

Supporting information

**Molecular Insights into NO-Promoted Sulfate Formation on Model TiO₂
Nanoparticles with Different Exposed Facets**

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The supporting information has 14 pages containing 9 figures and 1 table.

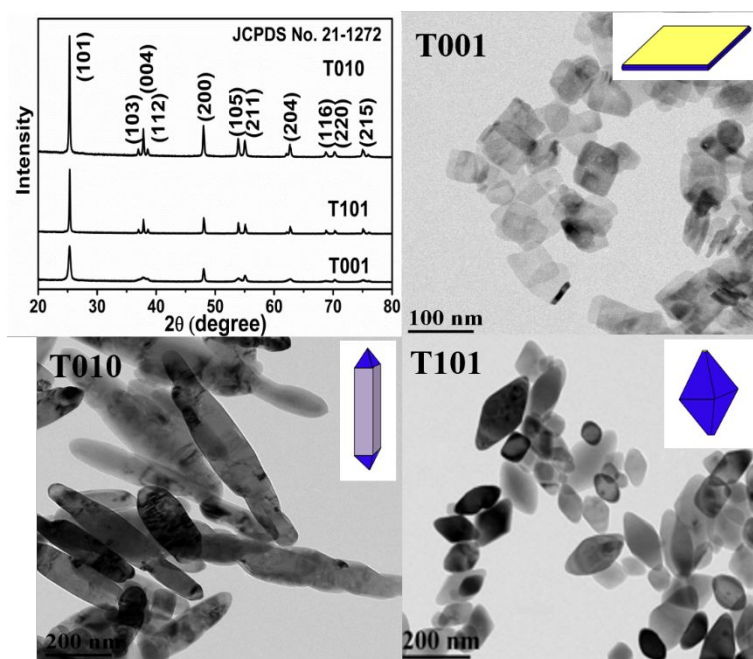


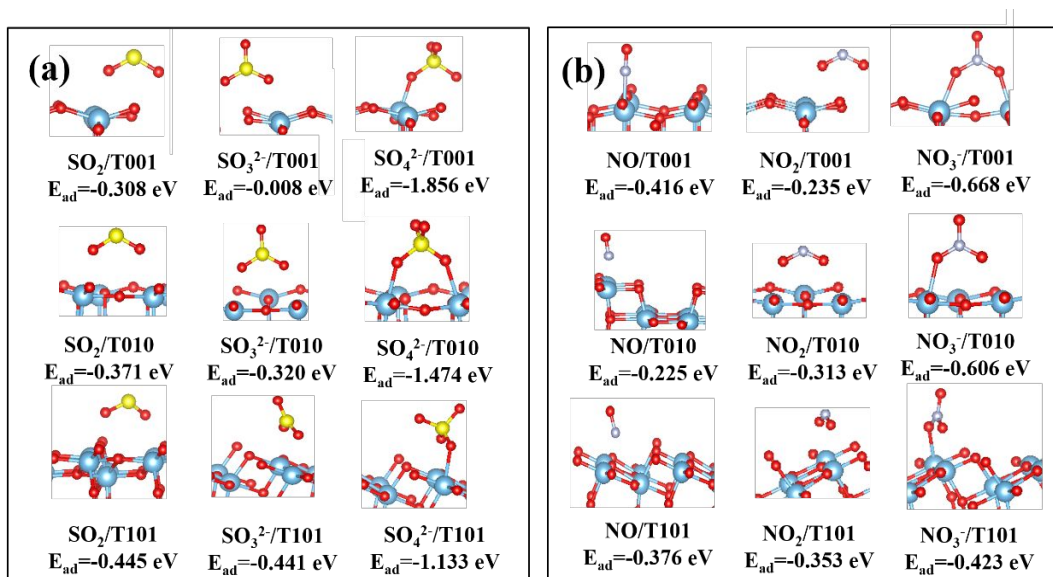
Figure S1. XRD and TEM patterns of the three TiO_2 samples

