SO₂ Initiates the Efficient Conversion of NO₂ to HONO on MgO Surface

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Supporting Information

ABSTRACT: Nitrous acid (HONO) is an important source of hydroxyl radical (OH) that determines the fate of many chemically active and climate relevant trace gases. However, the sources and the formation mechanisms of HONO remain poorly understood. In this study, the effect of SO₂ on the heterogeneous reactions of NO₂ on MgO as a mineral dust surrogate was investigated. The reactivity of MgO to NO₂ is weak, while coexisting SO₂ can increase the uptake coefficients of NO₂ on MgO by 2–3 orders of magnitude. The uptake coefficients of NO₂ on SO₂-aged MgO are independent of NO₂ concentrations in the range of 20–160 ppbv and relative humidity (0–70%RH). The reaction mechanism was demonstrated to be a redox reaction between NO₂ and surface sulfite. In the presence of SO₂, NO₂ was reduced to nitrite under dry conditions, which could be further converted to gas-phase HONO in humid conditions. These results suggest that the reductive effect of SO₂ on the heterogeneous conversion of NO₂ to HONO may have a significant contribution to the unknown sources of HONO observed in polluted areas (for example, in China).

INTRODUCTION

Nitrous acid (HONO) significantly enhances the atmospheric oxidative capacity due to the production of OH radical.¹ Field and modeling studies have shown that HONO photolysis contributes significantly to the OH production, with a total average contribution of up to 30–60% throughout the day.^{2–4} Because OH radical is the primary oxidant in the atmosphere and a main scavenger of gaseous pollutants, HONO affects the fate of many chemically active and climate relevant gases as well as the formation of ozone and secondary aerosols. HONO is also an important indoor pollutant due to its negative health effects.^{5,6} Therefore, investigation of HONO sources is of great environmental and health significance.

The currently known sources of HONO include direct emissions, gas-phase formation through the OH and NO reaction, heterogeneous reactions of NO₂ on the ground and particle surfaces, surface photolysis reactions, and biological processes.^{1,3,7–15} Among these sources, it is well-accepted that heterogeneous processes involving conversion of NO₂ on wet surfaces are the major formation pathway of HONO in the atmosphere. For example, HONO was produced during the hydrolysis of NO₂ on surfaces such as mineral dust, glass, and buildings.^{14,16–18} Redox reaction between NO₂ and soot was also proposed as a source of HONO.¹⁹ Because the reactive sites on soot decreased quickly after exposure to NO₂, the contribution of this process to HONO sources greatly depends on the content of reactive compounds on surface.^{20–23} A number of research projects have focused on the photo-enhanced conversion of NO₂ on surfaces such as soot,¹¹ humic

acids,^{24–26} organic compounds,^{27,28} and TiO₂-containing mineral dust^{29–32} due to their photocatalytic or photosensitive properties. These photochemical reactions of NO₂ on aerosol particles and ground surface have been considered as daytime HONO sources in the troposphere.^{10,15}

Although the mechanism of NO₂ conversion to HONO on surfaces has been widely studied, the role of aerosol on the formation of HONO is still controversial. Observations of HONO in the United States and Europe concluded that the ground surface is the major source of HONO, and reactions on aerosol particles are considered less-important.^{3,33–35} In contrast, the correlation between particulate matters and HONO were observed in the heavy haze episodes in China, and reactions on surfaces of high loading of aerosols were suggested as an important source of HONO.^{36–39} However, the mechanism is yet to be corroborated by laboratory results.

Mineral dust is a major component of aerosol over the world^{40,41} and particularly in China.^{40,42,43} It is estimated that 1000–3000 Tg of mineral aerosols are emitted annually into the atmosphere.⁴⁴ Field measurements observed a large ratio of HONO to NO₂ during dust storms, suggesting the highly efficient conversion of NO₂ to HONO on mineral dust particles.⁴⁵ However, the true uptake coefficients of NO₂ on mineral dust are very low,^{32,46,47} indicating that mineral dust is

