Synergistic reaction between SO₂ and NO₂ on mineral oxides: a potential formation pathway of sulfate aerosol†

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Sulfate is one of the most important aerosols in the atmosphere. A new sulfate formation pathway via synergistic reactions between SO₂ and NO₂ on mineral oxides was proposed. The heterogeneous reactions of SO₂ and NO₂ on CaO, α-Fe₂O₃, ZnO, MgO, α-Al₂O₃, TiO₂, and SiO₂ were investigated by in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (in situ DRIFTS) at ambient temperature. Formation of sulfate from adsorbed SO₂ was promoted by the coexisting NO₂, while surface N₂O₄ was observed as the crucial oxidant for the oxidation of surface sulfite. This process was significantly promoted by the presence of O₂. The synergistic effect between SO₂ and NO₂ was not observed on other mineral particles (such as CaCO₃ and CaSO₄) probably due to the lack of the surface reactive oxygen sites. The synergistic reaction between SO₂ and NO₂ on mineral oxides resulted in the formation of internal mixtures of sulfate, nitrate, and mineral oxides. The change of mixture state will affect the physicochemical properties of atmospheric particles and therefore further influence their environmental and climate effects.

1. Introduction

As a major constituent of atmospheric particulate matter, sulfate accounts for the largest mean mass fraction of both fine and coarse aerosol particles.7 In the atmosphere, sulfate aerosols can be transported several thousand kilometres and can have a mean lifetime of about one week.2,3 They can produce a cooling effect on the global climate by scattering solar radiation (direct effect)4–6 and can also act as cloud condensation nuclei (indirect effect).7–12 The global average direct forcing of sulfate aerosols ranges from −0.26 W m⁻² to −0.82 W m⁻², while indirect forcing on cloud albedo varies from −0.3 W m⁻² to −1.8 W m⁻²,13 indicating their competitive effect on the climate with greenhouse gases (1.5 W m⁻² for CO₂ and 0.95 W m⁻² for other greenhouse gases).14 Additionally, sulfate derived from anthropogenic emissions of SO₂ is a major contributor to the acidity of rainwater, giving rise to the severe environmental problem of acidification.15 On account of its key role in the global climate and air quality, the formation mechanism of sulfate is a pressing environmental concern.

Atmospheric secondary sulfate aerosols form by the oxidation of SO₂ either in gaseous phase reactions with hydroxyl radicals followed by condensation of sulfuric acid (e.g. reactions (1) and (2)), or in aqueous phase reactions within cloud and fog droplets (e.g. reaction (3) or (4)).7

\[
\begin{align*}
\text{SO}_2 + \text{OH} + \text{O}_2 & \rightarrow \text{SO}_3 + \text{HO}_2 \quad (1) \\
\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 \quad (2) \\
\text{SO}_3^{2-} + \text{O}_3 & \rightarrow \text{SO}_4^{2-} + \text{O}_2 \quad (3) \\
\text{HSO}_3^- + \text{H}_2\text{O}_2 & \rightarrow \text{HSO}_4^- + \text{H}_2\text{O} \quad (4)
\end{align*}
\]

However, large uncertainties still remain concerning the mechanism of sulfate formation. A number of models have been applied to predict the formation of sulfate on a global scale. Results have shown that SO₂ concentration is typically overestimated while sulfate concentration tends to be underestimated.16 Therefore, there must be some yet unknown pathways for the conversion of SO₂ to sulfate aerosols.

Recently, heterogeneous oxidation of SO₂ on the surface of mineral dust particles was investigated, showing that adsorption of SO₂ only leads to sulfite or bisulfite on the surface of mineral oxides.17–19 Oxidants, such as O₃, are needed in the conversion of sulfite to sulfate.20 In addition, NO₂, which is an important atmospheric pollutant with similar anthropogenic sources as SO₂, provides a promotive effect on the absorption and oxidation of SO₂ in flue gas desulfurization with high gaseous pollutant concentration and a reaction temperature of 423 K.21 Previous studies have also found that the formation of sulfate was enhanced by NO₂ on Sahara Desert mineral dust under ambient conditions.22 However, the interaction mechanism between SO₂ and NO₂ remains unclear. In our previous work,23...
we found that a synergistic effect existed in the heterogeneous reaction between SO$_2$ and NO$_2$ on $\gamma$-Al$_2$O$_3$. Since mineral dust originates from wind-blown soils, its chemical composition is similar to that of crustal rock. Besides Al$_2$O$_3$, the earth’s crust is also dominated by other oxides such as SiO$_2$, CaO, and $\alpha$-Fe$_2$O$_3$. However, the applicability of synergistic reactions between SO$_2$ and NO$_2$ on other mineral oxides is not known.