Material preparation. TiO_2 nanoparticles with dominant (001), (010) and (101) facets, denoted as T001, T010 and T101 in the following text, were prepared through a modified hydrothermal method reported by Li et al.¹ Typically, T001 is synthesized using a modified HF hydrothermal method. A hydrofluoric acid solution (4 mL, 40 wt.%) is added dropwise into tetrabutyl titanate (25 mL) in a Teflon-lined autoclave and heated at 200 °C for 24 h after strict magnetic stirring. The obtained white precipitate is washed with distilled water and ethanol, dried overnight at 60 °C in an oven and calcined at 550 °C for 2 h to remove F residuals. The T010 and T101 are prepared through a two-step hydrothermal method. In the first step, the Degussa P₂₅ (1 g), which is composed of approximately 70% anatase and 30% rutile crystallites, is dissolved in a KOH solution (70 mL, 10 M) in a Teflon-lined autoclave and heated at 200 °C for 48 h. The white nanowire is collected through filtration with distilled water, dried at 60 °C overnight and dispersed in water at a ratio of 1 mg:10 mL. After being stirred and sealed in the Teflon-lined autoclave, the mixture is heated at 200 °C and 170 °C for 24 h to obtain T010 and T101, respectively.

The crystal structures of the as-synthesized samples were confirmed by X-ray diffraction (XRD) using a computerized PANalytical X'Pert Pro diffractometer system equipped with

41 a Cu K α ($\lambda=0.15406$ nm) radiation source. High-resolution-transmission electron
42 microscopy (HR-TEM) was performed on an FEI Tecnai G² F20 electron microscope
43 operating at 200 kV with the supplied software for the automated electron tomography.
44 Brunauer-Emmet-Teller (BET) adsorption isotherm measurements were carried out to
45 obtain the surface area using a Quantachrome Quadrasorb SI-MP analyzer at 77 K over the
46 whole range of relative pressures. In the present study, the surface areas of the as-
47 synthesized T001, T010 and T101 are 84, 41 and 27 m² g⁻¹, respectively.

48 As shown in Figure S1, the XRD and HRTEM were performed to identify the crystal
49 structure and morphology of TiO₂ with different facets. No crystalline phase, e.g., rutile or
50 brookite, was observed, and typical anatase peaks at 25.2°, 36.9°, 37.8°, 38.5°, 48.0°, 53.8°,
51 55.0°, 62.6°, 68.7°, 70.2°, and 75.0° indexed to the (101), (103), (004), (112), (200), (105),
52 (211), (204), (116), (220) and (215) facets, respectively, appeared, indicating the pure
53 anatase phase of the as-synthesized samples (Figure S1a).² The HRTEM images for the
54 (001), (010) and (101) facets show that those facets are nanoscaled (Figure S1b-d). The
55 T001 is a nanosheet ranging from 40-60 nm in side length, and the T010 displays a
56 nanorod-like morphology approximately 300-600 nm in length and 50 nm in diameter. The
57 T101 is primarily composed of an octahedral bipyramid with an average side length of 80-
58 120 nm. Equivalent to the recently reported values by Chen et al.,³ the area percentages of
59 each predominant facet of (001), (010) and (101) occupying the total facets of TiO₂
60 prepared in the present study are 68.7%, 83.3% and 90.2%, respectively.



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64 **Figure S2.** Optimized adsorption structures of (a) SO₂, SO₃²⁻ and SO₄²⁻ and (b) NO, NO₂
 65 and NO₃⁻, and their adsorption energies (at the bottom) on different surfaces of anatase
 66 TiO₂. The red, blue, gray and yellow balls denote the O, Ti, N and S atoms, respectively.