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a minor medium for NO₂ reaction. Recently, a positive correlation (0.92) between gas-phase HONO and particulate sulfate was observed during dusty days,⁴⁸ and the authors attributed the correlation to a synergistic mechanism of adsorption and reaction between NO₂ and SO₂ on dust particles rather than the hydrolysis of NO₂. However, the mechanism is not clear yet. Oxidation of SO₂ or sulfite to sulfate in the presence of NO₂ in aqueous reactions has been considered as an important source of sulfate^{49,50} in which NO₂ was converted to nitrite or N₂O dependent on the reaction conditions.^{50–54} Compared to the liquid phase, the interaction of NO₂ and SO₂ on the particle surface is more-complicated and not well-studied. For example, NO₂ was found to have little effect relative to air on the conversion of SO₂ to sulfate on carbon particles.⁵⁵ However, in Santis and Allegrini's study, the interaction of SO₂ and NO₂ with the carbonaceous materials led to sulfate and different nitrogen-containing species depending on the type of carbonaceous materials.⁵⁶ Previous studies indicated that heterogeneous reactions SO₂ and NO₂ on mineral particles exhibit synergistic effect and promote the formation of sulfate.^{57–60} It should be noted that the concentrations of SO₂ or NO₂ used in these studies were much higher than atmospheric mixing ratios of these gases. Nevertheless, whether this synergistic effect relates to the formation of HONO is not clear. This inspired us to explore the effect of SO₂ on the conversion of NO₂ to HONO on mineral particles because minerals are ubiquitous in aerosol and soil.

SO₂ pollution is still severe in China due to the large combustion of fossil fuel. In haze episodes, the average concentration of SO₂ could be 60 ppbv, with the highest value close to 300 ppbv.³⁸ In the present study, we investigated the effect of coexisting SO₂ on the heterogeneous reaction of NO₂ on MgO using coated-wall flow tube reactor and in situ diffuse reflectance Fourier transformed infrared spectroscopy (in situ DRIFTS) at room temperature. MgO is an important component of mineral dust and soil, which has been always chosen as a representative of crustal oxides.^{40,59,61–64} A possible mechanism of the effect of SO₂ on the uptake and transformation of NO₂ was proposed. This work will contribute to a better understanding of the sources of HONO in polluted regions as well as in dust storms.

MATERIALS AND METHODS

Samples. MgO (Sigma-Aldrich) was used as purchased. A total mass of 1.0 g of MgO powder was dissolved in 20.0 mL of water. This suspension was dripped uniformly into a quartz tube (20.0 cm length, 1.1 cm i.d.) and dried overnight in an oven at 373 K. The resulting homogeneous film covered the entire inner area of the tube and was uniform in thickness. The specific surface area of the samples was measured to be 135.6 cm² mg^{−1} by nitrogen Brunauer–Emmett–Teller (BET) physisorption (Quantachrome Autosorb-1-C).

Coated-Wall Flow Tube Reactor. The uptake experiments were performed in a horizontal cylindrical coated-wall flow tube reactor (Figure S1), which has been described in detail elsewhere.^{23,47} The flow tube reactor was covered with aluminum foil to avoid the influence of light in the room. The experiments were performed at ambient pressure and maintained at 295 K by circulating water bath through the outer jacket of the flow tube reactor. High-purity synthetic air was used as carrier gas, and the total flow rate introduced in the flow tube reactor was 0.9 L·min^{−1}, ensuring a laminar regime.

The relative humidity (RH) was recorded during the whole experiment by a hygrometer (Omega RH-USB). NO₂ with designing concentrations was introduced into the flow tube through a movable injector with 0.3 cm (o.d.) radius. The concentrations of NO₂ and NO were online measured using two chemiluminescence analyzers (THERMO 42i). One analyzer used a molybdenum oxide (MoO) catalyst that converts NO₂, HONO, and other reactive nitrogen species, while the other is coupled with a highly selective photolytic converter that photodissociates NO₂ to NO at wavelengths of 380–410 nm (Droplet Measurement Technologies, model BLC).⁶⁵ The difference between these two analyzers is due to the existence of HONO, which was confirmed by comparative measurement of HONO with a long-path absorption photometer (LOPAP)^{66,67} (as seen in Figure S2).

