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\(_2\)O 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.
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$_2$SO$_3$, 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
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\(_2\)O 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\(_2\)O 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 (\(\gamma\)) was further determined from the reaction rate and collision rate of SO\(_2\) on surface of a single particle.

\[
\gamma = \frac{d[SO_4^{2-}]}{dt} \\
Z = \frac{1}{c} A \left[SO_2\right] \\
c = \sqrt{\frac{8RT}{\pi MN_{SO_2}}}
\]
where R is the gas constant, T is temperature, M_{SO_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 symmetrical stretching of carbonate (\nu_s(CO_3^{2-})) (Nakamoto, 1997). During the reaction, the peak at 1087 cm^{-1} decreased continuously 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 asymmetric stretching(\nu_a(SO_4^{2-})) of sulfate in gypsum (CaSO_4·2H_2O), respectively (Sarma et al., 1998). In addition, after the reaction, a broad envelope 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_4·2H_2O (Sarma et al., 1998; Ma et al., 2013).

During the multiphase reaction with SO_3/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_4·2H_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 O2. CaSO4 solid particle constituted most of the volume droplet here while in the absence
of O2 the few needle-shaped CaSO4 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 O2, where nitrate was formed first and sulfate was essentially
formed after the complete conversion of CaCO3 particle to Ca(NO3)2 droplet. Moreover, the time for
carbonate to be completely consumed was longer here than that in the absence of O2 (~120 min vs. ~40
min) when other conditions were kept the same.

3.3 Reactive uptake coefficient of SO2

The reactive uptake coefficient of SO2 for sulfate formation (γ) in the reaction of SO2 with
NO2/O2/H2O on CaCO3 in synthetic air and in O2/N2 carrier gas with varied O2 concentrations is shown
in Table 1. γ for the reaction of SO2 with NO2 in presence of O2 (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 N2 under similar conditions (Zhao et al., 2017). When other conditions were kept
constant, γ increased with O2 concentration. This indicates that O2 played a key role in enhancing the
oxidation of SO2.

The role of O2 in enhancing the reactive uptake of SO2 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 O2 concentration (0-5% by volume). Shen and Rochelle (1998) also found that in the presence of
O2, aqueous sulfite oxidation was enhanced. By investigating the oxidation of SO2 by NO2 in
mono-dispersed water droplets growing on carbon nuclei, Santachiara et al. (1990) found that sulfate
formation rate with 2% O2 is much higher than that without O2. Yet, our finding is in contrast to the
study by Lee and Schwartz (1983), who found that changing from N2 to air as carrier gas only increases
SO2 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 O2 diffusion from gas to condensed phase and
different mechanisms between multiphase reaction on particles and aqueous reaction.
3.4 Reaction mechanism

In the multiphase reaction of SO\textsubscript{2} with NO\textsubscript{2}/O\textsubscript{2}/H\textsubscript{2}O on CaCO\textsubscript{3} particles in synthetic air, we found CaCO\textsubscript{3} could react with NO\textsubscript{2} and H\textsubscript{2}O and produce Ca(NO\textsubscript{3})\textsubscript{2}, which could deliquesce, forming liquid water, and provide a site for aqueous oxidation of SO\textsubscript{2}. This process was similar to the reaction in N\textsubscript{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\textsubscript{2} can undergo multiphase reactions with NO\textsubscript{2}/O\textsubscript{2}. The detailed mechanism of the aqueous reaction of S(IV) with NO\textsubscript{2} is complex. Previous studies have proposed two different kinds of mechanism. One involves the SO\textsubscript{3}\•\- 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\textsubscript{2}, Lee and Schwartz (1983) suggest the following reaction equation, according to the reaction products and their yields,

\[ 2\text{NO}_2(aq) + \text{HSO}_3^-(aq) + H_2O \rightarrow 2\text{NO}_2^- (aq) + SO_2^{3-}(aq) + 3H^+(aq) \]  

(R1)

The yields of SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{2}\textsuperscript{-}, and H\textsuperscript{+} relative to the HSO\textsubscript{3}\textsuperscript{-} consumed are 1.0±0.05, 1.5±0.4, and 2.5±0.4, respectively, and the NO\textsubscript{2}\textsuperscript{-} formed relative to NO\textsubscript{2} consumed is 1.0±0.18.

