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## PAPER



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Biwu Chu (D<sup>abc</sup> and Hong He (D<sup>abc</sup>) In this study, a wall-coated flow tube reactor, *in situ* diffuse reflectance infrared Fourier transform spectro-

 $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>†

scopy (DRIFTS) and ion chromatography (IC) were used to investigate the effect of water on the heterogeneous reactions of SO<sub>2</sub> and NH<sub>3</sub> on the surfaces of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Flow tube results show that water exhibited little effect on the initial uptake coefficients ( $\gamma_{BET}$ ) of SO<sub>2</sub> but the addition of NH<sub>3</sub> increased the  $\gamma_{BET}$  at various relative humidity (RH) values on both  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The  $\gamma_{BET}$  of SO<sub>2</sub> in the presence of NH<sub>3</sub> was negatively RH dependent on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which decreased from (8.80 ± 2.30) × 10<sup>-6</sup> at 9% RH to (2.24 ± 0.71) × 10<sup>-6</sup> at 85% RH. In contrast, the  $\gamma_{BET}$  of SO<sub>2</sub> in the presence of NH<sub>3</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> increased from (1.32 ± 0.45) × 10<sup>-6</sup> at 10% RH to (2.56 ± 0.39) × 10<sup>-6</sup> at 74% RH. Surface product analysis by DRIFTS and IC shows that ammonium sulfate-like species formed, whereas the variation of SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> with RH differed on Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. With the increase of RH, sulfate tended to transform into bisulfate on Fe<sub>2</sub>O<sub>3</sub> with copresence of NH<sub>3</sub>, whereas surface-coordinated sulfite transformed to water-solvated sulfite and water-solvated sulfate species on Al<sub>2</sub>O<sub>3</sub> regardless of the presence of NH<sub>3</sub>. During this process, the amount of sulfate decreased with RH on Fe<sub>2</sub>O<sub>3</sub>, as opposed to that on Al<sub>2</sub>O<sub>3</sub>; yet the NH<sub>4</sub><sup>+</sup> was inhibited to form by adsorbed water on both surfaces. The different interaction mechanisms among water, NH<sub>3</sub>, and SO<sub>2</sub> on Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> as well as the atmospheric implications have been proposed.

The effect of water on the heterogeneous

reactions of SO<sub>2</sub> and NH<sub>3</sub> on the surfaces of

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### **Environmental significance**

Regional haze pollution has become a severe environmental issue in China owing to its increased frequency of occurrence in recent years. Heterogeneous reactions are considered of great importance in the production of secondary inorganic aerosol during haze episodes, wherein the fate of precursor gases, such as  $SO_2$  and  $NH_3$ , is closely associated with the presence of  $H_2O$ . This study reveals the different role of  $H_2O$  on the heterogeneous uptake of  $SO_2$  and  $NH_3$  on typical  $Fe_2O_3$  and  $Al_2O_3$  mineral dusts, which provides an insight into the  $H_2O$ -dependent distribution of gaseous pollutants on the gas-solid interface; relevant kinetic parameters of  $SO_2$  and  $NH_3$  presented here may provide important information for future model investigation in the atmosphere.

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## Introduction

Mineral dust is an important constituent of atmospheric particulate matter (PM), with an annual emission ranging from 1000 to 3000 Tg.<sup>1</sup> It can scatter and absorb solar and terrestrial radiation as well as act as a cloud condensation nucleus (CCN), accounting for a large uncertainty in the prediction of future global climate.<sup>2,3</sup> It also plays an important role in the migration and transformation of atmospheric species by providing reactive surfaces wherein heterogeneous reactions of SO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, water vapor and other atmospheric gases and in-cloud processing could occur.<sup>4-12</sup> Commonly, SO<sub>2</sub> adsorbs onto the surface of mineral dust as adsorbed sulfite, yet it can be oxidized into sulfate on encountering transition metal ions or other oxidants, like O<sub>3</sub>, NO<sub>x</sub> or OH radicals.<sup>13–20</sup> For instance, He *et al.* found that copresence with NO<sub>x</sub> could lead



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<sup>†</sup> Electronic supplementary information (ESI) available: XRD patterns of α-Fe<sub>2</sub>O<sub>3</sub> and γ-Al<sub>2</sub>O<sub>3</sub>; DRIFTS spectra of α-Fe<sub>2</sub>O<sub>3</sub> and its fitting peaks of integrated areas; individual reaction of SO<sub>2</sub> or NH<sub>3</sub> on α-Fe<sub>2</sub>O<sub>3</sub> and γ-Al<sub>2</sub>O<sub>3</sub>; linear mass dependence of the uptake coefficient of SO<sub>2</sub> on α-Fe<sub>2</sub>O<sub>3</sub> and γ-Al<sub>2</sub>O<sub>3</sub> at different RH; surface species stability test of α-Fe<sub>2</sub>O<sub>3</sub> and γ-Al<sub>2</sub>O<sub>3</sub>. See DOI: 10.1039/ c9en00574a

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to rapid conversion of  $SO_2$  to sulfate and contributed to the regional haze formation in China.<sup>21</sup> Moreover, Dupart *et al.* highlighted the importance of photooxidation of  $SO_2$  to sulfate on metal oxides (*e.g.* TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>), which act as atmospheric photocatalysts initiating the formation of gaseous OH radicals under UV irradiation.<sup>22</sup>