Uptake Coefficient. The kinetic behavior of the NO₂ can be described by assuming a pseudo-first-order reaction. The first-order rate constant (k_{obs}) is related to the geometric uptake coefficient (γ_{geo}) using eq 1:

$$\frac{d}{dt} \ln \frac{C_0}{C_i} = k_{\text{obs}} = \frac{\gamma_{\text{geo}} \langle c \rangle}{2r_{\text{tube}}} \quad (1)$$

where r_{tube} , t , and $\langle c \rangle$ are the flow tube radius, the exposure time, and the NO₂ average molecular velocity, respectively. C_0 and C_i are the NO₂ concentrations at $t = 0$ and $t = i$, respectively.

If the loss of NO₂ at the particle surface is too rapid to be recovered with the NO₂ supply, a radial concentration gradient in the gas phase will be formed, which may cause diffusion limitations. Therefore, a correction for diffusion in the gas phase was taken into account using the Cooney–Kim–Davis (CKD) method.^{68,69} Then, the true uptake coefficient (γ_{BET}) was obtained from the mass-dependence of γ_{geo} using eq 2:^{47,70}

$$\gamma_{\text{BET}} = \frac{S_{\text{geo}}}{S_{\text{BET}}} \times \text{slope} \quad (2)$$

where S_{geo} is the inner surface area of the sample tube (cm²), S_{BET} is the specific surface area of the particle sample (cm²·mg^{−1}), and slope is the slope of the plot of γ_{geo} versus sample mass in the linear regime (mg^{−1}).

In Situ DRIFTS. The heterogeneous reactions of SO₂ and NO₂ on MgO particles were measured by in situ diffuse reflectance Fourier transformed infrared spectroscopy (in situ DRIFTS, *is50*, Thermo Fisher Scientific), equipped with an in situ diffuse reflection chamber and a high-sensitivity mercury cadmium telluride (MCT) detector cooled by liquid N₂. Before the experiment, MgO particles were finely ground and placed into a ceramic crucible in the in situ chamber. The samples were first pretreated at 373 K for 120 min in a stream of synthetic air in a total flow of 100 mL·min^{−1}. After the temperature was cooled to room temperature (295 K), the samples were exposed to reactant gases. The infrared spectra were collected using a computer with OMNIC 6.0 software (Nicolet Corporation). All spectra were recorded at a resolution of 4 cm^{−1} for 100 scans in the spectral range of 600 to 4000 cm^{−1}, and then Kubelka–Munk (K–M) conversion was conducted. The low frequency cutoff of the spectra was due to the strong lattice oxide absorption of the samples.

Ion Chromatograph Analysis. Water-soluble inorganic anions were analyzed using an ion chromatograph (ICS-1000, Dionex Corporation), which consists of a guard column

Figure 1. Comparison of NO₂ uptake on MgO in the presence of various SO₂ concentrations: 0 ppbv (177.42 mg, black), 40 ppbv (43.15 mg, orange), 100 ppbv (33.47 mg, violet), and 1000 ppbv SO₂ (48.96 mg, olive). (A) NO₂ uptake and NO formation, (B) HONO formation. RH = 7.5%. Desorption of NO₂ occurred when the injector was pushed to the end of the flow tube after 120 min of reaction.

(AG14A) and an analytical column (AS14A). An electrolytic suppressor (ASRS 300 4 mm) was used to reduce the conductivity of the eluent. A concentrator (TAC-LP1) was installed. The analysis was performed by using 8 mM sodium carbonate and 1 mM sodium bicarbonate eluent at a flow rate of 0.6 mL min⁻¹. Multipoint calibrations were performed by using calibration standard solutions (Dionex Corporation, seven anion standards for anion). Good linearity of the calibration curve was obtained with $R^2 > 0.996$. The anions NO₂⁻, NO₃⁻, and SO₄²⁻ were analyzed. SO₃²⁻ was not analyzed because the column is not able to analyze SO₃²⁻ ion.

