Heterogeneous reactions of NO$_2$ with CaCO$_3$-$($NH$_4$)$_2$SO$_4$ mixtures at different relative humidities

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Abstract

In this work, the heterogeneous reactions of NO\textsubscript{2} with CaCO\textsubscript{3}-(NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} mixtures with a series of weight percentage (wt\%) of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} were investigated using a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) at different relative humidity (RH) values. For comparison, the heterogeneous reactions of NO\textsubscript{2} with pure CaCO\textsubscript{3} particles and pure (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} particles, as well as the reaction of CaCO\textsubscript{3} with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} particles were also studied. The results indicated that NO\textsubscript{2} did not show any significant uptake on (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} particles, and it reacted with CaCO\textsubscript{3} particles to form calcium nitrate under both dry and wet conditions. The heterogeneous reactions of NO\textsubscript{2} with CaCO\textsubscript{3}-(NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} mixtures were markedly dependent on RH. Calcium nitrate was formed from the heterogeneous reactions at all the RHs investigated, whereas CaSO\textsubscript{4}·0.5H\textsubscript{2}O (bassanite), CaSO\textsubscript{4}·2H\textsubscript{2}O (gypsum) and (NH\textsubscript{4})\textsubscript{2}Ca(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O (koktaite) were produced depending on RH. Under dry condition, the heterogeneous uptake of NO\textsubscript{2} on the mixtures was similar to that on CaCO\textsubscript{3} particles with neglectable effects from (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, the lasting time of initial stages and the NO\textsubscript{3}⁻ mass concentrations had negative linear relation with the mass fraction of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} in the mixtures. Under wet conditions, the chemical interaction of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} with Ca(NO\textsubscript{3})\textsubscript{2} enhance the nitrate formation, especially at medium RHs, while the coagulation of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} with CaCO\textsubscript{3} exhibits an increasing inhibiting effects with increasing RH at the same time. In addition, the heterogeneous uptake of NO\textsubscript{2} on the mixtures of CaCO\textsubscript{3} and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} was found to favor the formation of bassanite and gypsum due to the decomposition of CaCO\textsubscript{3} and the coagulation of Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2⁻}. A possible reaction mechanism was proposed and the atmospheric implications were discussed.
1. Introduction

Haze with high level of fine particulate matter with diameters less than 2.5 µm (PM$_{2.5}$) occurs frequently in China in recent years (Fang et al., 2009; Kulmala, 2015). Emissions of gaseous pollutants, e.g., SO$_2$, NO$_x$, NH$_3$, and volatile organic compounds (VOCs), result in a series of atmospheric chemical reactions, which are responsible for the formation of secondary particles and the occurrence of haze (Zhang et al., 2015; Wang et al., 2013; Guo et al., 2014). Chemical analyses show that sulfate, nitrate, and ammonium are the major aerosol constituents of PM$_{2.5}$ (Yang et al., 2011; Huang et al., 2014). Pathak et al. (2009) discovered that nitrate concentration showed a correlation with sulfate concentration as well as the RH value in ammonium-poor areas. Kong et al. (2014a) found strong negative correlation between the mass fraction of nitrate and that of sulfate in acidic atmospheric particles during air pollution episodes. Although atmospheric particulate sulfate, nitrate, and ammonium were found to be correlated by numerous field measurements in different locations (Sullivan et al., 2007; Quan et al., 2008; Duan et al., 2003; Possanzini et al., 1999; Querol et al., 1998), there is still a lack of knowledge to explain these phenomena.

Mineral dust is a major fraction of airborne particulate matter on a global scale (Tegen et al., 1996) with an estimated annual emission of 1000-3000 Tg of solids into the troposphere (Li et al., 1996). Mineral aerosols provide significant reactants and reactive sites for atmospheric heterogeneous reactions (Usher et al., 2003). Modeling studies indicated that mineral aerosols were highly associated with nitrate formation in the atmosphere (Dentener et al., 1996). Calcium carbonate represents an important and reactive mineral dust component, approximately accounting for 20-30% of the total dust loading (Usher et al., 2003; Li et al., 2006; Al-Hosney and Grassian, 2005; Prince et al., 2007). Calcium carbonate particle is converted to calcium nitrate after reaction with nitrogen oxides and HNO$_3$ in the atmosphere (Li et al., 2009; Laskin et al., 2005). Field measurements reveal that mineral dust particles are often mixed with ammonium sulfate aerosols through coagulation during long-range transport (Levin et al., 1996; Zhang et al., 2000). Korhonen et al. (2003) suggested that ammonium sulfate coating of mineral dust by heterogeneous nucleation of H$_2$SO$_4$, NH$_3$, and H$_2$O could occur at atmospheric sulphuric acid concentration. Additionally, Mori et al. (1998) have
found the coagulation between CaCO$_3$ and (NH$_4$)$_2$SO$_4$ could form koktaite and gypsum as a result of the interaction of ions under humid condition. Ma et al. (2013) also discovered that mixed CaCO$_3$-(NH$_4$)$_2$SO$_4$ particles had synergistic effects on the formation of gypsum in the humidifying-dehumidifying processes.

A few studies have shown that coexisting components play a role in the heterogeneous uptake of trace gases on atmospheric particles. Kong et al. (2014b) found that coexisting nitrate could significantly accelerate the formation rate of sulfate on hematite surface, resulting in surface-adsorbed HNO$_3$, gas-phase N$_2$O and HONO productions. Zhao et al. (2013) found that coexisting surface nitrate had different effects on the uptake of H$_2$O$_2$ on mineral particle surfaces depending on RH. The catalytic and basic additives, e.g., MgO and CaCO$_3$, could increase the basic property of the surface of NaCl and increase the formation of sulfate by facilitating the absorbance of SO$_2$ on the alkaline surface (Li et al., 2007). To the best of our knowledge, the heterogeneous reaction of atmospheric trace gases on mixed CaCO$_3$-(NH$_4$)$_2$SO$_4$ particles has not been reported.