Clifton et al. (1988) proposed that the reaction proceeds via NO\textsubscript{2}-S(IV) adduct complexes:

\[ \text{NO}_2(aq) + SO_2^{3-}(aq) \rightarrow [\text{NO}_2 - SO_3]^{2-}(aq) \]  

(R2)

\[ \text{NO}_2(aq) + [\text{NO}_2 - SO_3]^{2-}(aq) \rightarrow [\text{NO}_2 - SO_3 - NO_2]^{2-}(aq) \]  

(R3)

\[ [\text{NO}_2 - SO_3 - NO_2]^{2-}(aq) + OH^-(aq) \rightarrow [\text{NO}_2 - SO_4H - NO_2]^{3-}(aq) \]  

(R4)

\[ [\text{NO}_2 - SO_4H - NO_2]^{3-}(aq) \rightarrow 2\text{NO}_2^- (aq) + SO_2^{3-}(aq) + H^+(aq). \]  

(R5)

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

\[ 2\text{NO}_2(aq) + SO_2^{3-}(aq) + H_2O \rightarrow 2\text{NO}_2^- (aq) + SO_2^{3-}(aq) + 2H^+(aq). \]  

(R6)

The reaction R6 is similar to R1.

If the NO\textsubscript{2}-S(IV) adduct mechanism were the main mechanism in this study, there should be no significant difference in the SO\textsubscript{2} oxidation rate between the reaction in the presence of O\textsubscript{2} and in the absence of O\textsubscript{2}. In fact, in the presence of O\textsubscript{2} we observed a substantial enhancement in the SO\textsubscript{2} oxidation rate compared to the reaction in the absence of O\textsubscript{2}. Therefore, the NO\textsubscript{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\textsubscript{2} with aqueous sulfite, besides SO\textsubscript{3}\•\- and NO\textsubscript{2}\•\-, they detected S\textsubscript{2}O\textsubscript{6}\textsuperscript{2-} with an appreciable yield using Raman spectroscopy. Since S\textsubscript{2}O\textsubscript{6}\textsuperscript{2-} is known to be the combination reaction product of SO\textsubscript{3}\•\- (Eriksen, 1974; Hayon et al., 1972; Deister and Warneck, 1990; Brandt et al., 1994; Waygood and McElroy, 1992), SO\textsubscript{3}\•\- radical is proposed to be formed:

\[ \text{NO}_2(aq) + SO_2^{3-}(aq) \rightarrow \text{NO}_2^- (aq) + SO_2^{3-}(aq). \]  

(R7)
SO₃• can react via two pathways, forming either S₂O₆²⁻ or SO₄²⁻:

\[
SO₃⁻(aq) + SO₃⁻(aq) \rightarrow S₂O₆²⁻(aq) \quad \text{(R8)}
\]

\[
SO₃⁻(aq) + SO₃⁻(aq) \rightarrow SO₂⁻(aq) + SO₃ \quad \text{(R9)}
\]

\[
SO₃(aq) + H₂O \rightarrow SO₂⁻(aq) + 2H⁺(aq) \quad \text{(R10)}
\]

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 SO₃• radical in the aqueous reaction of S(IV) with NO₂, SO₃• was directly observed in the reaction of NO₂⁻ with SO₃²⁻ in an acidic buffer solution (pH=4.0) using electron spin resonance (ESR) (Shi, 1994). Since NO₂⁻ is formed in the aqueous reaction of SO₂ with NO₂ and S₂O₆ as the combination reaction product of SO₃• is observed (Littlejohn et al., 1993), SO₃• formation is plausible.

In the presence of O₂, Littlejohn et al. (1993) observed that the relative amount of S₂O₆²⁻ to SO₄²⁻ decreases and S₂O₆²⁻ is undetectable at low NO₂ concentrations (<5 ppm) in the aqueous reaction of NO₂ with sulfite. This indicates that O₂ suppresses the reaction pathway of S₂O₆²⁻ formation (R8).

Because SO₃• radical can react rapidly with O₂, forming SO₅• radical, and thus be consumed, the suppression of S₂O₆²⁻ is readily attributed to the reaction of SO₃• with O₂:

\[
SO₃⁻(aq) + O₂(aq) \rightarrow SO₅⁻(aq) \quad \text{(R11)}
\]

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):

\[
SO₅⁻(aq) + SO₃⁻(aq) + H⁺(aq) \rightarrow HSO₅⁻(aq) + SO₃⁻(aq) \quad \text{(R12)}
\]

\[
HSO₅⁻(aq) + SO₃⁻(aq) \rightarrow 2SO₃⁻(aq) + H⁺(aq) \quad \text{(R13)}
\]

\[
SO₅⁻(aq) + SO₃⁻(aq) \rightarrow SO₃⁻(aq) + SO₅⁻(aq) \quad \text{(R14)}
\]

\[
SO₅⁻(aq) + SO₃⁻(aq) \rightarrow SO₃⁻(aq) + SO₅⁻(aq) \quad \text{(R15)}
\]

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 SO₂ oxidation rate in the reaction of SO₂ with NO₂/O₂/H₂O with on CaCO₃ particles in synthetic air compared to that in N₂ can be attributed to the role of O₂. Although during the reaction in the absence of O₂, that is, the direct oxidation of SO₂ by NO₂, SO₃• radical can be formed (R7), the reaction chain cannot propagate (R11-15). Therefore, the S(IV) oxidation rate and the reactive uptake coefficient of SO₂ were much lower than that in the presence of O₂. According to the difference between the reactive uptake coefficient in the absence of O₂ and in presence of O₂, the sulfate production rate via chain reactions due to O₂ (20%) was two to three orders of magnitude faster than the direct oxidation of...
SO₂ by NO₂. This indicates that sulfate production was largely contributed by O₂ oxidation via the chain reaction pathway, i.e., “auto-oxidation” of S(IV) and O₂ was the main oxidant of SO₂.

