Significant formation of sulfate aerosols contributed by the heterogeneous drivers of dust surface

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Abstract. The importance of dust heterogeneous chemistry in the removal of atmospheric SO_2 and formation of sulfate aerosols is not adequately understood. In this study, the Fe, Ti, Al-bearing components, Na^+, Cl^-, K^+, and Ca^{2+} of the dust surface were discovered to be closely associated with the heterogeneous formation of sulfate. Regression models were then developed to make a reliable prediction for the heterogeneous reactivity based on the particle chemical compositions. Further, the recognized gas-phase, aqueous-phase and heterogeneous oxidation routes were quantitatively assessed and kinetically compared by combining the laboratory work with modeling study. In the presence of 55 μg m^{-3} airborne dust, heterogeneous chemistry accounts for approximately 28.6% of the secondary sulfate aerosols during nighttime, while the proportion decreases to 13.1% in the presence of solar irradiation. On the dust surface, heterogeneous drivers (e.g. transition metal constituents, water-soluble ions) are more efficient than surface adsorbed oxidants (e.g. H_2O_2, NO_2, O_3) in the conversion of SO_2, particularly during nighttime. Dust heterogeneous chemistry offers an opportunity to explain the missing sulfate source during severe haze pollution events, and its contribution proportion in the complex atmospheric environments could be even higher than the current calculation results. Overall, the dust surface drivers are responsible for the significant formation of sulfate aerosols and have profound impacts on the atmospheric sulfur cycling.

1   Introduction

25   As an important component of atmospheric particulate matters, sulfate exerts profound impacts on the Earth's climate system, air quality, and public health (Seinfeld and Pandis, 2016; Wang et al., 2021a). The rapid formation of sulfate was proven as largely responsible for London Fog and Beijing Haze (Wang et al., 2016; Cheng et al., 2016). Secondary sulfate aerosols originate predominately from the oxidation of sulfur dioxide (SO_2) obeying the laws of gas-phase chemistry in gaseous environments, aqueous-phase chemistry in liquid media, and heterogeneous chemistry on aerosol surfaces (Ravishankara, 1997;

30   Mauldin III et al., 2012; Su et al., 2020; Liu et al., 2021a). In recent years, the newly discovered sulfate formation pathways were kinetically compared with the documented ones to evaluate the relative importance of them (Cheng et al., 2016; Gen et al., 2019; Liu et al., 2020; Wang et al., 2020a). Additionally, the oxidation channels in mainstream were compared by aerosol observation or modeling investigations (Berglen et al., 2004; Sarwar et al., 2013; He et al., 2018; Ye et al., 2018; Fan et al., 2020; Tao et al., 2020; Zheng et al., 2020; Song et al., 2021; Tilgner et al., 2021; Liu et al., 2021b; Wang et al., 2022a). These

35   studies emphasized the importance of the aimed liquid reaction or compared the sulfate contributions of diverse gas- and aqueous-phase pathways. Nevertheless, heterogeneous reaction was scarcely involved in the relevant discussions, thereby hindering the deeper understanding of the atmospheric gas-solid interactions.

Heterogeneous reaction alters the concentrations of gas-phase SO_2 and particle-phase sulfate, and its atmospheric influences were considered by observation and modeling works (Fairlie et al., 2010; Alexander et al., 2012; Chen et al., 2017; Wang et

40   al., 2021b). As summarized by Table S1, when simulating the sulfate burst events, researchers observed the positive feedbacks after implementing heterogeneous chemistry into the WRF-Chem (Li et al., 2017), GEOS-Chem (Shao et al., 2019), CAMx (Huang et al., 2019) and CMAQ (Zhang et al., 2019a) models. However, these improved models highlighted the heterogeneous chemistry motivated by the surface adsorbed oxidants rather than the heterogeneous drivers of aerosol surface. To address the knowledge gap, the revised GEOS-Chem (Wang et al., 2014) and WRF-CMAQ (Zheng et al., 2015) models considered the

