_2 mainly acted as an initializer of the chain reactions. The synergy of NO_2 and O_2 resulted in fast oxidation of SO_2. Absence of either NO_2 or O_2 led to much slower SO_2 oxidation.

Using a method used in our previous study (Zhao et al., 2017), we assess the importance of the multiphase reaction of SO_2 with $NO_2/O_2/H_2O$ by estimating the lifetime of SO_2 due to multiphase reactions and the lifetime due to the gas phase reaction (with OH radical). The lifetime of SO_2 due to the multiphase reaction of SO_2 with NO_2/O_2 is estimated to be around 20 days using the reactive uptake coefficient of SO_2 of 1.2×10^{-5} and a typical particle surface area concentration for mineral aerosols in winter in Beijing (6.3×10^{-6} cm^2 cm^{-3}) (Huang et al., 2015). This lifetime is substantially shorter than the lifetime regarding the direct oxidation of SO_2 by NO_2 (~7000 days)(Zhao et al., 2017), and comparable to the lifetime of SO_2 due to the gas phase reaction with OH (~12 days assuming daytime OH concentration is 1×10^6 molecule cm^{-3}) (Zhao et al., 2017). Therefore, we conclude that the multiphase oxidation of SO_2 by O_2 in the presence of NO_2 is likely an important source of sulfate and sink of SO_2 in the ambient atmosphere, and can play a significant role in the sulfate formation in the heavily polluted haze episodes such as those frequently occurring in China. High sulfate concentrations are observed during these haze episodes, but the mechanism of sulfate formation is still not clear. Model simulation often substantially underestimate sulfate (Cheng et al., 2016; Gao et al., 2016; Wang et al., 2016; Zheng et al., 2015a). During the haze episodes, the high concentrations of SO_2 and NO_2 co-exist and relative humidity is often high (Zhang et al., 2014; Wang et al., 2016; Zheng et al., 2015b). Under these conditions, the multiphase oxidation of SO_2 by O_2 in the presence of NO_2 could proceed rapidly forming sulfate. The enhanced sulfate concentration due to multiphase reactions and resulted aerosol water content can further promote the multiphase oxidation of SO_2. The reaction thus proceeds in a self-accelerated way. Therefore, it can contribute significantly to sulfate formation.

Further understanding the mechanism of the multiphase reaction of SO_2 with $NO_2/H_2O/O_2$ in air is important to understand other atmospheric implications besides sulfate formation. The direct oxidation of SO_2 by NO_2 forms NO_2^- with a stoichiometry of 1: 1 and can further form HONO under acidic conditions. HONO can evaporate into the atmosphere and is an important source of OH radical. If NO_2 were the main oxidant of SO_2 in the multiphase reaction, the reaction would form one HONO for every sulfate formed. Thus the oxidation of SO_2 by NO_2 can simultaneously be an important source of HONO and OH radical and the SO_2 oxidation would be strongly coupled with reactive nitrogen chemistry. Yet, according to the mechanism of this study, NO_2 only acted as an initializer of chain reactions in SO_2 oxidation and essentially the entire SO_2 was oxidized by O_2. Therefore, HONO formation per sulfate formed was trivial. The oxidation of SO_2 by O_2/NO_2 is expected to neither be an important source of HONO and OH in the atmosphere nor significantly influence reactive nitrogen chemistry.

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Atmospheric Chemistry and Physics Discussions

426 **Table 1.** Reactive uptake coefficient of SO_2 for sulfate formation under 82% RH and different O_2
427 conditions.

