Kinetics and mechanisms of heterogeneous reaction of NO$_2$ on CaCO$_3$ surfaces under dry and wet conditions

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Abstract

Calcium nitrate (Ca(NO$_3$)$_2$) was observed in mineral dust and could change the hygroscopic and optical properties of mineral dust significantly due to its strong water solubility. The reaction of calcium carbonate (CaCO$_3$) with nitric acid (HNO$_3$) is believed the main reason for the observed Ca(NO$_3$)$_2$ in the mineral dust. In the atmosphere, the concentration of nitrogen dioxide (NO$_2$) is orders of magnitude higher than that of HNO$_3$; however, little is known about the reaction of NO$_2$ with CaCO$_3$. In this study, the heterogeneous reaction of NO$_2$ on the surface of CaCO$_3$ particles was investigated using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) combined with X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) under wet and dry conditions. Nitrate formation was observed in both conditions, and nitrite was observed under wet conditions, indicating the reaction of NO$_2$ on the CaCO$_3$ surface produced nitrate and probably nitrous acid (HONO). Relative humidity (RH) influenced both the initial uptake coefficient and the reaction mechanism. With RH<52%, surface –OH was formed through dissociation of the surface adsorbed water via oxygen vacancy, thus determining the reaction order. With RH>52%, a monolayer of water formed on the surface of the CaCO$_3$ particles, which reacted with NO$_2$ as a first order reaction, forming HNO$_3$ and HONO. The initial uptake coefficient $\gamma_0$ was determined to be $(1.66\pm0.38) \times 10^{-7}$ under dry conditions and up to $(0.84\pm0.44) \times 10^{-6}$ under wet conditions. Considering that NO$_2$ concentrations in the atmosphere are orders of magnitude higher than those of HNO$_3$, the reaction of NO$_2$ on CaCO$_3$ particle should have similar importance as that of HNO$_3$ in the atmosphere and could also be an important source of HONO in the atmosphere.

1 Introduction

It has been estimated that 1000–3000 Tg of mineral aerosols are emitted into the atmosphere annually (Jonas et al., 1995). The main components of mineral dust include...
quartz, feldspar, carbonate (e.g. calcite, dolomite) and clay. Each of these components provides surfaces and reactants for heterogeneous reactions in the atmosphere. Many gas phase species in the atmosphere could also condense or adsorb onto mineral dust during long-range transport to impact atmospheric chemistry and climate change (Chen, 1985; Quan, 1993; Carmichael et al., 1996; Zhang et al., 2000). Modeling studies suggested that approximately 40% of nitrate formation is associated with mineral aerosols (Dentener et al., 1996). Aerosol samples taken in East Asia showed a good correlation between nitrate and calcium (Zhuang et al., 1999; Song and Carmichael, 2001; Sullivan et al., 2007).

In fresh Asian mineral aerosols, calcium is found primarily in the form of calcium carbonate (CaCO$_3$) (Song et al., 2005; Okada et al., 2005). The observed association of nitrate with calcium in mineral dust samples after long range transport suggests that after exposure to nitrogen oxides in polluted region, calcium carbonate in mineral dust had been converted to calcium nitrate, which in turn can change the composition and morphology of calcium-containing aerosols and enhance their hygroscopicity and the rates of heterogeneous reactions, thus influence the atmospheric chemistry. Calcium nitrate can also alter the optical properties of aerosols to impact radiation, cloud formation, and global climate change.

Laboratory studies have demonstrated that nitric acid (HNO$_3$) can react with CaCO$_3$ to form calcium nitrate (Fenter et al., 1995; Goodman et al., 2000; Hanisch and Crowley, 2001; Krueger et al., 2003a, b). The measured uptake coefficient accounting for the BET area of the samples was determined to be (2.5±1)×10$^{-4}$ for HNO$_3$ on CaCO$_3$ under dry condition (Goodman et al., 2000). Johnson et al. (2005) determined the initial uptake coefficient of HNO$_3$ on CaCO$_3$ to be (2±0.4)×10$^{-3}$. The net reaction probability of HNO$_3$ on CaCO$_3$ particles was found to increase with increasing relative humidity, from 0.003 at RH=10% to 0.21 at 80% (Liu et al., 2008a). Vlasenko et al. (2006) reported an uptake coefficient of HNO$_3$ on CaCO$_3$ to be 0.11 at 33% relative humidity and a humidity dependence on Arizona Test Dust.

Compared to nitric acid, little is known about the reaction of NO$_2$ on CaCO$_3$. The
uptake coefficients of NO$_2$ on mineral oxide particles, such as Al$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$, have been determined to be on the order of $10^{-7}$ (Underwood et al., 1999); this is consistent with the results of the reaction of NO$_2$ on mineral dust samples from the Cape Verde Islands (Ullerstam et al., 2003).

No literature report about the uptake coefficient of NO$_2$ on CaCO$_3$ has been found. Considering that the concentration of NO$_2$ in the atmosphere is at least an order of magnitude higher than that of HNO$_3$, the reaction of CaCO$_3$ particles with NO$_2$ may comprise an important atmospheric reaction that lead to the formation of calcium nitrate during the long range transport of mineral dust. This reaction could be even more important in East Asia, where industrial regions with high NO$_2$ emissions are located in the path of long range transport of Asian Dust.