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68 **DFT calculation.** First-principles calculations were performed using the Vienna ab initio
 69 simulation package (VASP) based on density functional theory (DFT).⁴ The projector
 70 augmented wave (PAW) potentials were employed to model electron-ion interactions.⁵ The
 71 exchange and correlation effects for the structure relaxation were obtained by the
 72 generalized gradient approximation (GGA) using Perdew-Burke-Ernzerhof (PBE)
 73 functionals.^{6, 7} The cut-off energy was set at 450 eV for the plane-wave basis restriction in
 74 all calculations. The Monkhorst-Pack scheme was used to sample the K-points for the
 75 Brillouin-zone integration.⁸ The atomic structures were relaxed with a self-consistency
 76 accuracy of 10⁻³ eV and 10⁻⁴ eV for the ionic and electronic loops, respectively. For all
 77 surface models, a vacuum slab of 10 Å was used for surface isolation to prevent interactions
 78 between the two neighboring surfaces. Three surface layers were relaxed with all other
 79 atoms fixed to simulate the bulk structure. The adsorption energy is calculated by $E_{ad} =$
 80 $E_{\text{molecule}}^{\text{surface}} - E_{\text{surface}} - E_{\text{molecule}}^{\text{vacuum}}$ as reported by Huang et al.⁹

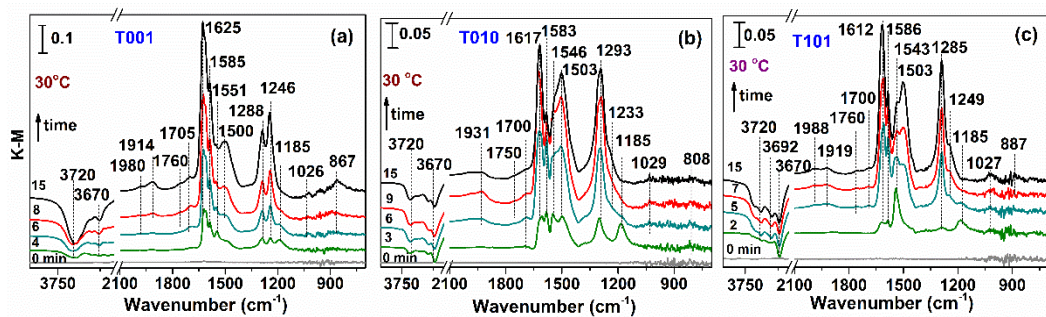
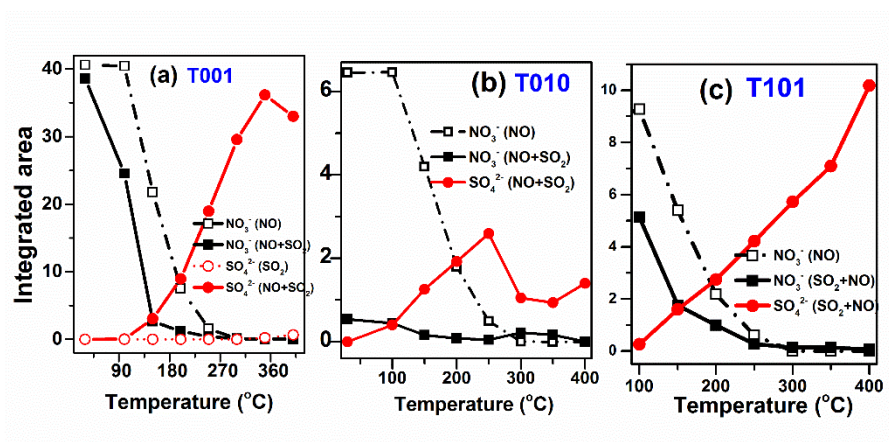


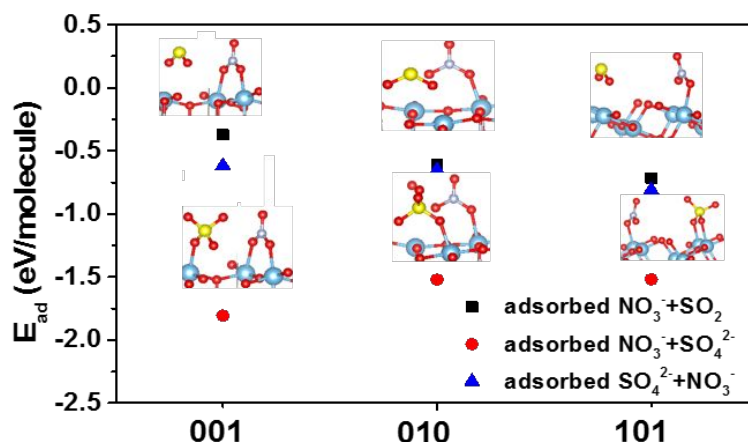
Figure S3. *In situ* DRIFTS spectra of the three facets exposed to 500 ppmv NO + 5 vol.% O₂ as a function of time at 30 °C.