In the present study, heterogeneous reactions of SO$_2$ and NO$_2$ on typical mineral oxides (CaO, $\alpha$-Fe$_2$O$_3$, ZnO, MgO, $\gamma$-Al$_2$O$_3$, TiO$_2$, and SiO$_2$) were investigated using in situ Diffuse Reflectance Infrared Fourier Spectroscopy (DRIFTS). The synergistic effect on the formation of sulfate was further elucidated. In addition, the difference in the heterogeneous reactions of SO$_2$ and NO$_2$ between mineral oxides and other typical atmospheric particles was compared. The aim of this work was to give an insight into the complex atmospheric chemistry of SO$_2$, NO$_2$, and atmospheric particles.

2. Experimental section

2.1 Sample preparation and characterization

The following mineral oxide particles were used in this study: CaO, $\alpha$-Fe$_2$O$_3$, ZnO, MgO, $\gamma$-Al$_2$O$_3$, TiO$_2$, and SiO$_2$. The $\gamma$-Al$_2$O$_3$ particles were prepared from boehmite (AlOOH, Shandong Aluminum Corporation) by calcining at 1473 K for 180 min. All other oxide particles were purchased from commercial sources. The BET surface areas were characterized by a physisorption analyzer (Autosorb-IC-TCD, Quantachrome) and sample particle sizes were measured by transmission electron microscopy (TEM, H-7500, Hitachi). The characterization results are listed in Table 1.

In addition to the mineral oxides listed in Table 1, other typical atmospheric particles, CaCO$_3$ (AR, Sinopharm Chemical Reagent Co. Ltd, China) and CaSO$_4$ (AR, Sinopharm Chemical Reagent Co. Ltd, China), were chosen as the representatives of other mineral particles. All these particles were used as purchased.

2.2 In situ DRIFTS measurements

The heterogeneous reactions of SO$_2$ and NO$_2$ on particles were measured by in situ DRIFTS (NEXUS 670, Thermo Nicolet Instrument Corporation), equipped with an in situ diffuse reflection chamber and a high-sensitivity mercury cadmium telluride (MCT) detector cooled by liquid N$_2$. Before the experiment, oxide samples were finely ground and placed into a ceramic crucible in the in situ chamber. In order to remove the adsorbed species (e.g. CO$_2$ and H$_2$O) on the surface, the samples were first pretreated at 573 K for 180 min in a stream of synthetic air (80% N$_2$ and 20% O$_2$) in a total flow of 100 mL min$^{-1}$. After 60 min the temperature was cooled to room temperature (303 K) and the samples were exposed to 200 ppmv SO$_2$ and/or 200 ppmv NO$_2$ balanced with 100 mL min$^{-1}$ synthetic air for at least 120 min. All reactive and carrier gases are of high-purity (99.9999%) in our study to ensure the absence of impurities (such as CO$_2$). The infrared spectra were collected using a computer with OMNIC 6.0 software (Nicolet Corporation, USA). All spectra were recorded at a resolution of 4 cm$^{-1}$ for 100 scans in the spectral range of 600 to 4000 cm$^{-1}$. The low frequency cutoff of spectra was due to the strong lattice oxide absorption of the samples.