To understand the importance of the heterogeneous reaction of NO$_2$ on mineral dust, it is important to measure the uptake coefficient of NO$_2$ on CaCO$_3$ particles. Similar to the reaction of HNO$_3$ on CaCO$_3$, the reaction of NO$_2$ on CaCO$_3$ may also change under the influence of surface water. Therefore, it is interesting to study the reaction mechanisms and to measure the uptake coefficient of the reaction of NO$_2$ on CaCO$_3$ particles under dry and wet conditions.

In this study, the reactions of NO$_2$ on CaCO$_3$ surfaces were investigated in situ using a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in combination with X-ray photoelectron spectroscopy (XPS), ion chromatography (IC), and scanning electron microscopy (SEM); initial uptake coefficients were measured and the reaction mechanisms were studied under different relative humidity (RH).

2 Experimental

The infrared (IR) spectrum of the particle surface was investigated on line with DRIFTS during the reaction. The reactor of DRIFTS is a vacuum reaction chamber (Model HVC-DR2) surrounding a Harrick Scientific diffuse reflectance accessory (Model DRA-2CS) located in the sampling compartment of a Nicolet Nexus FTIR Spectrometer equipped
with a mercury cadmium telluride (MCT) detector. Data from 128 scans, 4 cm\(^{-1}\) resolution, taken over about 80 s were averaged for one spectrum.

Besides online infrared spectroscopy measurements, for a number of selected experiments, the reaction products on the particle surface and extractable soluble components were also measured off line using X-ray photoelectron spectroscopy (XPS) and ion chromatography (IC), respectively. The morphological changes were observed using SEM. Further details of the instruments have been described previously (Li et al., 2006).

CaCO\(_3\) (>99.999%, Alfa Aesar) powder was prepared by grinding and the size of the grinded particle was about 1–10 \(\mu\)m with a mean value of 5.6 \(\mu\)m, as measured with a laser particle sizer (MasterSizer 2000, Malvern). The specific geometric surface area of the CaCO\(_3\) particles was calculated to be 0.37 m\(^2\) g\(^{-1}\) for cubic shape particles. About 20 mg of the sample was placed in the sample holder, pressed flat using a glass slide, and stored in a desiccator as previously described (Li et al., 2006). Water vapor was produced and gases were mixed using the apparatus displayed in Fig. A1. All tubes and surfaces were made of inert glass or Teflon with the exception of the stainless steel in situ reactor. Concentrations of NO\(_2\) entering the reactor were adjusted by mixing a NO\(_2\) standard gas (710 ppm in N\(_2\), Center of National Standard Material Research) with pure N\(_2\) (>99.999%) using two mass flow controllers (FC-260, Tylan, Germany). In the reactor, the NO\(_2\) diffused to the particle surface and reacted with CaCO\(_3\). The formation of the reaction products was monitored using DRIFTS. Humidity was regulated by mixing dry nitrogen with water vapor by bubbling through two glass grits in pure water (Millipore Corporation, Billerica, MA, USA). Humidity was monitored using a temperature sensor (PT100, Vaisala, Vantaa, Finland) and a humidity sensor (HM1500, Vaisala).

The volumetric BET (Brunauer, Emmett and Teller model) surface area of particles was measured with an ASAP2010 BET apparatus (Micromeritics Co., USA). The specific surface area, \(A_s\), was determined to be 4.91 m\(^2\) g\(^{-1}\), this is 13.3 times the specific geometric surface area of cubic shape CaCO\(_3\) particles with a size of 5.6 \(\mu\)m.
After the reactions, the absolute numbers of nitrate and nitrite ions formed during the reaction were determined with IC. The reacted CaCO$_3$ particles were sonicated in 10 mL of pure water (Millipore Corporation), and then the filtered solution was analyzed using an IC (Dionex DX-500 system), which was equipped with an Ionpac AS-11HC-4 mm analytical column and a conductivity detector. Details of analyzing conditions can be found in a previous paper (Li et al., 2006).

The XPS spectra were taken on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al K$_\alpha$ radiation (225 W, 15 mA, 15 kV) and low–energy electron flooding for charge compensation. To compensate for surface charges effects, binding energies were calibrated using C1s hydrocarbon peak at 284.80 eV. The data were converted into VAMAS file format and imported into CasaXPS software package for manipulation and curve-fitting.

3 Results

3.1 The influence of water vapor

Calcite is the main form of CaCO$_3$ in the environment and its (104) crystal plane has the lowest energy state (de Leeuw and Parker, 1998). Both laboratory and computer modeling studies have demonstrated that at certain relative humidity, a hydrated layer on CaCO$_3$ could be dissociated by oxygen vacancy to form stable –OH that remained surface-bound even in a high vacuum (Stipp et al., 1996; McCoy and LaFemina, 1997; de Leeuw and Parker, 1998). The results of Kuriyavar et al. (2000) and Stipp (1999) demonstrated that the dissociation of water could produce surface hydroxyl on CaCO$_3$ surfaces. Species including H$^+$, OH$^-$, HCO$_3^-$, Ca(OH)$^+$, and Ca(HCO$_3$)$^+$ can exist on the surfaces of calcite and alter its surface properties (Thompson and Pownall, 1989). XPS analysis of the CaCO$_3$ particle sample showed two peaks of O1s at 531.3 eV and 533.1 eV (Fig. A2), corresponding to the oxygen atoms of CaCO$_3$ and –Ca(OH) (Stipp, 1999). The oxygen atoms of –Ca(OH) accounted for 3.4–3.6% of the total number of
atoms. The presence of –Ca(OH) implied that water can have a major effect on the CaCO₃ surface properties. Therefore, understanding water adsorption on surfaces of CaCO₃ particles is very important.

