1   **Photoenhanced sulfates formation by the heterogeneous uptake of SO$_2$ on non-**

2   **photoactive mineral dust**

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7   **Short summary.** We provide evidence that light enhances the conversion of SO$_2$ to sulfates on

8   non-photoactive mineral dust, where triplet states of SO$_2$ (^{3}SO$_2$) can act as a pivotal trigger to

9   generate sulfates. Photochemical sulfate formation depends on H$_2$O, O$_2$, and basicity of mineral

10 dust. The SO$_2$ photochemistry on non-photoactive mineral dust contributes to sulfates,

11 highlighting previously unknown pathways to better explain the missing sources of

12 atmospheric sulfates.

14 **Abstract.** Heterogeneous uptake of SO$_2$ on mineral dust is a predominant formation pathway

15 of sulfates, whereas the contribution of photo-induced SO$_2$ oxidation to sulfates on the dust

16 interfaces still remains unclear. Here, we investigated heterogeneous photochemical reactions

17 of SO$_2$ on five mineral oxides (SiO$_2$, kaolinite, Al$_2$O$_3$, MgO, and CaO) without photocatalytic

18 activity. Light enhanced the uptake of SO$_2$, and its enhancement effects negatively depended

19 on the basicity of mineral oxides. The initial uptake coefficient ($\gamma_{0,\,BET}$) and the steady-state

20 uptake coefficient ($\gamma_{s,\,BET}$) of SO$_2$ positively relied on light intensity, relative humidity (RH)

21 and O$_2$ content, while they exhibited a negative relationship with the initial SO$_2$ concentration.

22 Rapid sulfate formation during photo-induced heterogeneous reactions of SO$_2$ with all mineral

23 oxides was confirmed to be ubiquitous, and H$_2$O and O$_2$ played key roles in the conversion of

24 SO$_2$ to sulfates. Specially, triplet states of SO$_2$ (^{3}SO$_2$) were suggested to be the trigger for

25 photochemical sulfate formation. Atmospheric implications supported a potential contribution

26 of interfacial SO$_2$ photochemistry on non-photoactive mineral dust to atmospheric sulfate

27 sources.

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Keywords: SO$_2$; Sulfates; Non-photoactive mineral dust; Heterogeneous photochemistry

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1 Introduction

As an important trace gas in the atmosphere, SO$_2$ is mainly emitted by volcanic eruption and fuel combustion. There is an uneven distribution of atmospheric SO$_2$ concentrations that show a distinctive seasonal and regional differentiation. Typical mixing ratios of SO$_2$ in the troposphere are below 0.5 ppb for clean weather days, rising to several hundred ppb during polluted days in urban regions (Ma et al., 2020). About half of SO$_2$ is oxidized to sulfate (He et al., 2012), which is a key component of fine particulates in the atmosphere. High sulfate loading in PM$_{2.5}$ was observed (Shao et al., 2019), especially in polluted regions where high-sulfur fuels are usually used (Olson et al., 2021). They significantly alter physicochemical properties of aerosols in terms of hygroscopicity, acidity and light absorption (Chan and Chan, 2003; Cao et al., 2013; Lim et al., 2018). Sulfates may lead to negative health outcomes, such as respiratory illness and cardiovascular (Shiraiwa et al., 2017). In addition, the deposition of sulfates leads to adverse effects on ecosystems via the acidification of soils and lakes (Golobokova et al., 2020). Therefore, the oxidation of SO$_2$ to form sulfates has attracted widespread attention in the past decades.

The conversion of SO$_2$ to sulfates in the atmosphere usually occurs in different phases: gas-phase oxidation of SO$_2$ by hydroxyl radicals (•OH) or Criegee intermediate radicals (Mauldin et al., 2012; Davis et al., 1979); aqueous-phase reaction of SO$_2$ with O$_3$, peroxides or transition metal ions dissolved in cloud and fog droplets (Alexander et al., 2009; Herrmann et al., 2000; Harris et al., 2013; Liu et al., 2020a; Li et al., 2020); and heterogeneous SO$_2$ uptake on aerosols including authentic mineral dust, soot, inorganic ion and organic compounds (Adams et al., 2005; He et al., 2018a; Ye et al., 2018; Wang et al., 2019; Yao et al., 2019; Zhang et al., 2020a; Liu et al., 2020; Liu et al., 2021). However, the oxidation of SO$_2$ in gas and aqueous phases fails to explain high sulfate concentrations in the polluted areas. Model simulation suggests

56 that the rapid sulfate formation can be attributed to the heterogeneous SO_2 uptake (Li et al.,

57 2017). A positive relationship between the fraction of sulfates and mineral dust in haze days

58 has been reported, implying that mineral dust may account for the formation of sulfates (Wang

59 et al., 2020a). Moreover, a large amount of sulfates was observed to be formed on the surface

60 of mineral dust after long-distance transport (Prospero, 1999). Thus, investigating the

61 heterogeneous oxidation of SO_2 on mineral dust can provide basic data for the model

62 calculation to evaluate atmospheric sulfates.

63   Mineral dust, as the dominant component of particulate matters in the atmosphere, accounts

64 for about 30%−60% mass fractions of global aerosols (Dentener et al., 1996; Peng et al., 2012).

65 It primarily contains SiO_2 (40%−80%), followed by Al_2O_3 (10%−15%), Fe_2O_3 (6%−13%),

66 CaO (3%−10%), MgO (1%−7%) and TiO_2 (0.1%−5%) (Urupina et al., 2021; Urupina et al.,

67 2019; Usher et al., 2003). Mineral dust can provide active sites for the adsorption and reaction

68 of gases. Up to now, the heterogeneous SO_2 uptake on authentic mineral aerosols and model

69 mineral oxides has been widely reported (Ma et al., 2019; Goodman et al., 2001; Wang et al.,

70 2018; Wang et al., 2020b), with the uptake coefficient (γ) of SO_2 varying from 10^{-9} to 10^{-4}

71 (Urupina et al., 2019; Usher et al., 2002).

72   It was recognized that light could significantly enhance the heterogeneous conversion of SO_2

73 to sulfates on the surface of photocatalytic mineral dust (Chen et al., 2021; Li et al., 2019; Wang

74 et al., 2020b). Electron-hole pairs are produced via photo-induced electrons from the valence

75 band to the conduction band of photocatalytic metal oxides, and then react with H_2O and O_2 to

76 generate reactive oxygen species (ROS), such as •OH and •O_2^- (Chu et al., 2019). Sulfates are

77 produced by the heterogeneous reactions of SO_2 with ROS (Park and Jang, 2016; Park et al.,

78 2017; Langhammer et al., 2020; Bounechada et al., 2017). In particular, due to the large

79 abundance of non-photoactive mineral dust (more than 85% mass of total mineral dust in the

80 atmosphere) (Usher et al., 2003; Liu et al., 2022), revealing the photooxidation processes of

81 SO_2 on these mineral dust is of great importance to better reevaluate the sulfate formation on

82 aerosols in the global scale.