NO_2/SO_2/O_2 concentration	**γ**
75 ppm/ 75 ppm/ 86 %	1.7×10^{-5}
75 ppm/ 75 ppm/ 20 %	1.2×10^{-5}
75 ppm/ 75 ppm/ 5 %	3.5×10^{-6}

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Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-900
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Discussion started: 4 October 2017

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Table 2. Summary of the mechanism of the reaction S(IV) with NO_2/O_2

Step	Reactions	
Initiation	$NO_2(aq) + SO_3^{2-}(aq) \rightarrow NO_2^-(aq) + SO_3^{\bullet-}(aq)$	(R8a)
	$NO_2(aq) + HSO_3^-(aq) \rightarrow NO_2^-(aq) + SO_3^{\bullet-}(aq) + H^+(aq)$	(R8b)
Progation	$SO_3^{\bullet-}(aq) + O_2(aq) \rightarrow SO_5^{\bullet-}(aq)$	(R11)
	$SO_5^{\bullet-}(aq) + SO_3^{2-}(aq) + H^+(aq) \rightarrow HSO_5^-(aq) + SO_3^{\bullet-}(aq)$	(R12)
	$SO_5^{\bullet-}(aq) + HSO_3^-(aq) \rightarrow HSO_5^-(aq) + SO_3^{\bullet-}(aq)$	(R12b)
	$HSO_5^-(aq) + SO_3^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + H^+(aq)$	(R13)
	$HSO_5^-(aq) + HSO_3^-(aq) \rightarrow 2SO_4^{2-}(aq) + 2H^+(aq)$	(R13b)
	$SO_5^{\bullet-}(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + SO_4^{\bullet-}(aq)$	(R14)
	$SO_5^{\bullet-}(aq) + HSO_3^-(aq) \rightarrow SO_4^{2-}(aq) + SO_4^{\bullet-}(aq) + H^+(aq)$	(R14b)
	$SO_4^{\bullet-}(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + SO_3^{\bullet-}(aq)$	(R15)
	$SO_4^{\bullet-}(aq) + HSO_3^-(aq) \rightarrow SO_4^{2-}(aq) + SO_3^{\bullet-}(aq) + H^+(aq)$	(R15b)
Termination	$SO_3^{\bullet-}(aq) + SO_3^{\bullet-}(aq) \rightarrow S_2O_6^{2-}(aq)$	(R8)
	$SO_3^{\bullet-}(aq) + SO_3^{\bullet-}(aq) \rightarrow SO_3^{2-}(aq) + SO_3$	(R9
	$SO_3(aq) + H_2O \rightarrow SO_4^{2-}(aq) + 2H^+(aq)$	(R10)
	$SO_4^{\bullet-}(aq) + SO_4^{\bullet-}(aq) \rightarrow S_2O_8^{2-}(aq)$	(R16)
	$SO_5^{\bullet-}(aq) + SO_5^{\bullet-}(aq) \rightarrow S_2O_8^{2-}(aq) + O_2(aq)$	(R17)

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-900
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 October 2017

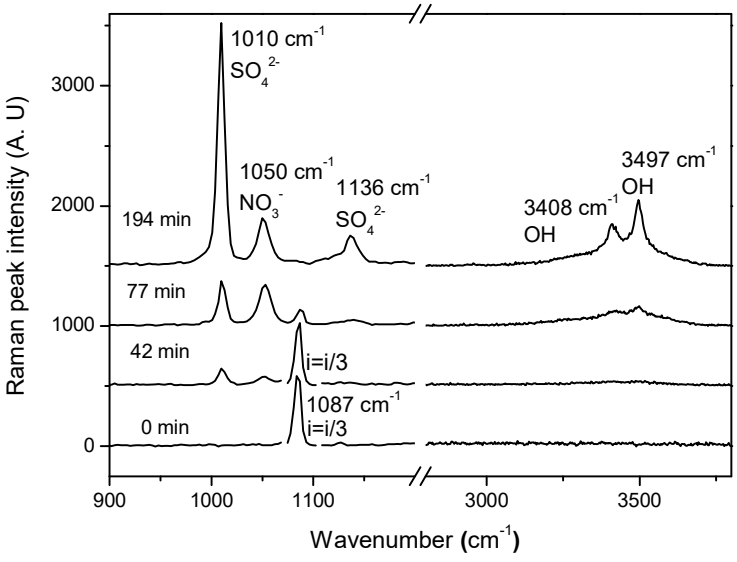

Figure 1. Raman spectra of a $CaCO_3$ particle during the multiphase reaction of SO_2 with $NO_2/O_2/H_2O$ on the particle in synthetic air. SO_2: 75 ppm, NO_2: 75 ppm, RH: 72%. The peak intensity of carbonate (1087 cm^{-1}) at 0 and 42 min was divided by three for clearness.