From the FTIR spectra of the CaCO₃ particle samples, we integrated the area of the stretching vibration of –OH from 3644 to 2983 cm⁻¹ and plotted it as a function of RH at 296 K (Fig. 1, left axis); it demonstrated that the proportion of surface bound water increased with RH. The experimental data were fitted using the three-parameter equation of BET adsorption to determine the equivalent number of molecular layers of water, and we concluded that a monolayer of water formed on the CaCO₃ surface at 52% RH (Fig. 1, right axis). This suggests that the mechanisms of the heterogeneous reactions on the surface CaCO₃ particles could be different when RH is lower or higher than 52%.

The NO₃⁻ production rate on the CaCO₃ particle samples can be expressed as:

\[
d\{\text{NO}_3^-\}/dt = k\{\text{CaCO}_3\}^m[H_2O]^q[\text{NO}_2]^n
\]

(1)

where \(\{x\}\) denotes the concentration of surface species (e.g. nitrate ions and active site on CaCO₃), \([x]\) denotes the concentration of species in gas phase, and m, n, and q are the reaction order for CaCO₃, NO₂ and H₂O, respectively. At the initial stage of the reaction, the number of NO₃⁻ ions formed on the surface of CaCO₃ is small compared to the surface active site, \{CaCO₃\}, which can be considered constant. At a constant NO₂ concentration, the production rate of NO₃⁻ is only a function of \([H_2O]\). The slope of double-log line of the NO₃⁻ production rate versus the water concentration should give the reaction order with respect to H₂O, q.

At a constant NO₂ concentration of 6.88×10¹⁵ molecules cm⁻³, the double-log curve of the NO₃⁻ production rate versus the water concentration is shown in Fig. 2. The reaction order of H₂O(g) was −0.44 when RH<50%, and 0.20 when RH>50%. This indicates that at low RH, H₂O(g) inhibits the formation of surface nitrate but at high RH it had very little influence on the formation of surface nitrate. This result is consistent with the observation that at low RH, the formation of the active site on the surface of the
CaCO₃, e.g. –OH, involved the adsorbed water and the existence of adsorbed water can alter the reactivity of the particle surface (Elam et al. 1998; Hass et al., 1998; Eng et al., 2000; Hass et al., 2000). Meanwhile, water could easily adsorb onto the surface –OH, and compete with the adsorption of NO₂ (Stumm, 1992). At RH>52%, water layer forms on the surface of CaCO₃ and changes the reaction on the calcite surface from gas-solid to gas-liquid reaction. Thus, the water vapor plays an important role in the heterogeneous reactions of NO₂ with CaCO₃.

3.2 Reaction under dry conditions

Experiments under dry conditions were carried out by first heating the CaCO₃ at 623 K for 2 h, thus eliminating nearly all of the adsorbed water. A mixture of NO₂ and N₂ without water vapor was admitted at 296 K.

Figure 3 shows typical IR spectra of CaCO₃ when reacted with NO₂ under dry conditions for 0 to 100 min. Nitrate was clearly observed on the CaCO₃ surface. The peak at 816 cm⁻¹ was assigned to the out-of-plane bending of nitrate ν₂. The peak at 1043 cm⁻¹ was assigned to the symmetric stretching of nitrate ν₁ and the peak at 748 cm⁻¹ was assigned to the in-plane bending of nitrate ν₄. Peaks at 1295, 1330, and 1350 cm⁻¹ were assigned to the asymmetric stretching of nitrate ν₃. The ν₃ mode of nitrate on the CaCO₃ surface has many peaks; this is different from the nitrate ions in Ca(NO₃)₂ that were attributable to the adsorbed nitrate of different coordination (monodentate, bidentate, and bridging), while the nitrate ions did not form on the CaCO₃ surface (Borensen et al., 2000).

The asymmetric stretching of adsorbed nitric acid has been reported to be at 1710/1680 cm⁻¹ (Nakamoto, 1997; Finlayson-Pitts et al., 2003). In our study, to confirm the vibration frequency of the adsorbed HNO₃, calcium sulfate (CaSO₄) particles were exposed to gas phase HNO₃. The IR absorption peaks of adsorbed HNO₃ were observed at 1670, and 1720 cm⁻¹; therefore, we can assign the peaks at 1670 and 1703 cm⁻¹ to adsorbed HNO₃, this suggests that HNO₃ was formed when NO₂ re-
acted with CaCO_3.

The peaks at 1630 and 3520 cm\(^{-1}\) were assigned to the bending and asymmetric stretching of crystal hydrate water. Compared with the vibration frequencies of the crystallized water in Ca(NO_3)_2\(\cdot\)4H_2O at 1640 cm\(^{-1}\) and 3490 cm\(^{-1}\), a shift of both peaks occurred, due to the decreased hydrogen bonding. The asymmetric stretching shifted to the higher wave number, and the bending shifted to the lower wave number. The peaks at 3140 and 3330 cm\(^{-1}\) were assigned to surface adsorbed water, both peaks decreased as the reaction proceeded until the peaks for crystal hydrate water at 1630 cm\(^{-1}\) and 3520 cm\(^{-1}\) appeared.