Furthermore, an increase in tropospheric NO$_2$ concentration has been observed in recent years across many developing regions due to fossil fuel combustion and biomass burning (Zhang et al., 2007; Sheel et al., 2010; Ghude et al., 2009; Shi et al., 2008; Richter et al., 2005; Irie et al., 2005). Atmospheric NO$_2$ concentration ranges from 70 part per billion (ppb) during photochemical smog events to hundreds ppb in polluted urban environment (Huang et al., 2015; Zamaraev et al., 1994). NO$_2$ is one such critical anthropogenic gaseous pollutant, which reduces air quality and affects global tropospheric chemistry. NO$_2$ plays a crucial role in the photochemical induced catalytic production of ozone, leading to photochemical smog and increasing tropospheric ozone concentration (Volz and Kley, 1988). Moreover, the heterogeneous reactions of NO$_2$ can also lead to the deposition of nitric acid, as well as the formation of gas phase HONO (Jaegle et al., 1998; Brimblecombe and Stedman, 1982; Goodman et al., 1999). Furthermore, the heterogeneous uptake of NO$_2$ on mineral aerosols was responsible for the nitrate accumulation in dust events (Usher et al., 2003). A number of laboratory studies investigated the heterogeneous reaction of NO$_2$ with mineral dust (Underwood et al. 1999b; Börensen et al., 2000; Finlayson-Pitts et al., 2003; Liu et al., 2015;
Guan et al., 2014). Miller and Grassian (1998) discovered that NO₂ reacted with Al₂O₃ and TiO₂ particles to form surface nitrite and nitrate. Underwood et al. (1999a) measured the uptake coefficients of NO₂ on Al₂O₃, TiO₂, and Fe₂O₃ particles using a Knudsen cell. Li et al. (2010) determined the Brunauer-Emmett-Teller (BET) area-corrected initial uptake coefficients to be 10^{-9} and 10^{-8} for the heterogeneous uptake of NO₂ on CaCO₃ particles under dry and wet conditions, respectively. However, there are big gaps between the results of modeling studies and field measurements about the quantities and accumulation of nitrate, especially in haze periods (Zheng et al., 2015).

In the present study, the heterogeneous reactions of NO₂ with the mixtures of CaCO₃ and (NH₄)₂SO₄, pure CaCO₃ particles, and pure (NH₄)₂SO₄ particles at different RHs were investigated using a DRIFTS reactor. The surface adsorbed products were monitored and the uptake coefficients of NO₂ were determined. The aim of this work is to explore the kinetics and mechanism of the heterogeneous reactions of NO₂ with CaCO₃-(NH₄)₂SO₄ mixtures and its relevance to RH. The results are helpful for further exploring the correlations among particulate nitrate, sulfate, and ammonium concentration in the atmosphere and partly contribute to understanding of multicomponent reaction systems in practical environment conditions.

2. Experimental

CaCO₃ (99.5 %) and (NH₄)₂SO₄ (99.9%) were purchased from Alfa Aesar. CaCO₃ and (NH₄)₂SO₄ were mechanically mixed and ground together in order to obtain uniform mixtures with 10-93wt% (mass percent) of (NH₄)₂SO₄ in the mixtures, which were denoted as FAS-10, FAS-20, FAS-40, FAS-57, FAS-75, FAS-87, and FAS-93, respectively. The BET surface areas of pure CaCO₃ and (NH₄)₂SO₄ particles were determined to be 8.15 and 0.19 m² g⁻¹, respectively, (Autosorb-1-MP automatic equipment (Quanta Chrome Instrument Co.)). The BET area of the mixtures were determined to be 8.06, 6.62, 4.54, 3.21, 2.34, 1.67, and 0.89 m² g⁻¹ corresponding to the mixtures mentioned above. NO₂ (0.1%, Beijing Huayuan Gas Chemical Industry Co., Ltd.) and N₂ (>99.999%, Beijing Tailong Electronics Co., Ltd.) were used in this study.
In the gas supply system, N\textsubscript{2} was split into two streams; one was dehumidified by silica gel and molecular sieve to insure RH less than 1\% which was called dry condition, the other one was humidified by bubbling through ultrapure water. The flux of dry N\textsubscript{2}, humid N\textsubscript{2}, and NO\textsubscript{2} were adjusted to reach desired RH (<1\%, 40\%, 60\%, and 85\% RH) conditions with the total flow of 400 sccm by using mass flow controllers (Beijing Sevenstar electronics Co., LTD). Concentration of NO\textsubscript{2} entering reactor was diluted to $2.6 \times 10^{15}$ molecules cm$^{-3}$ by mixing with N\textsubscript{2}. RH and temperature of the inflow of sample cell were measured using a commercial humidity and temperature sensor (HMT330; Vaisala) with a measurement accuracy of ±1\% RH and ±0.2°C, respectively.

In situ DRIFTS experiment was used to monitor reactions in real time without interrupting the reaction processes and provide mechanistic details and kinetic data (Vogt and Finlaysonpitts, 1994). Infrared spectra of sample surfaces were recorded with a Nicolet FTIR Spectrometer 6700, which was equipped with a liquid-nitrogen-cooled narrow band mercury-cadmium-telluride (MCT) detector and DRIFTS optics (Model CHC-CHA-3, Harrick Scientific Corp.). The DRIFTS equipment has been described elsewhere (Tong et al., 2010). The spectra were measured at a resolution of 4 cm$^{-1}$ in the spectral range from 4000 to 650 cm$^{-1}$. Each spectrum was generally averaged from 100 scans with a time resolution of 40 s. In situ DRIFTS experiments were carried out on CaCO\textsubscript{3}-(NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} mixtures, CaCO\textsubscript{3} particles, and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} particles, respectively. About 30 mg samples were placed into the stainless steel sample holder (10 mm diameter, 0.5 mm depth). The investigated samples were exposed to pure nitrogen with desired RH for 20 minutes to establish adsorption equilibrium. Then infrared spectra of the unreacted powder samples were collected as background so that reaction products were observed as positive adsorption bands while losses of surface species as negative adsorption bands. Subsequently, NO\textsubscript{2} was introduced into the reaction chamber at a stable RH for 120 min. All the spectra were automatically collected through a Series program in OMNIC software.