NH<sub>3</sub> is the most abundant basic gas in the atmosphere involved in the formation of secondary PM through neutralization of acidic aerosols (e.g. HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>).<sup>23-25</sup> Theoretical and experimental studies have found that NH<sub>3</sub> addition could facilitate the nucleation and growth of sulfate aerosols in the ternary H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O-NH<sub>3</sub> system.<sup>26,27</sup> Recent studies found that the presence of NH<sub>3</sub> promoted the formation of HONO via aiding the hydrolysis of hydrated NO<sub>2</sub> dimers at the waterair interface; a similar promotion effect has also been found in the transformation of SO<sub>3</sub> to sulfamic acid (SFA) that is specifically self-catalyzed by NH<sub>3</sub>.<sup>28,29</sup> Actually, it is reported that NH<sub>3</sub> emission abatement can mitigate fine particle pollution despite worsened acid rain precipitation.<sup>30</sup> Besides, a few studies involving sole NH<sub>3</sub> adsorption on PM, such as TiO<sub>2</sub>,<sup>31</sup> soot,<sup>32</sup> sulfuric acid monohydrate<sup>33</sup> and sulfuric acid aerosols,<sup>24</sup> have also been reported. However, these heterogeneous reactions are insufficient to cover these complicated atmospheric problems, especially under an atmosphere containing multiple gases. Under such a circumstance, the coexisting gases may affect each other in their heterogeneous reactions. For instance, our previous study has shown that a synergistic effect exists between SO<sub>2</sub> and NH<sub>3</sub> on typical mineral dusts (such as, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO and TiO<sub>2</sub>).<sup>34,35</sup>

Additionally, adsorbed water plays an important role in the heterogeneous reactions of gaseous pollutants on mineral dusts.<sup>8,14,36,37</sup> The gas-oxide interface can be modified by water molecules, which can dissociate into hydroxyl groups (OH) at low RH and form a liquid layer at elevated RH.<sup>38,39</sup> In consequence, the fluctuations of accessible OH or the resulting hydrolysis effect may render the water-occupied surface either favorable or deteriorated for the adsorption and reaction of gaseous reactants.<sup>8,40,41</sup> Among those investigated reactions containing water, the role of NH<sub>3</sub> has been gradually paid attention. For instance, previous studies found that NH<sub>3</sub> could accelerate the oxidation of SO<sub>2</sub> in the thin film of water on vessel surfaces or in droplets nucleated by soot or NaCl aerosols.42,43 Recently, a study has further revealed that the NO<sub>2</sub>-driven aqueous oxidation of SO<sub>2</sub> can be favored by NH<sub>3</sub> neutralization.<sup>44</sup> However, the effect of NH<sub>3</sub> with the presence of adsorbed water on the reactivity of mineral oxides to SO<sub>2</sub> is still not well known, given the abundant reactive sites present on oxides, including OH, defects, activated oxygen species and so forth.

 $Al_2O_3$  and  $Fe_2O_3$  are typical constituents of mineral dusts and are widely used as model oxides for studying the heterogeneous reactions of trace gases. In this work, the influence of RH on heterogeneous reactions of  $SO_2$  and  $NH_3$  on  $Al_2O_3$ and  $Fe_2O_3$  at room temperature and ambient pressure are investigated by using a flow tube reactor, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and ion chromatography (IC). The heterogeneous reaction mechanism and relevant atmospheric implications have also been proposed.

### Experimental

### Materials

 $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was purchased from SASOL and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was prepared using a precipitation method as reported before.<sup>34</sup> XRD patterns (Fig. S1<sup>†</sup>) were measured on a computerized PANalytical X'Pert Pro diffractometer equipped with a Cu K $\alpha$  radiation source. The average particle sizes were hence calculated through the Scherrer equation based on the XRD patterns, with 28.04 ± 3.42 nm and 10.96 ± 2.84 nm for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively. The Brunauer–Emmett–Teller (BET) surface areas of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were 185.8 and 24.5 m<sup>2</sup> g<sup>-1</sup>, which were obtained using a Quantachrome Quadrasorb SI-MP system at 77 K. The specifications of the gases used in this experiment are as follows: SO<sub>2</sub> (0.25%, SO<sub>2</sub>/N<sub>2</sub>, Beijing Huayuan), NH<sub>3</sub> (0.20%, NH<sub>3</sub>/N<sub>2</sub>, Beijing Huayuan), N<sub>2</sub> and O<sub>2</sub> (99.999% purity, Beijing Huayuan).

#### Methods

Flow tube reactor experiments. The uptake experiments were performed in a 20 cm × 1.0 cm (i.d.) horizontal cylindrical coated-wall flow tube reactor, which has been described in detail elsewhere.45,46 The temperature was maintained at 298 K by circulating water through the outer jacket of the flow tube reactor. Synthetic air as the carrier gas was introduced in the flow tube reactor at 770 ml min<sup>-1</sup> to ensure a laminar regime at ambient pressure. SO2 was introduced into the gas flow through a movable injector with 0.3 cm radius. The SO<sub>2</sub> concentration was 210  $\pm$  5 ppb and was measured using a SO<sub>2</sub> chemiluminescence analyzer (THERMO 43i) while the concentration of  $NH_3$  was estimated as  $210 \pm 5$  ppb according to the introduced amount of NH3 and the total flow volume. RH was adjusted by the ratio of dry air to wet air and was measured using a hygrometer (center 314). The powder samples were suspended in ethanol and dripped uniformly into the inner wall of a quartz tube and then dried overnight in an oven at 393 K. No uptake of SO<sub>2</sub> was observed when the reactant gases were introduced into the blank quartz tube.