The XPS spectrum of CaCO_3 particle that reacted with 1.06\(\times\)10^{15} molecules cm\(^{-3}\) NO_2 for 626 min (Fig. A3a) showed the peak of nitrogen of +5 valence at 407.3 eV, and confirmed the formation of nitrate. The formation of nitrate was further confirmed by IC analysis of reacted CaCO_3 particles (Fig. A3b). However, no nitrite was detected with both XPS and IC, this is probably due to the reason that HONO formed in the reaction was released into the gas phase and carried away by N\(_2\).

Figure 4 shows the formation of nitrate on CaCO_3 through the reaction of NO_2 as a function of time. The amount of nitrate formed is represented by the integrate absorbance \(I_A\) of the IR peak area between 1077 and 1013 cm\(^{-1}\). As the reaction proceeded, the nitrate concentration on the calcite surface increased and the rate of nitrate formation increased with higher NO_2 concentrations. The nitrate formation process could be divided into three stages: stage I lasted from the initiation of the reaction until \(I_A\) reached 0.3, stage II was the transition stage when the increase of \(I_A\) was slowing down between 0.3 and 0.4, and stage III was the growth stage when \(I_A\) > 0.4 and the increase rate of \(I_A\) reached to a constant.

The amount of nitrate ions formed on the particles \(\{\text{NO}_3^-\}\) was determined with a linear relationship between \(I_A\) in the range of 1073–1013 cm\(^{-1}\) and the amount of nitrate determined by ion chromatography \(\{\text{NO}_3^-\}\):

\[
\{\text{NO}_3^-\} = f \times I_A
\]

(2)
The conversion factor \( f \) was found to be independent of reaction time and NO\(_2\) concentration as long as the experiment was completed at a stage when the absorption of the nitrate band was still growing. For our study, \( f \) was calculated to be \( 1.89 \times 10^8 \) molecules/l.

Using \( f \), the production rate of nitrate \( d\{\text{NO}_3^-\}/dt \) was calculated, and the reaction order of NO\(_2\) on CaCO\(_3\) particles was obtained from the slope of the double-log plots of \( d\{\text{NO}_3^-\}/dt \) versus NO\(_2\) concentrations (Fig. 5). In stage I the reaction order of NO\(_2\) was 1.63±0.23 and in stage II 0.41±0.55. This means that the nitrate formation with respect to NO\(_2\) was a second-order reaction in the initial stage (I) and a zero-order reaction in the transition stage (II).

3.3 Reaction under wet conditions

Experiments of CaCO\(_3\) reaction with NO\(_2\) under wet conditions were carried out using non-heat-treated CaCO\(_3\) particles at 296 K with RH=60–71%. Figure 6 shows the typical IR spectra of CaCO\(_3\) when NO\(_2\) entered the reactor under wet conditions, at reaction times from 0 to 60 min.

The peak at 1048 cm\(^{-1}\) was assigned to the symmetric stretching \( \nu_1 \) of nitrate, the peak at 1344 cm\(^{-1}\) to the asymmetric stretching \( \nu_3 \) of nitrate. The peak at 1251 cm\(^{-1}\) was assigned to the asymmetric stretching \( \nu_3 \) of nitrite. The peak at 1688 cm\(^{-1}\) was assigned to the adsorption peak of HNO\(_3\) and the peak at 1636 cm\(^{-1}\) to the bending of the surface adsorbed water; the peak at 1472 cm\(^{-1}\) appeared in the range of peaks for the asymmetric stretching of carbonate and was assigned to the carbonate vibration peak. Compared to the corresponding peak observed under dry conditions, these peaks had all shifted more or less. We attributed these shifts to the changed environment caused by increased surface adsorbed water under wet conditions.

The peaks at 1525 and 1540 cm\(^{-1}\) were in the range of asymmetric stretching of bicarbonate and were assigned to the bicarbonate vibration peaks (Al-Hosney and Grassian 2004; Al-Abadleh et al., 2005). Negative peaks at 1472, 1525, and 1540 cm\(^{-1}\)
were similar to the negative peaks from the reaction of HNO$_3$ with CaCO$_3$ (Fig. A5). This indicated that the intermediate products HCO$_3^-$ and H$_2$CO$_3$ were formed during the reaction of NO$_2$ with CaCO$_3$. The result is consistent with the findings of Al-Hosney and Grassian (2004) that H$_2$CO$_3$ was the intermediate product when HNO$_3$, SO$_2$, HCOOH and CH$_3$COOH reacted with CaCO$_3$.

The formation of nitrate and nitrite was further confirmed by the XPS spectrum of CaCO$_3$ particles reacting with $1.06\times10^{15}$ molecules cm$^{-3}$ of NO$_2$ for 30 min at RH=80±2%, which demonstrated the existence of N of +5 valence and +3 valence as shown in Fig. A4a, and the formation of nitrate and nitrite was shown in IC chromatogram of Fig. A4b.

To obtain the change rate of each peak, Gaussian peak-fitting was used within the spectral range of 1750–1150 cm$^{-1}$ (Fig. 7a). Figure 7b shows the integrate absorbance of nitrate peak at 1344 cm$^{-1}$ increased during the reaction while that of the carbonate peaks at 1472, 1525, and 1540 cm$^{-1}$ decreased with time, indicating that nitrate was produced when CaCO$_3$ was consumed.

