Influence of relative humidity on heterogeneous kinetics of NO2 on kaolin and hematite†

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In order to obtain reliable kinetic parameters, it is required to measure the reaction kinetics of important heterogeneous reactions at ambient relative humidity (RH). In this study, the uptake coefficients and HONO yields for the heterogeneous reaction of NO2 on kaolin and hematite were measured at RH from 7% to 74% and at ambient pressure in the dark using a coated-wall flow tube reactor. The initial true uptake coefficient ($\gamma_{\text{uni}}$) of NO2 at RH 7% was measured to be $(1.44 \pm 0.10) \times 10^{-7}$ and $(1.58 \pm 0.13) \times 10^{-6}$ on kaolin and hematite, respectively, while it decreased notably on both minerals, accompanied by an increase of HONO yields, as RH increased. The average $\gamma_{\text{uni}}$ at 32–74% RH was $(4.42 \pm 1.17) \times 10^{-8}$ and $(2.83 \pm 0.84) \times 10^{-7}$ on kaolin and hematite, respectively. The corresponding mean HONO yield was $(36.0 \pm 16.1)\%$ and $(75.9 \pm 3.32)\%$, respectively.

Introduction

In the past few decades, due to their possible roles in atmospheric chemistry, considerable attention has been paid to heterogeneous reactions between nitrogen oxides (NOx) and atmospheric particulate matter (APM), including soot,\textsuperscript{1-4} mineral dust\textsuperscript{5-8} and sea salt.\textsuperscript{9,10} For example, heterogeneous reactions of NOx on soot and mineral dust can produce gaseous HONO\textsuperscript{3,4,11} which is a daytime source of OH radicals;\textsuperscript{12} while reactions between NOx and sea salt might be a source of Cl radicals.\textsuperscript{10} Mineral dust is an important component of APM, with a loading of 1000–3000 Tg per year.\textsuperscript{13} The presence of dust could also result in a decrease in concentrations of SO2, NOy (NO3 + N2O5 + HNO3), and H2O2 (OH + HO2 + H2O2) by 10.3–52.5%, 16.0–99.7%, and 11.3–59.4%, respectively, through heterogeneous reactions under typical dust storm conditions.\textsuperscript{14} In addition, it has been found that heterogeneous chemistry, including that of SO2 and NOx on dust, plays a significant role in regional haze formation in China.\textsuperscript{15-17}

The uptake coefficient ($\gamma$) is one of the key parameters in modelling studies. Several studies have measured the $\gamma$ of NO2 on dust from Saharan or Asian source regions\textsuperscript{5,18} and surrogate materials including CaCO3,\textsuperscript{7} Al2O3, Fe2O3, CaO, MgO, TiO2,\textsuperscript{5,19} and clay minerals.\textsuperscript{6} The $\gamma$ of NO2 on these samples varies from $10^{-4}$ to $10^{-9}$ depending on the substrates and experimental conditions,\textsuperscript{10} and was recommended to be $1.2 \times 10^{-8}$ by Crowley et al.\textsuperscript{21} Except for a few reaction systems, such as reactions of NO2 on TiO2,\textsuperscript{18,22,23} Saharan sand,\textsuperscript{23} and CaCO3,\textsuperscript{7} however, most of these $\gamma$ values were measured under dry conditions due to the limitations of the low pressure reactors used\textsuperscript{5,19} or at a single point of relative humidity ($\gamma$ was measured for NO2 on TiO2 and Saharan sand at RH = 25%).\textsuperscript{18,23} However, $\gamma$ has been found to show a strong dependence on humidity for some reactions. Both the increase and the decrease of $\gamma$ have been observed as a function of RH.\textsuperscript{7,22,24,25} Recently, it has been found that the heterogeneous uptake of NO2 on soil\textsuperscript{26} and montmorillonite\textsuperscript{27} was lowered notably by water.

In a recent work,\textsuperscript{16} the revised Community Multi-scale Air Quality Model (CMAQ), with simple heterogeneous chemistry, greatly minimized the gaps between the model and the observation results concerning inorganic components, while relatively large errors still remained. This means more refined kinetic parameters for the relevant reactions are required to further improve the model performance. In the real troposphere, RH typically varies from 20% to 90%. Thus, the quantitative dependence of $\gamma$ on RH needs to be investigated case by case for these important heterogeneous reactions.\textsuperscript{28} At the present date, reports on the RH dependent $\gamma$ of NO2 on kaolin and hematite are unavailable for modelling simulation.