The reaction kinetics  $(k_{obs})$  of SO<sub>2</sub> can be described in terms of the uptake coefficient, assuming a pseudo first-order reaction with respect to the concentration of SO<sub>2</sub> according to eqn (R1):

$$\frac{\ln(c_0/c_1)}{t} = k_{obs} = \frac{\gamma_{obs} \langle c \rangle}{2r_{tube}}$$
(R1)

where  $c_0$  and  $c_t$  represent the concentrations of SO<sub>2</sub> at t = 0 and t, respectively, and  $\gamma_{obs}$ ,  $\langle c \rangle$  and  $r_{tube}$  refer to the geometric uptake coefficient, the average molecular velocity of SO<sub>2</sub> and the flow tube radius, respectively. The geometric inner surface area of the whole sample was used to calculate

the  $\gamma_{obs}$ . The gas phase diffusion limitation is corrected using the Cooney–Kim–Davis (CKD) method.<sup>47</sup> Given the probability of SO<sub>2</sub> diffusion into the inner surface area of the porous sample,  $\gamma_{obs}$  is dependent on the sample mass within a linear range. Hence the initial uptake coefficient is considered as BET area-normalized  $\gamma_{obs}$ , *i.e.*  $\gamma_{BET}$ , as calculated *via* eqn (R2) below:

$$\gamma_{\rm BET} = \frac{\gamma_{\rm obs} \times S_{\rm geom}}{S_{\rm BET} \times M} \tag{R2}$$

where  $S_{\text{geom}}$  is the geometric area of the flow tube reactor,  $S_{\text{BET}}$  is the BET surface area of the sample and *M* is the sample mass.

In situ DRIFTS experiments. The *in situ* experiments were performed on an FTIR spectrometer (Nicolet iS50, Thermofisher Scientific Co., USA) equipped with a highsensitivity MCT/A detector cooled by liquid nitrogen. The sample was pretreated at room temperature (298 K) for 60 min in a stream of dry synthetic air (80% N<sub>2</sub> and 20% O<sub>2</sub>, 100 mL min<sup>-1</sup>) to remove adsorbed species and then saturated with water vapor at different RH followed by exposure to 200 ppmv SO<sub>2</sub> or/and 100 ppmv NH<sub>3</sub> balanced with synthetic air. The humidity was regulated by adjusting the ratio of dry nitrogen to pure water-bubbled nitrogen and was monitored using a hygrometer (CENTER 314). All the spectra were recorded at a resolution of 4 cm<sup>-1</sup> for 30 scans in the spectral range of 4000 to 600 cm<sup>-1</sup>. Each measurement was repeated at least three times.

IC measurements. The reaction product formed on the particle surface was analyzed by means of ion chromatography. The reacted particles were preserved with 1% formaldehyde to prevent sulfite oxidation and the mixture was diluted to 10 mL with ultrapure water (specific resistance = 18.2 M $\Omega$  cm) and then sonicated for 30 min. The leaching solution that was obtained through a 0.22  $\mu$ m PTFE membrane filter was analyzed using Wayee IC-6200 ion chromatograph equipped with a TSKgel Super IC-CR cationic or SI-524E anionic analytical column. An eluent (3.5 mM Na<sub>2</sub>CO<sub>3</sub>) was used at a FlowCAM flow rate of 0.8 mL min<sup>-1</sup>.

### Results and discussion

# Influence of $\rm NH_3$ on the initial uptake of $\rm SO_2$ on $\rm Fe_2O_3$ and $\rm Al_2O_3$ at varying RH

The uptake of SO<sub>2</sub> on Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> under different conditions was investigated by using a flow tube reactor. Typical uptake curves are shown in Fig. 1. Once Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> were exposed to SO<sub>2</sub>, an obvious decrease in the concentration of SO<sub>2</sub> was observed, followed by gradual recovery at both low and high RH. The uptake of SO<sub>2</sub> was enhanced by the copresence of NH<sub>3</sub> in all cases. With regard to Fe<sub>2</sub>O<sub>3</sub>, the uptake curve of SO<sub>2</sub> varied little from low (9%) to high RH (85%), while the presence of NH<sub>3</sub> resulted in increased bottom concentration at high RH, indicating a weakened initial uptake of SO<sub>2</sub> in this case. As for Al<sub>2</sub>O<sub>3</sub>, the uptake curve be-



Fig. 1 The uptake curves of SO<sub>2</sub> on (a and b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (c and d)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the absence (black) and presence (red) of NH<sub>3</sub> at low RH and high RH, respectively. The arrow indicates the exposure beginning.

came wider at high RH (71%) with reference to its low one (9%), especially with the presence of  $NH_3$ . It can be inferred that the uptake amount of  $SO_2$  (as indicated from the area covering the hollow curve) increased at high RH for  $Al_2O_3$ .

The initial geometrical uptake coefficients ( $\gamma_{obs}$ ) are calculated according to eqn (R1).<sup>46,48</sup> Given that the SO<sub>2</sub> can diffuse into the sublayer of the sample, the linear dependence of  $\gamma_{obs}$  on the sample mass was determined (see Fig. S2 in the ESI†). Then, the  $\gamma_{obs}$  was normalized to the BET surface area to obtain the initial uptake coefficient ( $\gamma_{BET}$ ) *via* eqn (R2) within the linear range (0–6 mg for Fe<sub>2</sub>O<sub>3</sub> and 0–2 mg for Al<sub>2</sub>O<sub>3</sub>), as shown in Fig. 2.