3. Results and discussion

3.1 Synergistic effect between SO$_2$ and NO$_2$ on CaO

Firstly, the heterogeneous reaction of SO$_2$ and NO$_2$ on CaO was investigated. The pretreated sample was exposed to SO$_2$ and NO$_2$ balanced with synthetic air in a total flow of 100 mL min$^{-1}$ at 303 K. The in situ DRIFTS spectra as a function of time are shown in Fig. 1. At the beginning of the reaction, several bands at 1000, 940, 895, and 850 cm$^{-1}$ were observed in the spectra. The bands at 940 and 850 cm$^{-1}$ are attributed to the symmetric stretching of monodentate sulfite, while bands at 1000 and 895 cm$^{-1}$ are assigned to the asymmetric stretching vibration of monodentate sulfite. As the reaction proceeded, these absorption features of sulfite decreased while bands at 1192, 1140, and 1099 cm$^{-1}$ increased. These bands could be assigned to the asymmetric vibration frequency of bidentate surface-coordinated sulfate. The symmetric stretching of sulfate at 950–1000 cm$^{-1}$ was overlapped by the absorption of sulfite. The increase of sulfate species as well as the decrease of sulfite species made it difficult to distinguish the absorption bands in this region of the spectra. Nevertheless, the results indicate that surface sulfite was converted to sulfate in the reaction process. In addition, the bands at 1638, 1519, 1336, and 815 cm$^{-1}$ grew with increased exposure time, which was attributed to the presence of nitrate species on the CaO surface. The band at 1519 cm$^{-1}$ is assigned to the asymmetric stretching...
mode of monodentate nitrate, while the bands at 1638 and 815 cm\(^{-1}\) are attributed to the asymmetric stretching and out-of-plane bend of bridging nitrate, respectively. Due to remnant water in the feed gas at room temperature, the water-solvated surface nitrate with asymmetric stretching mode at 1336 cm\(^{-1}\) appeared and acted as the dominant nitrate on the CaO surface. The symmetric stretching region of the surface nitrate (1000–1050 cm\(^{-1}\)) was overlapped by strong sulfate absorption (1000–1200 cm\(^{-1}\)), which was difficult to indicate in Fig. 1. In addition, two peaks at 1745 and 1295 cm\(^{-1}\) rapidly increased at the early stage of the reaction, then decreased in intensity as the reaction progressed. These two peaks are assigned to the asymmetric and symmetric stretching of the dimer of NO\(_2\), namely N\(_2\)O\(_4\), respectively. The reaction behavior of N\(_2\)O\(_4\) suggested it was an intermediate species in the synergistic reaction between SO\(_2\) and NO\(_2\).

Further quantitative analysis of surface species was conducted by integrating the absorbance band areas. As shown in Fig. 2, sulfite and N\(_2\)O\(_4\) species were dominant at the initial stage of the reaction, and reached maximum at 3 min and then gradually decreased to zero after 40 min. Additionally, a dramatic increase in sulfate species was observed after 3 min reaction, and it steadied after 40 min. It seems that the consumption of sulfite and N\(_2\)O\(_4\) accompanied the formation of sulfate. As for the formation of nitrate, the formation rate remained steady during the reaction.

In situ DRIFTS spectra of CaO exposed to individual SO\(_2\) or NO\(_2\) with synthetic air are displayed in Fig. 3a and b, respectively. For SO\(_2\) adsorption (Fig. 3a), formation of sulfite dominated the surface reaction and resulted in the broad band centered at 943 cm\(^{-1}\). This band is attributed to the stretching mode of monodentate sulfite species. The broad band at 1647 cm\(^{-1}\) is assigned to \(\delta(\text{HOH})\) vibration of molecularly adsorbed water. The flow of SO\(_2\) + air was switched to only air for 60 min to flush the surface; however, peak intensity of sulfite remained unchanged. This indicated that SO\(_2\) was chemisorbed on the surface. Further adsorption of NO\(_2\) on the SO\(_2\) pre-saturated CaO surface was conducted and the spectra are shown in Fig. 3a. As the exposure time increased, the sulfite species band at 943 cm\(^{-1}\) gradually decreased while the sulfate bands at 1099 and 1192 cm\(^{-1}\) increased. In addition, the features of N\(_2\)O\(_4\) at 1748 and 1300 cm\(^{-1}\) appeared at the early stage of the reaction but decreased in intensity with increasing reaction time. This implied that N\(_2\)O\(_4\) played a crucial role in the oxidation of surface sulfite to sulfate. Peaks due to bridging (1652, 815 cm\(^{-1}\)) and water-solvated (1338 cm\(^{-1}\)) nitrate were also detected on the CaO surface after SO\(_2\) pre-saturation.

