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$_2$ with CaCO$_3$–(NH$_4$)$_2$SO$_4$ mixtures with a series of weight percentage (wt %) of (NH$_4$)$_2$SO$_4$ were investigated using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) at different relative humidity (RH) values. For comparison, the heterogeneous reactions of NO$_2$ with pure CaCO$_3$ particles and pure (NH$_4$)$_2$SO$_4$ particles, as well as the reaction of CaCO$_3$ with (NH$_4$)$_2$SO$_4$ particles, were also studied. The results indicated that NO$_2$ did not show any significant uptake on (NH$_4$)$_2$SO$_4$ particles, and it reacted with CaCO$_3$ particles to form calcium nitrate under both dry and wet conditions. The heterogeneous reactions of NO$_2$ with CaCO$_3$–(NH$_4$)$_2$SO$_4$ mixtures were markedly dependent on RH. Calcium nitrate was formed from the heterogeneous reactions at all the RHs investigated, whereas CaSO$_4$·0.5H$_2$O (bassanite), CaSO$_4$·2H$_2$O (gypsum), and (NH$_4$)$_2$Ca(SO$_4$)$_2$·H$_2$O (koktaitie) were produced depending on RH. Under the dry condition, the heterogeneous uptake of NO$_2$ on the mixtures was similar to that on CaCO$_3$ particles with negligible effects from (NH$_4$)$_2$SO$_4$; the duration of initial stages and the NO$_2$ mass concentrations had a negative linear relation with the mass fraction of (NH$_4$)$_2$SO$_4$ in the mixtures. Under wet conditions, the chemical interaction of (NH$_4$)$_2$SO$_4$ with Ca(NO$_3$)$_2$ enhances the nitrate formation, especially at medium RHs, while the coagulation of (NH$_4$)$_2$SO$_4$ with CaCO$_3$ exhibits an increasing inhibiting effects with increasing RH at the same time. In addition, the heterogeneous uptake of NO$_2$ on the mixtures of CaCO$_3$ and (NH$_4$)$_2$SO$_4$ was found to favor the formation of bassanite and gypsum due to the decomposition of CaCO$_3$ and the coagulation of Ca$^{2+}$ and SO$_4^{2-}$. A possible reaction mechanism was proposed and the atmospheric implications were discussed.

1 Introduction

Haze with a high level of fine particulate matter with diameters less than 2.5 µm (PM$_{2.5}$) has occurred 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 relative humidity (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 (Uscher 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 (Uscher et al., 2003; Li et al., 2006; Al-Hosney and Grassian, 2005; Prince et al., 2007). Calcium carbonate particles are converted to calcium nitrate after reaction with nitrogen oxides and HNO3 in the atmosphere (Li and Shao, 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 H2SO4, NH3, and H2O could occur at atmospheric sulfuric acid concentration. Additionally, Mori et al. (1998) have found the coagulation between CaCO3 and (NH4)2SO4 could form koktaite and gypsum as a result of the interaction of ions under humid conditions. Ma et al. (2013) also discovered that mixed CaCO3-(NH4)2SO4 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 HNO3, gas-phase N2O and HONO productions. Zhao et al. (2013) found that coexisting surface nitrate had different effects on the uptake of H2O2 on mineral particle surfaces depending on RH. The catalytic and basic additives, e.g., MgO and CaCO3, could increase the basic property of the surface of NaCl and increase the formation of sulfate by facilitating the absorbance of SO2 on the alkaline surface (Li et al., 2007). To the best of our knowledge, the heterogeneous reaction of atmospheric trace gases on mixed CaCO3-(NH4)2SO4 particles has not been reported.