RESULTS AND DISCUSSION

Effect of SO₂ on NO₂ Uptake. Figure 1 shows NO₂ uptake on MgO particles in the presence of various SO₂ concentrations (0, 40, 100, and 1000 ppbv). When MgO was exposed to 100 ppbv NO₂ in the absence of SO₂, NO₂ concentrations decreased slightly and returned to the initial concentration in 10 min. This indicated the reaction of NO₂ on the fresh MgO surface is weak. In contrast, sharp decrease of NO₂ concentration was detected in all NO₂ uptake processes with the coexistence of SO₂. The uptake process lasted much more than 2 h, and the sample surfaces were quite beyond saturation. Blank experiment showed that no reaction between NO₂ and SO₂ on the quartz tube occurred under this reaction condition (as shown in Figure S3). Thus, this significant decrease of NO₂ concentration could be attributed to the uptake of NO₂ on MgO surface by coexisting SO₂. Increasing in SO₂ concentrations could increase the initial uptake coefficients as well as adsorption amounts of NO₂ on MgO, as seen in Figure 1A. This suggested NO₂ adsorption sites may relate to SO₂ adsorbed species on MgO surface.

For gaseous products, no NO was observed during all the uptake experiments, as can be seen in Figure 1A. This is in agreement with Liu et al., in which NO was not observed in the uptake of NO₂ on kaolin and hematite using coated-wall flow tube.⁴⁷ However, Underwood et al. observed NO as a predominant gas-phase product in the reaction of NO₂ with mineral oxides using Fourier transform infrared spectroscopy (FTIR) and Knudsen cell reactor.⁷¹ This difference is likely due to the various reaction conditions, such as NO₂ concentration, relative humidity, pressure, and oxygen content in reactor.^{31,47,62,71} For example, in Underwood et al., high NO₂ concentration was used, which favored a Langmuir–Hinshel-

wood (LH) or Eley–Rideal (ER) type mechanism of NO₂ and nitrite to produce NO and nitrate.⁷¹ Moreover, both the FTIR and Knudsen cell reactors are under vacuum condition in which the RH and oxygen content were very low.⁷¹ The O₂ (20% in volume) present in the flow tube reactor could inhibit the formation of NO.^{31,47} In the present study, NO was not observed, which was mainly due to the low concentration of NO₂ and the synthetic air conditions. In addition, the coexisting SO₂ may also change the reaction mechanism of NO₂.

Unlike NO, HONO was observed as a product in all NO₂ uptake processes in the presence of SO₂, as seen in Figure 1B. The concentration of HONO increased gradually as the reaction proceeded. In previous studies, Liu et al. found HONO was formed in the uptake of NO₂ on kaolin and hematite.⁴⁷ However, in the present study, the formation of HONO was not obvious in the reaction between NO₂ and MgO without SO₂. This may be due to the low reactivity of MgO to NO₂, which limited the formation of HONO. These results suggested that SO₂ could change the reaction mechanism of NO₂ on MgO particles. The role of SO₂ on the uptake of NO₂ and the formation of HONO will be discussed later.

Uptake Coefficients of NO₂. The initial geometric uptake coefficients (γ_{geo}) of NO₂ on MgO surface under different reaction conditions were compared in Figure 2. The SO₂-aged MgO samples were prepared by exposing MgO particles to 1000 ppbv SO₂ in synthetic air for 12 h. As seen in Figure 2, γ_{geo} of NO₂ on fresh MgO exhibited a linear mass effect, with a slope of $4.79 \times 10^{-8} \text{ mg}^{-1}$. This is due to the diffusion of NO₂ into underlying layers of the sample. The true uptake coefficients (γ_{BET}) were calculated using eq 2. γ_{BET} of NO₂ on fresh MgO is about 2.44×10^{-9} , indicating weak reactivity of fresh MgO particles to NO₂. This value is lower than that measured by Underwood et al., in which they reported a true uptake coefficient of 1.2×10^{-5} . This discrepancy may be due to the different measurement methods. Underwood et al. used a Knudsen cell in which samples were under vacuum condition. In the flow tube reactor, O₂ and H₂O in carrier gas may exhibit a competitive effect to NO₂ reaction and decreased the uptake coefficient of NO₂.^{31,47}