In the case of NO\(_2\) adsorption (Fig. 3b), the intensities of bands at 1635, 1336, 1040, and 815 cm\(^{-1}\) increased with reaction time. The most prominent band at 1336 cm\(^{-1}\) is assigned to \(\delta(\text{HOH})\) vibration of molecularly adsorbed water. Absorption peaks at 1635, 1040, and 815 cm\(^{-1}\) are attributed to asymmetric stretching, symmetric stretching, and out-of-plane mode of bridging nitrate, respectively. After saturation with nitrate species, the surface was purged by synthetic air for 60 min and was then exposed to SO\(_2\) for 120 min, but no spectral change was observed.

To illuminate the synergistic effect between SO\(_2\) and NO\(_2\) on the formation of surface species, the integrated areas of sulfite, sulfate, bridging nitrate, and solvated nitrate formed on CaO under different reaction conditions were compared and are shown in Fig. 4. Compared with the individual reaction of SO\(_2\), formation of sulfate was significantly promoted (Fig. 4a) while sulfite was quickly consumed (Fig. 4b) in the presence of NO\(_2\). As for nitrate, the presence of SO\(_2\) had no influence on the generation of bridging nitrate (Fig. 4c), but the formation...
3.2 Synergistic effect between SO2 and NO2 on other typical mineral oxides

To clarify the synergistic reaction between SO2 and NO2 on other mineral oxides, in situ DRIFTS experiments were carried out with SO2 and NO2 introduced simultaneously or individually onto other mineral oxides. The surface species formed during the reaction are summarized in Table 2. The integrated area of surface species was compared, as shown in Fig. 5. When SO2 was individually introduced into the reaction system with synthetic air, the only surface species observed on ZnO and TiO2 was the sulfate (1100–1200 cm\(^{-1}\)). For MgO, in addition to sulfate, the absorption band at 1150 cm\(^{-1}\) was due to surface adsorbed water originating from remnant water in the feed gas. The bands at 1346, 1416, and 1675 cm\(^{-1}\) that correspond to the bending mode of \(\nu_1(\text{HONO})\), \(\delta(\text{OH})\), and \(\nu_4(\text{HNO}_3)\) indicated the formation of adsorbed HNO3 on the SiO2 surface.32 Vibration mode \(\delta(\text{HON})\) at 1267 cm\(^{-1}\) was observed, implying the possible formation of HONO in the reaction.31,32 These results suggest that the reaction of NO2 with surface water was dominant on the SiO2 surface. Due to the inhibition of SO2 adsorption, formation of sulfate was not observed when NO2 was present in the system. This is expected because SO2 is an acidic oxide and not reactive to acidic SO2 and NO2. Therefore, surface nitrate and sulfate are hardly to form on SiO2.

3.3 Comparison of reactivity between mineral oxides and other atmospheric particles

The formation of sulfate due to the synergistic reaction between SO2 and NO2 was demonstrated on mineral oxides. To determine whether this effect occurred on other mineral particulate matters, the reactions of SO2 and NO2 on CaCO3 and CaSO4 were also tested. No surface reaction of SO2 and NO2 was observed on these particles (as seen from Fig. S1, ESI†). The difference between mineral oxides and other mineral particles on the reactivity of SO2 and NO2 was ascribed to their distinctive surface properties.

3.4 Possible mechanism of synergistic effect

The surface reaction mechanism of SO2 is different from that of NO2 on metal oxides.25 Initially, NO2 adsorbs on metal sites of metal oxide particles (for example, \(\gamma\)-Al2O3, \(\alpha\)-Al2O3, Fe2O3, and TiO2) to form nitrite and then nitrate via reaction with...
another nitrite in an Langmuir–Hinshelwood (LH) type mechanism or with NO₂ in an Eley–Rideal (ER) type mechanism.37,41

In the reactions shown below, M represents a metal atom of the oxides surface:

\[
\begin{align*}
\text{NO}_2(g) + M & \rightarrow M\text{NO}_2 \quad (5) \\
2\text{MNO}_2 & \rightarrow \text{MNO}_3 + \text{NO}_2(g) \quad (6) \\
\text{MNO}_2 + \text{NO}_2(g) & \rightarrow \text{MNO}_3 + \text{NO}(g) \quad (7)
\end{align*}
\]

