Multiphase Oxidation of SO₂ by NO₂ on CaCO₃ Particles

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Abstract. Heterogeneous/multiphase oxidation of SO₂ by NO₂ on solid or aqueous particles is thought to be a potentially important source of sulfate in the atmosphere, for example, during heavily polluted episodes (haze), but the reaction mechanism and rate are uncertain. In this study, in order to assess the importance of the direct oxidation of SO₂ by NO₂ we investigated the heterogeneous/multiphase reaction of SO₂ with NO₂ on individual CaCO₃ particles in N₂ using Micro-Raman spectroscopy. In the SO₂/NO₂/H₂O/N₂ gas mixture, the CaCO₃ solid particle was first converted to the Ca(NO₃)₂ droplet by the reaction with NO₂ and the deliquescence of Ca(NO₃)₂, and then NO₂ oxidized SO₂ in the Ca(NO₃)₂ droplet forming CaSO₄, which appeared as needle-shaped crystals. Sulfate was mainly formed after the complete conversion of CaCO₃ to Ca(NO₃)₂, that is, during the multiphase oxidation of SO₂ by NO₂. The precipitation of CaSO₄ from the droplet solution promoted sulfate formation. The reactive uptake coefficient of SO₂ for sulfate formation is on the order of 10⁻⁸, and RH enhanced the uptake coefficient. We estimate that the direct multiphase oxidation of SO₂ by NO₂ is not an important source of sulfate in the ambient atmosphere compared with the SO₂ oxidation by OH in the gas phase.
1 Introduction

Sulfate is a major component of atmospheric particulate matter. It contributes to a large fraction of atmospheric aerosol particles in both urban and rural areas (Seinfeld and Pandis, 2006; Zhang et al., 2007). Sulfate is either from primary source, such as sea spray, or from secondary source, i.e., by the oxidation of reduced sulfur compounds such as dimethyl sulfide (DMS), carbonyl sulfur (COS), and SO2 (Seinfeld and Pandis, 2006). In the continent, the main source of sulfate is the oxidation of SO2, an important air pollutant from fossil fuel combustion. SO2 can be oxidized in the gas phase, mainly by OH, or in the particle phase such as by H2O2, O3, or O2 catalyzed by transition metal ions in cloud or fog water (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts Jr., 1999) or by O3 or photochemical reactions on particle surface (Zhu et al., 2011; Li et al., 2006; Li et al., 2007; Shang et al., 2010; Li et al., 2011).

Although various pathways of SO2 oxidation are identified, the source of sulfate and relative importance of various pathways of SO2 oxidation forming sulfate in the atmosphere still remain uncertain. For example, during heavily polluted episodes (haze) in China in recent years, high concentrations of sulfate were observed, but the source of sulfate is elusive (Wang et al., 2016; Wang et al., 2014a; Zheng et al., 2015b; Guo et al., 2014). The relative contribution of regional transport versus local formation and physical and chemical mechanisms responsible for sulfate formation are still not clear. Recent studies have highlighted heterogeneous reactions of SO2 on solid or liquid particles to be a possibly important source of sulfate based on model, field and laboratory studies (Huang et al., 2014; Zhu et al., 2011; Cheng et al., 2016a; Gao et al., 2016; Zheng et al., 2015a; Wang et al., 2014b; He et al., 2014; Fu et al., 2016; Xue et al., 2016; Xie et al., 2015). During haze episodes, relative humidity (RH) is often high (Zhang et al., 2014; Wang et al., 2016; Zheng et al., 2015b) and particles or some components of particles can deliquesce forming liquid water. In particular, several recent studies propose that the multiphase oxidation of SO2 by NO2, another important air pollutant, on liquid particles may be a major pathway of sulfate formation (Cheng et al., 2016a; Wang et al., 2016; Xue et al., 2016; Xie et al., 2015). Both SO2 and NO2 are from fossil fuel combustion and both concentrations are often high during haze episodes, and their reaction may significantly contribute to sulfate formation.

In order to assess and quantify the role of the heterogeneous reactions of SO2 in sulfate formation, laboratory studies are needed to understand the reaction process and obtain kinetic parameters for modeling such as uptake coefficients of SO2. Among many studies investigating the heterogeneous reactions of SO2 on various particles (Goodman et al., 2001; Li et al., 2011; Shang et al., 2010; Huang et al., 2015; Huang et al., 2016; Zhou et al., 2014; Li et al., 2004; Kong et al., 2014; Passananti et al., 2016; Cui et al., 2008; Chu et al., 2016; Zhao et al., 2015; Li et al., 2006; Wu et al., 2011; He et al., 2014; Liu et al., 2012; Ma et al., 2008; Park and Jang, 2016; Ullerstam et al., 2002; Sorimachi et al., 2001; Ullerstam et al., 2003; Wu et al., 2013; Wu et al., 2015), only a few have investigated the heterogeneous reaction of SO3 in the presence of NO2 (He et al., 2014; Liu et al., 2012; Ma et al., 2008; Park and Jang, 2016; Ullerstam et al., 2003; Ma et al., 2017). These studies found that NO2 can promote sulfate formation from SO2 oxidation (He et al., 2014; Liu et al., 2012; Ma et al., 2008; Park and Jang, 2016; Ullerstam et al., 2003). However, the mechanism of this effect is still not clear and only few studies reported kinetic parameters such as uptake coefficient of SO2 due to the reaction with NO2. Importantly, most of these studies focused on the gas-solid reactions on particles. Very few laboratory studies have investigated the multiphase reaction of SO2 with NO2 on atmospheric aqueous particles or solid-aqueous mixed phase aerosol
particles, and the uptake coefficient of SO₂ on atmospheric aqueous particles due to the reaction with NO₂ is largely unknown. From several decades ago until now, a number of studies have investigated the aqueous reaction of soluble S(IV) species (H₂SO₃, HSO₃⁻, SO₃²⁻) with NO₂ in dilute bulk solution (Lee and Schwartz, 1983; Clifton et al., 1988; Littlejohn et al., 1993; Takeuchi et al., 1977; Nash, 1979; Ellison and Eckert, 1984; Shen and Rochelle, 1998; Tursic and Grgic, 2001) relevant to the conditions in cloud water. However, in aqueous aerosol particles, the reaction rate and process may be substantially different from those in bulk solution due to high ion strength resulted from high concentrations of solutes, potential interactions of sulfate with other ions, and low water activity in aerosol particles.