The reactive process of NO2 on dust is regarded as the adsorption and reaction of NO2 with the surface oxides, followed by secondary processes, or the heterogeneous hydrolysis of NO2 to yield HONO and HNO3.\textsuperscript{20} Besides surface nitrates and nitrates,\textsuperscript{19,29-31} HONO is
also detected as a gaseous product. Under ultra-violet irradiation, the HONO yield ($\gamma_{\text{HONO}}$) is 75%, 33% and 80% for reactions of NO$_2$ on pure TiO$_2$, 1% TiO$_2$/SiO$_2$ and Saharan sand, respectively. It has been postulated that the surface acidity, microstructure and other unknown factors control the production of HONO. However, the HONO yields for heterogeneous reactions of NO$_2$ on kaolin and hematite are as yet unclear, and how the RH affects the HONO yield for the reactions of NO$_2$ on these materials is also unknown.

In this study, kaolin and hematite, which have been identified as common mineralogical components of dust samples, were used as a proxy of mineral dust to investigate the effect of RH on the kinetics and HONO yields for reactions with NO$_2$. The uptake experiments were carried out at ambient RH and ambient pressure using a flow tube reactor. The quantitative dependence of uptake coefficients and HONO yields on RH on NO$_2$ on kaolin and hematite was obtained. The environmental implications were also discussed.

**Experimental section**

**Materials**

Hematite (AR) was obtained from Beijing Nanshang Chemicals Factory. Kaolin was supplied by Huaibei Junteng Kaolinite Co. Ltd and originated from Anhui province, China. The mineralogy was confirmed by X-ray diffraction (XRD) analysis (D/max-RB). The specific surface area of hematite and kaolin was 2.7 m$^2$ g$^{-1}$ and 12.4 m$^2$ g$^{-1}$, respectively, measured by nitrogen Brunauer–Emmet–Teller (BET) physisorption analysis (Quantachrome Autosorb-1-C). NO$_2$ standard gas (50 ppmv in N$_2$, Beijing Huayuan Gases Inc.), and high purity N$_2$ and O$_2$ (99.99%, Beijing AP BEIFEN Gases Inc.) were used as received.

**Experimental methods**

The experiments were performed in a 20 cm × 1.0 cm (i.d.) horizontal cylindrical coated-wall flow tube reactor in the dark (covered with aluminium foil) (Fig. S1, ESI†), which has been described in detail elsewhere and is similar to that used by Ndour et al. The temperature was maintained at 298 K by circulating water through the outer jacket of the flow tube reactor. Simulated air was used as the carrier gas, and the total flow introduced in the flow tube reactor was 770 ml min$^{-1}$, ensuring a laminar regime at ambient pressure. NO$_2$ was introduced into the flow tube through a movable injector with a 0.3 cm radius. The NO$_2$ concentration was measured using a NO$_2$ analyzer (THERMO 42i), in which a molybdenum catalyst converts NO$_2$ to NO, which is subsequently measured via chemiluminescence, after which NO is desorbed from both kaolin and hematite. This means that the reaction kinetics, $k_{\text{obs}}$, was reported in terms of the uptake coefficient, which was proportional to the measured first-order rate constant derived from the uptake curves when the Na$_2$CO$_3$ denuder was used, according to the following equation:

$$k_{\text{obs}} = \frac{\gamma_{\text{obs}}(c)}{2r_{\text{tube}}}$$

where $r_{\text{tube}}$, $\gamma_{\text{obs}}$ and $c$ are the flow tube radius, the geometric uptake coefficient and the average molecular velocity of NO$_2$, respectively. The $k_{\text{obs}}$ was determined by pulling the injector back to the end of the sample tube. Thus, the geometric inner surface area of the whole sample tube was used to calculate $\gamma_{\text{obs}}$. A correction for gas phase diffusion limitations was taken into account for $\gamma_{\text{obs}}$ calculations using the Cooney–Kim–Davis (CKD) method. Then, the true uptake coefficient ($\gamma_t$) was obtained from the mass dependence of $\gamma_{\text{obs}}$ as follows:

$$\gamma_t = \text{slope} \times \frac{A_g}{S_{\text{BET}}}$$

where [slope] is the slope of the plot of $\gamma_{\text{obs}}$ versus the sample mass in the linear regime (mg$^{-1}$); $A_g$ is the inner surface area of the sample tube (cm$^2$); and $S_{\text{BET}}$ is the specific surface area of the particle sample (cm$^2$ mg$^{-1}$).