The nitrite ion peak at 1251 cm$^{-1}$ and HNO$_3$ peak at 1688 cm$^{-1}$ increased initially and subsequently decreased, implying that the decrease of nitrite was related to the decrease of HNO$_3$. It was inferred that the increase of adsorbed nitric acid caused the release of nitrite in the form of gaseous HONO which led to the decreased of both nitrite ion and nitric acid. The adsorbed water peak at 1636 cm$^{-1}$ exhibited a linear increase initially but later reached a plateau, demonstrating that the CaCO$_3$ particle surface was gradually saturated with adsorbed water.

Figure 8 shows the nitrate formation as a function of time during the reaction of CaCO$_3$ with NO$_2$ under wet (RH=60–71%) conditions. The integrated absorbance was in the range of 1077–1013 cm$^{-1}$. Unlike the reaction under dry conditions, under wet conditions, the nitrate on the CaCO$_3$ surface increased linearly with time but did not become saturated during the experimental period, and the nitrate formation rate increased with the increasing of NO$_2$ concentrations.

Using the conversion factor $f=1.89\times10^8$ molecules/l$\lambda$, the integrate absorbance of
the nitrate peak in the range of 1077–1013 cm\(^{-1}\) was converted to the number of nitrate ions formed on CaCO\(_3\) particle surface \(\{\text{NO}_3^-\}\). The reaction order of NO\(_2\) was obtained from the slope of the double-log plot of the nitrate production rate \(d\{\text{NO}_3^-\}/dt\) versus the NO\(_2\) concentration (Fig. 9). The slope of the curve was 0.94±0.10; this means that under wet conditions, the NO\(_2\) reaction on CaCO\(_3\) particles is first order with respect to NO\(_2\).

3.4 Uptake coefficient

Reactive uptake coefficient or reaction probability, \(\gamma\), is defined as the ratio of reactive gas-surface collision rate to the total gas-surface collision rate. The reactive uptake coefficient of NO\(_2\) by the surface of the CaCO\(_3\) particles is

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

\[
Z = \frac{1}{4}A\omega n
\]

where \(N(\text{NO}_2)\) is the number of reactive NO\(_2\) collisions with the surface, \(Z\) is the total gas-surface collision rate of NO\(_2\) on the surface of CaCO\(_3\), \(A\) is the surface area of CaCO\(_3\) particles (BET surface area was used here), \(\omega\) is the mean speed of the gas molecule, and \(n\) is the concentration of gas phase species. The rate of reactive collisions can be obtained from the production rate of nitrate \(d\{\text{NO}_3^-\}/dt\), the reactive uptake coefficient then become:

\[
\gamma = \frac{2d\{\text{NO}_3^-\}/dt}{Z}
\]

Previous studies show that the reaction of NO\(_2\) with particles was through N\(_2\)O\(_4\) (Finlayson-Pitts et al., 2003), then the reactive NO\(_2\) loss rate in the gas phase is twice of the nitrate formation rate.
The nitrate formation rate \( \frac{d\{\text{NO}_3^-\}}{dt} \) could be calculated from the curve of nitrate formation as a function of time, and the nitrate formation rate in the initial stage of the reaction was used for calculating the initial uptake coefficient \( \gamma_0 \). Table 1 lists the initial uptake coefficient of \( \text{NO}_2 \) on \( \text{CaCO}_3 \) particles under both dry and wet (RH=60–71%) conditions. The initial uptake coefficient under dry conditions was \((1.09\pm0.25)\times10^{-7}\), while under wet conditions, it was slightly lower, with a value of \((0.63\pm0.33)\times10^{-7}\). To further investigate the influence of RH on the uptake of \( \text{NO}_2 \) on \( \text{CaCO}_3 \) particle, the initial uptake coefficient of the reaction was determined as a function of RH. Figure 10 shows the results. As RH increased, \( \gamma_0 \) decreased initially with increasing RH; at RH=45–53%, \( \gamma_0 \) showed a turning point and jumped to a higher value at RH=53%; with RH>53%, \( \gamma_0 \) started to increase slightly with the increasing RH.

The change of \( \gamma_0 \) with RH demonstrates the influence of water vapor on the reaction mechanism of \( \text{NO}_2 \) on \( \text{CaCO}_3 \) particles. When RH<53%, \( \text{H}_2\text{O} \) was competing with \( \text{NO}_2 \) molecules for reactive sites on the surface of \( \text{CaCO}_3 \) particles, the initial uptake coefficient of \( \text{NO}_2 \) was therefore decreasing with increasing RH.

As described in the above section, at RH=52±2%, a monolayer of adsorbed water was formed on the surface of the \( \text{CaCO}_3 \) particles, hence with RH>52%, the reaction of \( \text{NO}_2 \) on \( \text{CaCO}_3 \) particles was controlled by the reaction of \( \text{NO}_2 \) with surface condensed water on the \( \text{CaCO}_3 \) particles. This may explain why the increase of RH had little influence on \( \gamma_0 \) when RH was larger than 52%. The formation of a water layer on \( \text{CaCO}_3 \) particles suggests that the reaction mechanism of \( \text{NO}_2 \) on \( \text{CaCO}_3 \) became different from that when RH was lower than 52%.

