The effects of nitrate on the heterogeneous uptake of sulfur dioxide on hematite


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Abstract

Nitrate is often found to be associated with atmospheric particles. Surface nitrate can change the hygroscopicity of these particles, and thus impact their chemical reactivity. However, the influence of nitrate on the heterogeneous reactions of atmospheric trace gases is poorly understood. In this work, the effects of nitrate on heterogeneous conversion of SO$_2$ with hematite at 298 K were investigated using an in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and a White cell coupled with Fourier transform infrared spectroscopy (White cell-FTIR). It is found that nitrate participates in the heterogeneous reactions of SO$_2$, accelerates the formation rate of sulfate, and leads to the formation of surface-adsorbed HNO$_3$ and gas-phase N$_2$O and HONO, revealing that nitrate has a significant impact on the heterogeneous conversion of SO$_2$ to sulfate. The results indicate that small amounts of nitrate significantly enhance the reactivity of hematite-nitrate mixtures and favor the enhancement in SO$_2$ uptake and an increase in the amount of sulfate on hematite. For mixtures, the sample containing 24 % nitrate exhibits the highest sulfate formation rate, and its corresponding average sulfate formation rate is about 5 times higher than that of hematite alone. No uptake of SO$_2$ and formation of sulfate are observed on the pure nitrate. Evidence presented herein implies a significant contribution of the unreleased HNO$_3$ and HONO in the particles for the conversion of SO$_2$ and the enhanced formation of sulfate in the atmosphere. A possible mechanism for the influence of nitrate on the heterogeneous conversion of SO$_2$ on hematite is proposed, and atmospheric implications based on these results are discussed.

1 Introduction

Sulfur dioxide is a major component of air pollution. It is usually generated by the combustion of fossil fuels and by the atmospheric oxidation of biogenic organic sulfur compounds, particularly dimethyl sulfide. The oxidation of sulfur dioxide leads to sul-
fate particulate formation. Atmospheric sulfate particles play significant roles in adverse health effects, visibility degradation and rain water acidification (Seinfeld and Pandis, 2006). The conversion of SO$_2$ to sulfate in the atmosphere usually occurs via three well-known pathways, including gas-phase oxidation to sulfuric acid followed by condensation into the particulate-phase, aqueous-phase oxidation in cloud or fog droplets, and various heterogeneous reactions on the surfaces of aerosol particles (Kerminen et al., 2000). There have been a number of atmospheric chemistry models applied to predict the formation of sulfate aerosols on a global scale (Kasibhatla et al., 1997; Laskin et al., 2003). The results suggest that atmospheric SO$_2$ concentrations are typically overestimated while sulfate concentrations tend to be underestimated (Kasibhatla et al., 1997; Laskin et al., 2003), and the two pathways including gaseous oxidation by OH radical and aqueous oxidation in cloud or fog droplets are not enough to bridge the gap between field and modeling studies (Luria and Sievering, 1991), implying that the heterogeneous conversion of SO$_2$ to sulfate on aerosols may make an important contribution to the atmospheric sulfate concentration, or there are some unknown pathways for the formation of sulfate in the troposphere. The heterogeneous oxidation of SO$_2$ to sulfate on atmospheric aerosol has therefore received more and more attention in recent years. To date there have been a lot of studies regarding heterogeneous reactions of SO$_2$ on various model oxides and mineral dust particles (Dentener et al., 1996; Goodman et al., 2001; Usher et al., 2002; Ullerstam et al., 2003; Baltrusaitis et al., 2007; Lin et al., 2010; Zhu et al., 2011; Wu et al., 2011; Liu et al., 2012). However, the atmospheric heterogeneous reactions of SO$_2$ still have large uncertainties (Laskin et al., 2003), and the underlying formation mechanisms of sulfate on mineral aerosols are not completely understood (Dentener et al., 1996). For example, in the atmosphere, the heterogeneous reactions of SO$_2$ are unavoidably affected by other atmospheric species, but little concern has been paid to the effects of other species on the heterogeneous reaction of SO$_2$ in the laboratory studies up to now (Ullerstam et al., 2003; Lin et al., 2010; Wu et al., 2011; Liu et al., 2012).
Mineral dust aerosol, emitted from the arid and semi-arid regions with a global source strength of about 1000–3000 Tgyr$^{-1}$, is one of the most important contributors to the airborne particulate matter (Dentener et al., 1996). It is now widely recognized that mineral dust aerosols provide reactive surfaces for atmospheric trace gases, and the reactions on mineral dust particles change their size distribution, optical and hygroscopic properties and their lifetime in the atmosphere, which, in turn, can change the climate impact of these particles. Mineral oxide represents an important and reactive component of mineral dust aerosol. Being one of the typical oxide minerals, Fe$_2$O$_3$ contributes $\sim$ 6% by mass to the total dust burden in the atmosphere (Usher et al., 2003). Atmospheric chemical processing of Fe-containing dust particles during long-range transport can impact the amount of soluble iron (Zhuang et al., 1992; Meskhidze et al., 2003), while soluble iron will limit phytoplankton primary productivity in extensive regions of the ocean referred to as high-nutrient low-chlorophyll regions (Moore et al., 2002), which ultimately has implications for global climate, carbon and nitrogen cycles (Jickells and Spokes, 2001). Thus, there is interest in the atmospheric chemistry of Fe$_2$O$_3$. On the other hand, field studies have also observed that nitrate is one of the most common components of secondary particles. It’s often found to be associated with these mineral dust particles in the atmosphere (Dentener et al., 1996). Surface nitrate enhances the hygroscopic properties of the original particles and, in turn, changes their physicochemical properties (Hoffman et al., 2004), which inevitably impacts their chemical reactivity, and therefore leads to a remarkable difference in their heterogeneous chemistry. However, little concern has been paid to the influence of nitrate on the heterogeneous reactions of SO$_2$ on atmospheric aerosols up to now (Lin et al., 2010).

In the present study, the effects of nitrate on heterogeneous conversions of SO$_2$ on mineral particles at room temperature are investigated using an in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and a White cell coupled with Fourier transform infrared spectroscopy (White cell-FTIR). Hematite ($\alpha$-Fe$_2$O$_3$, one of the typical components in mineral aerosol) and sodium nitrate (a major form of
nitrate in sea-salt particles) were used as model components of particles. The heterogeneous conversion mechanism of SO$_2$ is proposed and atmospheric implications of the present study are discussed. The results are helpful for the further understanding of a new potential formation pathway of sulfate aerosol in the troposphere and the mutual influences between the formation processes of sulfate and nitrate, as well as the significant contribution of the unreleased HNO$_3$ and HONO in the particles for the conversion of SO$_2$ and the enhanced formation of sulfate in the atmosphere. Understanding this chemistry will also contribute to the elucidation of the formation of atmospheric N$_2$O.

2 Experimental

2.1 Materials

Hematite was prepared according to the procedure reported previously (Schwertmann and Cornell, 2000). Powder X-ray diffraction confirmed the prepared sample as pure hematite (Fig. S1 in the Supplement). The Brunauer–Emmett–Teller (BET) surface area was 12.1 m$^2$ g$^{-1}$ (Micromeritics TriStar 3000, Micromeritics Instrument Co., USA). Sodium nitrate (Analytical grade, Shanghai Ab Chem Co. Ltd.) was used without further purification. Gaseous oxygen, argon (99.999 % purity, Shanghai Yunguang Specialty Gases Inc.), and SO$_2$ (97 ppm, SO$_2$/N$_2$, Shanghai Yunguang Specialty Gases Inc.) were introduced through an air-dryer before use.

In order to systematically study the effects of nitrate on the heterogeneous reactions of SO$_2$ with atmospheric aerosols, a series of hematite-sodium nitrate mixtures with the mass fractions of sodium nitrate in the mixtures in the range of 2–90 % (w/w) (denoted as FN-2, FN-6, . . . , FN-90, respectively) were prepared. Hematite was impregnated with a saturated aqueous solution of sodium nitrate, and then the mixtures were stirred manually and dried under an infrared lamp. Considering that aerosol particles in the real atmosphere invariably contain surface-adsorbed water and the surface-adsorbed water plays an important role in the heterogeneous chemistry of atmospheric SO$_2$, all
the prepared particle samples were kept in a desiccator at 68% relative humidity (RH) at least for 48 h before further use. The humid samples were still loose fine powders after the saturation, and this treatment made some adsorbed water molecule layers be present on the samples.