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88 **Figure S4.** Comparison of integrated areas for nitrate ($1565\text{-}1661\text{ cm}^{-1}$) and sulfate
 89 ($1400\text{-}1340\text{ cm}^{-1}$) when NO or SO₂ (open symbols, dashed lines), and NO + SO₂ (solid
 90 symbols, straight lines) react on (a) T001, (b) T010 and (c) T101. Reaction conditions: 50
 91 ppmv SO₂, 500 ppmv NO and 5 vol.% O₂ balanced with N₂ in a total flow of 300
 92 mL/min.
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Figure S5. Adsorption energies of the most stable models for the adsorbed NO₃⁻ with SO₂ or SO₄, and the reverse order for the latter. The red, blue, gray and yellow balls denote the O, Ti, N and S atoms, respectively.

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In the DFT models, the SO₂ molecules adsorbed on the three surfaces in the presence of NO₃⁻ have a high adsorption energy, suggesting an unstable adsorption of SO₂. The adsorption energy of the SO₄²⁻ bound onto the NO₃⁻-adsorbed TiO₂ facets is much lower than that in the SO₂ and NO₃⁻ coexisting sample. The results indicate that weakly adsorbed SO₂ tends to transform into stable sulfate species in the presence of NO₃⁻. Noting the small difference between the adsorption energies of the black square and the blue triangle, the energy barrier for the decomposition of SO₄²⁻ into SO₂ is easy to reach at high temperatures (e.g., 250 °C) even in the presence of NO₃⁻ on the (010) surface. This result explains the abnormal phenomenon occurring on the (010) faceted-TiO₂ that has been found by DRIFTS in Figure 3c.

Although the optimized adsorption structures of NO₃⁻ on SO₄²⁻-occupied TiO₂ are the same as those for SO₄²⁻ over the NO₃⁻-occupied TiO₂ surfaces, the system is repulsive to the former due to dramatically increased adsorption energies from the red dot to the blue triangle. Therefore, it can be postulated that the formation of SO₄²⁻ on the TiO₂ sample would inhibit the further production of NO₃⁻. This conclusion is also in line with the DRIFTS results. We propose that an accumulation of sulfate species blocks the active sites available for the NO₃⁻.