The uptake coefficients obtained in NO₂ reaction on SO₂-aged MgO as well as in the reaction of NO₂ coexisting SO₂ are independent of sample mass in the mass range of 6–300 mg. A

Figure 2. Mass dependence of initial geometric uptake coefficients (γ_{geo}) of 100 ppbv NO_2 on different MgO surfaces at 7.5% RH: fresh MgO (black), SO_2 -aged MgO (red), and fresh MgO coexisting with 100 ppbv SO_2 (blue) and 40 ppbv SO_2 (olive).

further decrease in sample mass was not adopted because it is difficult to achieve complete coverage of the sample tubes. Because the diffusion of NO_2 or SO_2 into the underlying layers of powdered samples was found to readily occur, the BET surface area of the powdered samples was always used to calculate the true uptake coefficients.^{61,62} Therefore, we estimated the γ_{BET} based on the initial geometric uptake coefficients on sample with the minimum mass available. The true uptake coefficients of NO_2 were about 5.28×10^{-6} for SO_2 -aged MgO samples and about 2.87×10^{-6} and 1.03×10^{-6} for fresh MgO in the presence of 100 and 40 ppbv SO_2 , respectively. It should be noted that these results should be considered as lower-limit values.

The mass-independent initial geometric uptake coefficients of NO_2 depend on the concentration of SO_2 or SO_2 aging process (as seen in Figure S4). When the concentration of SO_2 was above 1000 ppbv, the uptake coefficients of NO_2 reached a plateau and were close to that on SO_2 -aged MgO. The saturation effect of SO_2 on uptake coefficients of NO_2 might be due to a Langmuir-type adsorption of SO_2 on MgO.⁶¹ These results further indicated a close relation between adsorbed SO_2 species and NO_2 adsorption sites on MgO surface.

The effect of concentrations and relative humidity on γ_{geo} of NO_2 on SO_2 -aged MgO was compared in Figure 3. Values of γ_{geo} were measured in mass-independent regime (10–15 mg). The error bars represent the standard deviation (σ) for three

independent experiments. As seen in Figure 3A, the uptake coefficients of NO_2 were independent of the concentration of NO_2 in the range of 20–160 ppbv, indicating a first order reaction of NO_2 on SO_2 -aged MgO. As for the humidity, increasing RH in the reactor had little influence on the initial geometric uptake coefficients of NO_2 on SO_2 -aged MgO (Figure 3B). It should be noted that the increase of relative humidity has always exhibited negative effect on the uptake of NO_2 on fresh particles, which was explained by competitive adsorption between NO_2 and H_2O on surface.^{29,31,47} These results in our study indicated that the adsorption sites for NO_2 on SO_2 -aged MgO may be not adsorbed water or surface species like reactive oxygen or hydroxyls. Instead, adsorbed SO_2 species should relate to NO_2 adsorption sites on MgO surface.

Yield of HONO. Formations of HONO were observed in all the NO_2 uptake experiments on MgO in the presence of SO_2 . The effect of relative humidity on the yield of HONO in the uptake of NO_2 on SO_2 -aged MgO was compared in Figure 4.

Figure 4. Effect of relative humidity on the yield of HONO on SO_2 -aged MgO particles. (Sample mass: 10–15 mg).

The measured yields of HONO were calculated by the ratio of HONO formed to NO_2 consumed. There was little HONO formation under dry conditions, while the generation of HONO was detected under humid conditions. This indicated that surface H_2O was necessary for the formation of HONO. However, the HONO yields were not influenced by RH. It should be noted that the γ_{geo} of NO_2 on SO_2 -aged MgO particles were also not influenced by RH (Figure 3B). These results suggested that surface H_2O was not involved in the initial reaction step of NO_2 on SO_2 -aged MgO. Instead, surface

Figure 3. Effect of (A) NO_2 concentrations (RH = 7.5%) and (B) RH on the γ_{geo} of NO_2 on SO_2 -aged MgO particles. (Sample mass: 10–15 mg).

Figure 5. In situ DRIFTS spectra of MgO exposed to (A) 1000 ppbv SO₂ and (B) 1000 ppbv SO₂ and 200 ppbv NO₂ as a function of time. RH = 4.5%.