2.2 In situ DRIFTS experiments

In situ DRIFTS spectra were recorded on the Nicolet Avatar 360 FTIR spectrometer, equipped with a high-sensitivity mercury cadmium telluride (MCT) detector and a Spectra-Tech diffuse reflectance accessory, just as described previously (Fu et al., 2007, also see Fig. S2 in the Supplement). 30 mg of sample was placed into the ceramic crucible in the in situ chamber, and a sample temperature controller was used to control reaction temperature. Before the reaction gas was introduced, the reaction chamber was purged with argon (100 mL min\(^{-1}\)) for 1 h, and then a background spectrum of the unreacted powder sample was collected. Subsequently, a mixture of SO\(_2\) (e.g. 3 ppm) and O\(_2\) (21% \(v/v\)) with argon carrier was introduced into the chamber at a total flow rate of 100 mL min\(^{-1}\), and then IR spectra were collected as a function of reaction time. The total reaction time is about 4–6 h. All spectra reported here were recorded at a resolution of 4 cm\(^{-1}\) for 100 scans. All of the measurements were repeated three times.

2.3 In situ White cell-FTIR experiments

An infrared cell (White cell reactor, Model 19-V, a variable-path long path cell with the optical path length from 2.4 to 24 m. Infrared Analysis, Inc.) coupled to a Fourier transform infrared spectrometer was used to measure trace gaseous reactants and the possible gaseous products formed from the heterogeneous reaction of SO\(_2\). The optical path length was set to the maximum for all of the measurements. The infrared cell was cleaned by ultra-pure water and then dried before every experiment. The infrared cell was connected to a vacuum system and a gas supply system. The apparatus has
been described in detail elsewhere (Fu et al., 2007; Zhang et al., 2006; also see Fig. S3 in the Supplement). For in situ FTIR measurements, the experiments were conducted in the absence of light. The infrared cell was flushed with pure argon with the aid of the vacuum system, and this cleaning process was repeated three times before the sample was placed into the infrared cell. The sample, weighing 30 mg, was put in a small reaction disc (inner diameter = 1 cm, depth = 0.1 cm) made of quartz, and then the disc was placed into the infrared cell. After the sample was placed, argon was filled into the cell again to $1.01 \times 10^5$ Pa, the background spectrum of the gases was collected, and then the infrared cell was evacuated to 20 Pa again. Argon was used as a carrier gas to load the reactive gases SO$_2$ and O$_2$ into the infrared cell through the gas supply system. After the infrared cell was filled to a pressure of $1.01 \times 10^5$ Pa, it remained at that pressure for 3 min to ensure homogeneous mixing of the gases in the infrared cell before starting to collect the in situ IR spectra. FTIR spectra were recorded on a Nicolet Avatar 360 FTIR equipped with a liquid nitrogen cooled MCT detector. 100 repeat spectral scans were averaged over a range of 600–4000 cm$^{-1}$ at a spectral resolution of 4 cm$^{-1}$. A single-beam spectrum was used as a reference spectrum, which was collected prior to the SO$_2$ exposure. In order to trace the formed gaseous species, sometimes a much longer reaction time scale (up to 20 h) was adopted. The peak areas of the characteristic peaks of SO$_2$ are shown to have a linear correlation with the concentration of SO$_2$ ($R^2 > 0.999$). Thus, the concentration of gaseous SO$_2$ can be determined by measuring the corresponding in situ FTIR spectra peak areas of gaseous SO$_2$. All of the measurements were repeated at least twice.

2.4 Heterogeneous reaction of SO$_2$ in the dark

Heterogeneous reactions of SO$_2$ (50 ppm) on humid hematite, FN-24 and FN-90 were performed in the presence of O$_2$ (21 % v/v) in three 42 mL brown glass bottles in the dark at room temperature for about 3–7 days, respectively. An about 30 mg sample, which was kept in a desiccator at 68 % RH for 48 h, was placed flatly on the bottom
of the glass bottle, in order to make sure that no sample particles were stuck on the interior wall of glass bottle. Before the reaction gas SO$_2$ was introduced, a mixture of Ar and O$_2$ (21 % v/v) was introduced into the bottle at a total flow rate of 100 mL min$^{-1}$ to expel air from the bottle for an hour, after which the inlet and the outlet of the bottle were closed. Then 2.1 µL of SO$_2$ (50 ppm) was injected through the septum into the bottle with a microsyringe. The bottle was packed in aluminum foil and then placed in the dark for 3–7 days.

### 2.5 Ion analysis and N$_2$O detection

The products formed on the sample surface were analyzed by ion chromatography after DRIFTS experiments. The method is similar to that in a previous study (Ullerstam et al., 2002). The reacted sample particles were extracted by sonication with ultrapure water (specific resistance $\geq$ 18.0 M$\Omega$ cm). The leaching solution contained 1 % formaldehyde as a preservative to suppress sulfite oxidation and was obtained through a 0.45 µm PTFE membrane filter. The filtered solution was analyzed using a Dionex DX 500 ion chromatography, which was equipped with a Dionex AS 14 analytical column and a CD20 conductivity detector. A weak base eluent (1.0 mM NaHCO$_3$ – 3.5 mM Na$_2$CO$_3$) was used for anion detection at a flow rate of 1.5 mL min$^{-1}$. Quality assurance of species measurement was routinely carried out by using standard reference materials produced by the National Research Center for Certified Reference Materials, China.

A solid phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS) method was also used to detect nitrous oxide (Drescher et al., 2006). SPME was carried out using a commercial SUPELCO 75 µm Carboxen/PDMS fiber to qualitatively analyze N$_2$O. Before the fiber was used for the first time, the fiber was conditioned at 280°C until a clean chromatogram was obtained under normal run conditions. In addition, to minimize background signals, the fibers were heated in the GC inlet for 2 to 5 min before each sampling. The SPME fiber was directly inserted in the White Cell reactor or brown glass bottle for 30 min at room temperature for
the collection of gas-phase N$_2$O. The analysis was performed using a GC-MS (Agilent, USA) fused-silica capillary column (HP-5MS, J & W Scientific, Folsom, CA, USA, 30 m × 0.25 mm I.D., 0.25 µm film thickness). The carrier gas was high purity helium (99.999%, 1.0 mL min$^{-1}$). The mass spectrometer was operated in the electron ionization (EI) mode at the electron energy of 70 eV. Thermal desorption of retained compounds on fiber was carried out at 260°C in splitless mode. Prior to running a sample analysis, a blank analysis had been performed.

3 Results and discussion

3.1 Effect of nitrate on surface species formed from the uptake of SO$_2$ onto hematite

In situ DRIFTS experiments were carried out on humid hematite, pure nitrate and a series of hematite-sodium nitrate mixtures with 2–90% of mass fractions of nitrate, respectively. Each experiment was performed at 298 K with 30 mg of sample to investigate the effects of nitrate on the uptake of gas-phase SO$_2$ onto the sample particle surface and the nature of the formed surface-bound species.