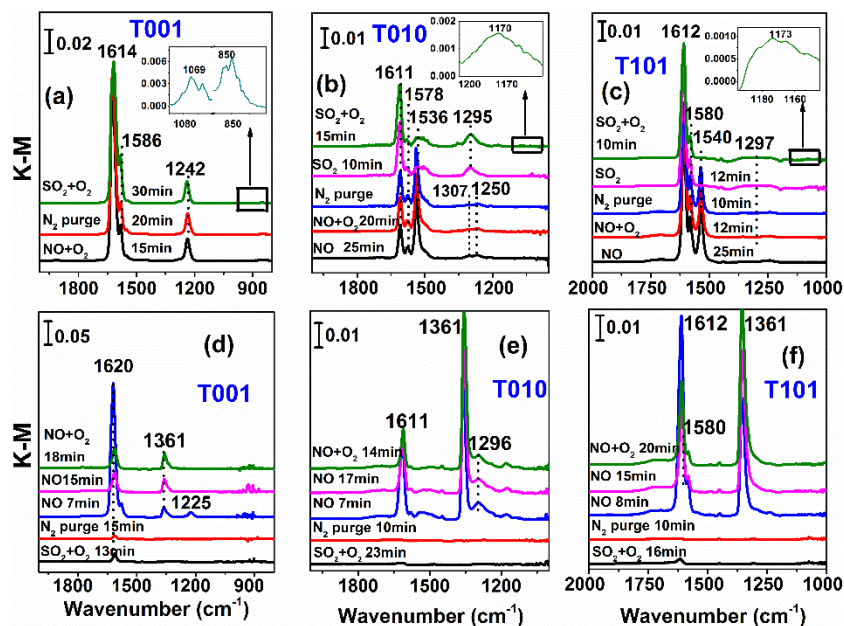


Figure S6. *In situ* DRIFTS spectra of reaction between SO_2+O_2 with pre-adsorbed $\text{NO}+\text{O}_2$ species, and the reverse order over (a) (d) T001, (b) (e) T010 and (c) (f) T101 at 180 °C. Reaction conditions: 50 ppmv SO_2 /500 ppmv NO , and 5 vol.% O_2 balanced with N_2 in a total flow of 300 mL/min

In Figure S6a, bridging nitrate (ca. 1614 cm^{-1}) and bidentate nitrate species (ca. 1586, 1242 cm^{-1}) were observed after saturation with $\text{NO}/\text{NO}+\text{O}_2$ on T001. Almost no change was found after purging with N_2 and the following introduction of $\text{SO}_2/\text{SO}_2+\text{O}_2$, except for the formation of a small amount of sulfite species at the band of 1080 cm^{-1} , (magnified in the inserted graph), indicating that SO_2 competes for the same sites that have been occupied by the strongly adsorbed nitrate species. This indicated that the gaseous SO_2 can hardly be oxidized directly by the surface-adsorbed nitrate.

In the case of pre-adsorbed SO_2 species (Figure S6d), the introduction of NO resulted in obvious formation of sulfate (1361 cm^{-1}). While the variation of sulfite in the purge of N_2 and subsequent introduction of $\text{NO}/\text{NO}+\text{O}_2$ are barely observed due to the poor signal in the region of 1200-800 cm^{-1} .

In the case of T010 (Figure S6b) and T101 (Figure S6c), the formed bidentate nitrate species (ca. 1536 cm^{-1}) tend to convert into monodentate nitrate (ca. 1295 cm^{-1}) under the

disturbance of SO₂ possibly due to the instability of the former. Besides, a small amount of sulfate species (1170-1173 cm⁻¹) was found on both facets. But this formation of sulfate was much weak compared to the case of the reverse order (Figure S6e and f), in which a significant formation of sulfate species (1361 cm⁻¹) occurred, accompanied by an obvious decrease of nitrate species (1611 cm⁻¹). Apparently, the nitrate (1611 cm⁻¹) consumption and sulfate (1361 cm⁻¹) formation trends are basically the same on all the three facets.

It is noted that the DRIFTS spectra of the NO/SO₂ reaction with and without O₂ are identical. This result is somehow different from those found over other TiO₂-based catalysts possibly due to the richness of the oxygen vacancies (or active oxygen species) produced on the facet-controlled TiO₂ in this study.⁹