In the case of the individual uptake of SO<sub>2</sub> on Fe<sub>2</sub>O<sub>3</sub> (Fig. 2a), the  $\gamma_{\text{BET}}$  varied little throughout the whole RH range. When NH<sub>3</sub> was introduced simultaneously with SO<sub>2</sub>, the  $\gamma_{\text{BET}}$  of SO<sub>2</sub> was promoted to increase at each specific RH. For instance, the  $\gamma_{\rm BET}$  increased from (2.41 ± 0.69) × 10<sup>-6</sup> (without NH<sub>3</sub>) to  $(8.80 \pm 2.30) \times 10^{-6}$  (with NH<sub>3</sub>) at 9%, whereas the increment became smaller at elevated RH. The  $\gamma_{\rm BET}$  at 85% was (2.16 ± 0.71) × 10<sup>-6</sup> in the absence of NH<sub>3</sub>, which rose slightly up to  $(2.24 \pm 0.71) \times 10^{-6}$  with the presence of NH<sub>3</sub>. Corresponding values have been listed in detail in Table 1. Obviously, the presence of NH<sub>3</sub> enables the enhancement of the initial uptake of SO<sub>2</sub> relative to that without NH<sub>3</sub>, whereas this promotion effect is negatively RH dependent. One possible reason can be that H<sub>2</sub>O competes with  $NH_3$  for surface active sites. In contrast to  $Fe_2O_3$ , the promotion of NH<sub>3</sub> for the increase of  $\gamma_{BET}$  (SO<sub>2</sub>) on Al<sub>2</sub>O<sub>3</sub> is favored



Fig. 2 Influence of RH on the  $\gamma_{BET}$  of SO<sub>2</sub> on (a) Fe<sub>2</sub>O<sub>3</sub> and (b) Al<sub>2</sub>O<sub>3</sub> in the absence and presence of NH<sub>3</sub>.

Table 1 Summary of the initial uptake coefficients ( $\gamma_{BET}$ ) of SO<sub>2</sub> on Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> under different conditions

Sample	RH (%)	$\gamma_{\rm BET}~(\times 10^{-6})$	
		$\gamma_{\rm BET}$ (SO <sub>2</sub> )	$\gamma_{\rm ini} \left( {\rm SO}_2 + {\rm NH}_3 \right)$
α-Fe <sub>2</sub> O <sub>3</sub>	9	$2.41 \pm 0.69$	8.80 ± 2.30
	28	$2.52 \pm 0.55$	$3.96 \pm 0.20$
	42	$2.50 \pm 0.47$	$2.98 \pm 0.73$
	85	$2.16 \pm 0.71$	$2.24 \pm 0.71$
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	10	$1.16 \pm 0.35$	$1.32 \pm 0.45$
	74	$1.18\pm0.25$	$2.56\pm0.39$

at elevated RH (Fig. 2b). The increment, *i.e.*, from  $(1.16 \pm 0.35) \times 10^{-6}$  without NH<sub>3</sub> to  $(1.32 \pm 0.45) \times 10^{-6}$  with NH<sub>3</sub> at 10% is enlarged at 74%, which is from  $(1.18 \pm 0.25) \times 10^{-6}$  to  $(2.56 \pm 0.39) \times 10^{-6}$ , as seen in Table 1. In this case, the presence of H<sub>2</sub>O facilitates the NH<sub>3</sub>-assisted uptake of SO<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub>.

The BET uptake coefficients ( $\gamma_{\text{BET}}$ ) of SO<sub>2</sub> on mineral dusts differed from each other in the literature. Usher et al. found that the  $\gamma_{BET}$  of SO<sub>2</sub> on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was in the order of 10<sup>-5</sup>-10<sup>-4</sup> using a Knudsen cell.<sup>49</sup> Kong et al. investigated the uptake of SO<sub>2</sub> on nitrate-modified  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and determined the  $\gamma_{\rm BET}$  ranging in the order of  $10^{-7}$  to  $10^{-6}$  via DRIFTS technique.<sup>18</sup> An early report by Adams et al. found that the  $\gamma_{\text{BET}}$  fell in the order of  $10^{-5}$  by using a flow tube reactor, regardless of the presence of O<sub>3</sub> or water vapor.<sup>50</sup> Lately, Huang et al. have adopted a filter-based flow reactor and introduced a corrected factor whereby the H<sub>2</sub>O<sub>2</sub>-assisted  $\gamma$  of SO<sub>2</sub> reached the order of 10<sup>-4.51</sup> Generally, the  $\gamma_{\rm BET}$ obtained via a Knudsen cell and flow tube reactor was higher than that via DRIFTS. This discrepancy was caused by the way of measurement evaluation, the different morphology of the sample, and the influence of other factors (such as RH,  $O_3$ ,  $H_2O_2$  or irradiation).<sup>13,52-55</sup> The Knudsen cell technique and flow tube reactor measure the loss rate of gaseous species during their exposure to the mineral dusts, whereas DRIFTS determines the formation rate of surface products and dismisses the physical adsorption or other possible adsorption forms of reactants. Furthermore, uptake experiments in the Knudsen cell reactor are typically under high vacuum conditions while those in a flow tube reactor are under ambient pressure; in the latter case, the residual impurities that occupy the surface may decrease the uptake of  $SO_2$ .<sup>53</sup> Therefore, our  $\gamma_{BET}$  (10<sup>-6</sup>) in this study is lower than that measured by the Knudsen cell technique.