The products formed on the samples after reaction with NO\textsubscript{2} were analyzed by ion chromatography. The filtered solution was analyzed by using a Dionex ICS 900 system, equipped with a Dionex AS 14A analytical column and a conductivity detector (DS5). The
reacted samples were sonicated for 20 min in 8 ml ultrapure water.

3. Results and discussion

3.1 Surface products characterization

Figure 1 represents the IR spectra of surface products when the samples were exposed to NO₂ for 120 min at different RHs. Under dry condition (Fig. 1a), absorption bands centered at 746, 816, 1040, 1300, and 1330 cm⁻¹ which were assigned to surface nitrate could be observed on CaCO₃ particle surfaces (FAS-0) and the mixtures (Goodman et al., 2001; Goodman et al., 2000; Al-Hosney and Grassian, 2005). Moreover, peaks at 1630 and 3540 cm⁻¹ were assigned to crystal hydrate water in calcium nitrate (Li et al., 2010). It suggested that calcium nitrate was formed on CaCO₃ particle surfaces and the mixtures of CaCO₃ and (NH₄)₂SO₄. The detailed vibrational assignments were listed in Table 1. Two peaks observed at 1689 and 838 cm⁻¹ could be attributed to the ν(C=O) and δₒₒₜ(CO₃) of adsorbed carbonic acid, respectively, indicating that carbonic acid acted as an intermediate production under dry condition (Al-Hosney and Grassian, 2004; Al-Abadleh et al., 2004). Besides, adsorbed nitric acid was also formed with peaks centered at 1710 and 1670 cm⁻¹, which were assigned to the asymmetric stretching of adsorbed nitric acid (Goodman et al., 1999). At the same time, negative bands ranging from 2800 to 3400 cm⁻¹ could be ascribed to the loss of surface adsorbed water and negative peaks at 3640 and 3690 cm⁻¹ were corresponding to the two types of hydroxyl ions on CaCO₃ particle surfaces (Kuriyavar et al., 2000). No obvious negative peaks could be observed when the samples exposed to dry pure nitrogen for 120 min which indicated that surface adsorbed water and hydroxyl ions participated in the reaction.

Compared with the spectrum of FAS-0, several additional weak absorptions appeared at 1008, 1096, 1155 cm⁻¹ on the CaCO₃-(NH₄)₂SO₄ mixtures, which could be attributed to the vibration modes of SO₄ tetrahedra in CaSO₄·0.5H₂O (bassanite) (Prasad, 2005; Liu et al., 2009). The vibration modes of water group in bassanite were too weak to be observed. In addition, the peak at 1215 cm⁻¹ slightly grew in intensity during the whole heterogeneous reaction period of NO₂ with the mixtures, whereas it grew fast at the early stage of the
reaction of NO\textsubscript{2} with CaCO\textsubscript{3} particles, and then diminished after reaching a maximum value at about 30 min (see Fig. S1). This band described before was ascribed to nitrite species, which would convert to nitrate as the reaction proceeded (Miller and Grassian, 1998; G. M. Underwood, 1999b; Wu et al., 2013). To probe this product, samples after reaction with NO\textsubscript{2} for different times were detected by IC. The results showed that nitrite was increased during the first 30 min in the reaction of NO\textsubscript{2} with CaCO\textsubscript{3} particles, whereas it was too little to be detected after the reaction lasted about 60 min.

At 40\% RH (Fig. 1b), the absorption bands of nitrate shifted from 1040 cm\textsuperscript{-1} to 1043 cm\textsuperscript{-1}, 746 cm\textsuperscript{-1} to 749 cm\textsuperscript{-1}, and 816 cm\textsuperscript{-1} to 828 cm\textsuperscript{-1}, respectively, compared to those under dry condition. Meanwhile, the shoulder peak at 1300 cm\textsuperscript{-1} belong to asymmetric stretching of nitrate became ambiguous. The frequency shifts of nitrate adsorption bands were caused by the phase transition of calcium nitrate. It was reported that calcium nitrate was in amorphous hydrates state at RH below 7\% (Liu et al., 2008), and it deliquesced to form a saturated solution droplet at 18\% RH (Tang and Fung, 1997). For the absorption bands of nitrate on the mixtures of CaCO\textsubscript{3} and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, there was a new shoulder peak at 1365 cm\textsuperscript{-1} which were attributed to the ν\textsubscript{3}(NO\textsubscript{3}) in NH\textsubscript{4}NO\textsubscript{3} (Schlenker et al., 2004). Moreover, the formation of CaSO\textsubscript{4}·0.5H\textsubscript{2}O was enhanced at 40\% RH compared to that under dry condition, as features became apparent at 1155, 1096, and 1008 cm\textsuperscript{-1}, concomitant with the appearance of the peaks at 1620, 3555, and 3605 cm\textsuperscript{-1} due to the vibration modes of water group in bassanite (Prasad et al., 2005). Additionally, signatures at 1670 cm\textsuperscript{-1}, 1570 cm\textsuperscript{-1} on the samples suggested the formation of nitric acid and HCO\textsubscript{3}\textsuperscript{-} during the heterogeneous reaction, respectively. And the signature at 1189 cm\textsuperscript{-1} (Schlenker et al., 2004) on the mixtures suggested that HSO\textsubscript{4}\textsuperscript{-} was produced.