For SO₂ adsorption on metal oxide surfaces, surface-coordinated sulfite/bisulfite forms on basic oxide anions (oxygen atoms or adsorbed hydroxyl), while weakly adsorbed SO₂ forms on acidic metal sites.19 Previous studies have proposed SO₂ as an electron acceptor on metal oxides (MgO, α-Al₂O₃, ZrO₂, TiO₂, and CeO₂) through adsorption on either surface oxygen sites to form strongly adsorbed sulfite species or on basic hydroxyl groups leading to the formation of hydrogen-sulfite species.42

In the present work, surface oxygen sites and hydroxyl groups contributed to SO₂ adsorption, while metal sites were the adsorption sites for NO₂. In some cases, the consumption of surface hydroxyl groups was not observed (e.g. CaO, Fig. S2, ESI†). Therefore, the number of surface oxygen sites may play a key role in the reaction.

It is proposed that gases such as O₂ adsorb on the surface of oxides and produce surface active oxygen species.43 Oxygen is also a key reactant in the oxidation of adsorbed SO₂ on the surface of iron oxides to form surface sulfate species at ambient temperatures.40 To explore the role of O₂ in the synergistic reaction between SO₂ and NO₂, an experiment without O₂ was carried out by exposing CaO to SO₂ and NO₂ in a 100 mL min⁻¹ N₂ flow. As is displayed in Fig. 8, peaks at 1624, 1581, 1322, 1035, 850, and 817 cm⁻¹ were observed after 600 min, which were quite different from those obtained in the presence of O₂ (Fig. 1). In the initial 180 min reaction, the formation of surface bidentate nitrite species (1230 cm⁻¹) dominated the surface reaction.44 This suggested that the reactivity of SO₂ and NO₂ decreased in the absence of O₂. Conversion of nitrite to water-solvated nitrate (1322 cm⁻¹), bidentate nitrate (1581 cm⁻¹), and bridging nitrate (1747, 1624, and 1024 cm⁻¹) was observed as exposure time increased,30 which implied that nitrite was the intermediate of NO₂ to nitrate. These results are consistent with previous studies.37 Sulfite at 850 cm⁻¹ was detected in the spectra until 120 min.43 However, the formation

<table>
<thead>
<tr>
<th>Surface species</th>
<th>Representation</th>
<th>CaO</th>
<th>α-Fe₂O₃</th>
<th>ZnO</th>
<th>TiO₂</th>
<th>MgO</th>
<th>α-Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monodentate nitrate</td>
<td>O=N-O</td>
<td>1519</td>
<td>1580</td>
<td>1521</td>
<td>1450</td>
<td>1540</td>
<td>1450</td>
</tr>
<tr>
<td>Bidentate nitrate</td>
<td>O=N-O</td>
<td>1288</td>
<td>1602</td>
<td>1568</td>
<td>1585</td>
<td>1585</td>
<td>1585</td>
</tr>
<tr>
<td>Bridging nitrate</td>
<td>O=N-O</td>
<td>815</td>
<td>1638</td>
<td>1240</td>
<td>1625</td>
<td>1244</td>
<td>1624</td>
</tr>
<tr>
<td>Water-solvated nitrate</td>
<td>NO₃⁻ (aq)</td>
<td>1336</td>
<td>1338</td>
<td>1299</td>
<td>1300</td>
<td>1317</td>
<td>1317</td>
</tr>
<tr>
<td>N₂O₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Physically adsorbed SO₂</td>
<td>SO₂(ad)</td>
<td>850</td>
<td>895</td>
<td>940</td>
<td>1000</td>
<td>955</td>
<td>990</td>
</tr>
<tr>
<td>Monodentate sulfite</td>
<td>O=S-O</td>
<td>850</td>
<td>895</td>
<td>940</td>
<td>1000</td>
<td>955</td>
<td>990</td>
</tr>
<tr>
<td>Bridging sulfite</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Bidentate sulfite</td>
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</tbody>
</table>

The superscript numbers are the sequence numbers of corresponding references.