It is worth noting that the obtained  $\gamma_{\text{BET}}$  in this study was 1–2 orders of magnitude lower than the above-mentioned  $\gamma_{\text{BET}}$  in Adams *et al.* and Huang *et al. via* a flow tube reactor.<sup>50,51</sup> One possible reason lies in the different concentration of SO<sub>2</sub> used. The SO<sub>2</sub> concentration (200 ppbv, ~4.91 × 10<sup>12</sup> molecules per cm<sup>3</sup>) in this study is ~10–200 times larger than that (2–40 × 10<sup>10</sup> molecule per cm<sup>3</sup>) in Adams *et al.* and much higher than that (5 ppbv) in Huang *et al.* A higher concentration of the reactants would give rise to a smaller initial uptake coefficient owing to the surface saturation effect.<sup>46,56</sup>

Another difference can be driven by the different mineralogy of the dust. Our dust component is single relative to the diversified ones in the cases of Adams *et al.* and Huang *et al.*, in which the various sites (*e.g.* Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, *etc.*) would enrich the surface in the adsorption and reaction of SO<sub>2</sub>, although the complex interaction among those components needs further investigation. Besides, the  $\gamma_{\text{BET}}$  presented in this study can be taken as a lower limit while that obtained in Huang *et al.* has been perfected based on a corrected factor.

# Surface products formed during the heterogeneous reactions of SO\_2 and/or NH\_3 on Fe\_2O\_3 and Al\_2O\_3 $\,$

Since flow tube reactor measured only the initial kinetic uptake of gaseous SO<sub>2</sub> on Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, the surface products formed on the two oxides were undetectable. Hence, DRIFTS experiments coupled with IC measurements were further carried out to trace the reaction processes as well as analyze the surface products. As shown in Fig. 3a, the DRIFTS spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> after exposure to SO<sub>2</sub> and NH<sub>3</sub> for 1 h are summarized as a function of RH. Under dry conditions (RH < 1%), four unresolved lines at 1294, 1243, 1159 and 1108 cm<sup>-1</sup> and a weak band at 1028 cm<sup>-1</sup> were observed, which were assigned to bidentate sulfate species.<sup>15,18</sup> Bands indicative of asymmetric and symmetric deformations of NH<sub>4</sub><sup>+</sup> at 1429 cm<sup>-1</sup> ( $\delta_{as}$  (NH<sub>4</sub><sup>+</sup>)) and 1698 cm<sup>-1</sup> ( $\delta_{s}$  (NH<sub>4</sub><sup>+</sup>)) were detected. Corresponding vibrational absorption of NH<sub>4</sub><sup>+</sup> at 3024 and 2842 cm<sup>-1</sup> was also observed. In addition, a weak absorption of NH<sub>3</sub> coordinated to a



Fig. 3 DRIFTS spectra of (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (b)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after reaction with 200 ppmv SO<sub>2</sub> and 100 ppmv NH<sub>3</sub> for 60 min at different relative humidity. The reacted  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are 32 mg and 21 mg, respectively.

Lewis acid site appeared at  $3214 \text{ cm}^{-1}$  ( $v_{s}$  (NH<sub>3</sub>)).<sup>57,58</sup> As the RH increased, two absorption bands at 3565 and 1640 cm<sup>-1</sup>, corresponding to the stretching and bending modes of surfaceadsorbed water, grew in intensity.<sup>59</sup> The absorption bands at 1294 and 1108 cm<sup>-1</sup> decreased, while bands at 1243 and 1159 cm<sup>-1</sup> red-shifted to 1223 and 1131 cm<sup>-1</sup>, respectively. This indicated that the sulfate coverage can be reduced with the introduction of water. Additionally, absorption bands of chemisorbed NH<sub>3</sub> species at 3214, 3024, 2842 and 1429 cm<sup>-1</sup> also weakened with increasing RH.

It is noteworthy that the band at *ca.* 1223 cm<sup>-1</sup> increased slightly with RH. Actually, its growth was reported to be caused by the transformation of sulfate to bisulfate, which would be favored in an acidification process.<sup>18,60</sup> In this study, the surface acidity is expected to be enhanced due to the inhibition effect of water on the adsorption of NH<sub>3</sub> at elevated RH. To confirm this, the change of this band on α-Fe<sub>2</sub>O<sub>3</sub> as a function of time at a low and high RH is analyzed and shown in Fig. S3.† All spectra are fitted using Gaussian-Lorentzian with a correlation coefficient  $(R^2)$  above 0.99 to deconvolute overlapping peaks and then the areas are integrated (shown in Fig. S4<sup>†</sup>). At low RH (Fig. S4a<sup>†</sup>), the band at *ca.* 1223 cm<sup>-1</sup> first reached a maximum in the early stage but then decreased obviously with time. This can be attributed to the buildup of bisulfate on the acidic surface at the beginning, whereas the formed bisulfate subsequently converted to sulfate upon accumulation of basic NH<sub>3</sub> species on the surface. In contrast, at high RH (Fig. S4b<sup>†</sup>), the adsorption of NH<sub>3</sub> was inhibited and the surface was kept more acidic. Therefore, the band of 1223 cm<sup>-1</sup> grew to a plateau and the value was maintained constantly till the end.