In this study, we present the findings of the multiphase reaction of SO₂ directly with NO₂, a reaction pathway proposed in a number of recent studies to be potentially important for sulfate formation (Cheng et al., 2016b; Wang et al., 2016; Xue et al., 2016). We investigated the heterogeneous reaction of SO₂ with NO₂ on CaCO₃ particles at the ambient RH. CaCO₃ is an important component of mineral aerosols, especially in East Asia (Cao et al., 2005; Song et al., 2005; Okada et al., 2005) and it is a very reactive component (Krueger et al., 2004; Li et al., 2010; Li et al., 2006; Prince et al., 2007a). It is also one of the few alkaline particles in the atmosphere, especially in northern China, which can neutralize acids on particles and increase the pH of aerosol water, thus promoting the apparent solubility and uptake of SO₂. The reaction of SO₂ with NO₂ on CaCO₃ has been suggested by field observations, which showed internal mixing of CaCO₃, CaSO₄, and Ca(NO₃)₂ in particles (Hwang and Ro, 2006; Li and Shao, 2009; Zhang et al., 2000). More importantly, as shown below, during the reaction on CaCO₃, aqueous phase can be formed, which allows us to investigate the multiphase reaction of SO₂ with NO₂. We studied the reaction of SO₂ and NO₂ on individual CaCO₃ particles in N₂ using Micro-Raman spectrometer with a flow reaction system. N₂ was used as carrier gas in order to avoid confounding effects of other oxidants including O₂ in SO₂ oxidation. Combining the chemical and optical information from Micro-Raman spectrometer, we systematically investigated the reaction process and quantified the reactive uptake coefficient of SO₂ due to the oxidation by NO₂ based on sulfate production rate. We further assessed the importance of the multiphase oxidation of SO₂ by NO₂ in the atmosphere.

2 Experimental

2.1 Apparatus and procedures

The experimental setup used in this study is illustrated in Fig. 1. The details of the setup have been described previously (Liu et al., 2008; Zhao et al., 2011). NO₂ and SO₂ of certain concentrations were prepared by adjusting the flow rates of standard gases of specified concentrations (NO₂: 1000 ppm in N₂, Messer, Germany; SO₂: 2000 ppm in N₂, National Institute of Metrology P.R. China) and high-purity nitrogen (99.999%, Beijing Haikeyuanchang Corp.). We used N₂ as a carrier gas to exclude the potential inference from other compounds in SO₂ oxidation such as O₂, which is key to investigate the direct oxidation of SO₂ by NO₂. RH was regulated by adjusting the flow rates of humidified N₂ and of dry N₂ and other dry gases. Humidified N₂ was prepared by bubbling N₂ through fritted glass in water. Flow rates of the gases were controlled by mass flow controllers (FC-260, Tylan, Germany). Mixed gases reacted with CaCO₃ particles in a stainless steel reaction cell. Individual CaCO₃ particles were deposited on a Teflon FEP film substrate annealed to a silicon wafer. The substrate was
then placed in the reaction cell, which has a glass cover on top of the center. Through this top window, a
Micro-Raman spectrometer (LabRam HR800, HORIBA Jobin Yvon) was used to acquire the Raman spectra of
particles. A 514 nm excitation laser was focused onto selected particles and back scattering Raman signals were
detected. The details of the instrument are described in previous studies (Liu et al., 2008; Zhao et al., 2011).

The RH and temperature of the outflow gas from the reaction cell were measured by a hygrometer (HMT100,
Vaisala). Experiments of individual CaCO$_3$ particles reacting with NO$_2$ (75-200 ppm) and SO$_2$ (75-200 ppm)
mixing gas diluted with N$_2$ were conducted under certain RH (17-72%). All the measurements were carried out at
25±0.5 °C. Each reaction was repeated for three times.

In this study, the size of CaCO$_3$ particles was around 7-10 μm. During a reaction, components of an
individual particle may distribute unevenly within the particle due to the formation of new aqueous phase or solid
phase, and particles may grow. Because particles are larger than the laser spot (~1.5 μm), Raman spectrum from
one point does not represent the chemical composition of the whole particle. Therefore Raman mapping was used
to obtain the spectra on different points of a particle in order to get the chemical information of the whole particle.
The mapping area is a rectangular slightly larger than the particle and mapping steps are 1×1 μm. Raman spectra
in the range 800-3900 cm$^{-1}$ were acquired with exposure time of 1 s for each mapping point. During each
mapping (7-10 min, depending on the mapping area), no noticeable change in composition was detected. The
mean time of a mapping period was used as reaction time. During the reaction, microscopic images of particles
were also recorded. Raman spectra were analyzed using Labspec 5 software (HORIBA Jobin Yvon). Raman
peaks were fit to Gaussian-Lorentzian functions to obtain peak positions and peak areas on different points of the
particle. The peak areas were then added up to get the peak area for the whole particle.