Furthermore, an increase in tropospheric NO2 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 NO2 concentration ranges from 70 parts per billion (ppb) during photochemical smog events to hundreds of parts per billion in polluted urban environments (Huang et al., 2015; Zamarayev et al., 1994). NO2 is one such critical anthropogenic gaseous pollutant, which reduces air quality and affects global tropospheric chemistry. NO2 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 NO2 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 NO2 on mineral aerosols was responsible for the nitrate accumulation in dust events (Uscher et al., 2003). A number of laboratory studies investigated the heterogeneous reaction of NO2 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 nitrate 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 Experiment

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 10–93 wt % (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 areas 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$_2$ was split into two streams; one was dehumidified by silica gel and molecular sieve to insure RH less than 1 %, which was called the dry condition; the other one was humidified by bubbling through ultrapure water. The flux of dry N$_2$, humid N$_2$, and NO$_2$ 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$_2$ entering reactor was diluted to 2.6 × 10$^{15}$ molecules cm$^{-3}$ by mixing with N$_2$. 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 Finlayson-Pitts, 1994). Infrared spectra of sample surfaces were recorded with a Nicolet FTIR (Fourier transform infrared) Spectrometer 6700, which was equipped with a liquid-nitrogen-cooled narrowband mercury-cadmium-telluride (MCT) detector and DRIFTS optics (Model CH-C-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$_3$–(NH$_4$)$_2$SO$_4$ mixtures, CaCO$_3$ particles, and (NH$_4$)$_2$SO$_4$ particles, respectively. Samples of about 30 mg 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 min 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 were observed as negative adsorption bands. Subsequently, NO$_2$ 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$_2$ were analyzed using ion chromatography (IC). The filtered solution was analyzed using a Dionex ICS 900 system, equipped with a Dionex AS 14A analytical column and a conductivity detector (D5S). 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 infrared (IR) spectra of surface products when the samples were exposed to NO$_2$ for 120 min at different RHs. Under the 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 CaCO$_3$ particle surfaces (FAS-0) and the mixtures (Goodman et al., 2001, 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 CaCO$_3$ particle surfaces and the mixtures of CaCO$_3$ and (NH$_4$)$_2$SO$_4$. 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 δ$_{oop}$(CO$_3^-$) of adsorbed carbonic acid, respectively, indicating that carbonic acid acted as an intermediate production under the 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$^{-1}$ corresponded to the two types of hydroxyl ions on CaCO$_3$ particle surfaces (Kuriyavar et al., 2000). No obvious negative peaks could be observed when the samples were exposed to dry pure nitrogen for 120 min, which indicated that surface adsorbed water and hydroxyl ions particiated in the reaction.