**Results and discussion**

Fig. 1 shows the typical uptake curves of NO$_2$ on kaolin and hematite as well as the corresponding evolution of the $\gamma_{\text{obs}}$ with time. The black and red lines show the data collected with 10 s and 1 min time resolution, respectively. As shown in Fig. 1A and B, once the kaolin or hematite sample was exposed to NO$_2$, a large initial NO$_2$ uptake was observed, followed by a quick recovery. After 20 min, a stable consumption of NO$_2$ was observed on both kaolin and hematite. The $c(=o)$ (20–30 min) was (0.869 ± 0.005) and (0.902 ± 0.006) for these two specific experiments, respectively. This steady uptake of NO$_2$ was always observed for all uptake experiments at different RH, which implies the occurrence of a catalytic reaction. When the samples were isolated from the reactant gas by moving the injector outside the reaction region, only a small amount of NO$_2$ (<4%) desorbed from both kaolin and hematite. This means that the reactive uptake should be the main contributor to the uptake of NO$_2$ on these samples.

Because NO is in thermodynamic equilibrium with NO$_2$, ~3% NO was always present in the reactant gas. Fig. S2 (ESI†)
As mentioned in the Experimental section, gas-phase diffusion was corrected for in \( \gamma_{\text{obs}} \) calculations using the

Additionally, gas phase HNO₃, NO₂ and HONO were detected.⁵,¹⁹ Based on these previous studies,⁴,⁹,¹⁹,³⁰,³⁹ the following reactions are summarized as the possible reaction pathways in the dark.

\[
\begin{align*}
\text{MO}^- + \text{NO}_2(g) & \rightleftharpoons \text{MO}^-\text{NO}_2(\text{ads}) \\
\text{MO} + 2\text{NO}_2(\text{ads}) & \rightleftharpoons \text{MO}-\text{N}_2\text{O}_4(\text{ads}) \rightleftharpoons \text{MO}-\text{NO}^+\text{NO}_3^{-}(\text{ads}) \\
\text{MO}-\text{NO}_2^{-}(\text{ads}) + \text{NO}_2(g) & \rightarrow \text{MO}^- + \text{MO}-\text{NO}_3^{-}(\text{ads}) + \text{NO}(g) \\
2\text{MO}-\text{NO}_2^{-}(\text{ads}) & \rightarrow \text{MO}^- + \text{MO}-\text{NO}_3^{-}(\text{ads}) + \text{NO}(g) \\
\text{M}^-\text{O}^- + \text{NO}_2(g) & \rightarrow \text{M}^-\text{NO}_2^{-}(\text{ads}) \\
2\text{M}^-\text{O}^- + \text{N}_2\text{O}_4(\text{ads}) & \rightarrow \text{MO}^-\text{NO}_2^{-}(\text{ads}) + \text{MO}^-\text{NO}_3^{-}(\text{ads}) \\
\text{MONO}_2^{-}(\text{ads}) + \text{MO}-\text{H}_2\text{O}(\text{ads}) & \rightarrow \text{MO}^-\text{OH}(\text{ads}) + \text{MO}^- + \text{HONO}(g) \\
\text{M}^-\text{OH} + \text{NO}_3^{-}(g) & \rightarrow \text{M}^-\text{O} + \text{HONO}(g) \\
\text{2NO}_3^{-}(g) + \text{MO}-\text{H}_2\text{O}(\text{ads}) & \rightarrow \text{MO}^-\text{HONO}_2(\text{ads}) + \text{HONO}(g) \\
2\text{M}^-\text{OH} + \text{2NO}_3^{-}(g) & \rightarrow \text{MO}^-\text{NO}_3^{-}(\text{ads}) + \text{MO}^-\text{NO}_2^{-}(\text{ads}) + \text{MO}^-\text{H}_2\text{O}(\text{ads}) \\
\end{align*}
\]