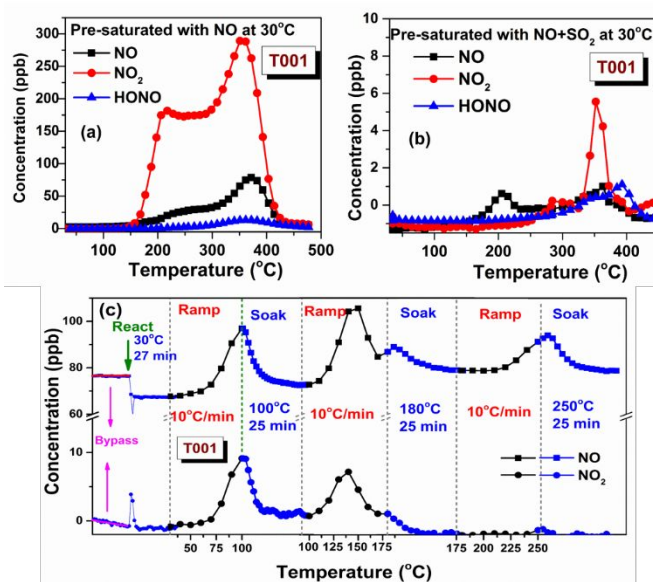


Figure S7. (a) (b) NO_x and HONO evolution over T001 as a function of temperature with a ramp rate of 10 °C/ min in an total flow of 1.9 L/ min. The T001 sample has been pre-saturated with (a) NO or (b) NO and SO₂ in the DRIFTS cell prior to the analysis. (c) Dynamic uptake and release of NO_x on T001 with a constant inlet concentration of NO (76 ppbv) as a function of temperature. The sample mass was the same under all conditions (16.5 mg).

Figure S7 (a) and (b) show the concentration profiles of gas products derived from the decomposition of adsorbed nitrate (that formed at 30 °C) as a function of temperature. The NO_x chemiluminescence analyzer (THERMO 42i) and HONO analyzer (ZHICHEN TECHNOLOGY, China) were used simultaneously to online measure the concentrations of NO_x and HONO with the increase of temperature. It is found that a large amount of nitrate species that formed at 30 °C (Figure 2, S3) decomposed into dominant NO₂ as well as small amounts of HONO and NO in the range of 180- 400 °C.¹⁰ While the simultaneous pre-adsorption of NO and SO₂ resulted in a significant reduction in the releases of NO_x and HONO, especially NO₂. This indicated that the decomposed NO₂ participated in the oxidation of SO₂. A small amount of NO₂ release was still observed possibly due to decomposition of redundant nitrate remaining on the surface.

170 To confirm the NO reactivity on TiO₂ at different temperatures, we introduced 76 ppbv
171 NO into the DRIFTS cell containing TiO₂ sample and online measured the outlet gas
172 concentrations of NO_x and HONO with varied temperature, as shown in Figure S7 (c) and
173 also below. Notably, the inlet NO concentration was kept constant throughout the whole
174 temperature range. Once exposure of the sample to NO at 30 °C, a uptake of NO occurred,
175 simultaneously observed with a NO₂ pulse signal. After NO reaction for 27 min at 30 °C,
176 the following increase of temperature resulted in simultaneous appearance of peak values
177 for NO and NO₂ at 100 °C and 150 °C. No NO₂ signal was detected beyond 180 °C while
178 the signal of NO was still present. The NO can be due to the physisorbed NO on TiO₂ at
179 30°C. As postulated above, the released NO₂ above 180 °C was derived from the
180 decomposition of nitrate/nitrite species that formed at low temperatures (Figure 2, Figure
181 S3, S7a). Since the exposure time and concentration of NO were short and low, the
182 formation of adsorbed nitrate species was limited, thus no observation of NO₂ above 180
183 °C in this case.