Besides the reaction of CaCO$_3$ with SO$_2$ and NO$_2$, other reaction systems including the reaction on Ca(NO$_3$)$_2$,
NaNO$_3$, and NH$_4$NO$_3$ particles with SO$_2$ or SO$_2$ and NO$_2$ mixing gas (summarized in Table 1) were also studied
in order to elucidate the reaction mechanism.

CaCO$_3$ (98%, Sigma) with diameters about 7-10 μm on average, Ca(NO$_3$)$_2$·4H$_2$O (ACS, 99-103%; Riedel-de
Haën), NH$_4$NO$_3$ (AR, Beijing Chemical Works), and NaNO$_3$ (AR, Beijing Chemical Works) were used without
further purification.

### 2.2 Quantification of reaction products on the particle phase

The Raman intensity of a sample is described as Equation (1):

$$ I(\nu) = I_0 \cdot A(\nu) \cdot J(\nu) \cdot \nu^4 \cdot D \cdot K $$

where $I_0$ is the intensity of incident laser, $A(\nu)$ is the collection efficiency function of a Raman spectrometer,
$J(\nu) \cdot \nu^4$ is the Raman scattering section of the sample, $D$ is the number density of the sample, and $K$ is the
effective depth of the sample. Raman intensity is not only determined by the amount of the sample molecules, but
also by the configuration of the instrument, whose influence cannot be eliminated unless internal standards are
used. For soluble compounds, water can be used an internal standard (Zhao et al., 2011; Liu et al., 2008).
However, in this study, one product (CaSO$_4$, see below) appeared as solid state. For solid particles of micro-scale,
it is hard to add internal standards into the system. Therefore it is difficult to establish the relationship between
Raman intensity and the amount of sample molecules, which makes the quantification very challenging.
In this study, we chose seven individual CaSO$_4$ particles varying in size as the standard for solid products. The profile of each particle can be obtained by scanning the particle using Raman mapping with steps of 1, 1, and 2 μm for x, y, and z dimension, respectively. The volume of each particle was calculated based on 3D profiles of the particles using a CAD software (AutoDesk). In order to minimize the influence of variations of incident laser on Raman intensity, these seven particles were measured before each experiment, which produced a calibration curve for each experiment (Fig. S1).

2.3 Determination of reactive uptake coefficient

In this study, sulfate was produced from the oxidation of SO$_2$. The reactive uptake coefficient $\gamma$ of SO$_2$ on individual particles was estimated from sulfate formation. $\gamma$ is derived as the rate of sulfate formation \( \frac{d\{SO_4^{2-}\}}{dt} \) divided by the rate of surface collisions with an individual particle (Z),

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

$$Z = \frac{2cA_s[SO_2]}{\pi R^2}, \quad (3)$$

$$c = \frac{R T}{e_{SO_2} M_{SO_2}}, \quad (4)$$

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. $Z$ is the collision rate between SO$_2$ and a particle. $\{SO_4^{2-}\}$ indicates the amount of sulfate on the particle phase in mole, and $[SO_2]$ indicates the concentration of SO$_2$ in the gas phase.

$\{SO_4^{2-}\}$ was determined by a calibration curve as stated above. In this study, since sulfate was mainly formed after the formation of Ca(NO$_3$)$_2$ droplet as shown below, $A_s$ was calculated by estimating the diameter of the droplet according to its microscopic image and using a shape of spherical segment defined by the contact angle of a water droplet on Teflon (Good and Koo, 1979). For each experiment, at least three particles with different diameters were measured to get an average reactive uptake coefficient.

3 Results and discussion

3.1 Reaction products and particle morphology changes

Figure 2 shows typical Raman spectra of a CaCO$_3$ particle during the reaction with SO$_2$ and NO$_2$. The peak at 1087 cm$^{-1}$ is assigned to the symmetric stretching mode of carbonate ($\nu_1$) (Nakamoto, 1997), which could be detected during the initial stage of the reaction. Shortly after the reaction started, a peak at 1050 cm$^{-1}$ was observed, which is attributed to the symmetric stretching mode of nitrate ($\nu_1$). This demonstrates that calcium nitrate (Ca(NO$_3$)$_2$) was produced during the reaction. A broad band at 2800-3800 cm$^{-1}$ was also observed together with the formation of Ca(NO$_3$)$_2$. It is assigned to $-$OH stretching of liquid water. The formation of liquid water is attributed to the deliquescence of Ca(NO$_3$)$_2$, which is very hygroscopic and can deliquesce at $\sim$10% RH (Liu et al., 2008; Al-Abadleh et al., 2003; Tang and Fung, 1997). After about 82 min, a new peak at 1013 cm$^{-1}$ was observed, which is attributed to the symmetric stretching mode of sulfate ($\nu_1$) in anhydrite (CaSO$_4$) (Sarma et al., 1998). This peak clearly demonstrates that sulfate was formed. CaSO$_4$ as a reaction product has also been found in the
reaction of CaCO$_3$ with SO$_2$ and NO$_2$ in a previous study (Ma et al., 2013b). Afterwards, no other Raman peaks than those of CaCO$_3$, Ca(NO$_3$)$_2$, and CaSO$_4$ were detected until 1050 min after the reaction.