H₂O reacted with the products of NO₂ reaction. Thus, the increase in RH may not increase the HONO yield.

In the presence of H₂O, the measured yields of HONO increased gradually as the reaction proceeded. The HONO yield beyond 50% was observed in the later stage of reaction, implying the formation of HONO maybe not through the hydrolysis reaction (disproportionation of NO₂ to equal HONO and HNO₃ with HONO yield less than 50%).^{14,16} Constant HONO yield as well as steady state uptake of NO₂ was not observed, indicating that this reaction is not a catalytic reaction. The reaction mechanism will be discussed later.

Besides, the measured yields of HONO also depended on sample mass (as seen in Figure S5). The observed yields of HONO decreased with increasing MgO mass. Due to the alkalinity of MgO, the formed HONO may tend to adsorb on the surface as nitrite species instead of releasing to gas phase if the sample mass was large. Desorption of HONO was also observed when the uptake process was stopped (as seen in Figure 1B). Otherwise, when the sample mass was small, HONO yield beyond 100% could be observed when the consumption of NO₂ was close to zero; namely, the surface was almost saturated (as seen in Figure S6). This may be caused by the equilibrium between the surface nitrite and gas-phase HONO. Thus, the surface species should be further analyzed.

Surface Products. To study the dynamic change of surface species, in situ DRIFTS measurements was used to characterize the reaction of NO₂, SO₂, and NO₂ and SO₂ on MgO. The reactivity of MgO to 200 ppbv NO₂ was quite weak, and no obvious surface species were observed (as seen in Figure S7), which was in good agreement with the results of flow tube experiments (Figure 1). As shown in Figure 5A, the reaction of SO₂ (1000 ppbv) on MgO resulted in the formation of sulfite (960 cm⁻¹) and sulfate (1015, 1040, 1164, 1193, and 1265 cm⁻¹).^{59,61} The sulfite was the dominant surface species in the individual SO₂ reaction, which was in consistent with previous studies.^{59,61,63,72} In the reaction of NO₂ and SO₂ on MgO (Figure 5B), surface species including sulfite (960 cm⁻¹), sulfate (1265, 1193, 1164, 1135, 1040, and 1015 cm⁻¹), and nitrite (1305 and 1220 cm⁻¹)^{73,74} were detected during the reaction. Compared to the individual SO₂ reaction (Figure 5A), the intensity of peak at 960 cm⁻¹ due to sulfite species decreased, while peaks at 1265, 1193, 1164, 1135, 1040, and 1015 cm⁻¹ (corresponding to sulfate) increased. These results suggested that the presence of NO₂ could enhance the conversion of SO₂ to sulfate.

For surface nitrogen-containing species, only surface nitrite (1305 and 1220 cm⁻¹) was observed. No peaks attributed to surface nitrate species (typically in the range of 1500–1650 cm⁻¹) was observed.^{59,71} These results indicated that SO₂ was oxidized to sulfate, while NO₂ was reduced to nitrite in the reaction between NO₂ and SO₂ on MgO surface, implying this was a redox reaction. The surface products were also confirmed by ion chromatography (IC) analysis (as seen in Figure S8). The main water-soluble ions were detected to be sulfate and nitrite with little nitrate. Thus, the final products of NO₂ reaction on MgO in the presence of SO₂ were HONO and nitrite, combined the results of flow tube and DRIFTS experiments. Considering the convertibility between HONO and nitrite, the yields of HONO (HONO and nitrite) in the present study could be regarded as 100%.

Proposed Reaction Mechanism. As shown above, the coexisting SO₂ was determined to enhance the uptake of NO₂ on MgO and the transformation to HONO and nitrite. This means SO₂ could change the reaction mechanism of NO₂ on MgO. There are several proposed mechanisms of NO₂ adsorption on mineral oxides in previous researches. For example, Underwood et al.⁷¹ suggested a two-step mechanism in which gas-phase NO₂ is initially adsorbed as a nitrite species that subsequently reacts with another nitrite (Langmuir–Hinshelwood type) or additional NO₂ (Eley–Rideal type) to form surface nitrate and gas-phase NO. This mechanism of NO₂ adsorption on mineral oxide surface may be mainly due to the high NO₂ concentration used. In the present study, much lower NO₂ concentration was used. In addition, neither gaseous NO nor surface nitrate species were observed. Thus, this mechanism was excluded from our results.