3.1.1 Surface sulfur-containing species

Figure 1a shows the in situ DRIFT spectra of surface species produced on pure hematite after exposure to SO$_2$. As can be seen in Fig. 1a, four prominent peaks at 1261, 1219, 1158 and 1056 cm$^{-1}$ and three weak shoulder peaks at 1361, 1337 and 1000 cm$^{-1}$ are readily observed in the spectra. The intensities of these peaks increase as the reaction proceeds. These peaks can be assigned to the adsorbed bisulfate and/or sulfate on the particle surface based on assignments in previous studies (Yamaguchi et al., 1986; Watanabe et al., 1994; Persson and Lovgren, 1996; Hug, 1997; Sugimoto and Wang, 1998; Nanayakkara et al., 2012). Watanabe et al. observed in-
indeed observed infrared absorption peaks at 1360, 1270, 1150 and 1020 cm$^{-1}$ for the sulfated hematite at 25°C (Watanabe et al., 1994), and suggested that the peak at 1270 cm$^{-1}$ was assigned to the symmetric stretching vibration mode of S=O and the peak at 1150 cm$^{-1}$ was assigned to the asymmetric stretching vibration mode of S-O. A transmission FTIR study on SO$_2$ reacted TiO$_2$ surface has also shown peaks at 1361, 1297, 1172, 1116, 1050 and 1000 cm$^{-1}$, which were assigned to adsorbed sulfate species. The observed peak at 1335 cm$^{-1}$ was also observed by Nanayakkara et al. and was thought to be most likely due to the formation of sulfate (Nanayakkara et al., 2012). Therefore, in the present study, the prominent peaks at 1261, 1158, 1056 and 1000 cm$^{-1}$ reflect the formation of adsorbed sulfate. Additionally, peak fitting using a mixture of Lorenztian and Gaussian lineshapes to deconvolute overlapping peaks of every single spectrum of an experiment shows that the peaks at 1261 and 1158 cm$^{-1}$ synchronously increase in intensity as the reaction time increases, while the peak at 1219 cm$^{-1}$ shows a completely different behavior. The peak at 1219 cm$^{-1}$ rapidly grows in the early stage of the reaction, reaches a plateau, and then decreases in intensity slightly as the reaction proceeds, implying that the peak at 1219 cm$^{-1}$ should be assigned to different surface species and this species undergoes secondary chemistry on the sample surface. Faguy et al. studied the structure of bisulfate or sulfate adsorbed on the Pt (111) surface by PDFTIR and found that a maximum at 1227–1250 cm$^{-1}$ was consistent with adsorbed bisulfate or adsorbed sulfate-H$_3$O$^+$ ternary complexes on the Pt (111) electrode surface (Faguy and Marinković, 1996). Hug (1997) found that a peak at or above 1200 cm$^{-1}$ appeared after drying of the hematite layer treated with sulfate at pH 3.6 or with hematite in contact with aqueous sulfate solutions acidified to below pH 2 with HCl. He thought that the conversion of aqueous sulfate to bisulfate occurred during acidification, and thus the peak around 1200 cm$^{-1}$ was assigned to the transformation from monodentate to bidentate coordination caused by drying or to the formation of bisulfate. Sugimoto and Wang (1998) further revealed that the adsorption mode of sulfate was changed from monodentate to bidentate with decreasing pH and that the bidentate adsorption on the $\{012\}$ and $\{1m0\}$ faces of hematite became dominant at
pH ≤ 1.0, and they thought that the enhancement of the peak at 1205 cm\(^{-1}\) with direct drying of a wet sample at pH 3.6, found by Hug (1997), seemed to be due to the pH drop during the drying process. Obviously, the attribution of the peak at around 1200 cm\(^{-1}\) remains arguable, however, the appearance of this peak undoubtedly reflects the enhancement of surface acidity. Therefore, in the present study, the increase in the peak intensity at 1219 cm\(^{-1}\) with the increase of reaction time indicates the increased surface acidity (Yamaguchi et al., 1986; Persson and Lovgren, 1996; Faguy and Marinković, 1996; Hug, 1997). Upon exposure of SO\(_2\), the surface-adsorbed H\(_2\)O was gradually consumed and the surface acidity of hematite was gradually enhanced. The transformation of the adsorption mode of the surface-formed sulfate would occur with the increase of the surface acidity and the drying of the particles, and then the peak at 1219 cm\(^{-1}\) appeared (Yamaguchi et al., 1986; Persson and Lovgren, 1996; Faguy and Marinković, 1996; Hug, 1997). The slight decrease in intensity of the peak at 1219 cm\(^{-1}\) after it reaches the maximum may be due to partial dissolution of hematite involving consumption of surface acidic species, which would lead to the formation of Fe\(^{3+}\) ions and some other surface species on the water-containing surface (Chun and Quon, 1973; Shi et al., 2011). Additionally, a broad peak containing several weak peaks, especially at the beginning of the reaction, is also observed between 1100 and 900 cm\(^{-1}\). Several peaks in this region can be assigned to the stretching motion of adsorbed sulfite and/or bisulfite based on previous studies on SO\(_2\) adsorption on different metal oxide surfaces (Zhang et al., 2006; Wu et al., 2011; Nanayakkara et al., 2012). These peaks can be overlapped by the symmetric stretching of sulfate in this region (Nanayakkara et al., 2012; Zhang et al., 2006), and it is difficult to distinguish these absorption peaks in this region due to the increase of surface sulfate species and the decrease of surface sulfite species during the reaction. These results indicate that surface S(IV) species such as adsorbed or surface-coordinated H\(_2\)SO\(_3\), HSO\(_3^-\), SO\(_3^-\) species were converted to sulfate in the reaction process and some S(IV) species have not been completely oxidized to sulfate on the pure hematite surface after the experiment.
Figure 1b shows the typical spectra of the oxidation of \( \text{SO}_2 \) on FN-24 recorded as a function of time in the range of 1500 to 900 cm\(^{-1}\). In Fig. 1b, a prominent peak at 1158 cm\(^{-1}\), a shoulder peak at 1190 cm\(^{-1}\) and two weak peaks at 1080 and 987 cm\(^{-1}\) are observed in the spectra. These peaks can be assigned to the peaks of surface-coordinated sulfate species, that is, bidentate surface sulfate complex (Zhang et al., 2006; Persson and Lovgren, 1996; Hug, 1997; Peak et al., 1999). Additionally, it is also possible that the feature at 1190 cm\(^{-1}\) is assigned to bisulfate (\( \text{HSO}_4^- \)) or sodium sulfate (\( \text{NaSO}_4^- \)) sorbed as a monodentate complex on the iron oxide surface, or monodentate sulfate that is hydrogen bonded to an adjacent surface site (Hug, 1997; Peak et al., 1999). In addition, \( \text{Fe}^{3+} \) ions is present due to the partial dissolution of hematite in the water-containing acidic surface during the reaction (Chun and Quon, 1973; Shi et al., 2011), and an iron (III) bisulfate complex (\( \text{Fe-HSO}_2^+ \)) can also potentially explain the observed feature at 1190 cm\(^{-1}\) (Peak et al., 1999). These results indicated that \( \text{SO}_2 \) can also be oxidized to sulfate on the surface of the hematite-nitrate mixture. Compared with that of hematite, the spectrum lineshapes are different from those of hematite, and the most apparent FTIR feature corresponding to the increase of surface product on FN-24 is the rapidly growing peak at 1158 cm\(^{-1}\) as the reaction proceeds, indicating that the adsorbed sulfate is the dominant oxidation product. Obviously, \( \text{NO}_3^- \) ions in the nitrate-hematite mixture promote the heterogeneous uptake of \( \text{SO}_2 \) and impact the formation of surface species and the adsorption mode of the formed surface species. A spectral peak-fitting program using mixed Gaussian–Lorentzian peak fitting is employed to fit peaks to the last spectrum in Fig. 1b. As shown in Fig. 2, the region from 1400 to 900 cm\(^{-1}\) is composed of three major peaks, which appear at 1094, 1155 and 1207 cm\(^{-1}\), respectively. A very weak peak at 986 cm\(^{-1}\) cannot even be seen in Fig. 2. The relative intensity of the observed peaks at 1207, 1155, 1094 and 986 cm\(^{-1}\) is approximately 5.6:16.1:2.2:0.1, respectively. The presence of the peak at 1207 cm\(^{-1}\) clearly indicates that the FN-24 surface after the experiment is still acidic. Moreover, compared with that of the hematite-only substrate, weak absorption peaks at 1080, 1050 and 966 cm\(^{-1}\) appear in the initial stage of heterogeneous conversion.
of \( \text{SO}_2 \) and then gradually disappear or are not easily observed with increased exposure time. These peaks should be assigned to the stretching motion of adsorbed sulfite and/or bisulfite (Zhang et al., 2006). The changes in intensity of these weak absorption peaks implies that the formation of \( \text{SO}_3^{2-} \) and/or \( \text{HSO}_3^- \) and their subsequently rapid consumption on the particle surface. The rapidly growing peak at 1158 cm\(^{-1}\) as the reaction proceeds also suggests that \( \text{SO}_3^{2-} \) and \( \text{HSO}_3^- \) are additionally oxidized in the presence of nitrate and less \( \text{SO}_3^{2-} \) and \( \text{HSO}_3^- \) are left when compared with that of hematite-only substrate.

### 3.1.2 Surface nitrogen-containing species

It should be noted that, compared to the peaks of the formed surface-adsorbed sulfate, some very low intensity signals appear in the region of 3800 to 1350 cm\(^{-1}\) during the same experiment (also see Fig. S4 in the Supplement). Figure 3 shows the DRIFTS spectra following \( \text{SO}_2 \) uptake on FN-24 particles as a function of increasing reaction time in this region in the same experiment. As shown in Fig. 3, negative peaks at 1599, 1587 and 1567 cm\(^{-1}\) decrease in intensity with increased exposure time. These peaks are assigned to bridging, bidentate and monodentate nitrate, respectively (Hixson et al., 2011; Underwood et al., 1999). This clearly indicates the loss of adsorbed nitrate on FN-24 and suggests that nitrate not only participates in the heterogeneous conversion of \( \text{SO}_2 \) on FN-24 but also have been consumed during the reaction. This result is consistent with the formation of nitrogen-containing species such as \( \text{N}_2\text{O} \) and HONO (discussed later in Sect. 3.4). However, it should be pointed out that the amount of the decay of nitrate is small during the reaction, which also results in small amounts of \( \text{N}_2\text{O} \) and HONO.