83   Hence, photochemical SO_2 uptake and sulfate formation on non-photoactive mineral oxides

were investigated using a flow reactor and an *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The SO_2 conversion to sulfates was examined under various conditions, and the roles of light intensity, SO_2 concentration, H_2O, O_2 and basicity of mineral oxides were determined. Reaction mechanisms and atmospheric implications were proposed, highlighting an important pathway accounting for the photochemical uptake of SO_2 to form sulfates on the non-photoactive surfaces.

2 Experimental methods

2.1 Materials

Analytical grade SiO_2 (Sinopharm Chemical Reagent Co., Ltd.), kaolinite (Sinopharm Chemical Reagent Co., Ltd.), Al_2O_3 (Alfa Aesar), MgO (Sigma-Aldrich), and CaO (Sigma-Aldrich) were used in the experiments. Through the nitrogen Brunauer-Emmett-Teller (BET) physisorption analysis, their specific surface areas were detected to be 0.419, 6.407, 8.137, 10.948 and 6.944 $m^2\,g^{-1}$, respectively. With $BaSO_4$ used as the reference, the ultraviolet-visible (UV-vis) light absorption spectra of samples (Figure S1) in the wavelength range of 300–800 nm were obtained by the Shimadzu UV-2550 spectrophotometer, which was equipped with diffuse reflection integrating sphere attachment. The solid powder (0.2−5 g) was uniformly dispersed into 10.0 mL ethanol solution. The mixed liquid was poured into a rectangle quartz sample dish (14.0 cm × 7.0 cm) and dried to form a solid coating in an oven at 353 K for 10 h. SO_2 standard gas (50 ppm in N_2, Shenyang Air Liquide Co., LTD) and high purity N_2 and O_2 (99.999 vol.%, Shenyang Air Liquide Co., LTD) were used as received. The solid sample powder (0.2 g) was immersed in 10 mL deionized water (20 $mg\,mL^{-1}$), and then the suspension was vigorously stirred for 10 min. The pH of SiO_2, kaolinite, Al_2O_3, MgO and CaO suspension was measured to be 6.27, 6.58, 9.33, 10.61 and 12.72 using a pH meter, respectively.

2.2 Rectangular flow reactor

The uptake experiments of SO_2 on mineral dust were performed in a horizontal rectangular flow reactor (26.0 cm length × 7.5 cm width × 2.0 cm height), which was depicted in Figure S2. In a previous study, a similar rectangular flow reactor was designed and the feasibility of

112 the reactor has been verified (Knopf et al., 2007). The reactor was made of quartz to allow the

113 transmission of light. The temperature was maintained at 298 K by circulating temperature-

114 controlled water through the outer jacket of the reactor. Synthetic air with a N_2/O_2 volume ratio

115 of 4:1 was introduced into the flow reactor, and its total flow rate was 1000 mL min^{-1}. The

116 Reynolds number (*Re*) was calculated to be 28.2 (*Re* < 200), as described in the Supporting

117 Information, indicating a laminar flow state. SO_2 together with high purity N_2 (100 mL min^{-1})

118 was introduced into the reactor through a movable T-shaped injector equipped with six exit

119 holes (0.2 mm diameter), so that the gas could be uniformly distributed over the width of the

120 reactor. The SO_2 concentration was 40−200 ppb and measured with a SO_2 analyzer (Thermo

121 43i). Wet N_2 generated with a bubbler containing deionized water was introduced by two

122 parallel inlets on the side of a T-shaped injector. Relative humidity (RH, 10%−75%) was

123 controlled by regulating the ratio of dry N_2 to wet N_2 and measured via a hygrometer (Center

124 314). The equivalent layer numbers of water on surface was 0.9−4.0 according to the Brunauer-

125 Emmett-Teller (BET) model (Sumner et al., 2004), and the thickness of the film of adsorbed

126 water varied between 2.7−12 nm at RH=10%−75%. There were three equally spaced exhaust

127 ports to mitigate the outlet turbulence. A xenon lamp (CEL-LAX500, China Education Au-light

128 Co., Ltd) was used to simulate sunlight and vertically located above the reactor. A filter was

129 placed on the reactor to remove the light with wavelengths shorter than 300 nm. The spectrum

130 irradiance of the xenon lamp was displayed in Figure S3 and measured using a calibrated

131 spectroradiometer (ULS2048CL-EVO, Avantes). The spectral irradiance was measured inside

132 the reactor, after passing the water cooling and in the absence of a sample. The total irradiance

133 (0−7.93 × 10^{16} photons cm^{-2} s^{-1}) on the coating can be adjusted by varying the distance of the

134 xenon lamp to the reactor.

135 **2.3 Uptake coefficient of SO$_2$**

136   The heterogeneous reaction kinetics of SO_2 with mineral dust can be described by a pseudo-

137 first-order reaction. Figure S4 showed a linear relationship between the natural logarithm of

138 the SO_2 concentration and the reaction time. The apparent rate constant (k_{obs, SiO_2}) of SO_2 with

139 SiO_2 can be calculated using equation 1,

140 $$\frac{\ln(C_0/C_t)}{t} = k_{obs, SiO_2} \quad (1)$$

141 where C_0 and C_t (ppb) are the initial SO_2 concentration and the SO_2 concentration, respectively;

142 t was calculated by diving the length of the reactive surface by the average flow velocity. The

143 loss of SO_2 on the internal wall of the reactor in blank experiments was carried out under

144 various conditions (Figure S5 as an example), and it has been deducted for the γ calculation.

145 Assuming that the wall loss was constant in the experiments with and without samples, the

146 geometric uptake coefficient (γ_{geo}) was determined by equation 2 (Knopf et al., 2007),

147 $$\gamma_{geo} = \frac{4Vk}{S\omega} \quad (2)$$

148 where k (s^{-1}), V (4×10^{-4} m^3), S (9.8×10^{-3} m^2) and ω (314.05 m s^{-1}) are the reaction rate

149 constant, the volume of the rectangular reactor, the surface area of the sample dish, and the

150 mean molecular speed of SO_2, respectively.