Previous studies also proposed that the hydrolysis of NO₂ on wet surfaces results in the generation of gaseous HONO and surface HNO₃.^{16–18,47,75} When NO₂ was in high concentration level, dimerization of gaseous NO₂ led to the formation of N₂O₄ intermediate, which then reacted with H₂O to form HONO and HNO₃.^{17,18} In the hydrolysis reaction of NO₂ with low concentration, it was proposed that dissociative chemisorption of H₂O to yield H_{ads} and OH_{ads} on the surface, which further reacted with NO₂ to form HONO and HNO₃.^{47,75} The yield of HONO should be less than 50% through this disproportionation reaction. Much higher yields than 50% were obtained in this work, however, indicating that the HONO formation on SO₂-aged MgO could not be attributed to hydrolysis reaction.

Recently, Kebede et al. demonstrated the formation of HONO in the redox reactions between NO_2 and $\text{Fe}^{2+}(\text{aq})$ present in water films on the surface of iron-bearing minerals.¹³ The yield of HONO could be larger than 50% when NO_2 underwent a redox reaction on surfaces.^{13,47} However, unlike Fe, Mg is not a valence-varied metal. This could explain no HONO formation in the uptake of NO_2 on MgO without SO_2 . Therefore, the conversion of NO_2 to HONO on MgO in the presence of SO_2 may be due to the redox reaction between NO_2 and surface sulfur-containing species.

It is well-known that adsorption of SO_2 on mineral particles leads to the formation of surface sulfite species, while additional oxidants like O_3 and NO_2 were needed to oxidize sulfite to sulfate.^{58,63,72} Although both sulfite and sulfate were observed during the adsorption of SO_2 on MgO, sulfite was the main surface species on MgO.^{59,61} In the present study, to confirm the role of surface sulfite species on the uptake of NO_2 , SO_2 -aged MgO samples were further exposed to 500 ppbv O_3 for forcing oxidation of sulfite to sulfate. NO_2 uptake decreased greatly on these samples (seen in Figure S9), indicating surface sulfite species were the reducing agent for the conversion of NO_2 to nitrite and HONO on MgO.

Therefore, we proposed a reaction mechanism of NO_2 on MgO in the presence of SO_2 , as seen in Scheme 1. First, initial

Scheme 1. Proposed Reaction Mechanism of NO_2 Adsorption on MgO in the Presence of SO_2

adsorption of SO_2 on MgO surface led to the formation of surface sulfite species (SO_3^{2-}), in which surface oxygen species (O^{2-}) was involved. These surface sulfite species then provided reactive sites for NO_2 adsorption. A redox reaction between NO_2 and sulfite occurred under dry condition and led to the formation of nitrite and sulfate species. If surface H_2O was present, HONO was produced through the conversion of nitrite by H_2O .

Recently, Liu et al. found that coexisting NO_2 could enhance the conversion of SO_2 to sulfate on typical mineral oxides, in which N_2O_4 was observed as an intermediate and nitrate was the final nitrogen-containing product on surfaces.⁵⁹ In the present study, the presence of SO_2 initiated the conversion of NO_2 to nitrite on MgO, and nitrate was not observed. This discrepancy may be due to the high concentration of NO_2 (100 ppm) used in Liu et al.,⁵⁹ which was prone to the dimerization of NO_2 and can favor the conversion of nitrite to nitrate through an Eley–Rideal (ER) type mechanism.⁷¹ When NO_2 concentration is in ppbv level (e.g., 100–200 ppbv in the present study), excess SO_2 could completely reduce NO_2 to HONO and nitrite on MgO surface. Therefore, nitrate species were not formed on the surface.