Concomitant with the formation of Ca(NO$_3$)$_2$ and CaSO$_4$, the microscopic morphology of the particle changed significantly. The initial CaCO$_3$ particle was a crystal close to a rhombohedron of about 9-10 μm (Fig. 3a). After reacting with NO$_2$/SO$_2$, the surface of the particle became smoother, and then a liquid layer formed surrounding the solid particle core (Fig. 3c). Raman spectra of the particle reveal that the outer liquid layer consisted of Ca(NO$_3$)$_2$ and water. As the reaction proceeded, the solid CaCO$_3$ core diminished gradually and finally CaCO$_3$ completely disappeared and a Ca(NO$_3$)$_2$ spherical droplet was formed (Fig. 3d). The whole particle became larger due to the growth of the outer liquid layer. The diameter of the Ca(NO$_3$)$_2$ droplet reached ~16 μm, and the droplet did not change much in the subsequent period of the reaction. Despite the invariant droplet diameter, a new solid phase of needle-shaped crystals was formed as the reaction proceeded, which distributed unevenly in the droplet. The Raman spectra of the new solid phase and Raman mapping (Fig. S2) reveal that this solid matter was CaSO$_4$. The amount of CaSO$_4$ increased gradually during the reaction, and its Raman peak could be observed more clearly at 1050 min.

3.2 Reaction process

In order to learn about the reaction process and mechanism, the amounts of Ca(NO$_3$)$_2$, CaSO$_4$, and CaCO$_3$, represented by the peak area at 1050, 1013, and 1087 cm$^{-1}$ in Raman spectra, respectively, were investigated as a function of reaction time. As shown in Fig. 4, Ca(NO$_3$)$_2$ was produced before CaSO$_4$. Nitrate was detected immediately after the reaction started, and reached a maximum at ~50 min whereas sulfate did not reach the detection limit until 82 min of the reaction. Sulfate increased slowly in the reaction and we did not observe it leveling off even after 1050 min.

According to the time series of carbonate, nitrate, and sulfate, this reaction consisted of two successive processes. The first process was the formation of Ca(NO$_3$)$_2$, which was accompanied with the decline of CaCO$_3$ (Fig. 4), indicating that Ca(NO$_3$)$_2$ was produced due to the reaction of CaCO$_3$ with NO$_2$. Ca(NO$_3$)$_2$ has been observed in the reaction of CaCO$_3$ with NO$_2$ in previous studies (Li et al., 2010; Tan et al., 2017). The formation of Ca(NO$_3$)$_2$ started with the reaction of NO$_2$ with adsorbed or liquid water, forming HNO$_3$ and HNO$_2$. Then HNO$_3$ reacted with CaCO$_3$ forming Ca(NO$_3$)$_2$ as well as CO$_2$, which was released to the gas phase. HNO$_2$ could evaporate into the gas phase due to the continuous flushing of reactant gases during the experiments and acidity of the droplet (see below). The reaction equations are as follows:

\[
\text{NO}_2(g) \leftrightarrow \text{NO}_2(aq) \quad \text{(R1)}
\]

\[
2\text{NO}_2(aq) + \text{H}_2\text{O}(aq) \rightarrow \text{HNO}_3(aq) + \text{HNO}_2(aq) \quad \text{(R2)}
\]

\[
\text{HNO}_3(aq) \rightarrow \text{H}^+(aq) + \text{NO}_3^-(aq) \quad \text{(R3)}
\]

\[
\text{CaCO}_3(s) + \text{H}^+(aq) \rightarrow \text{Ca}^+(aq) + \text{HCO}_3^-(aq) \quad \text{(R4)}
\]

\[
\text{HCO}_3^-(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{O}(aq) + \text{CO}_2(g) \quad \text{(R5)}
\]

\[
\text{HNO}_2(aq) \leftrightarrow \text{HNO}_2(g) \quad \text{(R6)}
\]

The detailed mechanism of the formation of Ca(NO$_3$)$_2$ in the reaction CaCO$_3$ with NO$_2$ have been studied by Li et al. (2010).
The second process was the formation of CaSO₄ through the oxidation of SO₂ by NO₂. CaSO₄ was mainly produced after CaCO₃ was completely reacted and increased steadily as the reaction proceeded. The amount of Ca(NO₃)₂ as the product of NO₂ uptake was overwhelmingly higher than that of CaSO₄ as the product of the reaction SO₂ with NO₂, which only reached detection limit after the complete conversion of CaCO₃. This indicates that the reaction of SO₂ with NO₂ did not contribute significantly to NO₂ uptake before CaCO₃ completely converted to Ca(NO₃)₂. Afterwards, the reaction of SO₂ with NO₂ promoted the reactive uptake of NO₂ by Ca(NO₃)₂ droplet.