151 The uptake process of SO_2 on SiO_2 depended on the reaction of SO_2 with SiO_2 and the mass

152 transport of SO_2 to the surface. It can be expressed by equation 3,

153 $$k'_{r, SiO_2} = \left[\frac{1}{k_{obs, SiO_2} - k_{obs, wall}} - \frac{a}{N_u D}\right]^{-1} \quad (3)$$

154 where k_{obs, SiO_2} and $k_{obs, wall}$ (s^{-1}) are the apparent rate constants measured with and without

155 SiO_2 samples, respectively. k'_{r, SiO_2} is the reaction rate constant of SO_2 accounting for the

156 diffusion effect; D (0.1337 cm^2 s^{-1}) is the diffusion coefficient of SO_2 in air; a (1 cm) is one

157 half height of the flow reactor; N_u is the Nusselt numbers obtained with a calculation method

158 from Solbrig and Gidaspow (1967), which represents the mass transport. Then, the corrected γ

159 can be calculated by equation 2 where k was replaced by k'_{r, SiO_2}. In our experiments, the

160 correction for γ was estimated to be 10%. Initial uptake coefficients (γ_0) and steady-state uptake

161 coefficients (γ_s) were calculated by averaging the signals within the 1.0 and 40−60 min reaction

162 time, respectively.

163 To understand the diffusion depth of SO_2 and determine the interaction of SO_2 with the

164 underlying layers of SiO_2, the uptake of SO_2 as a function of the SiO_2 mass under irradiation

165 was shown in Figure S6. The γ exhibited a linear increase in the SiO_2 mass range of 0.05−2.0

166 g, while it remained unchanged at the SiO$_2$ mass > 3.0 g. Therefore, the uptake coefficient of

167 SO$_2$ in the linear regions was normalized using the BET surface area of SiO$_2$ by equation 4

168 (Brunauer et al., 1938),

169 $$\gamma_{BET} = \frac{S_{geo} \times \gamma_{geo}}{S_{BET} \times m_{SiO_2}} \quad (4)$$

170 where γ_{BET} is the SO$_2$ uptake coefficient normalized to the BET surface area; S_{geo} (9.8 × 10^{-3}

171 m^2) is the geometric area of the sample dish; S_{BET} (0.419 m^2 g^{-1}) is the BET surface area of

172 SiO$_2$; m_{SiO_2} (0.05−2.0 g) is the SiO$_2$ mass. The same method was also used to calculate the

173 uptake coefficients of SO$_2$ on other mineral oxides.

2.4 In situ DRIFTS analysis

175 The changes in the chemical compositions on mineral oxides in the SO$_2$ uptake process were

176 investigated by the Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet iS50)

177 equipped with an *in situ* diffuse reflectance accessory and a mercury cadmium telluride (MCT)

178 detector. About 14 mg mineral oxides were placed into a stainless-steel cup inside the reaction

179 cell. To remove adsorbed impurities, SiO$_2$ was purged with a 150 mL min^{-1} airflow (N$_2$/O$_2$

180 volume ratio = 4:1) at RH=40% for 1 h. Then, a background spectrum of unreacted samples

181 was collected. SO$_2$ (2 ppm) was introduced into the reaction cell, and the IR spectra was

182 recorded as a function of time at a resolution of 4 cm^{-1} by averaging 100 scans. The light from

183 the xenon lamp (500 W) was transmitted into the DRIFTS reaction cell via a fiber. To verify

184 the role of intermediate, Ru(bpy)$_3$(Cl)$_2$) and NaHCO$_3$, acting as ^{3}SO$_2$ and •OH scavengers

185 (Bulgakov and Safonova, 1996; Gen et al., 2019a), respectively, were mixed with SiO$_2$ powder

186 in an agate mortar, and the mixture was put in the reaction cell of DRIFTS.

187

3 Results and discussion

3.1 Photo-enhanced uptake of SO$_2$

190 Acting as the most abundant mineral oxides, SiO$_2$ was used to investigate the uptake

191 behaviors of SO$_2$. As shown in Figure 1A, when SO$_2$ (80 ppb) was exposed to SiO$_2$ in the dark,

192 the SO$_2$ concentration decreased to 70 ppb, and then it quickly increased and reached a steady

193 state after 20 min. Upon exposure to SiO_2 under irradiation, the SO_2 concentration exhibited a

194 greater drop than that in the dark. The deactivation of SO_2 uptake on SiO_2 was very slight after

195 20 mins under irradiation. These suggest that light can promote the heterogeneous reaction of

196 SO_2 on SiO_2. Few studies observed the photochemical uptake of SO_2 on non-photoactive

197 minerals (Xu et al., 2021; Zhang et al., 2022). When SO_2 did not contact with SiO_2, its

198 concentration recovered rapidly. The desorption of SO_2 was observed when SO_2 was isolated

199 from SiO_2 in the dark and under irradiation, indicating that the physical adsorption partially

200 contributed to the SO_2 loss during the photochemical process. The proportion of the desorbed

201 SO_2 during the uptake process can be quantified by dividing the integral of reversible

202 desorption of SO_2 ($t = 80\text{–}100$ min) into the integral of the SO_2 uptake ($t = 20\text{–}80$ min), which

203 was calculated to be 95% and 12% in the dark and under irradiation, respectively. This implies

204 that SO_2 uptake in the dark was primarily ascribed to the physical adsorption of SO_2, while SO_2

205 uptake under irradiation was mainly attributed to chemical processes or irreversible adsorption.

206   The uptake coefficients of SO_2 on SiO_2 as a function of irradiation intensity were shown in

207 Figure 1B. The errors in all figures are the standard deviations of three repetitive experiments.

208 Both $\gamma_{0,\,BET}$ and $\gamma_{s,\,BET}$ displayed a well linear relationship with the irradiation intensity. The

209 $\gamma_{0,\,BET}$ and $\gamma_{s,\,BET}$ under the irradiation of 7.93×10^{16} photons $cm^{-2}\ s^{-1}$ were 1.75 and 2.25 times

210 of those in the dark, respectively. This further confirms the photochemical nature of the

211 reactions of SO_2 on SiO_2. In particular, $\gamma_{0,\,BET}$ and $\gamma_{s,\,BET}$ on SiO_2 under simulated solar

212 irradiation was comparable with those ($10^{-7}\text{–}10^{-6}$) on Gobi Desert dust (GDD) and Arizona

213 Test Dust (ATD) under UV irradiation, which contained photocatalytic metal oxides (Park et

214 al., 2017). As for the SO_2 uptake on TiO_2, $\gamma_{0,\,BET}$ and $\gamma_{s,\,BET}$ were measured to be 10^{-6} and 10^{-7},

215 respectively, by using the flow tube (Ma et al., 2019), which were similar to our results. It

216 should be pointed out that the similar uptake coefficient did not mean the comparable ability

217 of photoactive and non-photoactive mineral oxides to SO_2 uptake, since the uptake coefficient

218 was highly dependent on environmental conditions (SO_2 concentration, relative humidity,

219 mineral oxides mass, light source and pressure) and reactor type (chamber and flow tube

reactor). Table S1 shows that the fraction of SiO_2 in the sample was 99.02%, accompanied by a small amount of Al_2O_3, K_2O, Fe_2O_3 and CaO. Photoactive substances (Fe_2O_3) was very few in the sample, and they should not be the main contributor to the photochemical uptake of SO_2.