45   heterogeneous oxidation driven by aerosol surfaces, and successfully reproduced the rapid sulfate formation. Xue et al. (2016) moved forward to develop an observation-based model and found that heterogeneous chemistry contributed up to one third of the secondary sulfate in a typical haze-fog event. However, the "aerosol surface" mentioned in the previous works was not distinguished by its physical or chemical properties (Wang et al., 2014; Zheng et al., 2015; Xue et al., 2016), thereby making it difficult to compare the atmospheric importance of the diverse airborne surfaces. As discussed above, it is of great importance

50   to investigate the heterogeneous drivers of one selected aerosol surface, and further evaluate the atmospheric significance of the heterogeneous chemistry.

The resurgence of sandstorms in North China makes the air pollution situation more complex than ever before. The concentration of PM_{10} (particulate matter with an aerodynamic diameter of less than ten micrometers) in Beijing reached up to 3600 μg m⁻³, largely beyond the standards of World Health Organization and Chinese government (Li et al., 2021). As the

55   most abundant primary aerosol in the troposphere (Textor et al., 2006; Tang et al., 2016), dust particles could transport more

than one full circuit around the globe within ~ 2 weeks (Uno et al., 2009) and concurrently participate into an array of atmospheric reactions. Heterogeneous reactions over dust surface consume and produce various trace gases, thereby affecting the dust property and tropospheric oxidation capacity (Tang et al., 2016). One of the most extensive concerns is that the numerous surface sites of windblown dust provide opportunities for a variety of atmospheric reactions to occur, e.g. oxidation
60   of SO_2 and formation of sulfate (Usher et al., 2003). In the past decades, plenty of laboratory works have been performed to explore the heterogeneous behaviors of SO_2 on dust surfaces.

When discussing the heterogeneous chemistry on dust proxies, environmental factors including humidity, temperature, irradiance were frequently concerned. Adsorbed water accelerates the hydration of SO_2 but also competes with SO_2 for surface sites (Rubasinghege and Grassian, 2013). The exothermic adsorption of SO_2 results in the negative temperature dependence
65   (Clegg and Abbatt, 2001a), except for the positive effects observed below 250K (Wu et al., 2011) or during the initial reaction stage (Wang et al., 2018a). Light irradiation normally accelerates the transformation of (bi)sulfites to (bi)sulfates (Li et al., 2010; Nanayakkara et al., 2012; Han et al., 2021), while iron oxides may undergo photoreactive dissolution and reflect negative light effect (Fu et al., 2009). The reactivity can be enhanced by H_2O_2 (Huang et al., 2016), or O_3 (Li et al., 2006; Li et al., 2007; Zhang et al., 2018), or NO_x (Ma et al., 2008; Liu et al., 2012; He et al., 2014; Yu et al., 2018; Zhao et al., 2018; Yang et al.,
70   2018a; Wang et al., 2020b), or NH_3 (Yang et al., 2016; Yang et al., 2018b; Yang et al., 2019), or Cl_2 (Huang et al., 2017). By contrast, organic compounds, like CH_3CHO (Zhao et al., 2015), $HCOOH$ (Wu et al., 2013), CH_3COOH (Yang et al., 2020; Wang et al., 2022b) and C_3H_6 (Chu et al., 2019), were found to suppress the interactions due to the accumulation or production of particle-phase organic acids. In terms of particle property, size (Baltrusaitis et al., 2010; Zhang et al., 2016), morphology (Li et al., 2019) and crystal structure (Yang et al., 2017) exhibit varied impacts. Among the common mineral constituents,
75   Fe_2O_3 is more efficient than Al_2O_3 and SiO_2 (Chughtai et al., 1993; Zhang et al., 2006; He et al., 2014). Moreover, the addition of moderate nitrate (Kong et al., 2014; Du et al., 2019), or surfactant (Zhanzakova et al., 2019), or Al_2O_3 (Wang et al., 2018b) into the dust community could favor the heterogeneous uptake of SO_2. Relative to the environmental factors, the heterogeneous effects relevant to particle property are still under debate.