Table 2 Assignment of vibrational bands (cm⁻¹) of surface species formed when mineral oxides were simultaneously exposed to SO₂ and NO₂
Fig. 5 Comparison of the integrated area of surface species between 200 ppmv NO\textsubscript{2} and 200 ppmv SO\textsubscript{2} simultaneous reaction (solid points) and 200 ppmv SO\textsubscript{2} or 200 ppmv NO\textsubscript{2} individual reaction (hollow points) on (a) ZnO, (b) TiO\textsubscript{2}, (c) α-Al\textsubscript{2}O\textsubscript{3}, and (d) MgO.

Fig. 6 In situ DRIFTS spectra of (a) 200 ppmv SO\textsubscript{2} reaction, (b) 200 ppmv NO\textsubscript{2} reaction, and (c) SO\textsubscript{2} and NO\textsubscript{2} simultaneous reaction on the surface of α-Fe\textsubscript{2}O\textsubscript{3} as a function of time in a flow of 100 mL min\textsuperscript{-1} synthetic air (20% O\textsubscript{2}, 80% N\textsubscript{2}) at 303 K; (d) comparison of the integrated area of surface species between SO\textsubscript{2} and NO\textsubscript{2} simultaneous reaction (solid points) and SO\textsubscript{2} or NO\textsubscript{2} individual reaction (hollow points) on α-Fe\textsubscript{2}O\textsubscript{3}.
of both sulfate and N2O4 were not detected even as the reaction continued to 600 min, which demonstrated that the interaction between N2O4 and sulfite was necessary for the formation of sulfate. As discussed above, surface oxygen sites contributed to the adsorption of SO2. By providing abundant surface oxygen sites for initial adsorption of SO2, oxygen played a crucial role in the formation of sulfate. However, O2 was not considered as the direct oxidant of adsorbed SO2 as no oxidation of sulfite occurred on the mineral oxides (except a-Fe2O3) when SO2 was introduced into the system in the presence of O2. In addition, as seen in Fig. 1 and 8, surface N2O4 was also promoted by the presence of O2, which implied oxygen might also induce the formation of N2O4, although the mechanism remains unclear. Since nitrite, nitrate, and N2O4 all coexisted with sulfite during the simultaneous reaction of SO2 and NO2, all were possible oxidants for the conversion of sulfite to sulfate. As there was no formation of sulfate when nitrite and nitrate coexisted with sulfite (Fig. 8), neither species could oxidize sulfite. It is known that N2O4 could isomerize and autoionize to NO + NO3 in solution or at low temperatures, and can rapidly oxidize many organic and inorganic compounds. Therefore, N2O4 was considered the oxidant for the formation of sulfate in this work.

The reaction mechanism proposed for the synergistic effect between SO2 and NO2 on mineral oxides is illustrated in Scheme 1. Firstly, gaseous NO2 and SO2 adsorb on the surface to form adsorbed NO2(ad) and sulfite, respectively, and NO2(ad) dimerizes to N2O4(ad). The identification of active sites for N2O4 formation is difficult at present. Since Henry’s law coefficient for N2O4 in water is approximately two orders of magnitude larger than for NO2, the accumulation of N2O4 is more likely to occur when water is present on the surface. However, it has been demonstrated that pre-adsorbed water cannot lead to the formation of N2O4 on γ-Al2O3. Therefore, the formation of N2O4 might be related to the surface S(IV) species. In addition, the formation of N2O4 was also promoted by O2. Consequently, the autoionization of N2O4 leads to the formation of NO + NO3, which can oxidize sulfite to sulfate, while NO + NO3 is reduced to nitrite. Lastly, nitrite is converted to nitrate and gas phase NO in an LH type or ER type mechanism. The released NO is oxidized to NO2 and enters into the next reaction cycle. The reaction process may be as follows:

Stage 1:

\[
\text{NO}_2(g) \leftrightarrow \text{NO}_2(ad)
\]

\[
\text{SO}_2 + \text{MO} \rightarrow \text{MSO}_3
\]

Stage 2:

\[
\begin{align*}
\text{NO}_2(ad) & \leftrightarrow \text{N}_2\text{O}_4(ad) \\
\text{N}_2\text{O}_4(ad) & \rightarrow \text{NO}^+\text{NO}_3^-
\end{align*}
\]