When RH reached 60\% (Fig. 1c), water film was formed on particle surfaces with a band centered at 1650 cm\textsuperscript{-1} and a broad band composed of three peaks at 3260, 3400, and 3570 cm\textsuperscript{-1}, which could be assigned to the vibration modes of surface condensed water (Al-Abadleh et al., 2000). Meanwhile, the asymmetric stretching of surface nitrate appeared as a sharp peak at 1338 cm\textsuperscript{-1}. This was likely due to calcium nitrate incorporated into surface adsorbed water film and formed free aquated ions, based on the truth that only one sharp asymmetric
stretching peak existed for free aquated ions NO$_3^-$ (Gatehouse et al., 1957). The absorptions bands due to NH$_4$NO$_3$ could also be observed at 1365 cm$^{-1}$ for the mixtures of CaCO$_3$ and (NH$_4$)$_2$SO$_4$. Additionally, new peaks could be observed at 1168, 1145, and 1117 cm$^{-1}$, which were attributed to the $v_3$(SO$_4^-$) mode of gypsum. Although the IR absorption bands of bassanite and gypsum had some overlaps in the region between 1000 and 1250 cm$^{-1}$, there were some features that could be used to differentiate CaSO$_4$·0.5H$_2$O from CaSO$_4$·2H$_2$O. Gypsum showed two IR-active modes in the bending modes of crystal hydrate water at 1620 and 1685 cm$^{-1}$, while bassanite had only one band at 1620 cm$^{-1}$. And the two stretching modes of crystal hydrate water appeared at 3545, and 3400 cm$^{-1}$ for gypsum, at 3555 and 3610 cm$^{-1}$ for bassanite (Prasad, 2005). Furthermore, it should be noticed that the peak at 3400 cm$^{-1}$ from CaSO$_4$·2H$_2$O on the samples of FAS-40, FAS-57, FAS-75, and FAS-87 were much stronger than the peak at 3400 cm$^{-1}$ from condensed water on CaCO$_3$ particles. Therefore it can be inferred that Ca(NO$_3$)$_2$, NH$_4$NO$_3$, CaSO$_4$·nH$_2$O (gypsum and bassanite) were produced at 60% RH from the heterogeneous reaction of NO$_2$ with the CaCO$_3$·(NH$_4$)$_2$SO$_4$ mixtures.

The spectrum of FAS-0 in Fig. 1d was similar to that in Fig. 1c, while there were considerable changes for spectra of the mixtures as RH increased to 85%. Peaks observed at 981, 998, 1131, 1177 cm$^{-1}$ on the mixtures due to the stretching vibration modes of SO$_4^{2-}$ as well as peaks at 2860, 3064, 3192 cm$^{-1}$ assigned to the stretching vibration modes of NH$_4^+$ indicated the formation of (NH$_4$)$_2$Ca(SO$_4$)$_2$·H$_2$O (koktaite) (Jentzsch et al., 2012). The absorption band of nitrate overlapped with that of koktaite at 749 cm$^{-1}$. It can be inferred that koktaite, an intermediate production of gypsum, was formed rapidly as a result of the interaction of ions in the liquid film after the deliquesce of (NH$_4$)$_2$SO$_4$ and surface salts (Cziczo et al., 1997; Lightstone et al., 2000). Additionally, the IR absorption peaks at 1570 cm$^{-1}$ in Figure 1d are much stronger than those at 40% and 60% RH. The positive intensity is likely due to the increasing information of HCO$_3^-$, which is from the decomposition of the bulk CaCO$_3$ under wet conditions. It can be interpreted that the reaction of NO$_2$ can occur not only on the surfaces of CaCO$_3$ and the mixtures but also into the bulk of the samples under wet conditions. Also the acidity of surface condensed water is enhanced as a result of the
formation of HNO₃ and the dissolution of (NH₄)₂SO₄, which facilitates the decomposition of bulk CaCO₃.

In conclusion, NO₂ did not show any significant uptake on pure (NH₄)₂SO₄ particles (FAS-100) at all the RHs investigated. And the products formed from the heterogeneous reactions of NO₂ with CaCO₃-(NH₄)₂SO₄ mixtures were strongly dependent on RH. Ca(NO₃)₂ was produced under both dry and wet conditions, bassanite, gypsum and koktaite were formed depending on RH.

In another set of experiments, the mixture of FAS-57 was exposed to nitrogen without the introduction of NO₂ in order to investigate the solid-state reaction of CaCO₃ with (NH₄)₂SO₄. As shown in Fig. 2, no new absorption bands occurred after exposing to dry nitrogen for 120 min. The weak peak at 1189 cm⁻¹ due to HSO₄⁻ appeared as a main absorption peak and no obvious absorption band due to CaSO₄·nH₂O could be observed at 40% RH. The results suggested that little reaction occurred between CaCO₃ and (NH₄)₂SO₄ particles under dry condition and 40% RH. Therefore the chemical interaction of Ca(NO₃)₂ with (NH₄)₂SO₄ was responsible for the formation of bassanite in these conditions. This is likely due to the fact that Ca(NO₃)₂ is more hygroscopic and soluble than CaCO₃ particles. Furthermore, absorption bands attributed to bassanite, gypsum, koktaite, and surface water film could be observed at 60% and 85% RH, indicating that a chemical reaction in the coagulation of CaCO₃ and (NH₄)₂SO₄ particles actually occurred at 60% and 85% RH without the introduction of NO₂. This result was in good agreement with the results reported by Mori et al. (1998) that gypsum was formed from the chemical reaction between (NH₄)₂SO₄ and CaCO₃ with koktaite acting as an intermediate product at 70% RH. In addition, the integrated absorbance of bands between 1100 and 1250 cm⁻¹ for the sample of FAS-57 at 60% and 85% RH in Fig. 2 were about fifty percent and seventy percent of those for FAS-57 at corresponding RH in Fig. 1. Thus CaSO₄·nH₂O and koktaite products could be formed both from the chemical interaction of (NH₄)₂SO₄ with Ca(NO₃)₂ and the reaction of (NH₄)₂SO₄ with CaCO₃ at 60% and 85% RH.