The usage of simple mineral oxide as a substitution for natural dust may be problematic as such approach could undermine the
80   atmospheric importance of more complex mineralogy. Authentic dusts were utilized in laboratory works (Table S2). Some studies concerned single samples like Saharan dust (Ullerstam et al., 2002; Ullerstam et al., 2003; Adams et al., 2005; Harris et al., 2012), Arizona test dust (Park and Jang, 2016; Zhang et al., 2019a; Zhang et al., 2019b), China loess (Usher et al., 2002) and Asian dust (Ma et al., 2012). The comparison of diverse samples has been attracting increasing attention. Zhou et al. (2014) observed the positive temperature effect on Xinjiang sierozem, in contrast to the negative temperature dependence for Inner
85   Mongolia desert dust. Huang et al. (2015) discovered the accelerated oxidation of SO_2 by H_2O_2, and attributed the different moisture effects to the dusts' varying components. Maters et al. (2017) explored the heterogeneous uptake on volcanic ash and glass samples, and related the reactivity differences to the varying abundances of surface basic and reducing sites. Park et al. (2017) compared the heterogeneous reactions on Gobi desert dust and Arizona test dust, and linked the sulfate formation to the quantity of semi-conductive metals. Wang et al. (2019) discovered the enhanced uptake of SO_2 on clay minerals after the

simulated cloud processing, and explained this evolution by the modification of iron speciation. Urupina et al. (2019) discussed the kinetics of diverse volcanic dusts, and further experimentally proved that neither one selected pristine oxide nor a mixture of them can adequately typify the behavior of natural dust (Urupina et al., 2021). Recently, based on the measurement method for sulfite and sulfate (Urupina et al., 2020), they determined the associations between sulfate production and dust chemical properties like (Fe+Al)/Si and Na abundance (Urupina et al., 2022). The aforementioned works broaden the horizons of the heterogeneous drivers on dust surface. Up to now, the dominate dust surface drivers remain controversial due to the limited statistical linkages between the chemical composition of dust and the production rate of sulfate.

While the atmospheric relevance of the oxidation of SO_2 on dust has been widely recognized (Wu et al., 2020; Xu et al., 2020), the contribution of dust heterogeneous chemistry to secondary sulfate aerosols has not been quantitatively determined. By means of the improved WRF-CMAQ model, Wang et al. (2012) attributed a 27% decrement of SO_2 concentration and a 12% increment of sulfate concentration to the heterogeneous chemistry during an Asian dust storm. Moreover, Tian et al. (2021) recently simulated the heterogeneous formation of dust sulfate by the revised GEOS-Chem model and found that, during the dust episodes in North China, up to 30% of the secondary sulfate resulted from the heterogeneous chemistry on dust surface. However, the photocatalytic reactivity of dust was not considered by the advanced models. Yu et al. (2017) developed the atmospheric mineral aerosol reaction (AMAR) model based on the laboratory works, and suggested that the heterogeneous photocatalysis of mineral dust surface contributed more than half of the secondary sulfate. However, the heterogeneous reactivity was measured by quantifying all of the adsorbed SO_2 rather than calculating the yield of particle-phase sulfate. Moreover, limited gas- and aqueous-phase pathways were included in these models, and the heterogeneous reactivities of surface adsorbed oxidants and dust surface drivers have not been distinguished yet. Therefore, it is highly derisible to comprehensively compare the dust heterogeneous chemistry with other documented sulfate formation pathways.

Hereby, upon understanding the driving factors and driving force of the airborne dust surface, this work compared dust heterogeneous chemistry with gas- and aqueous-phase chemistries with respect to the formation rate of sulfate and atmospheric lifetime of SO_2. In order to characterize the sensitivity of heterogeneous reaction to dust loading, the scenarios with different dust concentrations were also considered. The joint influences of ionic strength and aerosol liquid water content on the aqueous-phase oxidation of SO_2 were further discussed to prove the significance of heterogeneous kinetics under diverse atmospheric conditions. The recently reported interfacial oxidations were additionally compared with the heterogeneous chemistry to emphasize the atmospheric relevance of dust surface drivers. This study attempted to verify the significant formation of sulfate aerosols contributed by the heterogeneous drivers of dust surface.