MO in the above reactions refers to mineral oxide. The reactions (3), (5), (7), and (10)–(12) should contribute to the loss of NO₂ from the gas phase during uptake experiments. The reactions (5), (6), and (9)–(11) involving the release of gas phase NO and HONO should be responsible for the uptake of NO₂ at a steady state after the surface species are saturated. However, as shown in Fig. S2 (ESI†), the release of NO was not observed on either kaolin or hematite under all of the tested RH values (7–47%). This means that reactions (5) and (6) should follow a minor reaction pathway under our reaction conditions, although they cannot be ruled out yet owing to the possibility of adsorption or reactions in the gas phase or on the surface. Thus, the uptake at the steady state should mainly be related to the reactions involving HONO formation. The contribution of reactions (9)–(11) to NO₂ uptake and HONO formation will be discussed later.

Fig. 1C and D show the evolution of the \( \gamma_{\text{obs}} \) with reaction time. The \( \gamma_{\text{obs}} \) decreased quickly with reaction time due to the surface saturation by surface species as mentioned above. Thus, the time resolution had a great effect on the uptake coefficient. For example, in these two specific experiments shown in Fig. 1, the \( \gamma_{\text{obs}} (10 \text{ s}) \) is 2.61 \( \times \) 10⁻⁵ (279.9 mg kaolin) and 4.03 \( \times \) 10⁻⁵ (247 mg hematite) at 298 K and 47% RH, while the corresponding \( \gamma_{\text{obs}} (1 \text{ min}) \) is 1.59 \( \times \) 10⁻⁵ and 2.78 \( \times \) 10⁻⁵, respectively. The \( \gamma_{\text{obs}} \) (SS) at the steady state (20–30 min) decreased to (2.28 \( \pm \) 0.10) \( \times \) 10⁻⁶ and (1.69 \( \pm \) 0.10) \( \times \) 10⁻⁶, respectively, with a decrease of one order of magnitude. Therefore, three values of \( \gamma_{\text{obs}} \) are reported here (\( \gamma_{\text{obs}} (10 \text{ s}), \gamma_{\text{obs}} (1 \text{ min}) \) and \( \gamma_{\text{obs}} \) (SS)).

Using infrared spectroscopy, surface species including nitrates and nitrites have been well characterized for heterogeneous reactions of NO₂ on kaolin⁴ and other mineral oxides.⁴,⁹,¹⁹,³⁰,³⁷,³⁸ The presence of surface nitrogen with oxidation states of +5, +4 and +3 was also confirmed using X-ray spectroscopy.¹¹
Cooney–Kim–Davis (CKD) method. In the coated-wall flow tube reactor, powder samples with multilayer thickness were usually generated. In order to determine the probe depth of NO2 in the multilayer samples, the response of γobs to the sample mass was measured. Fig. 2 shows the typical linear mass dependence of γobs on kaolin and hematite. Thus, the true uptake coefficient (γt) can be obtained using eqn (2). The γt (10 s), γt (1 min) and γt (SS) of NO2 on kaolin at 47% RH are (4.85 ± 0.39) × 10−8, (0.34 ± 0.16) × 10−8, and (3.74 ± 0.27) × 10−9, respectively. The corresponding values are (3.23 ± 0.23) × 10−7, (1.89 ± 0.18) × 10−7, and (1.50 ± 0.05) × 10−8, respectively, on hematite. The values of γt (10 s), γt (1 min) and γt (SS) at other levels of relative humidity are summarized in Table 1.

As shown in Table 1, both kaolin and hematite showed the largest γt of NO2 at 7% RH. The γt (10 s) was (1.44 ± 0.10) × 10−7 on kaolin, and it was (1.58 ± 0.13) × 10−6 on hematite at 7% RH. Fig. 3 shows the influence of RH on the γt of NO2 on the surface of kaolin and hematite. Assuming a Langmuir–Hinshelwood mechanism for the heterogeneous reaction of NO2 on these samples and that the adsorption of water vapour can be described independently by a Langmuir isotherm with an equilibrium constant KNO2, the NO2 surface coverage (θNO2) under humid conditions is given by,

\[
θ_{NO2} = \frac{K_{NO2}[NO2]}{1 + K_{NO2}[NO2] + K_{H2O}[H2O]}
\]  

where KNO2 and KH2O are the Langmuir adsorption equilibrium constants for NO2 and H2O, respectively, and [NO2] and [H2O] are the concentrations of NO2 and water vapor, respectively.