3.2 Uptake coefficients and kinetics
The formation rates of nitrate on CaCO₃ particle surfaces and the mixtures were studied. The nitrate formed during the reaction was presented by the integrated absorbance ($I_A$) of the IR peak area between 1390 and 1250 cm⁻¹. The peak at 1043 cm⁻¹ was not used to avoid the interruption of the absorptions of sulfates. The integrated nitrate absorbance over the $v_1$ region (1013-1073 cm⁻¹) and the $v_3$ region (1250-1390 cm⁻¹) could well overlap after the former multiplied by a constant on CaCO₃ particle surfaces (Figure S2). Figure 3 represents the integrated absorbance of nitrate as a function of time at different RHs. The formation of nitrate on sample surfaces could be divided into three stages under dry conditions. The integrated absorbance of nitrate increased linearly with time in initial stage and it slowed down at stable stage after a transition period. Furthermore, the lasting time of initial stages for the mixtures decreased nearly linearly with increasing mass fraction of (NH₄)₂SO₄ in the mixtures, e.g., it lasted about 80 min for FAS-0 (pure CaCO₃ particles), 30 min for FAS-57, 20 min for FAS-75 and 5 min for FAS-93. In another word, the reactive ability of the mixtures in initial stage had a positive linear relation with the CaCO₃ content in the mixtures. The possible reasons were that for the reaction of NO₂ with CaCO₃-(NH₄)₂SO₄ mixtures, nitrate was formed by the uptake of NO₂ on CaCO₃ particle surfaces without the participation of (NH₄)₂SO₄ and the reactions limited on the surfaces under dry condition. Moreover, the lasting time of initial stages were extended with increasing RH, e.g., it extended to 80 min for the mixture of FAS-75, to 50 min for the mixture of FAS-93, and even may longer than 120 min for the mixtures with mass fraction of (NH₄)₂SO₄ smaller than 57% at 40% RH. The boundaries between initial stages and transition stages became ambiguous at 60% RH and finally disappeared at 85% RH for all the CaCO₃-(NH₄)₂SO₄ mixtures. This was likely due to the fact that the reaction of NO₂ could react into the bulk of the particles under wet conditions.

The integrated absorbance ($I_A$) for nitrate ions on the samples had a linear relationship with the amount of nitrate determined by ion chromatography [$\{\text{NO}_3^-\}$]:

$$\{\text{NO}_3^-\} = (\text{integrated absorbance } I_A) \times f$$  \hspace{1cm} (1)

Here $f$ is conversion factor. It is calculated to be $(2.14 \pm 0.17) \times 10^{17}$ ions/int.abs at 85% RH
and \((3.32 \pm 0.13) \times 10^{17}\) ions/int.abs at 60% RH, 40% RH and dry condition (see Fig. S3). The conversion factor \(f\) may change with the chemical environment of surface nitrate which is related to surface condensed water and ion interaction (Li et al., 2010). Then nitrate formation rates \(d\{\text{NO}_3^-\}/dt\) can be calculated from \(f\) and the slope of integrated absorbance as a function of time.

As shown in Fig. 4, the initial nitrate formation rates for the samples showed a maximum value under dry condition, whereas the stable formation rates were much slower in this condition. The initial nitrate formation rates increased slightly as RH increased from 40% RH to 60% and 85% RH for the uptake of NO\(_2\) on CaCO\(_3\) particle surfaces (FAS-0). For the mixtures with mass fraction of \((\text{NH}_4)_2\text{SO}_4\) larger than 57%, it showed an opposite variation that initial nitrate formation rates at 40% RH were higher than that at 60% RH, followed by that at 85% RH. While for the mixtures with mass fraction of \((\text{NH}_4)_2\text{SO}_4\) smaller than 43%, the nitrate formation rates increased initially as RH elevated from 40% RH to 60% RH then it decreased obviously as RH increased to 85% RH. The differences in the tendency of nitrate formation rates with RH for the mixtures could be explained by the combined opposite effects from the interaction of \((\text{NH}_4)_2\text{SO}_4\) with \(\text{Ca(NO}_3)_2\) or CaCO\(_3\) at 60% RH.

Besides, nitrate formation rates decreased more evidently with increasing \((\text{NH}_4)_2\text{SO}_4\) content at 85% RH and dry condition than at 40% and 60% RH, e.g., the initial nitrate formation rates for the mixture of FAS-93 under dry condition, 40%, 60%, and 85% RH were 47%, 70%, 62%, and 34% of that for FAS-0 at corresponding RH, respectively. Furthermore as RH increased from dry condition to 40% and 60% RH, the initial nitrate formation rates decreased less for the reaction of NO\(_2\) with the mixtures than with CaCO\(_3\) particles, while it was opposite as RH increased to 85% RH, e.g., the initial nitrate formation rates for FAS-0 at 40%, 60%, and 85% RH were 64%, 67%, and 72% of that under dry condition, respectively, for the mixture of FAS-93, the initial nitrate formation rates at 40%, 60%, and 85% RH were 95%, 87%, and 60% of that under dry condition. In conclusion, the initial nitrate formation rates were accelerated to an extent at 40% and 60% RH, whereas it was inhibited slightly at 85% RH.
The reactive uptake coefficient ($\gamma$) is defined as the rate of the reactive collisions with the surface divided by the total number of surface collisions per unit time ($Z$).

$$\gamma = \frac{dN(\text{NO}_2)/dt}{Z}$$

(2)

$$Z = \frac{1}{4} A_{\text{surface}} [\text{NO}_2] \sqrt{\frac{8RT}{\pi M_{\text{NO}_2}}}$$

(3)

Where $N(\text{NO}_2)$ is the number of reactive NO$_2$ collisions with the surface, $A_{\text{surface}}$ is the effective surface area of samples and [NO$_2$] is the gas-phase concentration of NO$_2$. R represents the gas constant, T represents the temperature and $M_{\text{NO}_2}$ is the molecular weight of NO$_2$. The rate of reactive NO$_2$ collision with the surface can be quantified in terms of the nitrate formation rate $d\{\text{NO}_3\}^-/dt$, then the reactive uptake coefficients can be calculated by:

$$\gamma = \frac{d\{\text{NO}_3\}^-/dt}{Z}$$

(4)