Stage 3:

\[
\begin{align*}
\text{NO}^+\text{NO}_3^- + \text{MSO}_3 & \rightarrow \text{MSO}_4 + \text{NO}^+\text{NO}_2^- \\
\text{NO}^+\text{NO}_2^- + \text{MO} & \rightarrow 2\text{MNO}_2
\end{align*}
\]

Stage 4:

\[
\begin{align*}
2\text{MNO}_2 & \rightarrow \text{MNO}_3 + \text{NO}_2(g) \text{ LH} \\
\text{MNO}_2 + \text{NO}_2(g) & \rightarrow \text{MNO}_3 + \text{NO}_2(g) \text{ ER}
\end{align*}
\]

where M represents the surface metal sites, while MO represents the surface reactive oxygen sites. These reactive oxygen species include oxygen radicals (e.g. O2- and O-) and other coordinately unsaturated oxygen species. However, it is difficult to
identify and confirm them in the reaction. The synergistic effect between SO\textsubscript{2} and NO\textsubscript{2} was not observed on other mineral particles (such as CaCO\textsubscript{3} and CaSO\textsubscript{4}) probably attributes to the insufficient surface oxygen sites. Due to the scarcity of adsorption sites for SO\textsubscript{2}, further reaction is forbidden. The formation of nitrate in stage 3 was not detected by spectroscopic characterization in the SO\textsubscript{2} and NO\textsubscript{2} simultaneous reaction (e.g. Fig. 1), probably attributes to the rapid conversion to nitrate and gaseous product of NO. It should be noted that the relative humidity (RH) in the feed gas was less than 5% RH, therefore the present study could only represent dry conditions in the atmosphere. However, water plays an important role in atmospheric chemistry. For example, the adsorbed water film on CaCO\textsubscript{3} could enhance the uptake of sulfur dioxide and nitric acid on the surface.\textsuperscript{47} Therefore, the mechanism of synergistic reaction might change under high RH conditions, and it will be studied in future research.

4. Conclusions and atmospheric implications

A new formation pathway of sulfate in the atmosphere was proposed. The synergistic reaction between SO\textsubscript{2} and NO\textsubscript{2} on mineral oxides at ambient temperatures promoted the transformation of SO\textsubscript{2} to sulfate. The N\textsubscript{2}O\textsubscript{4} acted as an intermediate species and oxidized sulfite to sulfate. The oxidation process was greatly promoted by the presence of O\textsubscript{2} and NO\textsubscript{2}. Due to the lack of surface oxygen sites, the synergistic effect on other mineral particles, such as CaCO\textsubscript{3} and CaSO\textsubscript{4}, was not observed.

The heterogeneous reaction of mixed SO\textsubscript{2} and NO\textsubscript{2} with atmospheric concentration levels (500 ppbv SO\textsubscript{2} and 500 ppbv NO\textsubscript{2}) on CaO suggested the probability of this synergistic effect in the atmosphere, although longer experimental time was needed than that with higher concentration (Fig. S3, ESIf). Previous field measurement studies have suggested that sulfate is internally mixed with nitrate and mineral dust. The present study proposed a new formation pathway of mixed SO\textsubscript{2} and NO\textsubscript{2} with atmospheric concentration levels in the atmosphere via the synergistic reaction between SO\textsubscript{2} and NO\textsubscript{2} on mineral oxides. The variation in mixture state has a significant influence on the physicochemical properties of mineral oxides. The optical properties will change because sulfate does not absorb solar radiation. Therefore, direct climate forcing of the mixture will change as sulfate and nitrate have a cooling effect while mineral dust has a heating effect in the atmosphere.\textsuperscript{6,13} Since sulfate and nitrate are hygroscopic, mineral oxides internally mixed with them can absorb more water. Their cloud condensation nuclei potential is significantly enhanced, while indirect climate forcing of particles is changed.\textsuperscript{10} In addition, greater hygroscopicity may create an aqueous layer over the particles and therefore facilitate further adsorption and reaction of other pollutants under ambient atmospheric conditions. These results provide insight into the complex relationship between global sulfur and nitrogen circulation and atmospheric particles.

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Notes and references