It is puzzling to see from both Table 1 and Fig. 10 that under dry and wet conditions, \( \gamma_0 \) were varied within a narrow range of \( 0.6\times10^{-7}–1.2\times10^{-7} \). Mertes and Wagner (1995) have measured a lower limit of the mass accommodation coefficient of \( \text{NO}_2 \) on aqueous surfaces of \( \alpha\geq2\times10^{-4} \) at 278 K surface temperature. This suggests that at RH>52%, with the formation of water layer on the surface of \( \text{CaCO}_3 \) particles, \( \gamma_0 \) of \( \text{NO}_2 \) on \( \text{CaCO}_3 \) particles should have a value much higher than \( 10^{-7} \). The possible reason for a lower \( \gamma_0 \) value is that we used the specific BET surface area of \( \text{CaCO}_3 \)
particles (4.91 m² g⁻¹) to calculate γ₀, while at RH>52%, the water layer formed could make the surface of CaCO₃ particles smoother with less pores, and the available surface area for the reaction should be close to the geometric surface area of a cubic shape particle. Using 0.37 m² g⁻¹ as the specific geometric surface area of CaCO₃ particle samples, from Table 1 we calculated γ₀ at RH=60–71% to be (0.84±0.44) ×10⁻⁶; this should be the upper limit of γ₀ and is about ten times higher than γ₀ at RH<52%, when BET surface area was used. The uptake coefficient for HNO₃ on CaCO₃ was determined to be at a level of 10⁻⁴ (e.g. Goodmann et al., 2000). Considering that NO₂ concentrations in the atmosphere is orders of magnitude higher than that of HNO₃, at RH>52%, NO₂ may have similar importance of HNO₃ in the heterogeneous reactions with CaCO₃ particle in the atmosphere.

4 Discussion

We concluded from the above results that water vapor had a major influence on the heterogeneous reaction mechanism of NO₂ with CaCO₃. The reaction mechanism was different before and after a monolayer of water was formed. Prior to the formation of the monolayer of water on CaCO₃ surface, –OH was produced on the calcite surface via the dissociation of water by oxygen vacancy and this seems to be the rate determining factor for the reaction. After formation of a monolayer of water, surface condensed water participated in the reaction. We discuss the reaction mechanisms for both of these two conditions below.

4.1 Mechanism under dry conditions

Under dry conditions, the reaction mechanism proceeded as shown in Fig. 11a. At low RH, there was still some water vapor remaining and the surface adsorbed water on the
CaCO_3 surface equilibrated with water vapor, as shown in Reaction (R1):

\[ \text{H}_2\text{O}(g) \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \text{H}_2\text{O}(a) \]  
(R1)

Surface-adsorbed water existed on the CaCO_3 surface despite heating at 623 K for 2 h. The adsorbed water on the CaCO_3 surface was dissociated by an oxygen vacancy site (O) to form the active site S-(OH)H that was stable even at high temperature and high vacuum. When the surface-adsorbed water increased, the surface active site converted to adsorbed-water due to the action of the hydrogen bond:

\[ \text{site (O)} + 2\text{H}_2\text{O}(a) \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} \text{S} \cdot \text{(OH)H} + \text{H}_2\text{O}(a) \]  
(R2)

Finlayson-Pitts et al. (2003) found NO_2 was likely to form nitrogen dioxide dimmers (nitrogen tetraoxide, N_2O_4) at high concentrations, then N_2O_4 was adsorbed to the particle surface.

\[ 2\text{NO}_2(g) \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} \text{N}_2\text{O}_4(g) \]  
(R3)

\[ \text{N}_2\text{O}_4(g) \overset{k_4}{\underset{k_{-4}}{\rightleftharpoons}} \text{N}_2\text{O}_4(a) \]  
(R4)

N_2O_4 reacted with the surface active site forming adsorbed nitric acid HNO_3 and nitrous acid HONO, as illustrated in Reaction (R5):

\[ \text{N}_2\text{O}_4(a) + \text{S} \cdot \text{(OH)H} \overset{k_5}{\longrightarrow} \text{HNO}_3(a) + \text{HONO}(g) \]  
(R5)

Previous studies showed that HONO was unlikely to adsorb onto the calcite surface, but rather being released into the gas phase. Although we could not detect gas phase HONO, we did detect adsorbed HNO_3 with DRIFTS.
Surface adsorbed water was in equilibrium with water vapor, see Eq. (6), where \([x]\) indicates the concentration of gas phase species and \(\{x\}\) denotes the concentration of surface adsorbed species and active sites.

\[
\{\text{H}_2\text{O}\} = \frac{k_1}{k_{-1}} [\text{H}_2\text{O}] = K_1 [\text{H}_2\text{O}]
\] (6)

At the initial stage, surface-adsorbed water increased with RH, and the surface active site \(S\cdot(\text{OH})\text{H} \) was converted to adsorbed water.

\[
\{S \cdot (\text{OH})\text{H}\} = \frac{k_2}{k_{-2}} \{\text{site(}\text{O})\} \{\text{H}_2\text{O}\} = K_2 \{\text{site(}\text{O})\} \{\text{H}_2\text{O}\}
\] (7)

\(\text{NO}_2\) was in equilibrium with \(\text{N}_2\text{O}_4\) in the gas phase,

\[
[\text{N}_2\text{O}_4] = \frac{k_3}{k_{-3}}[\text{NO}_2]^2 = K_3[\text{NO}_2]^2
\] (8)

No adsorbed \(\text{N}_2\text{O}_4\) was observed on the particle surface, suggesting \(\text{N}_2\text{O}_4\) could be treated as an intermediate in the reaction:

\[
\frac{d\{\text{N}_2\text{O}_4\}}{dt} = k_4[\text{N}_2\text{O}_4] - k_{-4}\{\text{N}_2\text{O}_4\} - k_5\{\text{N}_2\text{O}_4\} \{\text{S} \cdot (\text{OH})\text{H}\} = 0
\] (9)