Compared with the spectrum of FAS-0, several additional weak absorptions appeared at 1008, 1096, and 1155 cm$^{-1}$ on the CaCO$_3$–(NH$_4$)$_2$SO$_4$ mixtures, which could be attributed to the vibration modes of SO$_4$ tetrahedra in CaSO$_4$ · 0.5H$_2$O (bassanite) (Prasad et al., 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 NO$_2$ with the mixtures, whereas it grew fast at the early stage of the reaction of NO$_2$ with CaCO$_3$ particles, and then diminished after reaching a maximum value at about 30 min (see Fig. S1 in the Supplement). This band described before was ascribed to nitrite species, which would convert to nitrate as the reaction proceeded (Miller and Grassian, 1998; Underwood et al., 1999b; Wu et al., 2013). To probe this product, samples after reaction with NO$_2$ for different times were detected by IC. The results showed that nitrite was increased during the first 30 min in the reaction of NO$_2$ with CaCO$_3$ particles, whereas there 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 to 1043 cm$^{-1}$, 746 to 749 cm$^{-1}$, and 816 to 828 cm$^{-1}$, respectively, compared to those under the dry condition. Meanwhile, the shoulder peak at 1300 cm$^{-1}$ 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 an amorphous hydrated 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$_3$ and (NH$_4$)$_2$SO$_4$, there was a new shoulder peak at 1365 cm$^{-1}$ which were attributed to the $\nu_3$(NO$_3$) in NH$_4$NO$_3$ (Schlenker et al., 2004). Moreover, the formation of CaSO$_4$·0.5H$_2$O was enhanced at 40 % RH compared to that under the dry condition, as features became apparent at 1155, 1096, and 1008 cm$^{-1}$, concomitant with the appearance of the peaks at 1620, 3555, and 3605 cm$^{-1}$ due to the vibration modes of water group in bassanite (Prasad et al., 2005). Additionally, new peaks could be observed at 1168, 1145, and 1117 cm$^{-1}$, which were attributed to the $\nu_3$(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$^{-1}$. Additionally, the two stretching modes of crystal hydrate water appeared at 3545 and 3400 cm$^{-1}$ for gypsum and at 3555 and 3610 cm$^{-1}$ for bassanite (Prasad et al., 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-75, FAS-75, and FAS-87 was much stronger than the peak at 3400 cm$^{-1}$ from condensed
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Table 1. Assignments of IR vibration frequencies of surface adsorbed species formed on CaCO\textsubscript{3} particle surfaces and CaCO\textsubscript{3}–(NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} mixtures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Species</th>
<th>v\textsubscript{1} (cm\textsuperscript{-1})</th>
<th>v\textsubscript{2} (cm\textsuperscript{-1})</th>
<th>v\textsubscript{3} (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(NO\textsubscript{3})\textsubscript{2}</td>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>1043</td>
<td>1050</td>
<td>1068</td>
</tr>
<tr>
<td>NH\textsubscript{4}NO\textsubscript{3}</td>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>816</td>
<td>830</td>
<td>1333, 1365</td>
</tr>
<tr>
<td>CaSO\textsubscript{4}·H\textsubscript{2}O</td>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>1003</td>
<td>1008</td>
<td>1117, 1145</td>
</tr>
<tr>
<td>Ca(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O</td>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>1003</td>
<td>1008</td>
<td>1117, 1145</td>
</tr>
<tr>
<td>Ca(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O</td>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>1005</td>
<td>1008</td>
<td>1117, 1145</td>
</tr>
<tr>
<td>Ca(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O</td>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>981, 998</td>
<td>1008</td>
<td>1108, 1131</td>
</tr>
<tr>
<td>Ca(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O</td>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>981, 998</td>
<td>1008</td>
<td>1108, 1131</td>
</tr>
</tbody>
</table>

\textsuperscript{a} from Schenkler et al. (2006); \textsuperscript{b} from Peters et al. (2005); \textsuperscript{c} from Jentzsch et al. (2012).

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\textsuperscript{-1} on the mixtures due to the stretching vibration modes of SO\textsubscript{4}\textsuperscript{2-} as well as peaks at 2860, 3064, 3192 cm\textsuperscript{-1} assigned to the stretching vibration modes of NH\textsubscript{4}\textsuperscript{+} indicated the formation of (NH\textsubscript{4})\textsubscript{2}Ca(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O (koktaite) (Jentzsch et al., 2012). The absorption band of nitrate overlapped with that of koktaite at 749 cm\textsuperscript{-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 deliquescence of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and surface salts (Cziczo et al., 1997; Lightstone et al., 2000). Additionally, the IR absorption peaks at 1570 cm\textsuperscript{-1} in Fig. 1d are much stronger than those at 40 and 60 % RH. The positive intensity is likely due to the increasing information of HCO\textsubscript{3}–, which is from the decomposition of the bulk CaCO\textsubscript{3} under wet conditions. It can be interpreted that the reaction of NO\textsubscript{2} can occur not only on the surfaces of CaCO\textsubscript{3} and the mixtures but also into the bulk of the samples under wet conditions. Additionally, the acidity of surface condensed water is enhanced as a result of the formation of HNO\textsubscript{3} and the dissolution of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, which facilitates the decomposition of bulk CaCO\textsubscript{3}.