Although the direct reaction of NO₂ with SO₂ only contributed a very small fraction to sulfate formation, NO₂ played an important role in SO₂ oxidation by initializing the chain reactions via producing SO₃•⁻ radical (R7). In the experiment without NO₂ while keeping other reaction conditions the same, we found that no sulfate was formed after 5 h of reaction. This indicates that O₂ by itself cannot initialize the chain reaction, although it favors chain propagation. Therefore, NO₂ initiated the oxidation of SO₂ by O₂ and it is the synergy of NO₂ and O₂ that resulted in the fast oxidation of SO₂ forming sulfate in this study. Without either NO₂ or O₂, the reaction proceeded much slower.

Based on the discussion above, we summarize the reaction mechanism of this study in Table 2. The reactions are classified as chain initiation, chain propagation, and chain termination. Due to the rapid inter-conversion between H₂SO₃, HSO₃⁻, and SO₄²⁻, reactions consuming one of these species will result in instantaneous re-establishment of the equilibria between them (Seinfeld and Pandis, 2006). Overall, the reaction can be written as follows, which shows clearly that O₂ was the main oxidant for sulfate formation:

\[
 2\text{NO}_2(aq) + 2\text{SO}_4^{2−}(aq) + (0 - 1)\text{O}_2 \rightarrow 2\text{NO}_3^−(aq) + S_2\text{O}_8^{2−}(aq) \quad \text{(R18)}
\]

\[
 2\text{SO}_3^−(aq) + \text{O}_2 \rightarrow 2\text{SO}_4^{2−}(aq) \quad \text{(R19)}
\]

\[
 2\text{HSO}_3^−(aq) + \text{O}_2 \rightarrow 2\text{SO}_4^{2−}(aq) + 2\text{H}^+(aq). \quad \text{(R20)}
\]

Once sulfuric acid was formed, it can further react with CaCO₃, forming CaSO₄:

\[
 2\text{CaCO}_3(s) + \text{SO}_4^{2−}(aq) + 2\text{H}^+(aq) + \text{H}_2\text{O}(aq) \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2(g).
\]

Overall, besides acting as the initializer of the chain reaction, NO₂ contributed to the formation of aqueous phase by the reaction with CaCO₃ forming Ca(NO₃)₂ as discussed above. The aqueous phase provided the site for S(IV) oxidation.

As mentioned above, compared with the reaction in N₂, CaCO₃ was consumed slower in the reaction in synthetic air. This difference can be attributed to two reasons. Firstly, the CaSO₄·2H₂O formed in the reaction can cover CaCO₃ surface and partly suppress the diffusion of aqueous ions such as proton and the contact of reactants with CaCO₃ surface, thus reducing CaCO₃ consumption rate. Secondly, compared with the reaction in N₂, a much higher fraction of CaCO₃ was converted to CaSO₄·2H₂O instead of Ca(NO₃)₂ due to the fast production of CaSO₄·2H₂O. Therefore, the volume of Ca(NO₃)₂ droplet was much smaller than that for the reaction in N₂ for a given CaCO₃ particle. Since the uptake rate of NO₂ was proportional to droplet surface and the NO₂ hydrolysis rate is proportional to droplet volume, the production rate of nitric acid from NO₂ hydrolysis and its reaction rate with CaCO₃ were reduced. Therefore, the CaCO₃ particle was consumed slower.
4 Conclusion and implications

We investigated the multiphase reaction of SO$_2$ with NO$_2$/O$_2$/H$_2$O on CaCO$_3$ particle in synthetic air. The reaction converted CaCO$_3$ particle to Ca(NO$_3$)$_2$ droplet with CaSO$_4$·2H$_2$O particle embedded in it. CaSO$_4$·2H$_2$O 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$_2$O 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 $1.2\times10^{-5}$ and a typical particle surface area concentration for mineral aerosols in winter in Beijing ($6.3\times10^{-6}$ 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 $1\times10^6$ 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$_2$O/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.