Assuming the \(\text{HNO}_3\) formed was quickly converted to \(\text{NO}_3^-\) on the surface of \(\text{CaCO}_3\), then

\[
\frac{d\{\text{NO}_3^-\}}{dt} = \frac{d\{\text{HNO}_3\}}{dt} = k_5 \{\text{N}_2\text{O}_4\} \{\text{S} \cdot (\text{OH})\text{H}\}
\] (10)

Combining Eqs. (6, 7, 8, 9, and 10), one can get

\[
\frac{d\{\text{NO}_3^-\}}{dt} = \frac{k_1 K_2 K_3 k_4 k_5 [\text{NO}_2]^2 \{\text{site(}\text{O})\}[\text{H}_2\text{O}]}{k_{-4} + K_1 K_2 k_5 \{\text{site(}\text{O})\}[\text{H}_2\text{O}]}
\] (11)
Equation (11) shows that, at the initial stage of the reaction, the amount of surface active site was relative large and formation of HNO$_3$ on the CaCO$_3$ surface was a second-order reaction with respect to NO$_2$; this is consistent with the measured reaction order of 1.63±0.23 obtained from Fig. 5.

4.2 Mechanism under wet conditions

In the above section, we showed that at RH>52%, water condensed on CaCO$_3$ forming a monolayer of adsorbed water. Here, the wet conditions refer to the conditions when RH>52%. The reaction mechanism under wet conditions was illustrated by the general scheme in Fig. 11b. NO$_2$ was adsorbed on CaCO$_3$ to form adsorbed NO$_2$(a):

$$\text{NO}_2(g) \xrightleftharpoons{k_6} k_{-6} \text{NO}_2(a) \quad (R6)$$

Previous studies have demonstrated that the disproportionation reaction of NO$_2$ with surface adsorbed water was a first-order reaction with the adsorption of NO$_2$ being the rate-limiting step (Svensson et al., 1987; Jenkin et al., 1988). The nitrite and nitrate formed on the particle surface was attributed to the reaction of surface-adsorbed water with NO$_2$; i.e., adsorbed NO$_2(a)$ reacted with condensed water H$_2$O(a) to form adsorbed HNO$_3(a)$ and gaseous HONO(g).

$$\text{H}_2\text{O}(a) + 2\text{NO}_2(a) \xrightarrow{k_7} \text{HNO}_3(a) + \text{HONO}(g) \quad (R7)$$

At the initial stage, HONO dissolved in adsorbed water to form nitrite. As the concentration of HNO$_3(a)$ increased, the surface pH decreased and nitrite was escaped from the surface as gaseous HONO. Meanwhile, HNO$_3(a)$ reacted with CaCO$_3$ to form H$_2$CO$_3$ and Ca(NO$_3$)$_2$.

$$2\text{HNO}_3(a) + \text{CaCO}_3(s) \xrightarrow{k_8} \text{Ca(NO}_3)_2(s) + \text{H}_2\text{CO}_3(a) \quad (R8)$$
Afterward, $\text{H}_2\text{CO}_3$ decomposed in adsorbed water to form $\text{H}_2\text{O}$ and $\text{CO}_2$, resulting in the decrease of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ on the surface.

$$\text{H}_2\text{CO}_3(a) \rightarrow \text{H}_2\text{O}(g) + \text{CO}_2(g) \quad (R9)$$

$\text{Ca(NO}_3)_2$ has strong hygroscopic property and the $\text{Ca(NO}_3)_2$ particles were in the form of solution droplets at RH>10% (Liu et al., 2008b); this caused the broadened peak for adsorbed water in the IR spectrum.

$$\text{Ca(NO}_3)_2(s) + n\text{H}_2\text{O}(a) \rightleftharpoons \text{Ca(NO}_3)_2 \cdot n\text{H}_2\text{O} \quad (R10)$$

Since the adsorption of $\text{NO}_2$ was the rate-limiting step and $\text{HNO}_3(a)$ was the intermediate product, the rate of nitrate production in the presence of excess surface water could be expressed as the following.

$$\frac{d[\text{NO}_3^-]}{dt} = \frac{1}{2} k_6[\text{NO}_2] \quad (12)$$

Equation (12) shows the surface nitrate formation with respect to $\text{NO}_2$ as a first order reaction; this is consistent with the experimental result of $0.94\pm0.10$ and results in the literature.

### 5 Conclusions

The initial uptake coefficient of $\text{NO}_2$ on $\text{CaCO}_3$ particles $\gamma_0$ was found to change with increasing relative humidity. Using BET surface area, $\gamma_0$ under dry conditions (RH~0%) was determined to be $(1.09\pm0.25) \times 10^{-7}$, while under “wet” conditions (RH=60–71%), it was slightly lower, with a value of $(0.63\pm0.33) \times 10^{-7}$. Our results show that relative humidity had a major influence on the surface properties of $\text{CaCO}_3$ particles by not only influencing the initial uptake coefficient but also by changing the reaction mechanism. At RH<52%, surface –OH produced via the dissociation of surface-adsorbed water
by an oxygen vacancy on the CaCO_3 surface was the rate determining factor in the reaction. Before surface –OH was depleted, the reaction was second order in NO_2. At RH>52%, a water layer of more than a monolayer was formed and NO_2 reacted with water on the surface of CaCO_3 to produce HNO_3 and HONO; at this stage, the reaction was the first order in NO_2.