3.3 Reaction mechanism

3.3.1 Mechanism of sulfate formation

Based on the results above, we found that a series of reactions of SO₂ and NO₂ on a CaCO₃ particle led to sulfate formation. Almost the entire sulfate was produced after a CaCO₃ particle was converted to a Ca(NO₃)₂ droplet (Fig. 4), although in some experiments a trace amount of sulfate could be observed when a small amount of CaCO₃ was still left in the Ca(NO₃)₂ droplet. The absence or low amount of sulfate before CaCO₃ was completely reacted might be due to the competition between the reaction of aqueous NO₂ with CaCO₃ and the reaction with SO₂. This result suggests that forming a Ca(NO₃)₂ droplet was key to the formation of sulfate. This finding is further supported by the results of the reaction of SO₂ with NO₂ on a Ca(NO₃)₂ droplet (Fig. 5 and Table 1). Using a Ca(NO₃)₂ droplet as the reactant, the reaction with SO₂/NO₂ at the same condition still produced CaSO₄, confirming CaCO₃ was not necessary for sulfate formation. The reaction with Ca(NO₃)₂ produced similar amount of sulfate to the reaction with CaCO₃ based on Raman spectra and microscopic images (Fig. 5), which indicates that Ca(NO₃)₂ droplet was important for sulfate formation. Therefore, we conclude that SO₂ was mainly oxidized via the multiphase reaction on the Ca(NO₃)₂ droplet while CaCO₃ mainly worked as a precursor of the Ca(NO₃)₂ droplet.

The oxidant of SO₂ can be NO₃⁻ or NO₂ in the Ca(NO₃)₂ droplet here. In a reaction between Ca(NO₃)₂ droplets and SO₂ (150 ppm) under 72% RH, we did not observe any sulfate formation on the basis of the Raman spectra and microscopic image after 5 h of reaction. This indicates that NO₃⁻ was not the oxidant for SO₂ in our study, which was also consistent with a previous study (Martin et al., 1981). Therefore, we conclude that SO₂ was oxidized by NO₂ in the Ca(NO₃)₂ droplet.

According to previous studies, NO₂ can oxidize sulfite and bisulfite ions into sulfate ion in aqueous phase (Ellison and Eckert, 1984; Shen and Rochelle, 1998; Littlejohn et al., 1993). The overall reaction equation was described to be (Clifton et al., 1988):

\[ 2\text{NO}_2(aq) + \text{SO}_3^{2-}(aq) + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{NO}_2^-(aq) + \text{SO}_4^{2-}(aq) \]  

\[ 2\text{NO}_2(aq) + \text{HSO}_3^-(aq) + \text{H}_2\text{O} \rightarrow 3\text{H}^+ + 2\text{NO}_2^-(aq) + \text{SO}_4^{2-}(aq) \]  

Under the experimental conditions of our study, water uptake of Ca(NO₃)₂ led to condensation of liquid water, which provided a site for aqueous oxidation of S(IV) by NO₂. The relative fractions of the three S(IV) species depend on pH and the equilibrium between them is fast (Seinfeld and Pandis, 2006). The pH of the droplet was mainly determined by the gas-aqueous equilibrium of SO₂ in this study and estimated to be ~3. The characteristic
time to reach the equilibrium in the gas-particle interface (~10^{-5} s) was estimated to be much less than the characteristic time for the aqueous phase reaction of SO_2 with NO_2 (10^{-2}-10^{-1} s) (Supplement S2). Therefore, aqueous S(IV) species can be considered to be in equilibrium with SO_2 in the gas phase. The concentrations of HSO_3^-, H_2SO_3, and SO_3^{2-} were estimate to be ~1.1×10^{-3}, 9.2×10^{-5}, and 6.6×10^{-8} mol L^{-1}, respectively, using the equilibrium constants in Seinfeld and Pandis (2006) (H_SO_2=1.23 mol L^{-1} atm^{-1}, K_1=1.3×10^{-2} mol L^{-1}, K_2=6.6×10^{-8} mol L^{-1}) and thus the main S(IV) species was HSO_3^-. Then SO_3^{2-} from S(IV) oxidation can react with Ca^{2+} forming CaSO_4 precipitation as observed in Raman spectra due to the low value of K_{sp} for CaSO_4 (Lide, 2009):

\[ \text{Ca}^{2+}(\text{aq})+\text{SO}_3^{2-}(\text{aq})\rightleftharpoons \text{CaSO}_4(s) \] (R8)

Some previous studies have shown that SO_2 can react with CaCO_3 to produce calcium sulfite (CaSO_3) (Li et al., 2006; Prince et al., 2007b; Ma et al., 2013a), and CaSO_3 can be oxidized to CaSO_4 by NO_2 (Rosenberg and Grotta, 1980; Ma et al., 2013a). In our study, we investigated the reaction between CaCO_3 and SO_2 (150 ppm) at 72% RH. We found that both sulfate and sulfite were lower than the detection limit of our Raman spectrometer (~5×10^{-14} mol for sulfate at a signal to noise ratio of 2 and ~3×10^{-14} mol for sulfite according to the relative Raman scattering cross-section of sulfate and sulfite (Meyer et al., 1980)) even after 300 min of the reaction. This indicates that forming CaSO_3 was not the main pathway in CaSO_4 formation in our study and CaCO_3 did not directly contribute to the formation of CaSO_4.