Fig. 3b shows the spectra of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with exposure to SO<sub>2</sub> and NH<sub>3</sub> with varying RH. At RH <1%, NH<sub>4</sub><sup>+</sup> bands at 3035, 2825 and 1461 cm<sup>-1</sup> were predominant on the surface.<sup>57,58</sup> The other two weak bands at 1080 and 960 cm<sup>-1</sup> are assigned to surface-adsorbed sulfite or bisulfite.<sup>61,62</sup> When the RH increased, bands at 3400 and 1640 cm<sup>-1</sup> attributed to H<sub>2</sub>O and the band at 960 cm<sup>-1</sup> attributed to sulfite increased.<sup>61</sup> Concomitantly, the band at 1080 cm<sup>-1</sup> disappeared while another new band at 1187 cm<sup>-1</sup> grew sharply. This is likely due to the conversion of surface-bound sulfite to water-solvated sulfate.<sup>62</sup> Similarly to the above observed on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the adsorption of NH<sub>3</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> weakened at elevated RH, as indicated by the decreased development of NH<sub>4</sub><sup>+</sup> bands at 3035, 2825 and 1461 cm<sup>-1</sup>, whereas a small amount of NH<sub>3</sub> coordinated to a Lewis acid site at 3207 cm<sup>-1</sup> still remained.

The individual reactions of SO<sub>2</sub> or NH<sub>3</sub> on these two oxides have also been investigated at different RHs, as shown in Fig. S5.† Briefly, a bisulfate/sulfate species (1225, 1155 cm<sup>-1</sup>) was the final product resulting from the oxidation of SO<sub>2</sub> on Fe<sub>2</sub>O<sub>3</sub> (Fig. S5a†), while solvated sulfate (1180 cm<sup>-1</sup>) and solvated sulfite (960 cm<sup>-1</sup>) cohabited on the surface of Al<sub>2</sub>O<sub>3</sub> (Fig. S5c†). The peak areas of surface products showed a slight change with RH on Fe<sub>2</sub>O<sub>3</sub> but increased remarkably with RH on Al<sub>2</sub>O<sub>3</sub>. These variations with RH are in close agreement to those found in the simultaneous reactions of SO<sub>2</sub> and NH<sub>3</sub>. Although the adsorption of  $NH_3$  also weakened with RH similar to that detected in the simultaneous reaction, it mainly resides on Lewis acid sites on both oxides (at the band at 1200 cm<sup>-1</sup> for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and 1261 cm<sup>-1</sup> for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; Fig. S5b and d†). It is likely that the copresence of SO<sub>2</sub> promoted the transformation of Lewis acid site-coordinated NH<sub>3</sub> to Brønsted acid site-bound NH<sub>4</sub><sup>+</sup>, as reported in our previous study.<sup>34</sup> These results indicated that the adsorbed water exerted different effects on the adsorption of SO<sub>2</sub> on Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, regardless of the presence of NH<sub>3</sub>, which will be discussed later.

In situ DRIFTS experiments have witnessed an opposite variation trend of S-containing species with RH on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and y-Al<sub>2</sub>O<sub>3</sub> but the same one for N-containing species on both oxides in the simultaneous reactions. IC was further used to quantitatively analyze the surface products that formed on the powder oxides at different RHs. As shown in Fig. 4, the amounts of  $SO_4^{2-}$  and  $NH_4^+$  basically decreased with increasing RH on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. In the case of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, there is a lesser increase of sulfate amount relative to its obvious band growth in the DRIFTS spectra (Fig. 3b) across the same RH range. It is deduced that the "solvation effect" of water may "magnify" the observation of bands in the DRIFTS spectra, whereas the decreased amount of  $NH_4^+$  on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with rising RH agrees well with the observation in the DRIFTS spectra. Notably, the stoichiometric ratio of NH<sub>4</sub><sup>+</sup> is much lower than that of  $SO_4^{2-}$ , which indicates that the ammonium sulfate-like species takes a small fraction relative to the rest of the sulfate. The adsorption of  $NH_3$  as  $NH_4^+$  can be retarded due to the competition effect of water for the active sites. Moreover, this suggested that the coated sulfate aerosols on both  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> tended to be acidic under NH<sub>3</sub>-poor conditions in this study. Basically, findings from DRIFTS and IC measurements further confirmed the varying trend of SO<sub>2</sub> reaction with RH on Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, as indicated from the flow tube reactor investigation.

#### Proposed mechanism

The heterogeneous reaction mechanisms of  $SO_2$  or  $NH_3$  on mineral dusts have been widely studied.  $SO_2$  most probably adsorbed on Lewis base sites (exposed oxygen atoms,  $O^{2-}$  or



Fig. 4 The amounts of sulfate and ammonium formed on (a)  $\alpha\text{-}Fe_2O_3$  and (b)  $\gamma\text{-}Al_2O_3$  at various RHs.

OH<sup>-</sup>) to form chemisorbed sulfite; while NH<sub>3</sub> tended to coordinate with Lewis acid sites (metal atoms) or bound onto Brønsted acid sites (OH sites) to form chemisorbed NH<sub>3</sub> or  $NH_4^+$ , respectively.<sup>15,34,61,63</sup> In this work, the obvious consumption of OH (3670 cm<sup>-1</sup> for Fe<sub>2</sub>O<sub>3</sub>; 3727 cm<sup>-1</sup> for Al<sub>2</sub>O<sub>3</sub>, Fig. 3) indicates that OH groups serve as important active sites for the simultaneous adsorption of SO<sub>2</sub> and NH<sub>3</sub> on the oxides, which gives rise to the formation of sulfate  $(SO_4^{2-})$ and ammonium  $(NH_4^+)$  species on Fe<sub>2</sub>O<sub>3</sub>, while sulfite  $(SO_3^{2-})$ and NH4<sup>+</sup> on Al<sub>2</sub>O<sub>3</sub> under dry conditions. Notably, NH<sub>3</sub> mainly adsorbed on Lewis acid sites in the individual reaction, whereas it favorably migrated to Brønsted acid sites to form  $NH_4^+$  with the copresence of SO<sub>2</sub>. It can be due to the enhanced Brønsted acidity caused by the adsorption of SO<sub>2</sub>, as reported in our previous study.34 The reactions can be expressed as follows:

$$SO_2(g) + O^{2^-}/OH^- \to SO_3^{2^-}/HSO_3^-$$
 (1)

$$NH_3(g) + OH^- \rightarrow O^{2-} - NH_4^+$$
 (2)

$$SO_2(g) + NH_3(g) + OH^- \rightarrow SO_3^{2-} - NH_4^+$$
(3)