Several weak peaks in the 1535–1440 cm\(^{-1}\) region grow with increasing exposure time. These peaks can be assigned to adsorbed nitrite. The peaks at 1506 and 1487 cm\(^{-1}\) are assigned to the \( \nu_3 \) mode of bridging nitro-nitrito \( \text{NO}_2^- \) and the \( \nu_3 \) mode of
bridging monodentate nitrito $\mathrm{NO}_2^-$ respectively, suggesting the formation of very small amounts of nitrite products (Hixson et al., 2011).

Molecularly adsorbed nitric acid and different nitric acid-water complexes, characterized by the peaks at 1676, 1686, 1697 and 1716 cm$^{-1}$ (McCurdy et al., 2002; Ramazan et al., 2006; Finlayson-Pitts et al., 2003), are also observed. These peaks are ascribed to the $\nu_2$ mode of the asymmetric NO$_2$ stretch in nitric acid (monomer or when complexed to water or another HNO$_3$) (McCurdy et al., 2002; Ramazan et al., 2006; Finlayson-Pitts et al., 2003), and the peaks at 1676, 1686, 1697 and 1716 cm$^{-1}$ are due to HNO$_3$·(H$_2$O)$_2$, (HNO$_3$)$_2$, HNO$_3$·H$_2$O, HNO$_3$·(H$_2$O)$_n$ on the surface, respectively. These peaks increase in intensity with increased exposure time. This result has confirmed that the adsorbed HNO$_3$ is formed from the combination of surface H$^+$ with NO$_3^-$ as the reaction proceeds. The formation of the HNO$_3$·H$_2$O complex indicates that nitric acid is stabilized by water on the particle surface (McCurdy et al., 2002; Ramazan et al., 2006; Finlayson-Pitts et al., 2003). As a result, no gas phase HNO$_3$ is observed in the White cell-FTIR experiments. Compared to the assignments of molecular adsorbed nitric acid, molecular nitric acid complexed to water and complexed to HNO$_3$ itself in the previous reports, these peaks have blue shifted by about 6 cm$^{-1}$ (McCurdy et al., 2002; Ramazan et al., 2006), indicating that the asymmetric NO$_2$ stretch in nitric acid may be affected by some other interaction, and the interaction may result in the distortion of the molecular symmetry of these complexes (Peak et al., 1999).

A weak shoulder peak at 1746 cm$^{-1}$ is seen to grow as the surface is exposed to SO$_2$. This peak overlaps with those of adsorbed HNO$_3$ and the amount of the adsorbed species corresponding to this peak increases with the amount of adsorbed nitric acid on the surface. The peak should be attributed to N$_2$O$_4$ adsorbed on the surface, indicating the formation of adsorbed N$_2$O$_4$. The peak has blue shifted by about 6 cm$^{-1}$ relative to previous studies (Goodman et al., 1999; Finlayson-Pitts et al., 2003), which may suggest that N$_2$O$_4$ is interacting with HNO$_3$ and/or HNO$_3$·H$_2$O water complexes on the surface through hydrogen bonds, perhaps in addition to the interactions with H$_2$O (Finlayson-Pitts et al., 2003). It further indicates that the formed N$_2$O$_4$ may be
held on the particle surface under the influence of nitric acid and H$_2$O, which is also consistent with the fact that no gas phase N$_2$O$_4$ is detected in the White cell-FTIR experiments. Surface N$_2$O$_4$, which can oxidize many organic and inorganic compounds, was observed as the crucial oxidant for the oxidation of surface sulfite (Liu et al., 2012). Therefore, the presence of a very small amount of N$_2$O$_4$ on particle surface may contribute to the oxidation of surface sulfite and the formation of sulfate and adsorbed nitrite.

### 3.1.3 Surface hydroxyl groups

Two negative absorption peaks are observed at 3661 and 3631 cm$^{-1}$ and grow in intensity as the reaction proceeds. These negative peaks have been previously reported and attributed to the loss of OH groups from the surface. The peaks at 3661 and 3631 cm$^{-1}$ are the stretching vibration modes of the isolated surface hydroxyl groups bonded to the surface iron ions of the octahedral sites and the tetrahedral sites, respectively (Watanabe et al., 1994), which implies that the surface OH groups are involved in the reaction and are the reaction active sites for SO$_2$ (Goodman et al., 2001). Pure hematite shows similar absorption. Another weak broad absorption peak extending from 2900 to 3500 cm$^{-1}$ increases in intensity slowly with the increase of reaction time. This broad peak is primarily associated with O-H vibration of hydrogen-bonded OH groups of acid and should be assigned to molecular nitric acid complexed to water or to some extent complexed to HNO$_3$ itself (Børensen et al., 2000; Ramazan et al., 2006; Finlayson-Pitts et al., 2003), which is consistent with the formation of surface-adsorbed HNO$_3$.

Overall, the results mentioned above clearly indicate that nitrate participates in the heterogeneous reactions of SO$_2$, changes the conversion pathway of SO$_2$ and the formation rate of sulfate, and leads to the formation of surface HNO$_3$, N$_2$O$_4$ and NO$_2^-$ species. A summary of the assignments for the surface species peaks observed in this study based on frequencies reported in earlier studies is given in Table 1.
3.2 Effect of nitrate on the rate of sulfate formation on hematite-nitrate mixture at 298 K

The formation rates of sulfate on different samples were investigated. All the DRIFTS experiments were performed at 298 K with 30 mg of sample, and the amount of sulfate on each sample after DRIFTS experiment was determined by ion chromatography to quantify the sulfate formation rate $\frac{d[SO_4^{2-}]}{dt}$. It is found that over a large concentration range the integrated sulfate absorption (1000 cm$^{-1}$ to 1400 cm$^{-1}$) is proportional to the sulfate concentration. The formation rate is therefore translated from the integrated sulfate absorbance of the spectrum to the total number of sulfate ions on the sample after the reaction by a conversion factor. The conversion factor is obtained from a calibration plot with integrated sulfate absorption vs. number of sulfate ions formed at the end of an experiment, and a value of $f = 2.89 \times 10^{18}$ ions g$^{-1}$ integrated absorption units$^{-1}$ is calculated. Since the absorption peaks of the different reaction product species overlap one another, sometimes the peaks are deconvoluted before integration.

The gas-phase concentrations of the reactive gases in a continuous flow were kept constant during the DRIFTS experiments and since O$_2$ was very abundant as compared to that of SO$_2$, the concentration of O$_2$ could be regarded as constant. The formation of sulfate generally proceeds via an initial stage (Wu et al., 2011), the number of sulfate ions formed at the initial stage is therefore considered to be small relative to the number of reactive surface sites. Therefore, the reaction order can be determined from a bilogarithmic plot of initial formation rate of sulfate ($\log(\frac{d[SO_4^{2-}]}{dt})$) vs. the concentration of SO$_2$ ($\log[SO_2]$), just as previously reported (Börensen et al., 2000; Wu et al., 2011), and hence the experiments with different SO$_2$ concentrations were performed. For the mixture such as FN-24 used in this study, the plot gave a slope of $1.02 \pm 0.12$ ($2\sigma$), which indicates a reaction order of 1 for SO$_2$. The reaction order with respect to SO$_2$ was also examined from White cell-FTIR experimental data by examining the rates of SO$_2$ decay. The calculated result is consistent with that using DRIFTS data (correlation coefficient of $\ln[SO_2]/[SO_2]$ vs. time ($t$) was greater than.
0.99). That is, the heterogeneous oxidation of SO\textsubscript{2} on the hematite-nitrate mixture was still a pseudo-first-order reaction.

Figure 4 shows the average sulfate formation rates for the reactions of SO\textsubscript{2} with hematite and a series of hematite-nitrate mixtures at 298 K. As shown in Fig. 4, the sulfate formation rate first increases and then decreases with increasing mass fraction of nitrate, and no sulfate formation is observed on pure sodium nitrate. For mixtures, the FN-24 sample presents the highest reactivity, and its corresponding average sulfate formation rate is about 5 times higher than that of hematite alone. Obviously, an appropriate amount of nitrate greatly enhances the reactivity of the hematite-nitrate mixtures and favors the formation of sulfate on hematite under the same reaction conditions. A further analysis for reaction uptake coefficients by DRIFTS is difficult because the evaluation of the diffusion depth and total actual reaction sample area are unavailable in this study. However, the results support that the reaction behavior of SO\textsubscript{2} adsorption on hematite is altered by the availability of nitrate. The promotion effect of a small amount of nitrate should cause close attention because the nitrate content is close to that in the ambient particles (Ho et al., 2003), and the promotion effect of nitrate may help to predict the formation of sulfate aerosols in the atmosphere.