At RH>52%, the water layer formed could make the surface smoother with less pores, and the surface area should be much smaller than the BET surface area. Using 0.37 m^2 g^{-1} as the specific geometric surface area of CaCO_3 particle samples, we calculated \( \gamma_0 \) at RH=60–71% to be (0.84±0.44)×10^{-6}; this is about ten times higher than that under dry conditions and could be used as the upper limit of \( \gamma_0 \). Considering the uptake coefficient for HNO_3 on CaCO_3 is at a level of 10^{-4} and NO_2 concentrations in the atmosphere is orders of magnitude higher than that of HNO_3, at RH>52 %, NO_2 should have similar importance of HNO_3 in the heterogeneous reactions with CaCO_3 particle in the atmosphere, and the NO_2 reaction with water adsorbed on CaCO_3 could also be an important source of HONO in the atmosphere. Further efforts to detect HONO formed in the reaction of NO_2 on CaCO_3 particles are under way.

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References


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Table 1. Initial uptake coefficient of NO$_2$ on CaCO$_3$ particles under dry and wet conditions. The RH was measured at 296 K.

<table>
<thead>
<tr>
<th>Replicate time</th>
<th>[NO$_2$] ($10^{15}$ molecule cm$^{-3}$)</th>
<th>$\gamma_0 \pm 2\sigma$ ($10^{-7}$)</th>
<th>RH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>6.90–16.84</td>
<td>1.09±0.25</td>
<td>dry</td>
</tr>
<tr>
<td>5</td>
<td>4.58–11.40</td>
<td>0.63±0.33</td>
<td>60–71</td>
</tr>
</tbody>
</table>
Fig. 1. Isotherm adsorption curve of water vapor on CaCO$_3$ particles at 296 K. IR absorbance of the stretching vibration of –OH of adsorbed water is integrated between 3644 and 2983 cm$^{-1}$. A monolayer of water was formed at 52% RH, based on the calculation using the BET equation (filled black square indicates the integration area of water; ○ denotes the number of single-molecule water layers).
Fig. 2. Double-log curve of NO$_3^-$ production rate versus [H$_2$O]. The reaction order with respect to H$_2$O(g) was $-0.44$ at RH<50%, and was 0.20 at RH>50%.
**Fig. 3.** Typical IR spectra of CaCO₃ particles after reaction with NO₂ at 296 K and reaction times of 0 to 100 min. RH was <10%, NO₂ concentration was 1.22×10¹⁶ molecule cm⁻³.
Fig. 4. Nitrate formation as a function of time during the reaction of CaCO$_3$ with NO$_2$. The nitrate concentration is represented by the integrated absorbance of the peak area between 1077 and 1013 cm$^{-1}$. The NO$_2$ concentration was changed from $4.81 \times 10^{15}$ to $1.22 \times 10^{16}$ molecule cm$^{-3}$. The data points and the error bars are the average value and the standard deviation of three duplicate experiments.
Fig. 5. Double-log curves of nitrate-producing rate versus NO$_2$ concentration. The data points and error bars are the average values and standard deviations of three replicate experiments. The reaction order was of NO$_2$ 1.63±0.23 in stage I, and 0.41±0.55 in transition stage II.
**Fig. 6.** Typical IR spectrum for CaCO$_3$ reacted with NO$_2$ under wet condition at reaction time of 0 to 60 min.
Fig. 7. (a) IR spectrum of CaCO$_3$ particles after reaction with $1.06 \times 10^{16}$ molecules cm$^{-3}$ of NO$_2$ for 60 min after Gaussian peak fitting. (b) Change in integrated absorbance of each peak with reaction time.
Fig. 8. Nitrate formation as a function of time during the reaction of CaCO$_3$ with NO$_2$ at 60–71%RH. The nitrate concentration is represented by the integrated absorbance of the peak area between 1077 and 1013 cm$^{-1}$. The NO$_2$ concentration was changed from $4.58 \times 10^{15}$ to $1.14 \times 10^{16}$ molecule cm$^{-3}$. The data points and the error bars are the average value and the standard deviation of three duplicate experiments.
Fig. 9. Double-log plot of the nitrate production rate versus the NO$_2$ concentration. The reaction was at 296 K and RH=66±2%. The data points and error bars are the average values and standard deviations of two or three replicate experiments.
Fig. 10. Initial uptake coefficient of NO$_2$ on CaCO$_3$ at different RH, the NO$_2$ concentration was $6.88 \times 10^{15}$ molecules cm$^{-3}$ for uniform format. The horizontal error bars are the errors of RH measurements.
Fig. 11. Schematics of the mechanism of NO$_2$ reaction on the surface of CaCO$_3$ particles under (a) dry and (b) wet conditions.
Fig. A1. Apparatus for gas preparation.
**Fig. A2.** XPS spectrum of O1s at the surface of CaCO$_3$ particles.
Fig. A3. Typical XPS spectrum (a) and IC chromatogram (b) of CaCO$_3$ particle after reacted with $1.06 \times 10^{15}$ molecules cm$^{-3}$ NO$_2$ for 626 min.
Fig. A4. XPS spectrum (a) and IC chromatogram (b) analysis of CaCO$_3$ particles after reaction with $1.06 \times 10^{16}$ molecules cm$^{-3}$ of NO$_2$ at RH=80±2% for 30 min. The dashed line in (a) was the Lorentzian peak fit.
Fig. A5. Typical IR spectrum of CaCO$_3$ after reacted with HNO$_3$ for 0 to 40 min.