The uptake coefficients of NO$_2$ on CaCO$_3$ particles and CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures were calculated using both BET and geometric surface area, which could be considered as two extreme cases (Ullerstam et al., 2002). The results are listed in Table 2. The initial uptake coefficients corresponding to BET surface area for NO$_2$ on CaCO$_3$ particle surfaces are $(3.34\pm0.14)\times10^{-9}$, $(2.04\pm0.07)\times10^{-9}$, $(2.23\pm0.22)\times10^{-9}$, and $(2.28\pm0.17)\times10^{-9}$ for dry condition, 40%, 60%, and 85% RH, respectively, well consistent with the previous measurement results (Li et al., 2010; Börensen et al., 2000). The $\gamma_{\text{BET}}$ is approximately a factor of $10^4$ smaller than the $\gamma_{\text{geometric}}$. The $\gamma_{\text{BET}}$ for the uptake of NO$_2$ on the mixtures was enhanced with increasing (NH$_4$)$_2$SO$_4$ content because of the decrease of BET surface area. On the contrary, the $\gamma_{\text{geometric}}$ decreased with increasing (NH$_4$)$_2$SO$_4$ content due to the decrease of nitrate formation rates.

The mass concentrations of NO$_3^-$ formed on the samples after reaction with NO$_2$ were detected by IC, as shown in Fig. 5. The NO$_3^-$ mass concentrations for CaCO$_3$ particles are $3.22\pm0.17$, $3.31\pm0.03$, $3.38\pm0.35$, and $3.47\pm0.32$ mg/g under dry condition, 40%, 60% and 85% RH, respectively. It suggests that the NO$_3^-$ mass concentration increase slightly with higher RH for the reaction of NO$_2$ with CaCO$_3$ particles. For the CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures, the
NO$_3^-$ mass concentrations under dry condition are obviously smaller than those at 85% RH, and it exhibits maximum values at 40% or 60% RH. In addition, it should be noticed that the NO$_3^-$ mass concentrations has a negative linear relation with (NH$_4$)$_2$SO$_4$ mass fraction in the mixtures under dry condition, the R$^2$ of liner fit is 0.993. This result is in good agreement with the conclusions of Figure 1a and Figure 3 that the reaction of NO$_2$ with CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures is very similar to the reaction of NO$_2$ with pure CaCO$_3$ particles under dry condition and that (NH$_4$)$_2$SO$_4$ has little effects on the formation of NO$_3^-$ in this condition. Moreover, the concentrations of NO$_3^-$ of the mixtures under wet conditions are markedly larger than those under dry condition. The nitrate concentrations for the mixtures of FAS-10 and FAS-20 at 40% and 60% RH are even larger than that for pure CaCO$_3$ particles. The NO$_3^-$ mass concentrations increase much more for the mixtures than for pure CaCO$_3$ particles as RH elevated from dry condition to wet conditions, e.g., the NO$_3^-$ mass concentrations for the mixture of FAS-57 are 3.23±0.09, 3.09±0.14, 2.42±0.07 mg/g at 40%, 60% and 85% RH, respectively, which are increased by a factor of 2.1, 2.0, and 1.6 in comparison with that for FAS-57 under dry condition (1.55±0.08 mg/g). For the reaction of NO$_2$ with FAS-0, the NO$_3^-$ mass concentrations just increase by a factor of 1.03, 1.05, 1.08, as RH increased from dry condition to 40%, 60% and 85% RH, respectively. Besides, no obvious NO$_3^-$ is formed on pure (NH$_4$)$_2$SO$_4$ particles under all conditions investigated. These results clearly reveal that the CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures exhibit promotive effects on nitrate formation in the heterogeneous reaction with NO$_2$ under wet conditions.

The results described above indicate that relative humidity plays a vital role in the heterogeneous reaction of NO$_2$ with CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures. Under dry condition, little reaction occurs between CaCO$_3$ and (NH$_4$)$_2$SO$_4$. Therefore, nitrate formed on the mixtures under dry condition is mainly produced from the reaction of NO$_2$ with CaCO$_3$ particles. At 40% RH, the solid-state reaction between CaCO$_3$ and (NH$_4$)$_2$SO$_4$ particles can be neglected, implying that the solid-state reaction has little effects on the heterogeneous reaction. Meanwhile, the chemical interaction of Ca(NO$_3$)$_2$ with (NH$_4$)$_2$SO$_4$ is enhanced with the deliquescence of Ca(NO$_3$)$_2$, resulting in the formation of microcrystallites of NH$_4$NO$_3$ and CaSO$_4$·nH$_2$O. Consequently, it may help to improve the ionic mobility of the surface ions.
(Allen et al., 1996), modify the surface structure and re-expose reactive sites (Al-Hosney and Grassian, 2005). Thus the chemical interaction of Ca(NO$_3$)$_2$ and (NH$_4$)$_2$SO$_4$ particles may exhibit promotive effects on the nitrate formation during the heterogeneous reaction of NO$_2$ with CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures. The nitrate formation rates and nitrate concentrations increase slightly when RH increased from 40% RH to 60% RH for the mixtures with mass percentage of (NH$_4$)$_2$SO$_4$ less than 43%. However, it was opposite for the mixtures with mass percentage of (NH$_4$)$_2$SO$_4$ larger than 57%. This could be possibly explained that there is a combined effect of the two opposing effects on nitrate formation from the interaction of (NH$_4$)$_2$SO$_4$ with Ca(NO$_3$)$_2$ or CaCO$_3$ during the heterogeneous reaction of the mixtures with NO$_2$. Since a chemical reaction in the coagulation of CaCO$_3$ with (NH$_4$)$_2$SO$_4$ actually occurred without the introduction of NO$_2$ at 60% RH, leading to the formation of CaSO$_4$·nH$_2$O. Consequently, CaCO$_3$ particles are partly consumed during the coagulation process and CaSO$_4$·nH$_2$O formed in the coagulation may block reactive sites for further reaction. Thus, the solid state reaction between CaCO$_3$ and (NH$_4$)$_2$SO$_4$ particles exhibits inhibiting effects on the formation of nitrate on the mixtures. As for 85% RH, the deliquescence of (NH$_4$)$_2$SO$_4$ and surface nitrate leads to more water uptake on the mixture surfaces. The inhibiting effects from the coagulation of CaCO$_3$ and (NH$_4$)$_2$SO$_4$ in water film become stronger at 85% RH than at 60% RH, resulting in the decrease of nitrate formation rates and nitrate concentrations at 85% RH in comparison with those at 40% and 60% RH.