### 3.3 Effect of nitrate on heterogeneous reactivity of SO\textsubscript{2} on hematite at 298 K

The White cell-FTIR can be used to trace gaseous reactants and the possible gaseous products formed from the heterogeneous reaction of SO\textsubscript{2}, but it cannot be used to observe surface species formed on the sample surface. In situ White cell-FTIR spectra collected from the exposure of FN-24 sample to 50 ppm of SO\textsubscript{2} at room temperature are shown in Fig. 5. The strong absorption peaks at 1373, 1360, and 1348 cm\textsuperscript{-1} and the weak ones at 1163 and 1135 cm\textsuperscript{-1} are readily observed in the spectra. These peaks are assigned to the characteristic peaks of gaseous SO\textsubscript{2} (Fu et al., 2007; Zhang et al., 2006). The intensities of these peaks in the spectra decrease rapidly as the reaction proceeds, indicating that the concentration of SO\textsubscript{2} decreases while it reacts on the surface of FN-24. The other FN series and pure hematite samples upon exposure...
to 50 ppm of SO$_2$ at room temperature show similar absorption but the difference in the consumption rate of SO$_2$, revealing that the sample reactivity varies with mass fractions of sodium nitrate. No uptake of SO$_2$ is observed on the pure sodium nitrate. The results indicate that the reactivity increases first and then decreases with increasing mass fraction of sodium nitrate in the samples, and FN-24 sample exhibits the highest reactivity. This is consistent with the rate of sulfate formation.

3.4 Effect of nitrate on gas-phase products from the heterogeneous uptake of SO$_2$ on hematite

It is worth noting that several absorption peaks of gaseous HONO appear in the spectra in the White cell-FTIR experiment by exposing the FN series samples to the lower concentrations of SO$_2$. Although the adsorbed HNO$_3$ has been detected during the DRIFTS experiments, gas phase nitric acid has not been observed by White cell-FTIR experiments, suggesting that molecular nitric acid is firmly adsorbed on the particle surface in the presence of water. Figure 6 shows the representative in situ FTIR spectra collected from the exposure of FN-90 sample to 12.5 ppm of SO$_2$ for different times. A difference spectrum shown in Fig. 6d is obtained by subtracting the spectrum in Fig. 6c from that in Fig. 6d. As shown in Fig. 6, there are no absorption peaks of gas-phase HONO before 430 min but several weak HONO absorption peaks centered at 1262, 850 and 790 cm$^{-1}$ are observed when the reaction time is prolonged to 1170 min (Fig. 6d) (Wingen et al., 2000). The difference spectrum shown in Fig. 6e further confirms the existence of HONO, revealing that a trace amount of gaseous HONO is formed during the reaction of SO$_2$ on the hematite-nitrate mixture. To the best of our knowledge, this is the first observation of the formation of HONO in such a nitrate-containing reaction system. Observation of HONO formation is of particular significance because it plays an important role in the degradation of most primary and secondary atmospheric pollutants by serving as a major source of hydroxyl radicals. HONO formed from heterogeneous reaction of nitrogen dioxide has been extensively studied on different materials like mineral dust particles and soot (Finlayson-Pitts et al.,...
2003; Arens et al., 2001), and HONO is known to be in equilibrium with NO and NO$_2$ in the gas phase via its self-reaction (Pitts et al., 1984). However, the heterogeneous reaction of nitrogen dioxide and the self-reaction of HONO may be negligible in our system because no detectable absorption peaks of gas-phase NO and NO$_2$ in the spectral range from 1200 to 1900 cm$^{-1}$ are observed. Maybe gaseous NO and NO$_2$ are present at concentrations below detection limits.

The result also suggests that the initial surface-formed HONO may be simultaneously consumed by some secondary reactions in this system. On the one hand, no detectable absorption peaks of HONO by exposing the FN series samples to 50 ppm SO$_2$ for the same reaction time were observed. This fact suggests that the possible consumption reactions of HONO may be the ones between HONO and the surface abundant reduced S(IV) species, such as sorbed or surface-coordinated H$_2$SO$_3$, HSO$_3^-$, SO$_3^{2-}$ species, which led to gaseous HONO levels below detection limits before the complete consumption of these species. On the other hand, the high concentration of SO$_2$ means that there are many more reduced S(IV) species existing on the sample surface than those formed from the low concentration of SO$_2$, and also implies that HONO will be observed within a longer reaction time if the high concentration of SO$_2$ is used. An earlier study of Martin et al. observed that S(IV) species can be rapidly oxidized to sulfate by HONO in acidic aqueous aerosols (Martin et al., 1981), which would support the secondary reactions of HONO with S(IV) species in our experiments and reveal the potential role of HONO in the heterogeneous conversion of SO$_2$. In addition, the absorption peaks between 1400 and 1800 cm$^{-1}$ are mainly attributed to H$_2$O molecule vibrations. These absorption peaks gradually grow in intensity with the increase of reaction time because H$_2$O molecules can evaporate slowly from the humid surface of FN sample which is placed in the White cell.

Rivera-Figueroa et al. found that the reaction between HNO$_3$ and SO$_2$ on silica surfaces in the presence of water films does not occur (Rivera-Figueroa et al., 2003). Martin and co-workers also reported that nitric acid in solution does not react with dissolved SO$_2$ (Martin et al., 1981). Furthermore, in our study the experiment in which
humid pure nitrate was exposed to SO\textsubscript{2} using White cell-FTIR or DRIFTS technique also shows that no detectable gas phase products are observed, indicating that pure nitrate cannot interact with SO\textsubscript{2}. Therefore, considering the species in the reaction systems mentioned above, these previous studies indicate that the reactions between HNO\textsubscript{3} and S(IV) species cannot occur. Moreover, reductive dissolution of Fe (III) oxides and reduction of Fe (III) by sulfite have been suggested as possible sources of Fe (II) (Behra and Sigg, 1990), and the formation of Fe\textsuperscript{2+} via heterogeneous reaction of SO\textsubscript{2} oxidation on the surface of Fe\textsubscript{2}O\textsubscript{3} has already been verified by measuring the amount of Fe\textsuperscript{2+} during the reaction (Zhang et al., 2007; Ansari et al., 1997). Therefore, among the possible surface species in our reaction system, Fe\textsuperscript{2+} is the only reduced species that can react with NO\textsubscript{3} in the presence of H\textsuperscript{+}. In other words, the only formation pathway of HONO is the reduction of NO\textsubscript{3} by the reductive Fe\textsuperscript{2+} in the presence of H\textsuperscript{+}, while the reductant Fe\textsuperscript{2+} can be fed from the recycle from the reduction of Fe\textsuperscript{3+} by dissolved SO\textsubscript{2}. HONO formation processes in the atmosphere are still under discussion, especially during daytime where large discrepancies are found between mixing ratios calculated from known gas phase chemistry and measured daytime mixing ratios (Kleffmann et al., 2005). Our results also suggest that the heterogeneous reaction of SO\textsubscript{2} on nitrate-containing hematite may serve as a potential source for HONO, which may have implications on the oxidant chemistry in the atmosphere. However, the low yield of gaseous HONO may suggest that the contribution of HONO formed by this pathway to the atmospheric gas phase HONO may be negligible, but the formation of unreleased HONO in the particles may be significant for the conversion of SO\textsubscript{2} and the formation of sulfate in the atmosphere.