### 3.3.2 Effects of cations in sulfate formation

Since sulfate was observed to precipitate as CaSO_4, we further analyzed the effect of precipitation reaction and cations on the aqueous oxidation of SO_2 by NO_2. In order to test effects of cations, we replaced Ca^{2+} with Na^{+} or NH_4^+. Based on Raman spectra, we found that in the reaction of a NaNO_3 or a NH_4NO_3 droplet with NO_2/ SO_2, sulfate, either as aqueous ion (at 984 cm^{-1} and 979 cm^{-1} for (NH_4)_2SO_4 and Na_2SO_4, respectively) or as in CaSO_4 crystal, was below the detection limit after 300 min in the same reaction conditions as Ca(NO_3)_2 and CaCO_3 (Fig. 6 and Table 1). Considering that the Raman scattering cross-section of sulfate in (NH_4)_2SO_4 aqueous aerosol particle is even higher than sulfate in CaSO_4 (Wright, 1973; Stafford et al., 1976), it can be concluded that the sulfate production rate was larger in the presence of Ca^{2+} compared to those in the presence of Na^{+} or NH_4^+. The difference can be explained by two possible reasons. The first possible reason may be due to the change of Gibbs energy. The spontaneity of the SO_2 oxidation by NO_2 for Reaction (R8) can be analyzed using the reaction Gibbs energy as follows:

\[ \Delta_r G = \Delta_r G^\theta + RT \ln \frac{a_\text{NO}_2^{a_\text{SO}_2^{2-}}} {a_\text{HSO}_3^-} \] (5)

where \( \Delta_r G \) is the reaction Gibbs energy, \( \Delta_r G^\theta \) is the standard reaction Gibbs energy, R is the gas constant, T is temperature, and \( a \) is the activity of various species.

\( \Delta_r G \) increases with increasing sulfate concentration. According to the different results between the reaction on Ca(NO_3)_2 droplet and the reaction on NaNO_3 and NH_4NO_3 droplet, there might be a backward reaction of SO_2 oxidation which consumed sulfate, although the detailed mechanism of the backward reaction is unknown at the moment. For NaNO_3 and NH_4NO_3 droplet, once sulfate concentration reached certain level, the reaction may stop due to the increase of \( \Delta_r G \). For Ca(NO_3)_2 droplet, the precipitation of CaSO_4 can substantially decrease the activity of SO_4^{2-}, and thus decrease \( \Delta_r G \) and promote the oxidation of SO_2 and sulfate formation. The second
possible reason is that sulfate may crowd the reaction environment and suppress the colliding probability of S(IV) species with NO₂ in aqueous phase and the uptake coefficient of SO₂ or NO₂ on the droplet. Precipitation of sulfate as CaSO₄ can cancel such suppressions and thus promote the reaction. Regardless of the reasons behind, we can conclude that the precipitation of less soluble CaSO₄ promoted sulfate formation.

3.4 Reactive uptake coefficient of SO₂

The reactive uptake coefficients of SO₂ (γ) for sulfate formation under different conditions are shown in Table 2. Each reaction was repeated for three times, during which, three particles with different size were selected. γ was higher at higher relative humidity, suggesting again that liquid water plays an important role in the formation of CaSO₄. At 17% RH, the reaction between CaCO₃ and NO₂ (the first process of the whole reaction) proceeded very slowly, and the amount of liquid water formed due to the water uptake of Ca(NO₃)₂ was very low. As a result, we did not observe the formation of CaSO₄ (the second process of the whole reaction) after 1000 min of the reaction and even at higher SO₂ and NO₂ concentrations (200 ppm SO₂, 200 ppm NO₂). Under higher relative humidity (46% and 72% RH), sulfate was observed soon after the reaction. It is interesting to note that there were no significant difference for γ between 46% and 72% RH. In either case, the reaction between CaCO₃ and NO₂ proceeded quickly and CaCO₃ was completely converted to a Ca(NO₃)₂ droplet within 100 min after the reaction. In the presence of enough liquid water, RH seemed to be no longer a limiting factor. In such conditions, an increase of NO₂ concentration (from 75 ppm to 200 ppm at 72% RH) promoted the reactive uptake of SO₂.

The reactive uptake coefficient of SO₂ for sulfate formation was determined to be on the order of 10⁻⁸ at 46% and 72% RH. This value is higher than the uptake coefficient (10⁻¹⁰) on mineral particles sampled from Cape Verde Islands (the main contents being potassium feldspars and quartz) obtained by Ullerstam et al. (2003) using NO₂/SO₂ mixing gas and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) technique. But the uptake coefficient in this study is lower than the uptake coefficient of SO₂ on Arizona Test Dust (ATD) particles in the presence of NO₂ ((2.10±0.08)×10⁻⁶) determined by Park and Jang (2016). γ here is also much lower than the γ of SO₂ on oxalic acid particles in the presence of NO₂ and NH₃ (10⁻⁶~10⁻⁴) determined at varying RH reported by Wang et al. (2016). The difference in these uptake coefficients is attributed to the different chemical composition of particles, reaction mechanism, reaction conditions, and the ways that the particle surface is determined. It is worth noting that in the studies of Ullerstam et al. (2003) and Park and Jang (2016), particles exist as solid state and sulfate formation is via gas-solid heterogeneous reaction, and in the study of Wang et al. (2016) sulfate formation is stated to be via aqueous reaction. In this study sulfate formation was via gas-liquid-solid multiphase reaction and liquid water played a key role.