Figure 1C shows the evolution of $\gamma_{0,\,BET}$ and $\gamma_{s,\,BET}$ at different SO_2 concentrations under irradiation. An inverse dependence of $\gamma_{0,\,BET}$ and $\gamma_{s,\,BET}$ on the SO_2 concentration was observed, meaning that the efficiency of SO_2 uptake decreased with increasing the SO_2 concentration. The uptake of gases on the solid surfaces usually follows the Langmuir-Hinshelwood (L-H) mechanism (Ammann et al., 2003; Zhang et al., 2020b), suggesting that gaseous molecules are quickly absorbed on the surfaces, and then the reactions occur among the absorbed species. Assuming that the adsorption of SO_2 on SiO_2 is in accord with the Langmuir isotherm, the dependence of γ on the SO_2 concentration can be described by equation 5 (Zhang et al., 2020b),

$$\gamma = \frac{(4V/S\omega)k[SiO_2]_T K_{SO_2}}{1 + K_{SO_2}[SO_2]_g} \quad (5)$$

where $[SO_2]_g$ is the concentration of gaseous SO_2; $[SiO_2]_T$ is the total number of active sites on SiO_2; k is the reaction rate constant of SO_2 absorbed on SiO_2; K_{SO_2} represents the Langmuir adsorption constant of SO_2. Because the SiO_2 mass remained constant during the reaction, equation 5 can be written as equation 6,

$$\gamma = \frac{a}{1 + K_{SO_2}[SO_2]_g} \quad (6)$$

where $a = (4V/S\omega)k[SiO_2]K_{SO_2}$. As shown in Figure 1C, equation 6 can well describe the correlation of the SO_2 uptake coefficient with the SO_2 concentration, suggesting that the L-H mechanism can explain the influence of the SO_2 concentration on $\gamma_{0,\,BET}$ and $\gamma_{s,\,BET}$.
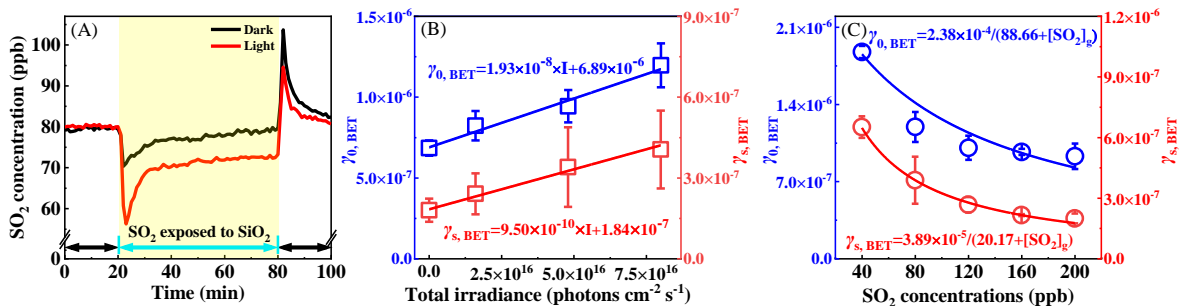
Figure 1. (A) The temporal variation of the SO_2 concentration on SiO_2 in the dark and under

242   irradiation (7.93×10^{16} photons cm^{-2} s^{-1}); The background changes of the SO$_2$ concentration

243   in the blank reactor have been deducted. (B) The $\gamma_{0,\,BET}$ and $\gamma_{s,\,BET}$ of SO$_2$ on SiO$_2$ as a

244   function of the light intensity. (C) The $\gamma_{0,\,BET}$ and $\gamma_{s,\,BET}$ of SO$_2$ on SiO$_2$ at different SO$_2$

245   concentrations under irradiation (7.93×10^{16} photons cm^{-2} s^{-1}); The fitting lines for $\gamma_{0,\,BET}$

246   and $\gamma_{s,\,BET}$ were based on the Langmuir-Hinshelwood mechanism using equation 6. Reaction

247   conditions: SiO$_2$ mass of 0.2 g, temperature of 298 K, RH of 40% and O$_2$ content of 20%.

248   **3.2 Photo-induced formation of sulfates by the SO$_2$ uptake**

249   To investigate the products formed on SiO$_2$, *in situ* DRIFTS spectra were recorded, as shown

250   in Figure 2. The band at 1359 cm^{-1} was assigned to physically-adsorbed SO$_2$ on SiO$_2$ (Urupina

251   et al., 2019). The bidentate sulfate and bisulfate contributed to the bands at 1260 and 1229/1074

252   cm^{-1} (Urupina et al., 2019; Yang et al., 2020), respectively. The bands at 1038 cm^{-1} may be

253   related to the monodentate sulfite (Yang et al., 2019; Wang et al., 2019). It was noted that the

254   intensity of physically-absorbed SO$_2$ (1359 cm^{-1}) under irradiation was lower than that in the

255   dark (Figure S7), which may be ascribed to further conversion of SO$_2$ absorbed on SiO$_2$ under

256   irradiation. Especially, the sulfate bands (1260, 1229 and 1074 cm^{-1}) only appeared under

257   irradiation, while the sulfites (1038 cm^{-1}) were only detected in the dark. This suggests that

258   light changed the SO$_2$ conversion pathways on SiO$_2$. As shown in Figure S7, the bands at

259   1157/1055 cm^{-1} were assigned to the asymmetric stretching of Si−O (Hu et al., 2003). Sulfate

260   generated on the surface may interact with SiO$_2$, leading to a decrease in the intensity of peaks

261   (1157/1055 cm^{-1}).