2 Methods

2.1 Technique route

120 This study attempted to investigate whether the heterogeneous oxidation of SO_2 on dust surface, particularly that induced by the dust surface drivers, makes great impacts on the loss of gaseous SO_2 and formation of sulfate aerosols (Text S1, Fig. S1). The gas- and aqueous-phase pathways were assessed by the documented methodologies and parameterizations (Cheng et al., 2016; Seinfeld and Pandis, 2016; Shao et al., 2019; Song et al., 2021), as briefly introduced by Sect. 2.2 (more details in Supporting Information). The heterogeneous conversion of SO_2 comprises dust-mediated and dust-driven modes, emphasizing

125 the oxidants co-adsorbed with SO_2 and the drivers of dust surface, respectively. In the dust-mediated mode, dust surface functions as a reaction medium supporting the interactions between adsorbed oxidants and SO_2. In the dust-driven mode, the oxidation of adsorbed SO_2 is initiated by the active components of dust surface. The former mode was assessed by the particle properties based on the reported methodology, while the later mode was quantitatively characterized by the laboratory works.

2.2 Gas- and aqueous-phase chemistries

130 The gas-phase oxidation of SO_2 is initiated by hydroxyl radical (OH), stabilized Criegee intermediates (CIs) and nitrate radical (NO_3). The former two oxidants promote the sulfate formation during daytime, while the latter one works mainly during nighttime. More details can be found in Text S2.

The aqueous-phase sulfate formation is pH-dependent and can be quantified based on the published documents and the references cited therein (Cheng et al., 2016; Su et al., 2020; Liu et al., 2021a). Herein, aqueous-phase chemistry refers to the

135 liquid SO_2 conversion accelerated by the transition-metal ion-catalyzed oxygen (TMI-O_2), ozone (O_3), hydrogen peroxide (H_2O_2), nitrogen oxide (NO_2), methyl hydroperoxide (CH_3OOH), peroxyacetic acid (CH_3COOOH), hypochlorous acid (HOCl), hypobromous acid (HOBr), dissolved nitrous acid (HONO), as well as the photosensitization and nitrate photolysis only considered for daytime. More details can be found in Text S3 and Tables S3-S4.

The oxidant concentration data were derived from the atmospheric observation campaigns performed in Beijing, North China.

140 The measurements in warm seasons were considered in priority to correspond the experimental temperature of this study. Considering the relatively high irradiance used in the laboratory experiments, the oxidant parameters for daytime discussion were selected from the observations performed at noon time. The influences of dust loading on the oxidant concentrations, nitrate photolysis kinetics and TMI abundances were considered to reflect the linkages between different reactions. More details can be found in Text S4 and Table S5.

145 2.3 Heterogeneous chemistry-particle characterizations

Five airborne clay minerals, including Nontronite (NAu), Chlorite (CCa), Montmorillonite (SWy), Kaolin (KGa) and Illite (IMt), were obtained from the Source Clay Minerals Repository (Purdue University, West Lafayette, Indiana, USA). The

purchased clays were sent for the following measurements.

The clay minerals were analyzed by X-ray fluorescence spectrometer (Axios Advanced, PANalytical, Netherlands) for element distributions (Table S6). The Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) of NAu, CCa, SWy, KGa and IMt were measured by a Quantachrome Nova 1200 BET apparatus to be 19.76, 5.67, 22.64, 18.77 and 20.05 m^2 g^{-1}, respectively. Particles were suspended in Milli-Q water (18.2 MΩ.cm at 25 °C) before the size measurement (ViewSizer[TM] 3000, MANTA Instruments, USA). The particle diameters range mostly from 50 to 1000 nm and are averaged to be 399 nm for NAu, 272 nm for CCa, 438 nm for SWy, 396 nm for KGa, and 366 nm for IMt (Fig. S2).