In conclusion, NO\textsubscript{2} did not show significant uptake on pure (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} particles (FAS-100) at all the RHs investigated. Additionally, the products formed from the heterogeneous reactions of NO\textsubscript{2} with CaCO\textsubscript{3}–(NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} mixtures were strongly dependent on RH. Ca(NO\textsubscript{3})\textsubscript{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 NO\textsubscript{2} in order to investigate the solid-state reaction of CaCO\textsubscript{3} with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}. As shown in Fig. 2, no new absorption bands occurred after exposing to dry nitrogen for 120 min. The weak peak at 1189 cm\textsuperscript{-1} due to HSO\textsubscript{4}\textsuperscript{-} appeared as a main absorption peak and no obvious absorption band due to CaSO\textsubscript{4}·nH\textsubscript{2}O could be observed at 40 % RH. The results suggested that little reaction occurred between CaCO\textsubscript{3} and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} particles under the dry condition and 40 % RH. Therefore the chemical interaction of Ca(NO\textsubscript{3})\textsubscript{2} with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} was responsible for the formation of bassanite in these conditions. This is likely due to the fact that Ca(NO\textsubscript{3})\textsubscript{2} is more hygroscopic and soluble than CaCO\textsubscript{3} 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 CaCO\textsubscript{3} and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} particles actually occurred without the introduction of NO\textsubscript{2} at 60 and
85 % RH. This result was in good agreement with the results reported by Mori et al. (1998) that gypsum was formed from the chemical reaction between (NH_4)_2SO_4 and CaCO_3, with kocktait 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 50 and 70 % of those for FAS-57 at corresponding RH in Fig. 1. Thus CaSO_4 \cdot nH_2O and kocktait products could be formed both from the chemical interaction of (NH_4)_2SO_4 with Ca(NO_3)_2 and the reaction of (NH_4)_2SO_4 with CaCO_3 at 60 and 85 % RH.

3.2 Uptake coefficients and kinetics

The formation rates of nitrate on CaCO_3 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 CaCO_3 particle surfaces (Fig. 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 the dry condition. 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 duration of initial stages for the mixtures decreased nearly linearly with increasing mass fraction of (NH_4)_2SO_4 in the mixtures; e.g., it lasted about 80 min for FAS-0 (CaCO_3 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 CaCO_3 content in the mixtures. The possible reasons were that for the reaction of NO_2 with CaCO_3–(NH_4)_2SO_4 mixtures, nitrate was formed by the uptake of NO_2 on CaCO_3 particle surfaces without the participation of (NH_4)_2SO_4 and the reactions limited on the particle surfaces under the dry condition. Moreover, the duration of initial stages was 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 be longer than 120 min for the mixtures with mass fraction of (NH_4)_2SO_4 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 CaCO_3–(NH_4)_2SO_4 mixtures. This was likely due to the fact that the reaction of NO_2 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 \([NO_3^-]\):

\[
\{NO_3^-\} = I_A \times f \tag{1}
\]

Here \(f\) is the 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, 40 % RH, and the 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 \(d\{NO_3^-\}/dt\) 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 maximum values under the 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 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 (NH_4)_2SO_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 (NH_4)_2SO_4 smaller than 43 %, the nitrate formation rates increased initially as RH elevated from 40 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 possibly explained by the combined opposite effects from the interaction of (NH_4)_2SO_4 with Ca(NO_3)_2 or CaCO_3 at 60 and 85 % RH.

Besides, nitrate formation rates decreased more evidently with increasing (NH_4)_2SO_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 the 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 the 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.
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 ($Z$):

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

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

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 $[\text{NO}_2]$ 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 $d\{\text{NO}_3^\text{-}\}/dt$, then the reactive uptake coefficients can be calculated by