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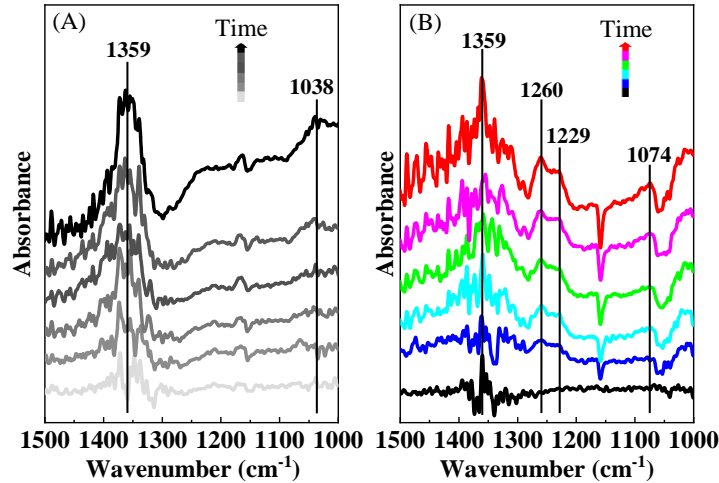
Figure 2. *In situ* DRIFTS spectra of SiO_2 during the uptake process of SO_2 (2 ppm) in the dark (A) and under irradiation (B). Reaction conditions: RH of 40%, temperature of 298 K and O_2 content of 20%.

3.3 Key roles of H_2O and O_2 in photochemical conversion of SO_2 to sulfates

Figure S8A shows temporal variations of the SO_2 concentration in the reaction with SiO_2 at RH=10% and 60% under irradiation. The uptake of SO_2 was very weak at RH=10%, whereas it was obvious at RH=60%. Moreover, H_2O prolonged the time to reach the steady-state uptake of SO_2. This means that H_2O plays an enhancement role in the photochemical uptake of SO_2. As shown in Figure 3A, $\gamma_{0,\,BET}$ had a continuous increase from $(1.20 \pm 0.04) \times 10^{-7}$ to $(1.54 \pm 0.07) \times 10^{-6}$ with increasing the RH in the 10%−60% range, but it decreased to $(1.05 \pm 0.09) \times 10^{-6}$ at RH=75%. The $\gamma_{s,\,BET}$ linearly depended on the RH, and linear fitting to $\gamma_{s,\,BET}$ versus RH yielded an equation $\gamma_{s,\,BET} = 1.31\times10^{-8}\times RH - 1.02\times10^{-7}$. Adsorbed H_2O promoted the hydration and dissociation of SO_2 (Huang et al., 2015), and it may generate reactive oxygen species (ROS) such as •OH or HO_2 radicals to oxidize SO_2 under irradiation (Li et al., 2020; Ma et al., 2019), which would lead to positive effects of RH on the SO_2 uptake. Adsorbed H_2O also occupied adsorptive and active sites on the surface, leading to a decrease in SO_2 adsorption. When this competitive role was dominated, the uptake of SO_2 would be hindered.

The DRIFTS spectra of SiO_2 during the SO_2 uptake at different RHs are shown in Figure

281   S9A. The band intensities of sulfates (1260 and 1229 cm^{-1}) at RH=60% were stronger than

282   those at RH=10%, suggesting that H_2O promotes the sulfate formation. To further investigate

283   the influence of H_2O on the sulfate formation, the integrated area of sulfates in the DRIFTS

284   spectra (1289−1202 cm^{-1}) as a function of the time at different RHs is illustrated in Figure 3B.

285   Sulfates exhibited a fast formation in the initial 30 min, and then they were continuously

286   generated at a relatively slow rate. SO_2 absorption on the surface would be blocked because of

287   the accumulation of H_2O and products (sulfites and sulfates), resulting in the gradual

288   deactivation of the surface. It was noted that sulfates formation was more prominent at higher

289   RH, revealing that H_2O can act as an important participator in the production of sulfates by the

290   photochemical uptake of SO_2 on SiO_2.

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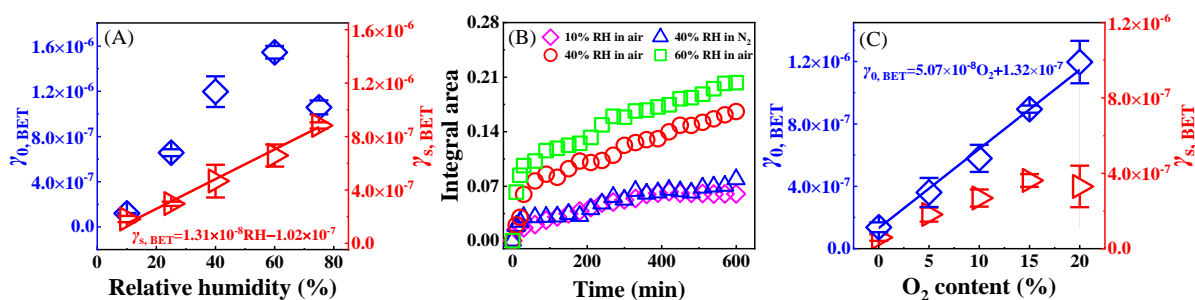


Figure 3. (A) The dependence of $\gamma_{0,\,BET}$ and $\gamma_{s,\,BET}$ on RH. (B) Integrated area of sulfates in

DRIFTS spectra (1289−1202 cm^{-1}) as a function of time. (C) The dependence of $\gamma_{0,\,BET}$ and

$\gamma_{s,\,BET}$ on O_2. Reaction conditions: SiO_2 mass of 0.2 g, irradiation intensity of 7.93×10^{16}

photons cm^{-2} s^{-1}, temperature of 298 K, O_2 content of 20% for (A) and RH of 40% for (B).

296   Figure S8B displays effects of O_2 on the photochemical uptake of SO_2 on SiO_2. Negligible

297   SO_2 uptake occurred in N_2, while there was a significant decrease in the SO_2 concentration in

298   air. The $\gamma_{0,\,BET}$ greatly increased from $(1.37 \pm 0.45) \times 10^{-7}$ under anaerobic condition to (1.19

299      $\pm\ 0.13) \times 10^{-6}$ under 20% O_2 content condition (Figure 3C), confirming that O_2 was involved

300   in the reaction of SO_2 on SiO_2. The $\gamma_{s,\,BET}$ increased from $(7.10 \pm 2.85) \times 10^{-8}$ under anaerobic

301   condition to $(4.37 \pm 0.58) \times 10^{-7}$ under 15% O_2 content condition, whereas it remained

302   unchanged with further increasing the O_2 content.