Particles were ultrasonically extracted in Milli-Q water, followed by the filtration through a polytetrafluoroethylene membrane filter. The obtained solution was analyzed by an ion chromatography (883 Basic, Metrohm, Switzerland) for the concentrations of anions ($HCOO^-$, Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+. NH_4^+, K^+, Mg^{2+}, Ca^{2+}) (Fig. S3) by the reported methods (Wang et al., 2020c). The water-soluble ions account for 4.6‰, 0.1‰, 8.5‰, 0.3‰ and 0.8‰ of the mass contents of NAu, CCa, SWy, KGa and IMt, respectively.

A mixture, denoted as natural dust hereafter, was prepared by mechanically mixing the studied clay minerals by their atmospheric abundances. Because the clays in Kaolinite group (NAu, KGa), Montmorillonite group (SWy), Illite group (IMt) and Chlorite group (CCa) occupy respectively 6.6%, 4.0%, 53.8% and 4.3% mass fractions of the airborne dust (Usher et al., 2003), the prepared natural dust sample comprises 8.8 wt% of NAu, 8.8 wt% of KGa, 5.3 wt% of CCa, 71.4 wt% of IMt, and 5.7 wt% of CCa.

2.4 Heterogeneous chemistry-DRIFTS measurements

The *in-situ* DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) spectra were collected using a FTIR spectrometer (Tracer-100, Shimadzu, Japan) equipped with a mercury-cadmium-telluride detector cooled by liquid nitrogen. A gas supply system was constructed by linking the experimental units through Teflon tubes. Mass flow controllers (D07-19, Severstar, China) adjusted the reactant gases to the expected reactant concentration and relative humidity (RH). Gas cylinders: high-pure air (79% N_2 and 21% O_2), SO_2 (2.46×10^{15} molecules cm^{-3} diluted by N_2).

Before each experiment, a ceramic cup holding particles was placed into the reaction chamber. The particles were treated in a stream of dry air (300 ml min^{-1}) for 30 min to minimize the surface water and impurities (Wang et al., 2018a, 2018c). After the pretreatment, the sample was exposed to humidified air (RH = 50%) to reach moisture saturation, followed by the collection of background spectrum and then the introduction of reactant gas for 240 min. The SO_2 concentration was 3.69×10^{13} molecules cm^{-3} in a total flow rate of 100 ml min^{-1}.

The simulated solar irradiation with an actinic flux of 6.51×10^{15} photons cm^{-2} s^{-1} was provided by an Xenon lamp (TCX-250, Ceaulight, China). The reaction temperature (296.8K) was controlled by a heater attached to a recirculating cooling water system and determined by a calibration curve introduced previously (Wang et al., 2018a). The gas- and aqueous-phase parameters were correlated by the experimental temperature. All of the exposures were performed in triplicates. The experimental setups are displayed by Fig. S4, and the recorded spectra are shown in Fig. S5 and S6.

2.5 Heterogeneous chemistry-acidity and kinetics

The recorded spectra were analyzed by referring to the previous literatures and the references cited therein (Persson and Vgren, 1996; Peak et al., 1999; Goodman et al., 2001; Zhang et al., 2006; Wu et al., 2011; Liu et al., 2012; Nanayakkara et al., 2012; Nanayakkara et al., 2014; Huang et al., 2016; Ma et al., 2017; Yang et al., 2017). Totally six sulfur-containing species can be identified: hydrated SO_2 ($SO_2 \cdot H_2O$), bisulfite, sulfite, solvated sulfate, coordinated sulfate, bisulfate, and the assignments are summarized by Table S7. The overlapping bands were further analyzed by Gaussian/Lorentzian deconvolution to obtain the product distributions (Fig. S7). The consistent deconvolution procedure was performed for the infrared spectra derived from the repeated experiments.