■ ATMOSPHERIC IMPLICATIONS

Although HONO has been widely investigated in laboratory studies and field measurements, its sources are still not fully understood.^{9,12,15,35} Here, we suggest a new potential formation pathway of HONO in polluted environments with high concentration of SO_2 . The coexisting SO_2 was found to increase the true uptake coefficients of NO_2 on MgO by 2–3

orders of magnitude. Mg is the seventh most abundant element in Earth's crust, making it a major component of soil and windblown mineral dust.⁴⁰ Thus, this reaction could happen on both mineral dust and the ground surface, which could contribute to HONO sources in polluted region with high concentration of SO_2 .

First, this redox reaction mechanism may help explain the high HONO concentrations observed in dust storms. Mineral particles account for a large fraction of global emissions of aerosol particles and can undergo long-range transport.^{40,41} Mineral dust can encounter SO_2 during the transport, which could form sulfite on particle surfaces.^{63,72} These SO_2 -aged mineral particles could provide reactive sites for the conversion of NO_2 to HONO. For example, the observations of high correlation between HONO and sulfate in dusty days⁴⁸ might be partially due to the redox reaction between SO_2 and NO_2 on mineral particles. Nie et al.⁷⁶ recently reported observational evidence on new particle formation and growth in the remote ambient atmosphere during heavy dust episodes mixed with anthropogenic pollution and attributed photoinduced heterogeneous reactions of NO_2 to the source of HONO and OH. Considering the high concentrations of mineral particles, SO_2 , and NO_2 observed in these dust events, the reaction between SO_2 and NO_2 on mineral particles could also contribute to the source of HONO.

Second, the redox reaction between SO_2 and NO_2 on surfaces may contribute to the formation of HONO in the haze episodes in China because high SO_2 concentration was always observed in the haze episodes. Haze in China has been increasing in frequency of occurrence as well as the area of the affected region, especially in the wintertime in the North China plain.⁶⁰ High concentrations of HONO were observed in the severe haze period in Beijing.^{38,39} As demonstrated in the present study, the true uptake coefficient of NO_2 on MgO in the presence of SO_2 could be in the range of $1.0\text{--}5.2 \times 10^{-6}$, with a yield of HONO and nitrite about 100%. If a constant surface area to volume ratio (S/V) value of 0.3 m^{-1} for ground surface was used,^{77,78} HONO formation rates could be $0.18\text{--}0.96\% \text{ h}^{-1}$ with an average loading (1.7%) of MgO in soil in north China (see detail in the Supporting Information). If the upper limit γ (mass-independent uptake coefficients) was considered, the formation rate would further increase. However, mineral dust is also a major component ($\sim 35\%$ in mass) of aerosol in the North China plain.^{40,43} A recent study reported that the concentrations of $\text{PM}_{2.5}$ and NO_2 in a heavy haze episode could reach $228\text{--}545 \mu\text{g m}^{-3}$ and $20\text{--}80 \text{ ppbv}$, respectively.³⁸ According to the average ratio of $\text{PM}_{2.5}/\text{PM}_{10}$ (0.5) during haze-fog episodes⁷⁹ and a surface area to volume ratio measured in Beijing,⁸⁰ the formation rate of HONO via the redox reaction of NO_2 and SO_2 on MgO in mineral dust is estimated to be $0.43\text{--}21.2 \text{ pptv h}^{-1}$ (see detail in the Supporting Information). Considering that the S/V value of aerosol ($<0.01 \text{ m}^{-1}$) is much lower than that of ground surface ($\sim 0.3 \text{ m}^{-1}$), the redox reaction between SO_2 and NO_2 on surfaces as a relevant HONO source will be more important on ground than on aerosol, even in the severe haze episodes in China. Accordingly, coexisting gases, especially SO_2 , should be considered in future study of NO_2 conversion to HONO.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05724.

Additional information about the diagram of coated-wall flow tube, the description of LOPAP and comparative measurement of HONO by LOPAP and two NO_x analyzers, blank tube experiment, effect of SO₂ concentration on the uptake coefficients, mass effect on yield, the measured yields of HONO in the uptake of NO₂ on 8.08 mg SO₂-aged MgO, DRIFTS spectra of MgO exposed to 200 ppb NO₂, description of IC and measurement, and uptake experiment on O₃-SO₂-aged MgO and the description of the calculation of HONO formation rates. (PDF)

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Notes

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