303   DRIFTS spectra of SiO_2 during the SO_2 uptake in N_2 and air were compared in Figure S9B.

304   In both air and N_2, the bands of absorbed SO_2 (1359 cm^{-1}), sulfates (1260, 1229 and 1074

305   cm^{-1}). Nevertheless, their intensities in N_2 were weaker than those in air. According to the

306   integrated area of sulfates in the DRIFTS spectra (1289−1202 cm^{-1}), the formation trends of

307   sulfates were similar in N_2 and air (Figure 3B), while the sulfate formation rate in N_2 was

308   obviously lower than that in air, meaning that O_2 enhanced the sulfate production. It was

309   reported that the production rate of sulfates from the SO_2 uptake on TiO_2 and by the photolysis

310   of nitrates under UV irradiation in N_2 was also smaller than that in air (Ma et al., 2019; Gen et

311   al., 2019b). In addition, it was noted that sulfates can be generated in N_2, meaning that O_2 was

312   not necessary and some pathways contributed to sulfates without O_2.

313   **3.4 Ubiquitously photoenhanced conversion of SO_2 to sulfates**

314   To better assess the potential for photochemical conversion of SO_2 to sulfates, the SO_2 uptake

315   experiments were further performed on typical mineral oxides without photocatalytic activity.

316   As displayed in Figure S10, more obvious SO_2 uptake on kaolinite, Al_2O_3, MgO and CaO were

317   observed under irradiation compared to those in the dark. Figure 4A shows that there was the

318   largest $\gamma_{s, BET}$ for CaO among five minerals, and $\gamma_{s, BET}$ positively depended on the basicity (pH)

319   of mineral oxides. Basic oxides generally contains more surface hydroxyls, which enhanced

320   the heterogeneous uptake of SO_2 (Zhang et al., 2006). The ratios of steady-state uptake

321   coefficients under irradiation to those in the dark ($\gamma_{s, Light}/\gamma_{s, Dark}$) were larger than 1.0 for all

322   mineral oxides (Figure 4B). The experiments for the pH dependence on SiO_2 have been also

323   performed (Figure S11). The pH of SiO_2 suspension was adjusted to pH = 9, and $\gamma_{s, BET}$ and

324   $\gamma_{s, Light}/\gamma_{s, Dark}$ were determined to be $(8.79 \pm 0.85) \times 10^{-6}$ and 1.31, respectively (Figure 4A and

325   4B). These results suggest that light can generally enhance the SO_2 uptake on minerals at a

326   wide pH range. However, the $\gamma_{Light}/\gamma_{Dark}$ had smaller values with an increase in the basicity,

327   suggesting that the promotion effect of the light was less remarkable for basic oxides.

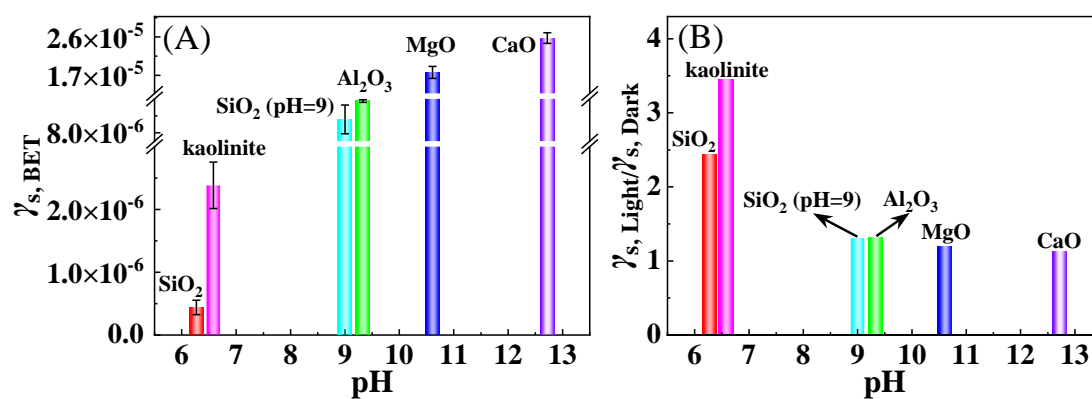



Figure 4. (A) The dependence of $\gamma_{s,\,BET}$ under irradiation on the basicity (pH) of mineral oxides. (B) The ratios of steady-state uptake coefficients under irradiation to those in the dark ($\gamma_{s,\,Light}/\gamma_{s,\,Dark}$). Reaction conditions: mineral oxides mass of 0.2 g, irradiation intensity of 7.93×10^{16} photons $cm^{-2}\ s^{-1}$, temperature of 298 K, RH of 40% and O_2 content of 20%.

As shown in Figure 5A and B, the band at 1300 cm^{-1} should be ascribed to the sulfate. The intensity of sulfate (1300 and 1220 cm^{-1}) under irradiation was larger than those in the dark. Compared to weaker peaks of sulfates (1200 and 1260 cm^{-1}) for Al_2O_3 in the dark (Figure 5C), a stronger band of bisulfates appeared at 1220 cm^{-1} under irradiation (Figure 5D). By contrast to the generation of sulfates for kaolinite and Al_2O_3, both sulfites and sulfates formations were observed for MgO and CaO (Figure 5E−H). Sulfites were dominant in the dark, as shown by the peaks at 966 and 1020 cm^{-1} for MgO and 943 cm^{-1} for CaO, whereas the sulfate formation was significantly enhanced under irradiation according to peak intensities at 1163 cm^{-1} for MgO and 1137 cm^{-1} for CaO. It should be noted that these mineral oxides were non-photoactive because of their poor light absorption property (Figure S1). Nevertheless, the light can promote the formation of sulfates via the SO_2 uptake process on mineral oxides without photocatalytic activity.