The γ of SO₂ was further compared with the reaction rate constants of the aqueous reaction of NO₂ with sulfite and bisulfite in bulk solution in the literature by deriving γ from rate constants using the method in Davidovits et al. (2006). The detailed method can be referred to the supplement S1. Lee and Schwartz (1983) determined the rate constant of the reaction of NO₂ with bisulfite to be >2×10⁶ mol⁻¹ L s⁻¹ at pH 5.8 and 6.4. Clifton et al. (1988) determined the rate constant of the reaction of NO₂ with sulfite/bisulfite to be (1.24-2.95)×10⁷ mol⁻¹ L s⁻¹ at pH 5.6-13 and further reported a rate constant of 1.4×10⁵ mol⁻¹ L s⁻¹ at pH 5 from the study of Lee and Schwartz (1983). The different rate constants were attributed to the different approaches to
determine the reaction rate by Clifton et al. (1988). Clifton et al. (1988) determined the reaction rate from the consumption rate of reactant, NO₂, which corresponds to the first reaction step of NO₂ with S(IV). Yet, Lee and Schwartz (1983) determined the reaction rate from the production rate of products (their conductivity), which is expected to be much slower than NO₂ consumption since formation of products needs more steps. In this study, we determined \( \gamma \) using sulfate production rate, and thus our data are comparable to the study of Lee and Schwartz (1983). Yet, the study of Lee and Schwartz (1983) only covers a pH range of 5-6.4 and has no overlap with the pH (~3) in our study, therefore uptake coefficients from both studies are not directly comparable. Nevertheless, the reaction rate of \( 1.4 \times 10^5 \text{ mol L}^{-1} \text{ s}^{-1} \) at pH 5 corresponds to the uptake coefficient of \( 4.3 \times 10^{-7} \), which is around one order of magnitude higher than the uptake coefficient in our study determined at pH ~3 for the droplet. The difference may be due to the different pH between these two studies, the different mechanisms between the multiphase reaction on particles and bulk aqueous reaction, and the different concentrations of each S(IV) species since the different species may have different reactivity with NO₂. The reaction rate of S(IV) has been found to decrease with decreasing pH and the reactivity of sulfite with NO₂ seems to be higher than bisulfite (Lee and Schwartz, 1983; Clifton et al., 1988; Takeuchi et al., 1977). In addition, the ionic strength in the droplet of this study (15-55 mol Kg⁻¹) was much higher than that in the bulk solution in previous studies (on the order of \( 10^{-6} \text{ - } 10^{-1} \text{ mol Kg}^{-1} \)), which may also influence the reaction rate.

In the ambient atmosphere, the reactive uptake coefficient of SO₂ due to the multiphase oxidation by NO₂ is influenced by various factors such as RH, NO₂ concentration, pH, sulfate concentration, and the presence of other ions in aerosol particles. For example, NO₂ concentrations in the atmosphere are much lower than those used in this study. At lower NO₂ concentrations, the uptake coefficient of SO₂ decreases, because the oxidation rate of SO₂ in aqueous phase decreases with decreasing NO₂ concentration. In addition, aqueous sulfate concentrations in aerosol particles in the atmosphere are often high. According to the effect of cations (Section 3.3.2), while reduced sulfate concentration by CaSO₄ precipitation likely led to the enhanced sulfate production rate in the reaction of SO₂ on Ca(NO₃)₂, higher sulfate concentration could increase the reaction Gibbs energy \( \Delta G \) (as shown in Eq. 5) and reduce the colliding probability of S(IV) species with NO₂ in the aqueous phase as discussed above and thus suppress the reaction of SO₂ and NO₂. This can reduce the uptake coefficient of SO₂. Therefore, the reactive uptake coefficient of SO₂ obtained in this study \( (10^{-8} \text{ at } 46-72\% \text{ RH and } 75 \text{ ppm NO}_2) \) can be regarded as an upper limit of the reactive uptake coefficient of SO₂ due to the multiphase reaction with NO₂ in the ambient atmosphere.

4 Conclusion and implications

We investigated the heterogeneous reaction of SO₂ directly with NO₂ on individual CaCO₃ particles in N₂ using Micro-Raman spectrometry. The reaction first converted the CaCO₃ particle to the Ca(NO₃)₂ droplet via the reaction with NO₂ in the SO₂/NO₂/H₂O/N₂ gas mixture and the deliquescence of Ca(NO₃)₂, and then formed needle-shaped CaSO₄ crystals in the Ca(NO₃)₂ droplet via the multiphase reaction of SO₂ with NO₂. The sulfate formation was observed only during the multiphase oxidation by NO₂, that is, after the complete conversion of CaCO₃ to Ca(NO₃)₂ droplet. The precipitation of CaSO₄ from solution promoted sulfate formation. The reactive uptake coefficient of SO₂ for sulfate formation in the multiphase reaction with NO₂ is on the order of \( 10^{-8} \) under
the experimental conditions of this study (RH: 46-72%, NO2: 75 ppm). The reactive uptake coefficient of SO2 was found to be enhanced at higher RH.

In order to assess the importance of the multiphase reaction of SO2 directly oxidized by NO2 to sulfate in the atmosphere, we compare the lifetime of SO2 due to the multiphase oxidation of SO2 by NO2 with the lifetime due to the gas phase oxidation of SO2 by OH. Using a daytime OH concentration of 1×10^6 molecule cm^-3 (Lelieveld et al., 2016; Prinn et al., 2005), the lifetime of SO2 in the atmosphere due to gas phase OH oxidation is around 12 days. The lifetime of SO2 due to the multiphase oxidation by NO2 is around 7000 days using the uptake coefficient of SO2 from this study (3.22×10^-8) 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). Using an annual average particle surface area concentration of PM10 in Beijing (1.4×10^-5 cm^2 cm^-3) (Wehner et al., 2008) results in a SO2 lifetime of 3300 days due to the multiphase oxidation by NO2. In the atmosphere, the lifetime of SO2 due to the multiphase oxidation by NO2 should be even longer than these values because the uptake coefficient of SO2 used here (3.22×10^-8) is an upper limit of the uptake coefficient of SO2 in the ambient atmosphere as discussed above. This comparison indicates that the direct multiphase oxidation of SO2 by NO2 is unlikely to be an important sink of SO2 and source of sulfate compared with the oxidation of SO2 by OH.