The pseudo first-order rate coefficient of the NO2 reaction follows

\[
k_{1,NO2} = \frac{k_{2,SS}[SS]K_{NO2}[NO2]}{1 + K_{NO2}[NO2] + K_{H2O}[H2O]}
\]  

where k2,SS is the second-order surface reaction rate constant and [SS]s is the adsorption site on the particle. By replacing eqn (14) with eqn (15) and (16),

\[
\gamma = \frac{4k_{1,NO2}}{A_s\langle c_{NO2} \rangle}
\]

the influence of RH on the uptake coefficient can be described as

\[
\gamma = \frac{4k_{2,SS}[SS]K_{NO2}[NO2]}{A_s\langle c_{NO2} \rangle + K_{NO2}[NO2]A_s\langle c_{NO2} \rangle (P_{H2O}^0[RH]K_{H2O}A_s\langle c_{NO2} \rangle)}
\]  

where a = 4k2,SS[SS]KNO2, b = ⟨cNO2⟩ + KNO2[NO2]⟨cNO2⟩, and c = P0H2O/KH2O⟨cNO2⟩; As is the surface area of the particles.

### Table 1 Summary of the measured NO2 uptake coefficients (γt) and HONO yields (γHONO) for the heterogeneous reaction of NO2 on kaolin and hematite at 298 K

<table>
<thead>
<tr>
<th></th>
<th>Kaolin</th>
<th>Hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH (%)</td>
<td>γtini (10 s)</td>
<td>γtini (1 min)</td>
</tr>
<tr>
<td>7</td>
<td>14.4 ± 0.01</td>
<td>8.69 ± 0.01</td>
</tr>
<tr>
<td>15</td>
<td>8.93 ± 0.39</td>
<td>3.89 ± 0.15</td>
</tr>
<tr>
<td>32</td>
<td>5.32 ± 0.21</td>
<td>3.30 ± 0.15</td>
</tr>
<tr>
<td>47</td>
<td>4.85 ± 0.39</td>
<td>3.46 ± 0.25</td>
</tr>
<tr>
<td>74</td>
<td>3.10 ± 0.14</td>
<td>2.03 ± 0.29</td>
</tr>
</tbody>
</table>
As shown in Fig. 3, like the $\gamma$ (10 s), the $\gamma$ (1 min) of NO2 also decreases with RH on kaolin and hematite. In particular, the curves in the low RH regions (<20%) are much steeper than those in the high RH regions. The decline of the initial $\gamma$ with RH can be ascribed to competitive adsorption between H2O and NO2 similar to the competitive adsorption of O2, NO2 or COS with H2O on mineral oxides.22,24,25 It has been found that a monolayer of H2O on kaolin is achieved at 13% RH,6 and at 10% RH on hematite.24 The initial $\gamma$ of H2O on mineral dust (4.2 ± 0.7 × 10−2)42 is much larger than that of NO2, as discussed above. This means that adsorption of H2O is preferred over NO2 when the RH is lower than the RH of monolayer of water. This satisfactorily explains the quick decrease of the initial $\gamma$ of NO2 in the low RH range. In addition, the $\gamma$ (1 min) is more sensitive to RH than that of $\gamma$ (10 s) in the low RH range, because the longer exposure time is favorable to formation of a monolayer of water. However, as shown in the inset graphs in Fig. 3, the $\gamma$ (SS) was not very sensitive to RH on hematite, while a decrease followed by an increase with RH was observed on kaolin.