In addition, it is interesting to note that N\textsubscript{2}O is formed in the process of the heterogeneous uptake of SO\textsubscript{2} on the hematite-nitrate mixtures at low or high SO\textsubscript{2} concentrations. Just as shown in Fig. 6, two N\textsubscript{2}O absorption peaks at 2235 and 2208 cm\textsuperscript{-1} gradually appear and slowly grow in intensity with the increase of reaction time (Hussain and Rahman, 2006), indicating that gas-phase N\textsubscript{2}O is produced in the FT-IR experiments. The concentration of N\textsubscript{2}O gradually increases and ultimately reaches a constant
(ca. 418 ppb) as the reaction proceeds (see Fig. 6f). The gas-phase concentrations of N\textsubscript{2}O are determined according to a linear relationship between the integrated area of the gaseous N\textsubscript{2}O absorption peaks in the range 2258–2160 cm\textsuperscript{-1} and its concentration ($r^2 = 0.996$). The linear relationship is obtained using in situ White cell-FTIR and different concentrations of N\textsubscript{2}O standard gas. The observed formation of N\textsubscript{2}O is of particular importance because it is an extremely influential greenhouse gas and directly involved in global warming as well as in the destruction of ozone in the stratosphere. It has been reported that sulfur (IV) species such as H\textsubscript{2}SO\textsubscript{3} can be easily oxidized by HONO at low pH (0.6–3.2) and the gas phase product is N\textsubscript{2}O (Martin et al., 1981). Therefore, it is reasonable to speculate that N\textsubscript{2}O is formed from the reduction of HONO by S(IV) species such as sorbed or surface-coordinated H\textsubscript{2}SO\textsubscript{3}, HSO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{2}\textsuperscript{−} species on the mixture sample surface before HONO is released (Pires et al., 1996, 1997). This observation provides evidence for the formation of nitrous oxide from the hematite-nitrate mixtures at ambient temperature, and suggests a new potential atmospheric source of N\textsubscript{2}O. The result may help to explain why the sources of N\textsubscript{2}O exceed the estimated sinks in the atmosphere and the observed increase in atmospheric N\textsubscript{2}O. This source of N\textsubscript{2}O is currently not accounted for in the global N\textsubscript{2}O budget, but the relative importance of this source needs further study.

To further confirm the formation of HONO and N\textsubscript{2}O, we also performed heterogeneous reactions of SO\textsubscript{2} (50 ppm) on humid hematite, FN-24 and FN-90 in the presence of O\textsubscript{2} (21 % v/v) in three brown glass bottles in the dark for 3–7 days. The dark condition is selected to avoid the photolysis of HONO and the photochemistry of adsorbed nitrate (Schuttlefield et al., 2008). The selected long reaction time favors the release of the produced HONO and the accumulation of N\textsubscript{2}O. Figure 7 shows the digital photos of the three samples after reaction with SO\textsubscript{2} in the dark at laboratory temperature for about 7 days. Interestingly, the heterogeneous reactions of SO\textsubscript{2} on the surfaces of FN-24 and FN-90 present unique phenomena, and some liquid drops cover the interior walls of glass bottles, which is different from that presented by the reaction of SO\textsubscript{2} on the pure hematite. The latter does not show the similar phenomenon. The
liquid drops shows strong acidity which has been measured with pH test paper. Ion chromatography analysis shows that the liquid drops mainly contain sulfate ions while the concentration of nitrate ion is below the detection limit. These results indicate that the liquid drop is sulfuric acid. Obviously, the appearance of the liquid drops should be attributed to the presence of gas phase HONO. Gas phase HONO transforms SO$_2$ that is present in the gas-phase or adsorbed on the bottle walls into sulfuric acid, while reactive HONO is produced from the heterogeneous reaction of SO$_2$ on the surface of the hematite-nitrate mixture and the subsequent release. The HONO vapor adsorbs onto the interior wall of the glass bottle, and together with H$_2$O initiates the oxidation of SO$_2$ and the subsequent formation of H$_2$SO$_4$. Additionally, the gas-phase species in the three glass bottles were analyzed by using SPMS/GC-MS technique, and N$_2$O is only found from the reactions of SO$_2$ on FN-24 and FN-90, no NO, NO$_2$ and N$_2$O$_4$ are detected (see Fig. S5 in the Supplement). Therefore, considering the experimental results mentioned above, the formation of HONO and N$_2$O during the reaction of SO$_2$ on the hematite-nitrate mixture has been further verified by this experiment, which is consistent with the observations from in situ White Cell-FTIR experiments. This experiment also verifies that N$_2$O and HONO can be produced from the reaction of SO$_2$ on the hematite-sodium nitrate mixtures not only in daytime but also at night. Although the concentration of the formed HONO cannot be accurately measured during the process of the heterogeneous uptake of SO$_2$ on the hematite-nitrate mixture because the formed HONO is being continuously consumed on the particle surface, it may be important not only in daytime but also at night for the conversion of atmospheric SO$_2$ and the formation of atmospheric sulfate. Such aspects should be further explored in future studies.

### 3.5 Effect of nitrate on the morphology of surface product formed from the uptake of SO$_2$ onto hematite

Scanning electron micrographs of sample particles before and after reaction with gaseous SO$_2$ were obtained from a Philips XL-30 scanning electron microscope.
equipped with an energy dispersive X-ray spectrometer (SEM-EDX). Figure 8 shows the SEM images of FN-24 and FN-90 particles before (Fig. 8a and c) and after (Fig. 8b and d) exposure to gaseous SO$_2$ in the DRIFTS experiments. The two unreacted samples show the morphology of aggregated particles and consist of primary particles with an average particle size of over 100 nm. After comparing these images, we notice that after the reaction with SO$_2$, there are some flaky substances covering some particle surfaces. EDX analysis shows that the flaky substance is composed of 57.89% O, 11.70% Na, 11.48% S and 18.93% Fe (Fig. 8e). The characteristic peaks in the EDX spectrum indicates that no nitrogen is detected on the flaky substance, clearly indicating the formation of sulfate on the particle surface and the change in particle morphology. This result should be attributed to the enhanced formation of sulfate on the hematite surface due to the presence of nitrate. It should be noted that we cannot observe a similar phenomenon on the pure hematite after exposure to SO$_2$.

### 3.6 Role of surface adsorbed water under the influence of nitrate

Previous studies indicate that surface-adsorbed water plays an important role in the heterogeneous chemistry of atmospheric SO$_2$ (Nanayakkara et al., 2012). However, little is known about the role of surface-adsorbed water in the heterogeneous oxidation of SO$_2$ on hematite-nitrate mixture. Therefore, the role of surface-adsorbed water in the heterogeneous oxidation of SO$_2$ on FN-24 was further investigated using in situ DRIFTS. In order to prevent the sample particles from being brought out from the in situ chamber when the vacuum was applied, the sample was first pretreated at preset temperature for 60 min in a stream of Ar in a total flow of 100 mL min$^{-1}$. The preset temperatures were 298, 303, 373, 473 and 573 K, respectively. After 60 min the heated sample in the reaction chamber was cooled to 298 K under Ar flow and a background spectrum of the unreacted powder sample was collected. Subsequently, IR spectra were collected as a function of reaction time after being exposed to gaseous reactants. The results are shown in Fig. 9. Obviously, the pre-treated sample at 373 and 423 K enhances the reactivity of hematite, and the average formation rate of sulfate at 423 K
increases by a factor of 1.2 compared with that at 298 K. However, with a further increase in pre-treated temperature the reactivity decreases, and the sample pre-treated at 473 K shows even lower reactivity than that at 298 K. Pre-treatment of the sample is known to mainly remove surface-adsorbed water, and, at higher temperature, surface dehydration occurs. The observed increases in the reactivity of the sample pre-treated at 373 and 423 K are due to the partly removal of physiadsorbed water, which may serve as an inhibitor for the SO$_2$ oxidation by blocking access to the active sites. Samples pre-treated at higher temperatures (473 K) displays removal of the physiadsorbed water along with partly desorption of surface hydroxyl groups (Egashira et al., 1981), resulting in a decrease in the sample reactivity. In agreement with other studies, surface hydroxyl groups can be the active sites for the conversion of SO$_2$.