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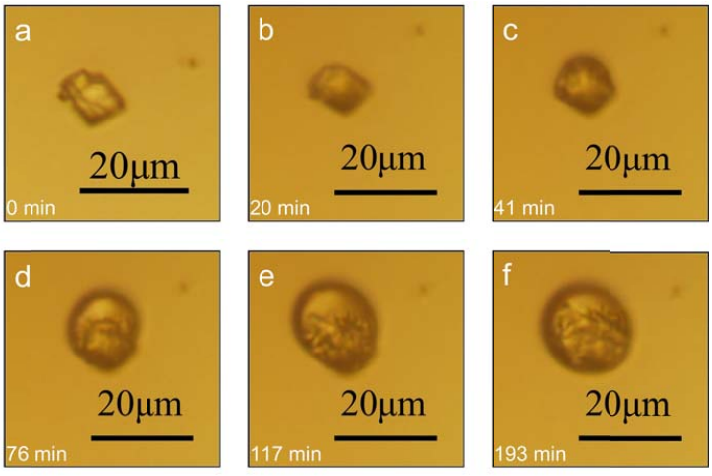
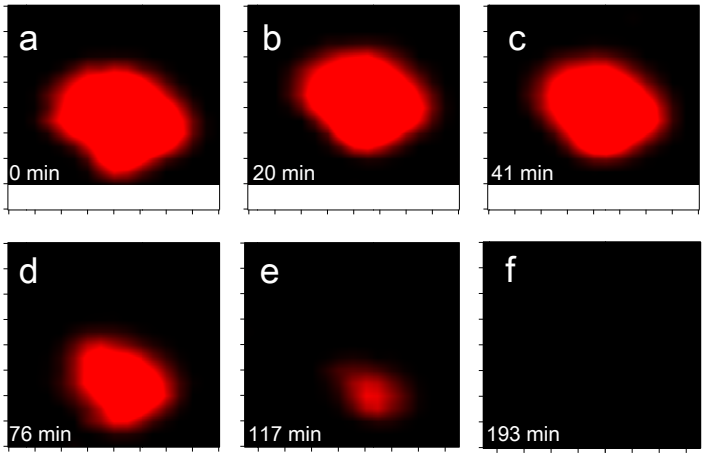
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 October 2017

Atmospheric Chemistry and Physics Discussions



(i)



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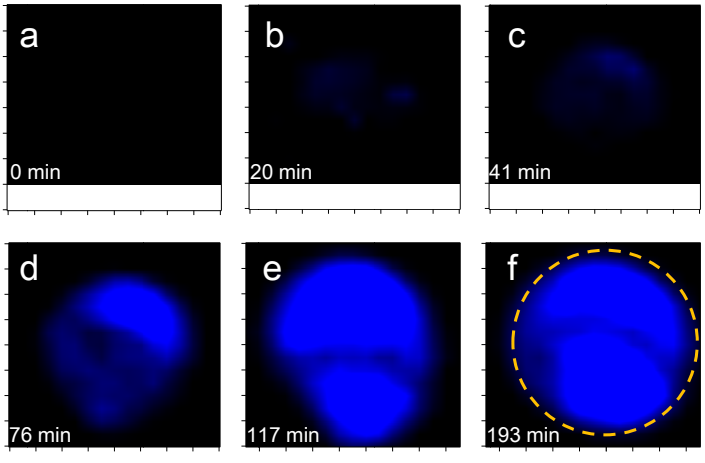