**HONO formation and HONO yields**

Besides surface nitrates,19,29,30,37,38 the presence of HONO(g) was qualitatively confirmed during the heterogeneous reaction of NO2 on SiO211 and kaolin26 using UV spectroscopy. Using a Long Path Absorption Photometer (LOPAP)20 or a NO analyzer,18,22,23 the yields of HONO were also measured directly or indirectly for the photochemical reaction of NO2 on TiO2 and Saharan sand.18,22,23 The formation of HONO can be explained by reactions (9)–(11). In fact, when reaction (3) and the dissociation reaction of H2O to form the surface OH group are coupled with reactions (9) and (10), a catalytic cycle from NO2(g) to HONO(g) can be realized by the reaction of the surface OH group as shown below. Thus, reactions (9)–(11) can be regarded as catalytic reactions.

\[
\text{NO}_2(g) \rightarrow \text{HONO}(g)
\]

(21)

In the above experiments, a Na2CO3 denuder between the outlet of the reactor and the NO2 analyzer was used to trap the formed HONO. In order to investigate the HONO yields, uptake experiments without the Na2CO3 denuder were performed at 7–74% RH. Fig. S4 (ESI†) shows a comparison of the typical uptake curves of NO2 on kaolin and hematite at 47% RH with or without the Na2CO3 denuder. As can be seen from this figure, the integrated uptake capacity (the total amount of NO2 uptake by the sample within 30 min) for NO2 with a Na2CO3 denuder was clearly larger than that without a Na2CO3 denuder on both kaolin and hematite. Thus, the difference between them represents the amount of HONO formed during the reaction. It should be pointed out that the Na2CO3 denuder can adsorb a small amount of NO2 (2.8 ± 0.8% regardless of RH, Fig. S5, ESI†). This difference might also partly result from the gaseous reaction between NO2 and H2O. However, in the experiments with a Na2CO3 denuder, adsorption of NO2 or HONO from a gaseous reaction was saturated or subtracted before the
samples were exposed to NO2 gas. Therefore, the difference between uptake curves with and without the Na2CO3 denuder strongly supports the formation of HONO during the reactions of NO2 on kaolin and hematite, and represents the net production of HONO from a heterogeneous reaction.

In the uptake experiments, uptake curves of NO2 for different sample masses were independently measured. As discussed above, the integrated uptake capacity linearly depends on the sample mass over a wide mass range (Fig. S6, ESI†). Thus, by dividing the differential uptake capacity (the amount of NO2 uptake by the sample within 1 min) by the sample mass, the normalized differential uptake capacity with or without a Na2CO3 denuder was obtained and is shown in Fig. 4. The error bars in Fig. 4A and B represent the standard deviation (σ) of 5–7 independent experiments. The averaged differential uptake capacity of NO2 with a Na2CO3 denuder is clearly higher than that without a Na2CO3 denuder on both kaolin and hematite. Fig. 4C and D shows the evolution of HONO yield with reaction time. The error bars were calculated considering error propagation.

On kaolin, the initial yHONO was around 30%, and then it gradually increased to 60%, while it increased quickly from 5% to 85% within 3 min on hematite. These results indicate that reactions (3), (5) and (7), which lead to surface nitrates and nitrites, mainly contribute to the initial uptake of NO2 on either kaolin or hematite. This also satisfactorily explains the quick deactivation for uptake of NO2 on kaolin and hematite (Fig. 1). However, at the steady state, the uptake of NO2 should be mainly ascribed to reactions (9)–(11). Angelini et al.6 proposed that reaction (9) might be related to HONO formation on kaolin because nitrites were not detected using both IR (at 1235 cm−1) and ion chromatography. However, reactions (10) and (11) cannot be ruled out yet because a non-zero initial HONO yield was observed on kaolin (shown in Fig. 4C). In particular, the yHONO on kaolin is around 50% at the steady state, which implies the importance of the disproportionation reaction (reaction (11)) in HONO formation on kaolin. On hematite, however, a very small initial yHONO (5%) and a larger yHONO at the steady state (>50%) indicate that reactions (9) and (10) should be the main pathway for HONO formation.

The accumulation of surface nitrites should explain the quick increase of yHONO with time (Fig. 4D). Therefore, these results imply different mechanisms of HONO formation on different dust samples.