### 3.7 Proposed mechanism of SO$_2$ uptake on hematite-nitrate mixture

On the basis of the experimental observations described above, a reaction mechanism for the heterogeneous reaction of SO$_2$ on the hematite-nitrate mixture is proposed. Previous studies have shown that nitrate ions can be readily solvated by adsorbed water molecules under ambient conditions due to their hygroscopic nature (Hoffman et al., 2004), and thus nitrate in mixture sample will make more water molecules be adsorbed on the particles when the prepared mixture sample is kept in a desiccator at 68 % RH for 48 h. The adsorbed water will favor the uptake of SO$_2$ and the formation of S(IV) species (Zhang et al., 2007; Preszler Prince et al., 2007). Therefore, in the initial stage of heterogeneous conversion of SO$_2$ on the nitrate-hematite mixture, the following reactions will occur (Zhang et al., 2007):

\[
\begin{align*}
\text{SO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_3 \\
\text{H}_2\text{SO}_3 & \rightarrow \text{H}^+ + \text{HSO}_3^- 
\end{align*}
\]  

Earlier studies of SO$_2$ adsorption on metal oxides have clearly shown that Lewis acid sites, hydroxyl groups and oxygen vacancies can all play a role in the surface
Surface hydroxyl groups are involved in the adsorption of sulfur dioxide, and in particularly, sulfur dioxide reacts with either one surface O-H group to yield adsorbed bisulfite or two surface O-H groups to yield adsorbed sulfite and water. In the current study, the used nitrate-hematite mixtures are still loose fine powders after they are saturated at 68 % RH for 48 h, and there may be several water molecule layers resisting on humid sample surfaces. Therefore, surface sulfate and/or bisulfate can also be produced on the nitrate-hematite mixture particles through surface active oxygen and hydroxyl, while the active oxygen and hydroxyl can be formed from the interaction of O₂ and H₂O with the surface of hematite (Baltrusaitis et al., 2007). The formation mechanism of the surface sulfate and/or bisulfate during initial reaction stages should also be the same as that reported previously (Goodman et al., 2001; Baltrusaitis et al., 2007; Fu et al., 2007; Zhang et al., 2007). That is, the gaseous S₂O reacts with surface active oxygen and hydroxyl to form surface S(IV) species (i.e. adsorbed sulfur species and surface-coordinated HSO₃⁻, SO³⁻), and then these S(IV) species are further oxidized to surface S (VI) species including SO₄²⁻ and/or HSO₄⁻ in the presence of O₂ and H₂O (Fu et al., 2007; Zhang et al., 2007; Preszler Prince et al., 2007).

The reactions mentioned above will lead to the formation of an acidic surface. On the acidic surface, hematite will be partially dissolved to give Fe³⁺ ions in the water-rich surface (Chun and Quon, 1973; Shi et al., 2011), which in turn oxidizes HSO₃⁻ to form SO₄²⁻. As previously reported, Fe²⁺ ions are generated during this process (Behra and Sigg, 1990; Ansari et al., 1997; Zhang et al., 2007).

\[
6H^+ + Fe_2O_3 \rightarrow 2Fe^{3+} + 3H_2O \tag{3}
\]

\[
2Fe^{3+} + HSO_3^- + H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 3H^+ \tag{4}
\]

It is well established that the nitrate ion is a strong oxidizing agent in highly acidic solutions that is capable of changing the oxidation state of reduced species (Burley and Johnston, 1992). As the above reactions proceed, the surface of the mixed hematite-nitrate sample becomes more acidic, and adsorbed nitric acid and nitric acid-water...
complexes are gradually formed on the surface. Once the surface becomes sufficiently acidified, the interaction between nitric acid and Fe$^{2+}$ ion occurs on acidic surface, and the Fe$^{2+}$ ion is oxidized and HONO is produced (Summers, 2005), as given in the following ionic equation:

$$2\text{Fe}^{2+} + 3\text{H}^+ + \text{NO}_3^- \rightarrow 2\text{Fe}^{3+} + \text{HONO} + \text{H}_2\text{O}$$  \hspace{1cm} (5)

The re-generated Fe$^{3+}$ further oxidizes the S(IV) species to S (VI) species and produces Fe$^{2+}$ ions. With the cycle of the above reactions, more and more sulfates and HONO are produced. As shown in previous studies, S(IV) species can be rapidly oxidized to sulfate by HONO, and HONO can be reduced to N$_2$O in acidic aqueous aerosols (Martin et al., 1981; Pires et al., 1996, 1997). Thus, the formed HONO is also considered to react promptly with surface S(IV) species (i.e. sorbed H$_2$SO$_3$, HSO$_3^-$, SO$_3^{2-}$) before it escapes to the gas phase, which also results in the formation of N$_2$O and more sulfates on the particle surface. As reported previously (Martin et al., 1981), the stoichiometry should be as follows:

$$2\text{HONO} + 2\text{H}_2\text{SO}_3 \rightarrow 2\text{H}_2\text{SO}_4 + \text{N}_2\text{O} + \text{H}_2\text{O}$$  \hspace{1cm} (6)

$$2\text{HONO} + 2\text{HSO}_3^- \rightarrow 2\text{SO}_4^{2-} + \text{N}_2\text{O} + \text{H}_2\text{O} + 2\text{H}^+$$  \hspace{1cm} (7)

$$2\text{HONO} + 2\text{SO}_2^{2-} \rightarrow 2\text{SO}_4^{2-} + \text{N}_2\text{O} + \text{H}_2\text{O}$$  \hspace{1cm} (8)

An alternate mechanism involving consumption of HONO and formation of sulfate is based on that proposed by Finlayson-Pitts et al. (2003) and Liu et al. (2012). That is, reaction of the surface formed HONO with HNO$_3$ on the surface generates NO$^+\text{NO}_3^-$. This reaction can be thought of as a reaction of NO$_3^-$ with NO$^+$ formed from the reaction of HONO with the HNO$_3$, i.e., the reverse of the overall NO$_2$ hydrolysis reaction. The reaction process may be as follows:

$$\text{HONO}_{(\text{surface})} + \text{HNO}_3(\text{surface}) \rightarrow \text{NO}^+\text{NO}_3^-_{(\text{surface})} + \text{H}_2\text{O}$$ \hspace{1cm} (9)
Some \( \text{NO}^+\text{NO}_3^- \) (surface) isomerizes to surface asymmetric \( \text{ONONO}_2 \), and then \( \text{ONONO}_2 \) converts to small amount of \( \text{N}_2\text{O}_4 \) (Finlayson-Pitts et al., 2003; Liu et al., 2012). The formed \( \text{N}_2\text{O}_4 \) interacts strongly with water or adsorbed \( \text{HNO}_3 \) and would be more likely present on the surface (Finlayson-Pitts et al., 2003). Some \( \text{NO}^+\text{NO}_3^- \) (surface) oxidizes surface S(IV) species to sulfate, while \( \text{NO}^+\text{NO}_3^- \) itself is reduced to nitrite (M represents the surface metal sites). This can be used to explain the small amount of \( \text{N}_2\text{O}_4 \) and nitrite observed in our study:

\[
\text{NO}^+\text{NO}_3^- \rightarrow \text{ONONO}_2 \rightarrow \text{N}_2\text{O}_4
\]

(10)

\[
\text{NO}^+\text{NO}_3^- + \text{MSO}_3 \rightarrow \text{MSO}_4 + \text{NO}^+\text{NO}_2^- \quad \text{(11)}
\]

Once the surface S(IV) species have been completely consumed, the remaining \( \text{NO}^+\text{NO}_3^- \) will react with surface adsorbed water to generate HONO and adsorbed \( \text{HNO}_3 \) (Finlayson-Pitts et al., 2003), and subsequently the formed HONO through the reaction of \( \text{NO}^+\text{NO}_3^- \) with water and the unconsumed HONO by S(IV) species will be slowly released into the gas phase. Accordingly, HONO rather than \( \text{N}_2\text{O}_4 \) is responsible for the formation of \( \text{H}_2\text{SO}_4 \) liquid drops on the interior wall of the glass bottle in the dark.

\[
\text{NO}^+\text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3
\]

(12)

Therefore, the appearance of HONO will favor the oxidation of S(IV) species on the surface and lead to the formation of more sulfates (Martin et al., 1981). With the cycle of the above reactions, more and more sulfates and \( \text{N}_2\text{O} \) are produced. Once the reduced S(IV) species on the surface have been completely consumed, the remaining and subsequently formed HONO will slowly escape into the gas phase, and be detected by FTIR at last.

In addition, it is well-known that \( \text{N}_2\text{O} \) can be formed during the heterogeneous hydrolysis of gas-phase \( \text{NO}_2 \) via HONO on acidic oxide surfaces (Finlayson-Pitts et al., 2003; Wiesen et al., 1995). Therefore, another possibility for the formation of \( \text{N}_2\text{O} \) is similar
to the conversion proposed by Finlayson-Pitts et al. and Wiesen et al. (Finlayson-Pitts et al., 2003; Wiesen et al., 1995). That is, reaction of HONO and its protonated forms (H₂ONO⁺ or possibly NO⁺) generates hyponitrous acid, HON=NOH. The self-reaction of (HON)₂ then decomposes to N₂O under acidic conditions. Similar chemistry has also been proposed for the formation of N₂O under acidic conditions in the presence of SO₂ (Pires et al., 1997).