Acknowledgements

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References


Spindler, G., Hesper, J., Bruggemann, E., Dubois, R., Muller, T., and Herrmann, H.: Wet annular denuder measurements of nitrous acid: laboratory study of the artefact reaction of NO$_2$ with S(IV) in aqueous solution and comparison with field measurements, Atmos. Environ., 37, 2643-2662, 10.1016/s1352-2310(03)00209-7, 2003.


Table 1. Reactive uptake coefficient of SO$_2$ for sulfate formation under 82% RH and different O$_2$ conditions.

<table>
<thead>
<tr>
<th>NO$_2$/SO$_2$/O$_2$ concentration</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 ppm/ 75 ppm/ 86 %</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>75 ppm/ 75 ppm/ 20 %</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>75 ppm/ 75 ppm/ 5 %</td>
<td>$3.5 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
Table 2. Summary of the mechanism of the reaction S(IV) with NO$_2$/O$_2$

<table>
<thead>
<tr>
<th>Step</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation</td>
<td>$NO_2(aq) + SO_3^{2-}(aq) \rightarrow NO_2^-(aq) + SO_3^{-}(aq)$ (R8a)</td>
</tr>
<tr>
<td></td>
<td>$NO_2(aq) + HSO_3^-(aq) \rightarrow NO_2^-(aq) + SO_3^{-}(aq) + H^+(aq)$ (R8b)</td>
</tr>
<tr>
<td>Propagation</td>
<td>$SO_3^{-}(aq) + O_2(aq) \rightarrow SO_3^{2-}(aq)$ (R11)</td>
</tr>
<tr>
<td></td>
<td>$SO_3^{2-}(aq) + SO_3^{2-}(aq) + H^+(aq) \rightarrow HSO_3^-(aq) + SO_3^{-}(aq)$ (R12)</td>
</tr>
<tr>
<td></td>
<td>$SO_3^{-}(aq) + HSO_3^-(aq) \rightarrow HSO_3^-(aq) + SO_3^{-}(aq)$ (R12b)</td>
</tr>
<tr>
<td></td>
<td>$HSO_3^-(aq) + SO_3^{2-}(aq) \rightarrow 2SO_3^{-}(aq) + H^+(aq)$ (R13)</td>
</tr>
<tr>
<td></td>
<td>$HSO_3^-(aq) + HSO_3^-(aq) \rightarrow 2SO_3^{-}(aq) + 2H^+(aq)$ (R13b)</td>
</tr>
<tr>
<td></td>
<td>$SO_3^{2-}(aq) + SO_3^{2-}(aq) \rightarrow SO_3^{4-}(aq) + SO_3^{-}(aq)$ (R14)</td>
</tr>
<tr>
<td></td>
<td>$SO_3^{-}(aq) + HSO_3^-(aq) \rightarrow SO_3^{2-}(aq) + SO_3^{-}(aq) + H^+(aq)$ (R14b)</td>
</tr>
<tr>
<td></td>
<td>$SO_3^{-}(aq) + SO_3^{2-}(aq) \rightarrow SO_3^{4-}(aq) + SO_3^{-}(aq)$ (R15)</td>
</tr>
<tr>
<td></td>
<td>$SO_3^{4-}(aq) + HSO_3^-(aq) \rightarrow SO_3^{2-}(aq) + SO_3^{-}(aq) + H^+(aq)$ (R15b)</td>
</tr>
<tr>
<td>Termination</td>
<td>$SO_3^{2-}(aq) + SO_3^{-}(aq) \rightarrow S_2O_6^{2-}(aq)$ (R8)</td>
</tr>
<tr>
<td></td>
<td>$SO_3^-(aq) + SO_3^{2-}(aq) \rightarrow SO_3^{2-}(aq) + SO_3$ (R9)</td>
</tr>
<tr>
<td></td>
<td>$SO_3(aq) + H_2O \rightarrow SO_3^{2-}(aq) + 2H^+(aq)$ (R10)</td>
</tr>
<tr>
<td></td>
<td>$SO_3^{-}(aq) + SO_3^{2-}(aq) \rightarrow S_2O_6^{2-}(aq)$ (R16)</td>
</tr>
<tr>
<td></td>
<td>$SO_3^{-}(aq) + SO_3^{2-}(aq) \rightarrow S_2O_6^{2-}(aq) + O_2(aq)$ (R17)</td>
</tr>
</tbody>
</table>
Figure 1. Raman spectra of a CaCO$_3$ particle during the multiphase reaction of SO$_2$ with NO$_2$/O$_2$/H$_2$O 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.
Figure 2. Microscopic image (i) and Raman mapping image of carbonate (ii), nitrate (iii), and sulfate (iv) on the CaCO₃ particle during the multiphase reaction SO₂ with NO₂/O₂/H₂O on the particle in synthetic air. A-f corresponds to reaction time of 0, 20, 41, 76, 117, and 193 min. SO₂: 75 ppm, NO₂: 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.
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$_2$O 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.