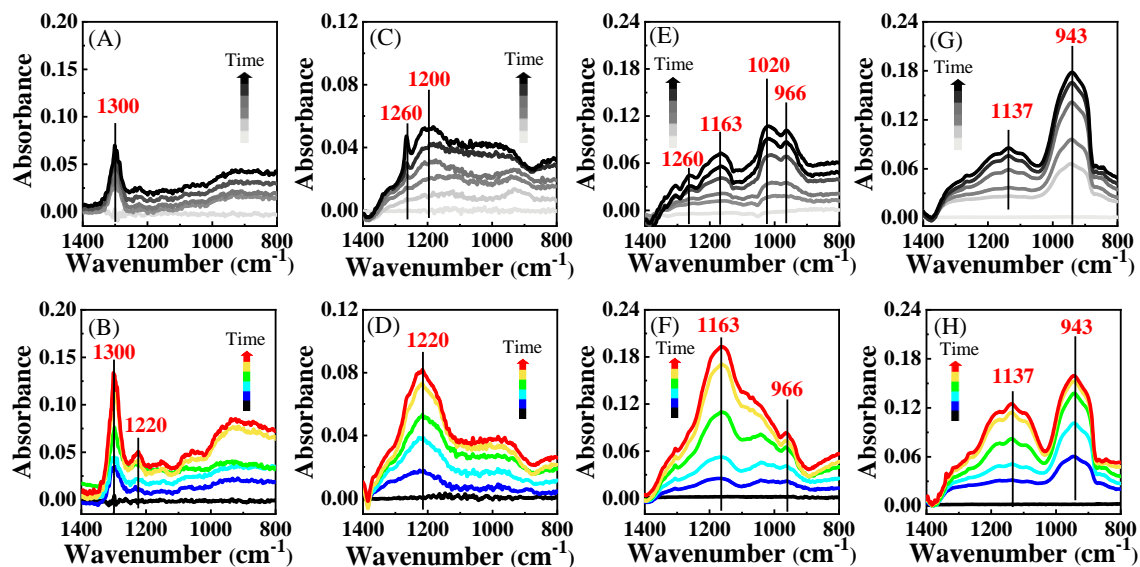



Figure 5. *In situ* DRIFTS spectra of kaolinite (A and B), Al_2O_3 (C and D), MgO (E and F), CaO (G and H) during the uptake process of SO_2 (2 ppm) for 600 min in the dark (black lines) and under irradiation (colorful lines). Reaction conditions: RH of 40%, temperature of 298 K and O_2 content of 20%.

3.5 Conversion mechanisms of SO_2 to sulfates

Heterogeneous photochemical reaction mechanisms of SO_2 on non-photoactive mineral dust were proposed in light of experimental observations (Figure 6). Gaseous SO_2 was adsorbed on the surface (R1), and then reacted with H_2O to form sulfites (R2). Under irradiation, adsorbed SO_2 accepted photons to form its singlet states ($^1SO_2$) and $^3SO_2$ (R3−5) (Sidebottom et al., 1972; Martins-Costa et al., 2018). The reaction between $^3SO_2$ and H_2O resulted in the formation of HOSO• and •OH (R6), which can combine with SO_2 to produce HOSO$_2$• (R7). HOSO• and HOSO$_2$• can be transformed into SO_3, which reacted with H_2O to drive the sulfate formation (R8 and R9). The interaction between $^3SO_2$ and O_2 may also generate SO_3 directly, which would be converted to sulfates subsequently (R10). Theoretical calculations suggested that the multistep reactions between $^3SO_2$ with H_2O and O_2 had small energy barriers or were barrier-free (Gong et al., 2022), which could enhance the generation of ROS and the transformation of S(IV) to S(VI). As displayed by R11 and R12, SO_2 and H_2SO_3 adsorbed on the surface may be oxidized to form sulfates via the reactions with ROS including •O, •OH or HO$_2$• , which were

364   produced in R6 and R8−10. In addition, gaseous SO_2 could be dissolved into adsorbed H_2O to

365   generate bisulfites, which would be finally converted to sulfates by ROS (R13) (Urupina et al.,

366   2019). As displayed in Figure S12A, the IR peaks of sulfates were not observed when tris (2,2′-

367   bipyridine) ruthenium dihydrochloride ($Ru(bpy)_3(Cl)_2$) was employed as the quencher of $^3SO_2$.

368   The peaks were assigned to the vibrations of excited $Ru(bpy)_3(Cl)_2$ (Mukuta et al., 2014). This

369   definitely proves that $^3SO_2$ is the key trigger for the sulfate formation. Figure S12B shows that

370   the peaks of sulfates were weaker in the presence of $NaHCO_3$, confirming the dominant

371   contribution of •OH formed in R6 and R9 to the formation of sulfates.

372   Several photochemical mechanisms have been reported to explain the sulfate formation via

373   the SO_2 uptake on various surfaces. Photoactive mineral oxides (such as TiO_2, F_2O_3 and ZnO)

374   can accept photons to produce electron-hole pairs, which generated ROS for the conversion of

375   SO_2 to sulfates (Ma et al., 2019; Li et al., 2019; Wang et al., 2020b). For example, •OH and

376   HO_2•, generated from the reaction of hole with H_2O and electron with O_2, respectively, can act

377   as oxidizing agents for the reaction with SO_2 (Ma et al., 2019). Similarly, the reaction of SO_2

378   with photo-induced •OH obviously enhanced the formation of sulfate on diesel soot and actual

379    $PM_{2.5}$ (Zhang et al., 2022; Zhang et al., 2020c). NO_2 and NO_2^-/HNO_2 can be formed in the

380   nitrates photolysis, and primarily contribute to the oxidation of SO_2 to sulfates on nitrates (Gen

381   et al., 2019b; Gen et al., 2019a). Theoretically, the mechanism proposed in this study should

382   also occur on photo-excited substrates. Taking TiO_2 as an example, SO_2 competed with TiO_2

383   for photons, and the production efficiency of $^3SO_2$ and excited state of TiO_2 (TiO_2*) depended

384   on their light absorption properties. Meanwhile, $^3SO_2$ had a competition electron-hole pairs

385   generated from TiO_2* for O_2 and H_2O. Thus, the dominant mechanism for the SO_2 uptake on

386   TiO_2 should be related to light absorption properties of precursors and the reactivity for $^3SO_2$

387   and TiO_2* to O_2 and H_2O. By contrast, all mineral oxides used here cannot be excited under

388   irradiation according to their light absorption spectra (Figure S1). Nevertheless, SO_2 adsorbed

389   on mineral oxides can absorb the ultraviolet radiation (290−400 nm) to form the excited states

390   of SO_2 (SO_2*) (Kroll et al., 2018), which subsequently reacted with H_2O and O_2, finally

391   converting SO_2 to sulfates. The SO_2 uptake experiment in the dark and the visible light (>420

392   nm) was carried out (Figure S13). An ignorable difference was observed for the SO_2

393   concentration with or without visible light, suggesting that visible light had a minor contribution

394   to the photoenhanced SO_2 uptake.