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

<table>
<thead>
<tr>
<th>(NH4)2SO4 (wt %)</th>
<th>Dry condition</th>
<th>40 % RH</th>
<th>60 % RH</th>
<th>85 % RH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_{\text{BET}}$ ($\times 10^{-9}$)</td>
<td>$\gamma_{\text{geo}}$ ($\times 10^{-6}$)</td>
<td>$\gamma_{\text{BET}}$ ($\times 10^{-9}$)</td>
<td>$\gamma_{\text{geo}}$ ($\times 10^{-6}$)</td>
</tr>
<tr>
<td>0</td>
<td>3.34 ± 0.14</td>
<td>10.4 ± 0.44</td>
<td>2.04 ± 0.07</td>
<td>6.36 ± 0.22</td>
</tr>
<tr>
<td>10</td>
<td>3.19 ± 0.21</td>
<td>9.83 ± 0.65</td>
<td>2.06 ± 0.21</td>
<td>6.34 ± 0.45</td>
</tr>
<tr>
<td>20</td>
<td>3.77 ± 0.24</td>
<td>9.54 ± 0.61</td>
<td>2.51 ± 0.34</td>
<td>6.28 ± 0.86</td>
</tr>
<tr>
<td>40</td>
<td>5.34 ± 0.17</td>
<td>9.25 ± 0.29</td>
<td>3.50 ± 0.42</td>
<td>6.07 ± 0.72</td>
</tr>
<tr>
<td>57</td>
<td>6.82 ± 0.33</td>
<td>8.38 ± 0.41</td>
<td>4.70 ± 0.51</td>
<td>5.78 ± 0.63</td>
</tr>
<tr>
<td>75</td>
<td>7.74 ± 0.94</td>
<td>6.94 ± 0.84</td>
<td>6.12 ± 0.37</td>
<td>5.49 ± 0.23</td>
</tr>
<tr>
<td>87</td>
<td>9.04 ± 0.73</td>
<td>5.78 ± 0.46</td>
<td>7.68 ± 0.50</td>
<td>4.92 ± 0.32</td>
</tr>
<tr>
<td>93</td>
<td>14.4 ± 1.07</td>
<td>4.90 ± 0.36</td>
<td>13.6 ± 0.93</td>
<td>4.63 ± 0.32</td>
</tr>
</tbody>
</table>

The $\gamma_{\text{BET}}$ is approximately a factor of $10^4$ smaller than the $\gamma_{\text{geo}}$. The $\gamma_{\text{BET}}$ for the uptake of NO2 on the mixtures was enhanced with increasing (NH4)2SO4 content because of the decrease of BET surface area. On the contrary, the $\gamma_{\text{geo}}$ decreased with increasing (NH4)2SO4 content due to the decrease of nitrate formation rates.

The mass concentrations of NO3− formed on the samples after reaction with NO2 were detected by IC, as shown in Fig. 5. The NO3− mass concentrations for CaCO3 particles are 3.22 ± 0.17, 3.31 ± 0.03, 3.38 ± 0.35, and 3.47 ± 0.32 mg g$^{-1}$ under the dry condition, 40, 60, and 85 % RH, respectively. It suggests that the NO3− mass concentration increases slightly with higher RH for the reaction of NO2 with CaCO3 particles. For the CaCO3–(NH4)2SO4 mixtures, the NO3− mass concentrations under the 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 NO3− mass concentrations nearly have a negative linear relation with (NH4)2SO4 mass fraction in the mixtures under the dry condition. This result is in good agreement with the conclusions of Figs. 1a and 3 that the reaction of NO2 with CaCO3–(NH4)2SO4 mixtures is very similar to the reaction of NO2 with pure CaCO3 particles under the dry condition and that (NH4)2SO4 has little effect on the formation of NO3− in this condition. Moreover, the concentrations of NO3− in the mixtures under wet conditions are markedly larger than those under the dry condition. The NO3− mass concentrations increase much more for the mixtures than for pure CaCO3 particles as RH elevated from the dry condition to wet conditions; e.g., the NO3− mass concentrations for the mixture of FAS-57 are 3.23 ± 0.09, 3.09 ± 0.14, and 2.42 ± 0.07 mg g$^{-1}$ 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 the dry condition (1.55 ± 0.08 mg g$^{-1}$). For the reaction of NO2 with FAS-0, the NO3− mass concentrations just increase by a factor of 1.03, 1.05, and 1.08, as RH increased from the dry condition to 40, 60, and 85 % RH, respectively. These results clearly reveal that the CaCO3–(NH4)2SO4 mixtures exhibit promotive effects on nitrate formation in the heterogeneous reaction with NO2 under wet conditions.