### 3.3 Mechanism

According to the experimental observations described above, a reaction mechanism for the heterogeneous reactions of NO$_2$ with CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures was proposed. Gas phase NO$_2$ attached to surface OH groups on CaCO$_3$ particle surfaces, as shown in (R1), where (g) is the gas phase and (ads) is the adsorbed phase.

\[ \text{S-OH} + \text{NO}_2(\text{g}) \rightarrow \text{S-OH}...\text{NO}_2(\text{ads}) \quad (\text{R1}) \]

Börens en et al. (2000) proposed that two adsorbed-phase NO$_2$ molecules result in surface
nitrate and nitrite products through a disproportionation reaction. Underwood et al. (1999b) suggested that \( \text{NO}_2 (g) \) reacted to form adsorbed nitrite species initially and then react with another surface nitrite or with gas-phase \( \text{NO}_2 \) to form nitrate. Nitrite was detected by FTIR and IC in this study. The reaction process can be described as:

\[
\text{S} \cdots \text{OH} \cdots \text{NO}_2(\text{ads}) \rightarrow \text{S} \cdots \text{NO}_3(\text{ads}) + \text{S} \cdots \text{NO}_2(\text{ads}) + \text{H}_2\text{O} \quad \text{(R2)}
\]

\[
2\ \text{S} \cdots \text{NO}_2(\text{ads}) \rightarrow \text{S} \cdots \text{NO}_3(\text{ads}) + \text{NO}(g) \quad \text{(R3)}
\]

\[
\text{S} \cdots \text{NO}_2(\text{ads}) + \text{NO}_2(g) \rightarrow \text{S} \cdots \text{NO}_3(\text{ads}) + \text{NO}(g) \quad \text{(R4)}
\]

Under dry condition, the surface nitrate was in equilibrium with surface adsorbed water and adsorbed \( \text{HNO}_3 \) species (R5). Adsorbed \( \text{H}_2\text{CO}_3 \) can exist on \( \text{CaCO}_3 \) particle surfaces (R6) and there was weak chemical interaction between \( \text{Ca(NO}_3)_2 \) and \( (\text{NH}_4)_2\text{SO}_4 \) (R7).

\[
\text{S} \cdots \text{NO}_3(\text{ads}) + \text{S} \cdots \text{H}_2\text{O}(\text{ads}) \rightarrow \text{S} \cdots \text{HNO}_3(\text{ads}) + \text{S} \cdots \text{OH} \quad \text{(R5)}
\]

\[
2\ \text{S} \cdots \text{HNO}_3(\text{ads}) + \text{CaCO}_3 \rightarrow \text{Ca(NO}_3)_2 + \text{S} \cdots \text{H}_2\text{CO}_3(\text{ads}) \quad \text{(R6)}
\]

\[
\text{Ca(NO}_3)_2 \cdot \text{nH}_2\text{O} + (\text{NH}_4)_2\text{SO}_4 \rightarrow \text{CaSO}_4 \cdot \text{nH}_2\text{O} + 2\text{NH}_4\text{NO}_3 \quad \text{(R7)}
\]

At 40% RH, \( \text{Ca(NO}_3)_2 \) deliquesced to form a solution droplet and reacted with \( (\text{NH}_4)_2\text{SO}_4 \):

\[
\text{Ca}^{2+} + 2\text{NO}_3^- + (\text{NH}_4)_2\text{SO}_4 + 0.5\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} + 2\text{NH}_4\text{NO}_3 \quad \text{(R8)}
\]

At 60% RH, the interaction between \( \text{CaCO}_3 \) and \( (\text{NH}_4)_2\text{SO}_4 \) in the presence of surface adsorbed water film can be expressed as R9:

\[
2\text{CaCO}_3 + 3(\text{NH}_4)_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{Ca(SO}_4)_2 \cdot \text{H}_2\text{O} + \text{CaSO}_4 \cdot \text{nH}_2\text{O} + 4\text{NH}_3 + 2\text{CO}_2 \quad \text{(R9)}
\]

It should be noticed that \( \text{NH}_3 \) was detected by PTR-MS (Proton-transfer-reaction mass spectrometry) under wet conditions in this study. \( \text{NH}_3 \) can also be released from the decomposition of \( \text{NH}_4\text{NO}_3 \) (R10).

\[
\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3 \quad \text{(R10)}
\]

At the same time, the heterogeneous reaction of \( \text{NO}_2 \) with surface adsorbed water has been demonstrated to form adsorbed \( \text{HNO}_3(\text{ads}) \) and gaseous \( \text{HONO}(g) \) (Svensson et al., 1987; Jenkin et al., 1988; Goodman et al., 1999).
\[
H_2O(\text{ads}) + 2\text{NO}_2(\text{ads}) \rightarrow \text{HNO}_3(\text{ads}) + \text{HONO}(g) \quad \text{(R11)}
\]

At 85% RH, the interaction of ions in the water film can be expressed as:

\[
2\text{Ca}^{2+} + 3\text{SO}_4^{2-} + 2\text{NH}_4^+ + n\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot n\text{H}_2\text{O} + (\text{NH}_4)_2\text{Ca(SO}_4)_2\cdot \text{H}_2\text{O} \quad \text{(R12)}
\]

4. Conclusions and atmospheric implications

The surface products and kinetics of the heterogeneous reactions of NO\(_2\) with CaCO\(_3\) particles, (NH\(_4\))\(_2\)SO\(_4\) particles, and CaCO\(_3\)−(NH\(_4\))\(_2\)SO\(_4\) mixtures were investigated under various RHs, using DRIFTS technique. And the solid-state reaction between CaCO\(_3\) and (NH\(_4\))\(_2\)SO\(_4\) particles were studied for comparison. All these reactions can occur in practical atmospheric conditions, which can be expressed in Fig. 6. The findings in this study have important atmospheric implications.