Fig. S6 (ESI†) shows the linear dependence of the integrated uptake capacity on the sample mass within 30 min. The slopes of these lines represent the integrated uptake capacity per unit sample mass. For example, at 47% RH, the slope was (1.09 ± 0.07) × 10−10 mol mg−1 when a Na2CO3 denuder on kaolin, while it was (6.40 ± 0.19) × 10−11 mol mg−1 when a Na2CO3 denuder was not used. For hematite, the corresponding slope was (1.03 ± 0.04) × 10−10 mol mg−1 and (2.25 ± 0.24) × 10−11 mol mg−1. Therefore, using these values, the integrated HONO yield was calculated and summarized in Table 1. The influence of RH on the integrated uptake capacity and yHONO is shown in Fig. 5.

As shown in Fig. 5, if a Na2CO3 denuder was not used, the integrated uptake capacity of both kaolin and hematite for NO2 gradually decreased with RH within 30 min, whereas different responses of the integrated uptake capacity to RH were observed between these two minerals when a Na2CO3 denuder was used. On hematite, from 7% to 15% RH, the integrated uptake capacity decreased by about a factor of two owing to competitive adsorption and it did not change any more with a further increase in RH (dotted line). However, the integrated uptake capacity on kaolin decreased with RH from 7% to 32%, and then increased with a further increase in RH. This change trend was also observed for its γ1 (SS) as shown in Fig. 3.

It should be noted that kaolin consists of neutral layers containing one octahedral aluminium hydroxide sheet bonded to one tetrahedral silicon oxide sheet through a plane of shared oxygen atoms.8 Although kaolin has a low shrink-swell capacity compared to montmorillonite, it swells slightly with increased water adsorption,43 which should make more reactive sites (M–O or M–OH) available. Thus, an increase of γ1 (SS) and the integrated uptake capacity was observed when the RH was higher than 32%. This is similar to the reaction of HNO3 on Na–montmorillonite, on which the γ increases clearly at higher RH.44 As shown in Fig. 5 and Table 1, the integrated HONO yield within 30 min increased from (3.4 ± 2.4)% to (49.4 ± 2.8)%.
on kaolin, and from (19.4 ± 0.4)% to (77.4 ± 0.1)% on hematite, when the RH increased from 7% to 74%. As discussed above, the values of the $\gamma_{\text{HONO}}$ also suggest that reaction (11) (disproportionation reaction with a HONO yield of 50%) should be the main mechanism for HONO formation on kaolin at high RH, while reactions (9) and (10) (with a HONO yield of 100%) should be important for HONO formation on hematite when the RH was larger than 32%.

It should be pointed out that HONO from the gas-phase reaction between NO$_2$ and H$_2$O at high RH might result in a positive bias for the measured heterogeneous HONO yields. However, this effect should be negligible in this study for the following reasons. Firstly, we measured the difference between the initial NO$_2$ concentrations with and without the Na$_2$CO$_3$ denuder at different RH values. If the gas phase reaction significantly contributes to the monitored HONO signal, the fraction of the removed HONO (measured as NO$_2$ and formed in the gas phase reaction) by the Na$_2$CO$_3$ denuder should positively respond to RH. However, as shown in Fig. S5 (ESI†), the relative ratio of NO$_2$ removed by the Na$_2$CO$_3$ denuder to the initial NO$_2$ concentration was constant (2.8 ± 0.8%), regardless of the RH value. Secondly, if gas phase reactions significantly contribute to the monitored HONO signal, a non-zero intercept should be expected when linearly fitting the uptake coefficient or the integrated uptake capacity to the sample mass at a fixed RH value, because the NO$_2$ converted to HONO in the gas phase should be a non-zero constant at the same residence time, NO$_2$ concentration and RH. However, as shown in Fig. 2 and Fig. S5 (ESI†), both the uptake coefficient and the integrated uptake capacity were linearly related to the sample mass with zero intercepts regardless of the RH values and sample types. Therefore, we are confident with the conclusion that the measured HONO yield was related to heterogeneous reactions on these samples.