Despite the less important role in sulfate formation, the multiphase oxidation of SO2 by NO2 on CaCO3 particles helps interpreting the findings from field studies. For example, internally mixed CaCO3 with Ca(NO3)2 and CaSO4 particles with varying reacted fractions of CaCO3 were observed in the field (Hwang and Ro, 2006; Li and Shao, 2009), but how the internally mixed particles are formed is not clear. In this study we showed that CaSO4 can be formed inside the Ca(NO3)2 droplet after the deliquescence of initially produced Ca(NO3)2 through the reaction of SO2 with NO2. In this way, internally mixed CaCO3 with Ca(NO3)2 and CaSO4 particles can be formed. Moreover, Hwang and Ro (2006) found that CaSO4-containing particles were observed to be almost always internally mixed with nitrate. The multiphase reaction process of SO2 with NO2 on CaCO3 particles found in this study can also explain this finding.

Acknowledgements

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References


Table 1 Summary of the results obtained in different reaction systems

<table>
<thead>
<tr>
<th>Particle</th>
<th>Gases</th>
<th>RH (%)</th>
<th>Whether sulfate was detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$</td>
<td>SO$_2$(75 ppm)+NO$_2$(75 ppm)</td>
<td>72</td>
<td>Yes</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$ droplet</td>
<td>SO$_2$(75 ppm)+NO$_2$(75 ppm)</td>
<td>72</td>
<td>Yes</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>SO$_2$ (150 ppm)</td>
<td>72</td>
<td>No</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$ droplet</td>
<td>SO$_2$ (150 ppm)</td>
<td>72</td>
<td>No</td>
</tr>
<tr>
<td>NaNO$_3$ droplet</td>
<td>SO$_2$(75 ppm)+NO$_2$(75 ppm)</td>
<td>72</td>
<td>No</td>
</tr>
<tr>
<td>NH$_4$NO$_3$ droplet</td>
<td>SO$_2$(75 ppm)+NO$_2$(75 ppm)</td>
<td>72</td>
<td>No</td>
</tr>
</tbody>
</table>
Table 2. Reactive uptake coefficient of SO$_2$ for sulfate formation ($\gamma$) during the reaction of SO$_2$ with NO$_2$ on individual CaCO$_3$ particles under different conditions at 298 K.

<table>
<thead>
<tr>
<th>[SO$_2$] (ppm)</th>
<th>[NO$_2$] (ppm)</th>
<th>RH (%)</th>
<th>$\gamma$ ($\times 10^{-8}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>75</td>
<td>72</td>
<td>3.22±0.90$^b$</td>
</tr>
<tr>
<td>75</td>
<td>200</td>
<td>72</td>
<td>16.0±3.12</td>
</tr>
<tr>
<td>75</td>
<td>75</td>
<td>46</td>
<td>3.22±0.90</td>
</tr>
<tr>
<td>75</td>
<td>75</td>
<td>17</td>
<td>0$^a$</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>17</td>
<td>0$^a$</td>
</tr>
</tbody>
</table>

$^a$: Sulfate was below the detection limit.

$^b$: The uncertainties are the standard deviations of $\gamma$ from duplicate experiments.

Fig. 1. Schematic diagram of the experimental setup. MFC: mass flow controller.
Fig. 2. Raman spectra of an individual CaCO$_3$ particle during the reaction with NO$_2$ (75 ppm) and SO$_2$ (75 ppm) at 72% RH at the reaction time of 0, 8, 30, 95, and 1050 min.
Fig. 3. Microscopic images of an individual CaCO$_3$ particle (same as in Fig. 2) reacting with NO$_2$ (75 ppm) and SO$_2$ (75 ppm) at 72% RH. a-f corresponds to the reaction time of 0, 6, 29, 37, 94, and 1050 min, respectively.
Fig. 4. Raman peak intensity of carbonate, nitrate (left axis), and sulfate (right axis) as a function of time during the reaction of an individual CaCO$_3$ particle with NO$_2$ (75ppm) and SO$_2$ (75ppm) at 72% RH (same as in Fig. 2 and 3). Note that the scales of the left axis and right axis are different. The intensity of NO$_3^-$, SO$_4^{2-}$, and CO$_3^{2-}$ show the peak area at 1050, 1013, and 1087 cm$^{-1}$, respectively, in Raman spectra obtained by Raman mapping. By 118 min, CaCO$_3$ was completely converted to Ca(NO$_3$)$_2$. Carbonate had decreased to zero and nitrate had reached a plateau. Therefore no further data of carbonate and nitrate were shown.
Fig. 5. Raman spectra (a) and microscopic image (b) of a Ca(NO₃)₂ droplet reacting with NO₂ (75 ppm) and SO₂ (75 ppm) at 72% RH at a reaction time of 300 min. The peak at 1014 cm⁻¹ in Raman spectra and crystals from the microscopic image indicate CaSO₄ was formed in this reaction.
Fig. 6. Raman spectra of a NH$_4$NO$_3$ (a) and NaNO$_3$ (b) droplet reacting with NO$_2$ (75 ppm) and SO$_2$ (75 ppm) at 72% RH at the reaction time of 300 min.