On Fe<sub>2</sub>O<sub>3</sub>, the sulfate species is the final product. Hence a redox process involving the oxidation of  $SO_3^{2^-}$  by lattice Fe<sup>3+</sup> in Fe<sub>2</sub>O<sub>3</sub> would further occur under this circumstance, as shown below:<sup>14,15</sup>

$$\text{Fe}^{3+}-\text{O}^{2-} + \text{SO}_3^{2-}/\text{HSO}_3^{-} \rightarrow \text{Fe}^{2+}-\Diamond^- + \text{SO}_4^{2-}/\text{HSO}_4^{-}$$
 (4)

$$Fe^{2+} - 0^{-} + O_2(g) \rightarrow Fe^{3+} - O_2^{-}$$
 (5)

where molecular oxygen activation on the left oxygen vacancy  $(\diamond^-)$  possibly involves the regeneration of lattice Fe<sup>3+</sup> (eqn (5)), as reported by Baltrusaitis *et al.*<sup>14</sup> Then those metal sites connecting to SO<sub>4</sub><sup>2-</sup> acquired improved Lewis acidity. Once they encounter H<sub>2</sub>O (which is inevitably present even under dry conditions), additional Brønsted acid sites (M–OH<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, as shown in eqn (6)) can be created, thus facilitating the formation of NH<sub>4</sub><sup>+</sup>.<sup>34,64</sup>

$$M-SO_4^{2-} + H_2O \rightarrow M-OH^- + HSO_4^{-}$$
(6)

At low RH, we have observed the transformation of  $HSO_4^-$  to  $SO_4^{2-}$ , coinciding with the gradual formation of  $NH_4^+$  (Fig. S4a<sup>†</sup>). This indicates that the adsorbed  $NH_3$  on Lewis acid sites may migrate onto adjacent  $HSO_4^-$  sites to grab  $H^+$ , or the gaseous  $NH_3$  directly interacts with  $H^+$  in  $HSO_4^-$  to form  $NH_4^+$ . This process is preferred at low RH, as quantitatively confirmed by the IC results (Fig. 4a).

Actually, the question is raised about the role of  $H_2O$  in the formation  $SO_4^{2-}$  and  $NH_4^+$  on Fe<sub>2</sub>O<sub>3</sub>. A popular proposal is that the Fe<sup>3+</sup> ions arising from dissolved Fe<sub>2</sub>O<sub>3</sub> in acidic aerosol water can also accelerate the oxidation of sulfite *via* eqn (7):<sup>18,20,65</sup>

$$2Fe^{3+} + HSO_3^- + H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 3H^+$$
(7)

in which the  $H^+$  yielded via eqn (7) can be neutralized by basic NH<sub>3</sub> and hence give rise to more NH<sub>4</sub><sup>+</sup>. However, this contradicted with our findings in this study. The formation of SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> appeared to be inhibited with increased adsorption of water, especially at high RH. In the present study, the heterogeneous reactions of SO<sub>2</sub> and NH<sub>3</sub> may still be at the initial stage. At such stage, reactions (1)-(6) will take priority over reaction (7) in the formation of  $SO_4^{2-}$  and  $NH_4^+$ , wherein the surface OH and  $O^{2-}$  and lattice  $Fe^{3+}$  that anchors in Fe<sub>2</sub>O<sub>3</sub> rather than that dissolved in water play principal roles. For instance, DRIFTS spectra show that the OH is obviously consumed albeit decreased formation of SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> with increasing RH. It can be inferred that H<sub>2</sub>O molecules interacted with those OH sites, thus blocking those sites available for the further adsorption of SO<sub>2</sub> and NH<sub>3</sub>. Such a competition effect can also occur on the sites of  $O^{2-}$  and lattice  $Fe^{3+}$ .<sup>46,66-68</sup> As a consequence, the promotion effect of NH3 for the heterogeneous uptake of SO2 on Fe2O3 weakened with increasing RH.