Calcium nitrate was produced from the heterogeneous reaction of NO\(_2\) with CaCO\(_3\)−(NH\(_4\))\(_2\)SO\(_4\) mixtures under both dry and wet conditions, and bassanite, gypsum and koktaite were formed depending on RH. It suggested that chemical composition in particulate phase was changed during the heterogeneous process, which can affect the physicochemical characteristics of atmospheric particles, including hygroscopicity, optical properties, and chemical reactivity. Besides, koktaite was detected in aerosols collected in Beijing, while it was absent in the soil where the dust originates (Mori et al., 2003), large uncertainties remain about its formation in the atmosphere. The results presented here provide evidence that the heterogeneous reactions of mixed CaCO\(_3\)−(NH\(_4\))\(_2\)SO\(_4\) particles with atmospheric acid trace gases was a possible source of koktaite. Also, the results indicated that the uptake of NO\(_2\) and the formation of nitrate promoted removing SO\(_4^{2-}\) from water soluble species to insoluble gypsum species, which could reduce the atmospheric water soluble sulfate content.

Gas phase products such as NH\(_3\) could be released during the heterogeneous reaction of NO\(_2\) with CaCO\(_3\)−(NH\(_4\))\(_2\)SO\(_4\) mixtures. In the atmosphere NH\(_3\) is mainly emitted from agriculture activities (such as fertilization and animal feeding) and biomass burning, and it plays an important role in nucleation and the growth of ion cluster and nanoparticles. The
results in this study suggest that heterogeneous uptake of NO₂ on CaCO₃ particles with the presence of (NH₄)₂SO₄ may be a potential pathway for the transformation of NH₃ from particulate phase to gas phase.

Furthermore, the uptake-coefficients of NO₂ on CaCO₃-(NH₄)₂SO₄ mixtures were determined, providing kinetic data for modeling studies. The results illustrate that the presence of (NH₄)₂SO₄ exhibits a promotive effect on the nitrate formation under wet conditions as a result of the interaction between Ca(NO₃)₂ and (NH₄)₂SO₄. On the contrary, the reaction between CaCO₃ and (NH₄)₂SO₄ particles has an inhibiting effect on the formation of nitrate during the heterogeneous reaction process, especially at high RH. Considering the abundance of (NH₄)₂SO₄ in the atmospheric aerosols, its mixtures with mineral dust may affect nitrate formation and the content of nitrate in atmospheric particles. The multicomponent reaction systems under ambient RH conditions play potentially vital role in atmospheric processes. To better understand the role of heterogeneous reactions in the atmospheric chemistry, the effects of ambient RH as well as multicomponent reaction systems should be considered.

The Supplement related to this article is available online.

Author contributions. Fang Tan and Shengrui Tong contribute equally to this work.

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Table 1. Assignments of IR vibration frequencies of surface adsorbed species formed on CaCO₃ particle surfaces and CaCO₃-(NH₄)₂SO₄ mixtures

<table>
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<tr>
<th>Samples</th>
<th>Stretch mode</th>
<th>ν₁ (cm⁻¹)</th>
<th>ν₂ (cm⁻¹)</th>
<th>ν₃ (cm⁻¹)</th>
<th>ν₄ (cm⁻¹)</th>
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<td>748</td>
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<tr>
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<td>830</td>
<td>1333, 1365</td>
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a from Schlenker et al. (2004). b,c from Prasad et al. (2005). d from Jentzsch et al. (2012)
Table 2. Initial uptake coefficients calculated using BET surface area and geometric surface area for the reaction of NO₂ with CaCO₃ particle surfaces and CaCO₃-(NH₄)₂SO₄ mixtures at various RHs.

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<th>40% RH</th>
<th>60% RH</th>
<th>85% RH</th>
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<td>γgeo (×10⁻⁶)</td>
<td>γΒΕΤ (×10⁻⁹)</td>
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Figure 1. DRIFTS spectra of CaCO$_3$ particles (FAS-0), CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures (FAS-10 - FAS-93), and (NH$_4$)$_2$SO$_4$ particles (FAS-100) after reaction with NO$_2$ at (a) dry condition, (b) 40% RH, (c) 60% RH, (d) 85% RH for 120 min. The concentration of NO$_2$ was 2.6×10$^{15}$ molecule cm$^{-3}$.
Figure 2. In situ DRIFTS spectra of surface products when the mixture of FAS-57 were exposed to nitrogen at dry condition (black), 40% RH (green), 60% RH (blue) and 85% RH (red) for 120 min.
Figure 3. The integrated absorbance of the peak area between 1390 and 1250 cm$^{-1}$ for nitrate on pure CaCO$_3$ particle surfaces (FAS-0), and CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures (FAS-10 - FAS-93) at (a) dry condition, (b) 40% RH, (c) 60% RH, and (d) 85% RH. The NO$_2$ concentration was 2.6×10$^{15}$ molecule cm$^{-3}$. 
Figure 4. Initial nitrate formation rates at dry condition (rhombus), 40% RH (triangle), 60% RH (fall triangle), 85% RH (roundness) and stable nitrate formation rates (pentagon) under dry condition versus the mass percentage of (NH$_4$)$_2$SO$_4$ in the mixtures. The data points and the error bars are the average value and the standard deviation of three duplicate experiments.
**Figure 5.** The mass concentration of NO$_3^-$ for CaCO$_3$ particles and the CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures after reacted with NO$_2$ for 120 min as a function of the mass percentage of (NH$_4$)$_2$SO$_4$ in the mixtures. The data points and the error bars are the average value and the standard deviation of three duplicate experiments.
Figure 6. Schematic illustrating the possible heterogeneous processes of NO$_2$ with CaCO$_3$-(NH$_4$)$_2$SO$_4$ mixtures and the possible atmospheric implications.