(iii)

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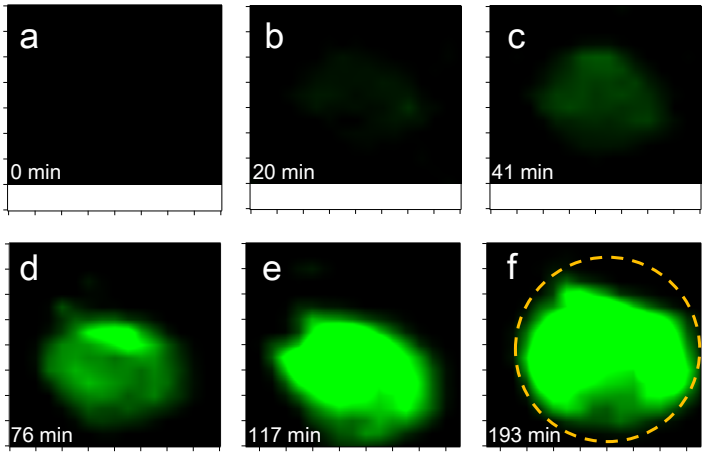

(iv)

Figure 2. Microscopic image (i) and Raman mapping image of carbonate (ii), nitrate (iii), and sulfate (iv) on the $CaCO_3$ particle during the multiphase reaction SO_2 with $NO_2/O_2/H_2O$ on the particle in synthetic air. A-f corresponds to reaction time of 0, 20, 41, 76, 117, and 193 min. SO_2: 75 ppm, NO_2: 75 ppm, RH: 72%. The mapping image of carbonate, nitrate, and sulfate are made using the peak area at 1050, 1010, and 1087 cm^{-1}, respectively. The red, blue, and green colors indicate the peak intensity of carbonate, nitrate, and sulfate, respectively. The dashed lines in panel iii-f and iv-f indicate the shape of the droplet at the end of the reaction.

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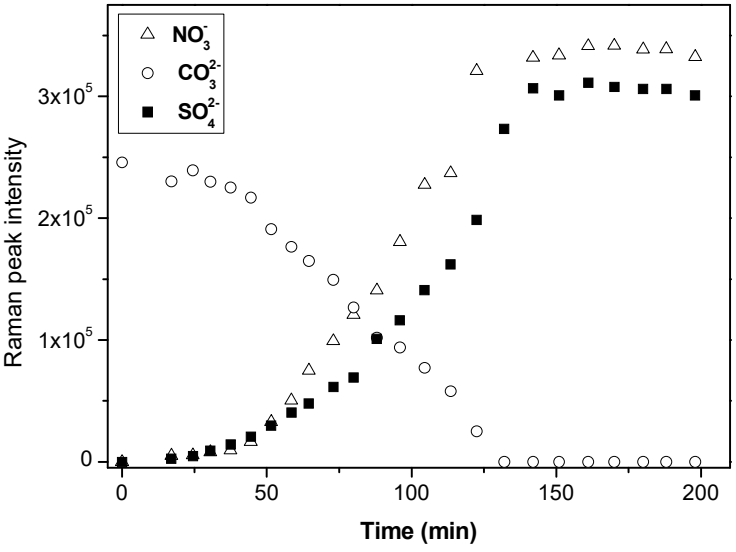

Figure 3. Time series of the Raman peak intensity of the carbonate, nitrate, and sulfate during the reaction of SO_2 with $NO_2/O_2/H_2O$ on $CaCO_3$ particles in synthetic air. SO_2: 75 ppm, NO_2: 75 ppm, RH: 72%. The intensity of NO_3^-, SO_4^{2-}, and CO_3^{2-} show the peak area at 1050, 1010, and 1087 cm^{-1}, respectively, in Raman spectra obtained by Raman mapping.