395   According to the experimental results, some surfaces, providing absorptive sites for SO_2, can

396   enhance the photooxidation of SO_2 to sulfates. However, the promotion effect would vary with

397   different substances. For example, the current experiments on some basic minerals indicate that

398   light plays a minor enhancement role in the SO_2 uptake (Figure 4), but it could still enhance the

399   sulfate formation (Figure 5). The solubility and effective Henry's law constant of SO_2 were

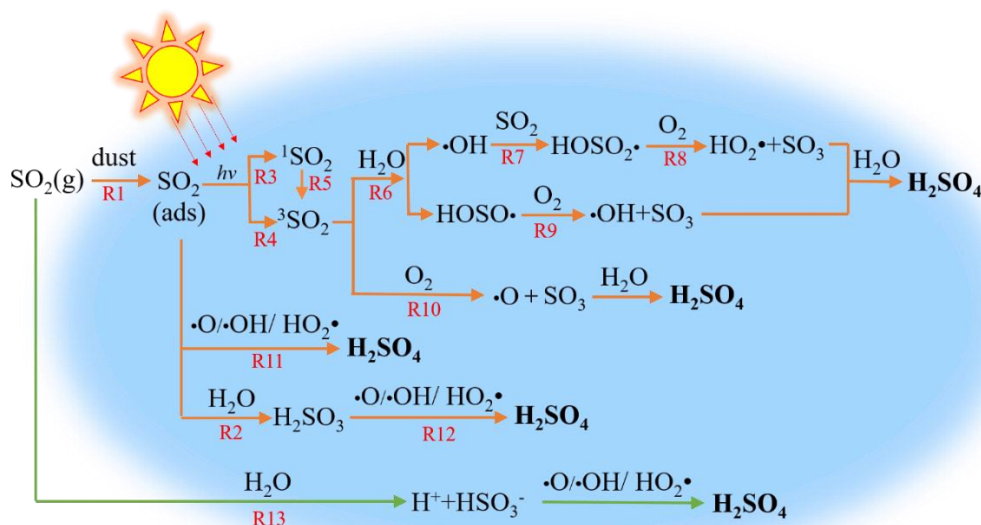
400   positively dependent on pH. Thus, SO_2 was more liable to be dissolved to form HSO_3^-/SO_3^{2-}

401   on more alkaline surface, leading to a strong SO_2 uptake in the dark (Figure 4A and 4B), and

402   abundant sulfites on surfaces (Figure 5). Nevertheless, gaseous SO_2 tends to be adsorbed on

403   kaolinite and Al_2O_3 due to less solubility of SO_2 on these surfaces, and then converted to sulfate

404   under irradiation (Figure 6). Accordingly, a promotion effect of light on SO_2 uptake was

405   observed on neutral and weakly alkaline surfaces (Figure 4B).

406

407   **Figure 6.** The proposed photochemical conversion mechanisms of SO_2 to sulfates on non-

408   photoactive mineral dust.

4 Atmospheric implications

410   The lifetime (τ) for photochemical loss of SO_2 on mineral dust was given using equation 7,

411 $$\tau = \frac{4}{\gamma \omega A} \quad (7)$$

412 where γ and ω are the uptake coefficient and the mean molecular speed of SO_2, respectively; A

413 is the surface area density of mineral dust, and it is estimated to be $(1.4–4.8) \times 10^{-5}$ cm^2 cm^{-3}

414 (Zhang et al.,2019; He et al., 2018b). In this work, $\gamma_{s, BET}$ of SO_2 on several mineral oxides

415 were measured to be 4.39×10^{-7}–3.45×10^{-5} (Reaction conditions: SO_2 concentration of 40

416 ppb, irradiation intensity of 7.93×10^{16} photons cm^{-2} s^{-1} and RH of 40%). Thus, the τ of SO_2

417 with respect to the photooxidation on mineral dust was calculated to be 0.9–240 days, which

418 was shorter than that (54 years) for the photochemical uptake of SO_2 on TiO_2 and the

419 corresponding one (346 days) for the heterogeneous oxidation of SO_2 on ATD in the presence

420 of nitrates (Ma et al., 2019; Zhang et al., 2019). The reaction conditions in this study and those

421 in the literatures are different in some respects, and the previously reported SO_2 uptake

422 coefficient (10^{-7}–10^{-6}) had a lower value (Ma et al., 2019). The huge difference in the τ of SO_2

423 was also ascribed to the variation in the surface area density. The content of TiO_2 in mineral

424 dust was only about 1%, and thus the surface area density of TiO_2 was about 10^{-7} cm^2 cm^{-3},

425 leading to a longer τ (54 years) for SO_2 on TiO_2 (Ma et al., 2019). It was comparable to the

426 lifetime (3.6–20 days) of SO_2 for the gas-phase reaction with $\cdot OH$ at a concentration of $\sim 10^{-6}$

427 molecules cm^{-3} (Huang et al., 2015; Zhang et al., 2019). Therefore, the photochemical process

428 with the excited state SO_2 acting as a driver on mineral dust was an important pathway for the

429 SO_2 sink in the atmosphere.

430   Sulfates show significant influences on the atmosphere, such as an important contributor to

431 the haze formation, affecting the activity of aerosols acting as cloud condensation nuclei (CCN)

432 and ice nuclei (IN), and modifying optical property and acidity of aerosols. A sulfate formation

433 rate (R) can be obtained using γ by equation 8 (Cheng et al., 2016),

434 $$R = \frac{d\left[SO_4^{2-}\right]}{dt} = \left[\frac{R_p}{D} + \frac{4}{\gamma \omega}\right]^{-1} A\left[SO_2\right] \quad (8)$$

435 where R_P is the radius of mineral dust, which can be estimated using equation 9 (Li et al., 2020),

436 $R_P = (0.254 \times [PM_{2.5}]/(\mu g\ m^{-3}) + 10.259) \times 10^{-9}$ m $\quad (9)$

437 where [PM$_{2.5}$] was average PM$_{2.5}$ mass concentration, and 300 μg m^{-3} was used for the polluted

438 periods in typical China cities (Li et al., 2020; Guo et al., 2014). It was assumed that mineral

439 dust accounted for 50% mass of PM$_{2.5}$ (Tohidi et al., 2022), and the mass fraction of SiO$_2$,

440 Al$_2$O$_3$, MgO, and CaO in mineral dust was 60%, 12.5%, 4% and 6.5%, respectively (Urupina

441 et al., 2021; Urupina et al., 2019; Usher et al., 2003). Thus, R was determined to be 2.15 μg

442 m^{-3} h^{-1}. This suggests that the SO$_2$ uptake on non-photoactive surfaces may be an important

443 sulfate formation pathway under irradiation in some dust-rich conditions.

444

Author contributions

446 CH, WY and JM designed and conducted experiments; CH, WY and JM analyzed the data and

447 prepared the paper with contributions from HY; FL conducted experiments; CH supervised the

448 project.

449

Competing interests

451 The authors declare that they have no conflict of interest.

452

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