Conclusions and atmospheric implications

Under dry conditions, the $\gamma_{\text{ini}}$ of NO$_2$ on kaolin and hematite was $2.55 \times 10^{-7}$ and $6.63 \times 10^{-6}$, respectively. The values are comparable with those reported in the literature when the reaction conditions are taken into account.$^{5,6,19}$ However, the RH typically varies from 20% to 90% in the real troposphere. As found in this work, the $\gamma_{\text{ini}}$ decreases with RH. Therefore, the $\gamma_{\text{ini}}$ measured under dry conditions should overestimate the uptake ability of mineral dust toward NO$_2$. Using the measured $\gamma_{\text{ini}}$ in the RH range of 32–74%, we recommend that the $\gamma_{\text{ini}}$ of NO$_2$ on kaolin should be $(4.42 \pm 1.17) \times 10^{-8}$ at ambient RH, and $(2.83 \pm 0.84) \times 10^{-7}$ on hematite. These values are slightly larger than the values recommended by Crowley et al.$^{21}$ According to the model results, the $\gamma_{\text{ini}}$ should be greater than $10^{-4}$ to observe an appreciable impact on NO$_2$ and O$_3$ concentrations for the interactions of NO$_2$ with mineral dust.$^{7}$ Thus, the small uptake coefficients measured at ambient RH in this work imply that heterogeneous reactions of NO$_2$ on mineral dust might be unimportant for NO$_x$ and O$_3$ concentrations. At the present date, secondary inorganic aerosol (SIA) has attracted much attention for China’s air pollution because SIA often abruptly increases during severe haze days.$^{15-17}$ The role of heterogeneous reaction in SIA formation has been confirmed in field measurements, laboratory and modelling studies. As the typical RH has often varied in the range of 40–80% in haze days in China,$^{15}$ the influence of RH dependent kinetics on particulate species formation needs to be evaluated with modelling studies in the future.

As a daytime source of OH radicals, HONO formation attracts much attention. In this work, the uptake of NO$_2$ at the steady state was found to be mainly related to HONO formation. Similar to the recommended $\gamma_{\text{ini}}$ at ambient RH, we also recommend the $\gamma_{\text{ss}}$ of NO$_2$ at ambient RH to be $(3.52 \pm 0.87) \times 10^{-9}$ and $(1.35 \pm 0.14) \times 10^{-8}$ on kaolin and hematite, respectively. The corresponding HONO yield is $(36.0 \pm 16.1)\%$ and $(75.9 \pm 3.32)\%$. Thus, the uptake coefficient for HONO formation at the steady state ($\gamma_{\text{ss},\text{HONO}}$) was calculated to be $(1.27 \pm 0.88) \times 10^{-9}$ and $(1.02 \pm 0.15) \times 10^{-8}$ on kaolin and hematite, respectively. Assuming the tropospheric concentration of NO$_2$ to be in the range from 10 ppb to 50 ppb$^{45}$ and that of mineral dust from 40 μm$^2$ cm$^{-3}$ to 150 μm$^2$ cm$^{-3}$ with a fraction of hematite of 6%,$^{13,46}$ the possible formation rate of HONO via the reaction of NO$_2$ on hematite in mineral dust varies from $4.8 \times 10^4$ to $9.0 \times 10^4$ molecules cm$^{-3}$ per day using the estimated $\gamma_{\text{ss},\text{HONO}}$ of hematite. Even if the $\gamma_{\text{ss},\text{HONO}}$ of mineral dust is equal to that of hematite, the formation rate of HONO is estimated to be from $8.0 \times 10^5$ to $1.5 \times 10^7$ molecules cm$^{-3}$ per day. This value is much lower than that on soot samples.$^{4}$ Therefore, the contribution of the heterogeneous reaction of NO$_2$ on mineral dust to tropospheric HONO might be negligible under typical atmospheric conditions. However, the mass loading of dust is often increased on severe haze days.$^{47}$ An et al.$^{48}$ found that heterogeneous reactions significantly enhance the concentrations of HONO and other particulate species in the North China Plain. This means that more comprehensive modelling studies based upon our kinetics should be carried out to fully evaluate the role of HONO formation from heterogeneous reactions on dust in regional air quality. It should be pointed out that the kinetic data were measured in the dark in this work, and other factors such as adsorbed HNO$_3$ have not been considered. It is necessary to investigate in the future whether irradiation has an enhancement effect on these reactions like that on Saharan sand$^{23}$ and whether the co-absorbed species, such as HNO$_3$, which were found to promote HONO decomposition on borosilicate glass surfaces,$^{19}$ have an influence on the HONO yield.

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References