The results described above indicate that relative humidity plays a vital role in the heterogeneous reaction of NO2 with CaCO3–(NH4)2SO4 mixtures. Under dry condition, little reaction occurs between CaCO3 and (NH4)2SO4. Therefore, nitrate formed on the mixtures under the dry condition is mainly produced from the reaction of NO2 with CaCO3 particles. At 40 % RH, the solid-state reaction between CaCO3 and (NH4)2SO4 particles can be neglected, implying that the solid-state reaction has little effect on the heterogeneous reaction. Meanwhile, the chemical interaction of Ca(NO3)2 with (NH4)2SO4 is enhanced with the deliquescence of Ca(NO3)2, resulting in the formation of microcrystallites of NH4NO3 and CaSO4·nH2O. 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(NO3)2 and (NH4)2SO4 par-

Figure 5. The mass concentration of NO3− for CaCO3 particles and the CaCO3–(NH4)2SO4 mixtures after they reacted with NO2 for 120 min as a function of the mass percentage of (NH4)2SO4 in the mixtures. The data points and the error bars are the average value and the standard deviation of three duplicate experiments.

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Particulate 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 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, 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 Reaction (R1), where (g) is the gas phase and (ads) is the adsorbed phase.

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

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

\[ 2\text{S-\text{OH}...\text{NO}_2(ads)} \rightarrow \text{S...NO}_3^-(ads) + \text{S...NO}_2^-(ads) + \text{H}_2\text{O} \quad (R2) \]
\[ 2\text{S...NO}_2^-(ads) \rightarrow \text{S...NO}_3^-(ads) + \text{NO}(g) \quad (R3) \]
\[ \text{S...NO}_2^-(ads) + \text{NO}_2(g) \rightarrow \text{S...NO}_3^-(ads) + \text{NO}(g) \quad (R4) \]

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

\[ \text{S...NO}_3^-(ads) + \text{S...H}_2\text{O}(ads) \rightarrow \text{S...HNO}_3(ads) + \text{S-\text{OH}} \quad (R5) \]
\[ 2\text{S...HNO}_3(ads) + \text{CaCO}_3 \rightarrow \text{Ca(NO}_3)_2 + \text{S...H}_2\text{CO}_3(ads) \quad (R6) \]
\[ \text{Ca(NO}_3)_2 \cdot \text{nH}_2\text{O} + \text{(NH}_4)_2\text{SO}_4 \rightarrow \text{CaSO}_4 \cdot \text{nH}_2\text{O} + 2\text{NH}_4\text{NO}_3 \quad (R7) \]

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

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

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

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

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

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

At the same time, the heterogeneous reaction of NO$_2$ with surface adsorbed water has been demonstrated to form adsorbed HNO$_3$(ads) and gaseous HONO(g) (Svensson et al.,...
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1987; Jenkin et al., 1988; Goodman et al., 1999):

H2O(ads) + 2NO2(ads) → HNO3(ads) + HONO(g).  \( \text{(R11)} \)

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

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

\( \text{R12} \)

4 Conclusions and atmospheric implications

The surface products and kinetics of the heterogeneous reactions of NO2 with CaCO3 particles, (NH4)2SO4 particles, and CaCO3–(NH4)2SO4 mixtures were investigated under various RHs, using the DRIFTS technique. The solid-state reaction between CaCO3 and (NH4)2SO4 particles was also 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 NO2 with CaCO3–(NH4)2SO4 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. In addition, 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 CaCO3–(NH4)2SO4 particles with atmospheric acid trace gases were a possible source of koktaite. The results also indicated that the uptake of NO2 and the formation of nitrate promoted removal of SO4^{2-} from water-soluble species to insoluble gypsum species, which could reduce the atmospheric water soluble sulfate content.

Gas-phase products such as NH3 could be released during the heterogeneous reaction of NO2 with CaCO3–(NH4)2SO4 mixtures. In the atmosphere, NH3 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 a potentially vital role in atmospheric processes. To better understand the role of heterogeneous reactions in the atmospheric chemistry, the effects of ambient RH (Rubaisingerhe and Grassian, 2013) as well as multicomponent reaction systems should be considered.

5 Data availability

All data are available upon request from the corresponding authors.

The Supplement related to this article is available online at doi:10.5194/acp-16-8081-2016-supplement.

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