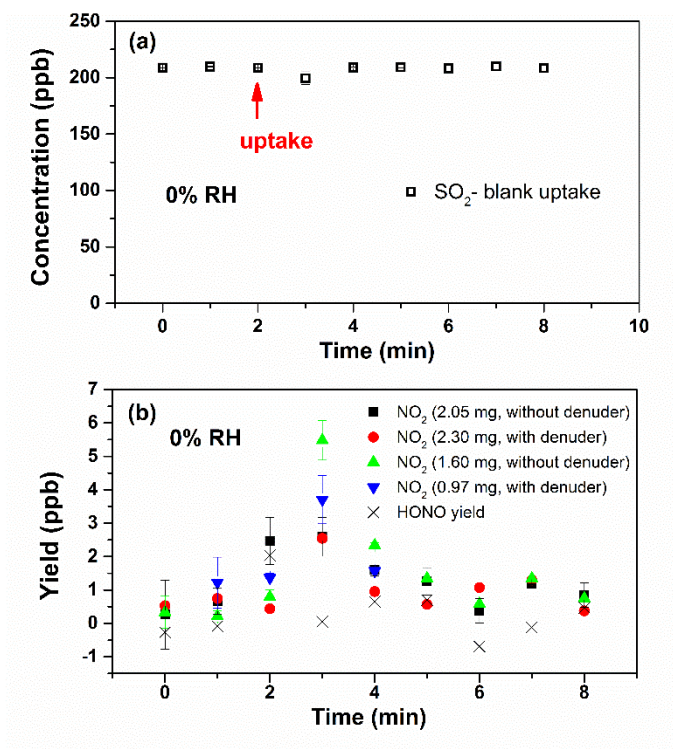


Figure S8. (a) The uptake of SO_2 in the blank experiments under dry condition. (b) The NO_x and HONO species detected with and without Na_2CO_3 denuder in the sampling line. The yield of HONO was estimated based on the difference of the NO_2 value with (2.30 mg, with denuder) and without Na_2CO_3 (2.05 mg, without denuder).

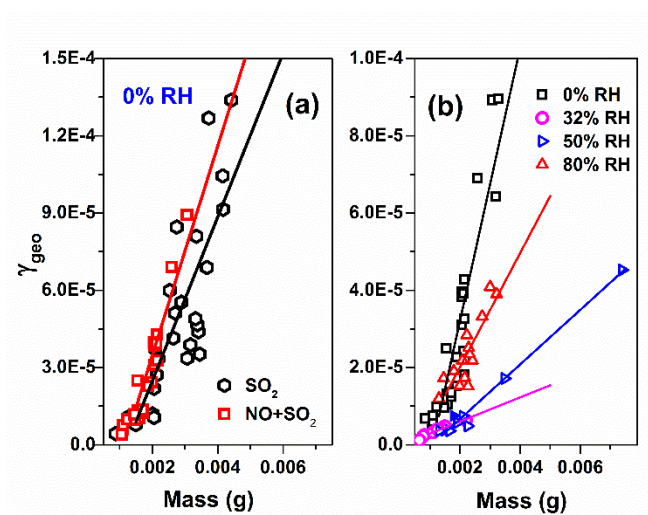


Figure S9. (a) Mass dependence of initial geometric uptake coefficients (γ_{geo}) of SO_2 on T001 in the absence and presence of NO at 0% RH. (b) RH influence on mass-dependent T001.

γ_{geo} of SO₂ on T001 in the presence of NO.

Table S1. The initial true uptake coefficient (γ_t) of SO₂ on T001 obtained under different conditions.

RH (%)	True uptake coefficient (γ_t)	
	SO ₂ reaction	SO ₂ +NO reaction
0	$(1.39 \pm 0.59) \times 10^{-6}$	$(1.95 \pm 0.45) \times 10^{-6}$
32	$(2.84 \pm 0.72) \times 10^{-7}$	$(2.62 \pm 0.53) \times 10^{-7}$
50		$(2.90 \pm 0.67) \times 10^{-7}$
80	$(1.22 \pm 0.36) \times 10^{-6}$	$(1.08 \pm 0.11) \times 10^{-6}$

Uptake coefficient. The reaction kinetics (k_{obs}) of SO₂ can be described in terms of the initial uptake coefficient, assuming a pseudo first-order reaction with respect to the concentration of SO₂ according to equation 1:

$$k_{\text{obs}} = \frac{\gamma_{\text{geo}} <c>}{2r_{\text{tube}}} \quad (\text{S1})$$

where γ_{geo} , $<c>$ and r_{tube} refer to initial geometric uptake coefficient, average molecular velocity of SO₂ and the flow tube radius. The geometric inner surface area of the whole sample was used to calculate the γ_{geo} . The gas phase diffusion limitation is corrected using the Cooney-Kim-Davis (CKD) method.¹¹ A probability of SO₂ diffusion into underlying layers of the sample can take place, and then the initial true uptake coefficient (γ_t) was obtained from the mass dependence of γ_{geo} :

$$\gamma_t = \frac{\gamma_{\text{geo}} \times S_{\text{geom}}}{S_{\text{BET}} \times M} \quad (\text{S2})$$

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

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