Above all, the consumed nitrate during the reaction will favor the uptake of more SO₂ molecules and produce more surface sulfate, while secondary chemistry of intermediate HONO will also result in the formation of gas phase N₂O. Furthermore, more adsorbed or surface-coordinated S(IV) species produced from higher concentrations of SO₂ also indicate that it will take a longer reaction time to observe the formation of gaseous HONO. The proposed mechanism provides new insights into some unsolved atmospheric problems such as unknown sources of N₂O and potential HONO, unknown SO₂ sinks and unknown sulfate formation pathways in the troposphere, and this chemistry also helps to explain the discrepancy between model-predicted sulfate and field observations of sulfate in the atmosphere (Laskin et al., 2003). The reaction mechanism of the heterogeneous oxidation of SO₂ on hematite in the presence of nitrate is summarized in Fig. 10.

4 Conclusions

The effects of nitrate on heterogeneous conversion of SO₂ on hematite at room temperature have been investigated. It is found that nitrate participates in the heterogeneous reactions of SO₂, changes the conversion pathway of SO₂, and leads to the formation of HNO₃, N₂O, HONO and more sulfate, revealing that nitrate has a significant impact on the heterogeneous conversion of SO₂ to sulfate. Compared with hematite solely, the heterogeneous uptake of SO₂ on hematite is clearly enhanced by a small amount of nitrate, and more sulfates are formed on hematite. For mixtures, the sample containing 24% nitrate exhibits the highest sulfate formation rate, and its corresponding average
sulfate formation rate is about 5 times higher than that of hematite alone. The enhanced formation of sulfate on particle surface and the change of particle surfaces would affect the hygroscopicity, optical properties and lifetime of the particle in the atmosphere. The observed formation of HONO and N$_2$O is of particular importance. The formation of potential HONO by this pathway may be significant for the conversion of SO$_2$ and the formation of sulfate in the atmosphere. The observed formation of N$_2$O may help to explain the difference between the sources of N$_2$O and the estimated sinks in the atmosphere and the observed increase in atmospheric N$_2$O. This study not only reveals the effects of nitrate on heterogeneous conversion of SO$_2$ on hematite but also provides new pathways for the formation of secondary sulfate aerosols, N$_2$O and potential HONO.

Results from this study have important atmospheric implications. Firstly, the results suggest that the heterogeneous conversion of SO$_2$ in the atmosphere will be affected by the availability of nitrate, and further emphasize that the complexity of the reaction of SO$_2$ on mineral dust. This chemistry may occur on surfaces of airborne dust particles that are known to be transported and play a role in the chemistry of the troposphere, which would affect the estimation of the amount of global atmospheric sulfate, and further affect the previously estimated radiative forcing and cooling effect of sulfate aerosols in the atmosphere (Dentener et al., 1996). Secondly, Fe (II) in airborne particles has been observed (Zhu et al., 1997; Zhuang et al., 2001) and its concentration in dust increased continuously during long-range transport (Zhuang et al., 2001). Also, in the real atmospheric systems, sulfuric acid is a common component of particles (Finlayson-Pitts and Pitts, 2000), PM$_{2.5}$ is generally acidic due to partial neutralization of acidic sulfate and nitrate under some atmospheric conditions (Huang et al., 2011), and even dust particle might become acidified to pH < 2 in the troposphere (Meskhidze et al., 2003). The Fe (II)-containing airborne particles will inevitably be loaded by nitrate and be acidified through contact with acidic particles such as sulfuric acid aerosols and acidic PM$_{2.5}$ particles, or become the heterogeneous reaction interface of SO$_2$ and NO$_2$ in the atmosphere. Hence, we can expect the production of potential HONO dur-
ing these processes. The results presented here may imply that such a heterogeneous conversion pathway of low concentration SO$_2$ on nitrate-containing airborne dust particles may be a potential and yet unknown daytime and nighttime significant source of HONO, and reveal that the presence of nitrate on mineral dust aerosol may play a role in the chemistry of HONO in the troposphere. In the meantime, these particles containing potential HONO may become the oxidizing carriers for the oxidation of atmospheric reduced gases, and thereby enhance the atmospheric oxidation ability. Understanding this chemistry will contribute to the elucidation of the potential contribution of the unreleased HONO in the particle for the conversion of SO$_2$ and the enhanced formation of sulfate in the atmosphere in the daytime and at night. Finally, several studies indicated that the photolysis of aqueous nitrate (Dubowski et al., 2001; Roca et al., 2008) and adsorbed nitrate (Schuttlefield et al., 2008) is a source of NO$_x$ (i.e., NO + NO$_2$), OH radicals and O ($^3$P). All of these products represent highly reactive oxidants in the gas phase and in other environmentally relevant phases. The production of hydroxyl radicals will favor the conversion of SO$_2$ to particulate sulfate, while the photolysis of aqueous or adsorbed nitrate will lead to a loss of nitrate in the particulate phase. Furthermore, according to our experimental results and discussion above, small amounts of nitrate will significantly promote the heterogeneous conversion of SO$_2$ and the formation of sulfate on airborne hematite-containing mineral dust particles, while the heterogeneous uptake of SO$_2$ on nitrate-containing mineral dust in the atmosphere will also bring a loss of adsorbed nitrate on the particle surface with the concomitant formation of gas-phase products including HONO and N$_2$O. Therefore, these studies mentioned above will aid in understanding the negative linear correlation between sulfate and nitrate contents in ambient particles (Kong et al., 2014). However, the reasons for the negative correlation are unknown. There is still lack of corresponding research on the formation mechanism of the negative correlation up to now, and all these aspects need to be further investigated.
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References


Table 1. Assignment of vibrational frequencies of surface species formed on hematite particle surfaces and on hematite-nitrate mixture surfaces.

<table>
<thead>
<tr>
<th>Surface species</th>
<th>Hematite (cm⁻¹)</th>
<th>Hematite-nitrate mixture (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃²⁻/HSO₃⁻</td>
<td>1056</td>
<td>1080, 1050, 966</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1361, 1337, 1261, 1158, 1056, 1000</td>
<td>1158, 1190, 987</td>
</tr>
<tr>
<td>Acidic species</td>
<td>1219</td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td></td>
<td>1599, 1587, 1567</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td></td>
<td>1506, 1487</td>
</tr>
<tr>
<td>Adsorbed HNO₃</td>
<td></td>
<td>1676, 1686, 1697, 1716</td>
</tr>
<tr>
<td>O-H region</td>
<td>3664, 3631</td>
<td>3664, 3631</td>
</tr>
</tbody>
</table>
Fig. 1. DRIFT spectra of different samples recorded upon exposure to SO$_2$ at 298 K. (a) Hematite. (b) FN-24.
Fig. 2. Peak fit of the last DRIFT spectrum of the products on FN-24 shown in Fig. 1 by mixed Gaussian–Lorentzian peak fitting.
**Fig. 3.** DRIFT spectra of FN-24 as a function of time after exposure to SO$_2$ in the range of 3800 to 1350 cm$^{-1}$. The inset shows expanded region from 1630 to 1550 cm$^{-1}$. 

- Wave number cm$^{-1}$
Fig. 4. Average formation rates of sulfate on 30 mg of particle samples after exposure to 3 ppm SO₂ for 4 h under the same experimental conditions.
Fig. 5. In situ White cell-FTIR spectra of FN-24 recorded upon exposure to 50 ppm SO$_2$ + 21% O$_2$ at room temperature for different reaction times.

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Fig. 6. In situ FTIR spectra of FN-90 recorded upon exposure to 12.5 ppm SO$_2$ + 21% O$_2$ at room temperature for different times. (a) 10 min. (b) 60 min. (c) 430 min. (d) 1170 min. (e) difference spectrum: (d) minus (c). (f) The concentration of the formed N$_2$O as a function of time during the reaction of FN-90 sample with SO$_2$. 
Fig. 7. Digital photos of different samples after reaction with 50 ppm SO$_2$ + 21 % O$_2$ in the dark at 298 K for about 7 days.
Fig. 8. SEM images and EDX spectrum. Top panels: SEM images of FN-24 (a, b) and FN-90 (c, d) particles before (left) and after (right) exposure to 3 ppm SO$_2$ at 298 K for 240 min. Bottom panel: typical EDX spectrum of the flaky substance.
Fig. 9. Average formation rates of sulfate on 30 mg of FN-24 after exposure to 3 ppm SO$_2$ for 4 h under different pre-treatment temperatures.
Fig. 10. Schematic of the reaction mechanism of the heterogeneous oxidation of SO$_2$ on hematite in the presence of nitrate.