The case of Al<sub>2</sub>O<sub>3</sub> was somewhat different from that of Fe<sub>2</sub>O<sub>3</sub> regardless of the presence of NH<sub>3</sub>. The initial uptake coefficient of SO<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub> increased at high RH, accompanied by the slightly enhanced formation of solvated sulfite and solvated sulfate species, namely, water seemed to contribute to the heterogeneous oxidation of SO<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub>. Results from the stability test of surface-adsorbed species (by purging water vapor onto the SO<sub>2</sub> + NH<sub>3</sub>-aged Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> surfaces at elevated RH; see more details in the ESI,† Fig. S6) show that the surface-adsorbed sulfite species on Al<sub>2</sub>O<sub>3</sub> is easily transformed into solvated sulfite and solvated sulfate species with the introduction of water while the adsorbed NH<sub>4</sub><sup>+</sup> can be easily purged away by increased water vapor fraction. The adsorbed species are found to be less stable on Al<sub>2</sub>O<sub>3</sub> than on Fe<sub>2</sub>O<sub>3</sub>, which is possibly due to the weaker interaction of Al2O3 with surface-adsorbed species than with H<sub>2</sub>O. Or rather, Al<sub>2</sub>O<sub>3</sub> appears to be more hydrophilic than Fe<sub>2</sub>O<sub>3</sub>. It is reported that the RH corresponding to the monolayer of surface-absorbed water comes earlier on Al<sub>2</sub>O<sub>3</sub> than on Fe<sub>2</sub>O<sub>3</sub>.<sup>69</sup> A fully aqueous interface may be favored to form on the surface of Al<sub>2</sub>O<sub>3</sub>, whereas a deeper reason behind this needs to be further investigated.

Similarly to Fe<sub>2</sub>O<sub>3</sub>, the formation of surface-bound NH<sub>4</sub><sup>+</sup> on Al<sub>2</sub>O<sub>3</sub> declined with RH. This trend differed from that occurring in the case of surface-adsorbed SO<sub>2</sub> species. Just as those previously reported on TiO<sub>2</sub> by Nanayakkara *et al.*, in this study, the adsorbed SO<sub>2</sub> (*e.g.* SO<sub>3</sub><sup>2-</sup>/HSO<sub>3</sub><sup>-</sup>) may become solvated in the water on Al<sub>2</sub>O<sub>3</sub> that is driven by the hydrolysis effect, as shown in eqn (8) and (9).<sup>70,71</sup>

$$SO_3^{2^-} + H_2O \Rightarrow SO_2 \cdot H_2O + O^{2^-}$$
 (8)

$$HSO_3^- + H_2O \rightleftharpoons SO_2 \cdot H_2O + OH^-$$
(9)

A SO<sub>2</sub>·H<sub>2</sub>O complex formed herein. In particular, with the presence of NH<sub>3</sub>, the NH<sub>3</sub> can donate a lone pair to the H atom in H<sub>2</sub>O (possibly forming a H bond), which makes the

O atom in  $H_2O$  more basic, thus attracting  $SO_2$  to approach it to form a  $SO_2$ · $H_2O$  complex.<sup>72–74</sup> This may explain the increased uptake of  $SO_2$  in the presence of  $NH_3$  at elevated RH. In eqn (8) and (9), the released  $O^{2-}$  and  $OH^-$  sites can be captured by surface-adsorbed water, since the consumption of OH corresponded well with the growth of adsorbed-water bands (Fig. 3). Meanwhile, part of the surface-coordinated sulfite would convert to solvated sulfate in the presence of water, as similarly found in the case of MgO by Goodman *et al.*<sup>61</sup> The solvation effect magnified the images of sulfite (960 cm<sup>-1</sup>) and sulfate (1180 cm<sup>-1</sup>) in the DRIFTS spectra because the increment of these species, such as that of sulfate from 27% RH to 85% RH (Fig. 4), is minor compared to the obvious rising of their bands in the DRIFTS spectra (Fig. 3).

### Conclusions

The heterogeneous reactions of SO<sub>2</sub> and NH<sub>3</sub> on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at different RHs were investigated by using a flow tube reactor, DRIFTS and IC techniques. It was found that sulfate dominated on the surface of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> whereas solvated sulfate and solvated sulfate species cohabited on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the presence of water. The adsorbed water had an inhibition effect on the uptake of SO<sub>2</sub> on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> despite the presence of NH<sub>3</sub>. As to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the increased RH slightly enhanced the formation of sulfate species yet suppressed the formation of ammonium. The different responses of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> to the varying RH regarding the heterogeneous reaction of SO<sub>2</sub> can be possibly linked to their different affinity toward water, although further investigation is needed.

Results from this study provided information for the atmospheric processes involving water vapor, SO<sub>2</sub> and NH<sub>3</sub> on iron- or aluminum-containing oxides. In an aerosol system under humid conditions, the aerosol mineralogy and the water content in the atmosphere play important roles in the transformation of pollutant precursors. For instance, the increased water vapor is expected to lower the initial uptake of SO<sub>2</sub> on iron oxides but promote its uptake on aluminum oxide, which possibly alters the atmospheric transportation of SO<sub>2</sub> under complicated atmospheric conditions. However, a detailed experimental investigation involving the abundance and chemical components of mineral dusts is needed to evaluate its role. The iron and aluminum oxides share some similarities in their reactivity towards NH<sub>3</sub> under humid conditions. The increased water content on the surface of oxides in the atmospheric system may reduce the adsorption of NH<sub>3</sub> on the surfaces and then influence its distribution in the gas-solid interface. On the other hand, results from DRIFTS and IC reveal that the sulfate species coated onto the surfaces of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> tended to be acidic under relatively NH<sub>3</sub>poor conditions. It has been reported that a low particle acidity or high pH value can be attached to a further enhanced SO<sub>2</sub> oxidation or organic formation involving the copresence of NO2 and/or toluene with NH3 or dissolution of other transition metal ions in aerosol water.<sup>19,75,76</sup> Given complexly polluted conditions in the real atmosphere, a relationship between  $NH_3$  variation and multi-gas pollutants in the formation of surface species on aerosol water needs to be established; and the role of the mineralogy of dust merits further investigation in such a reaction that is expected to be extrapolated to the real atmosphere.

### Conflicts of interest

There are no conflicts to declare.

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