Because part of the measured ions exist in the surface coordinated forms or crystalline states, the particle acidity (pH) may not be accurately characterized by the proxy methods (Hennigan et al., 2015). Herein, the ionization equilibrium of dissolved SO_2 in the water layers of particle surface is considered to be associated with particle acidity. As reported, the dissolved SO_2 would transform from $SO_2 \cdot H_2O$ to HSO_3^-, and then to SO_3^{2-} as the medium evolves from the extremely acidic to the nearly alkaline (Haynes, 2014; Zhang et al., 2015). The relative abundance of $SO_2 \cdot H_2O$ and SO_3^{2-}, as assumed to be equivalent to the relative integral area of their characteristic peaks, is utilized to calculate the particle acidity (more details in Text S3-2 of Supporting Information). The relative abundance of HSO_4^- and SO_4^{2-}, which can be used to calculate the aerosol acidity (Rindelaub et al., 2016; Ault, 2020), was not considered by the present study because the characteristic signals of bisulfate cannot be observed in some of the recorded infrared spectra.

Heterogeneous kinetics can be assessed by the reactive uptake coefficient (γ) by assuming a first-order loss of SO_2. The γ for dust-driven heterogeneous chemistry can be calculated by:

$$\gamma = \frac{d[SO_4^{2-}]/dt}{Z} \tag{1}$$

$$Z = \frac{1}{4} \times A_S \times [SO_2] \times v_{SO_2} \tag{2}$$

$$v_{SO_2} = \sqrt{\frac{8RT}{\pi M_{SO_2}}} \tag{3}$$

Where $d[SO_4^{2-}]/dt$ is the rate of sulfate production on dust surface (ion s^{-1}), A_s is the reactive surface area (m^2), $[SO_2]$ is the experimental concentration of SO_2 (molecules m^{-3}), v_{SO_2} is the molecular velocity of SO_2 (m s^{-1}), R is gas constant (J mol^{-1} K^{-1}), T is the experimental temperature (K), M_{SO_2} is the molecular weight of SO_2 (kg mol^{-1}). Because the infrared intensity is proportional to the amount of surface product, $[SO_4^{2-}]$ can be translated by the integral area of the sulfate characteristic peaks:

$$[SO_4^{2-}] = f \times (integral\ area) \tag{4}$$

Where f is the conversion factor and represents the number of SO_4^{2-} corresponding to per unit integral area. The sulfate production rate of dust surface can be translated by the calibration curves by mixing weighed Na_2SO_4 with the target particle sample to a set of concentrations (Martin et al., 1987; Li et al., 2006; Wu et al., 2011; Wang et al., 2020d). The conversion

factors are calculated to be 1.32×10^{18}, 4.62×10^{17}, 6.97×10^{17}, 8.20×10^{17}, 9.44×10^{17}, and 9.25×10^{17} for NAu, CCa, SWy, KGa, IMt, and natural dust, respectively. Because the sulfate standard item was thoroughly mixed with the particles, S_{BET} was used to calculate the reactive uptake coefficient.

215   All of the particle samples except SWy presented steady sulfate production potentials over the entire experiment, while the products on SWy increased by reaction time in the beginning and then gradually remained unchanged (Fig. S8). Accordingly, the process on SWy was assessed by the experimental data of the first 30 min of reaction, and the kinetics of other samples were calculated by the spectra recorded throughout the experiment.

Besides the dust surface drivers, the heterogeneous conversion of SO_2 can be additionally initiated by the gaseous oxidants (O_3, H_2O_2, NO_2, HOCl, HOBr, CH_3OOH, CH_3COOOH, HONO) co-adsorbed with SO_2. Considering that the adsorption of

220   oxidant onto dust surfaces would produce gas- and particle-phase species (Usher et al., 2003; Tang et al., 2017), the dust-mediated heterogeneous oxidation can be assumed to primarily proceed in the surface water layers. Such assumption can be experimentally proved as the acceleration of SO_2 oxidation induced by the co-oxidant (e.g. H_2O_2, NO_2, O_3) becomes more significant under higher humidity (Huang et al., 2015; Park et al., 2017; Zhang et al., 2018). Based on the previous studies (Hanson et al., 1994; Jacob, 2000; Shao et al., 2019), the γ for dust-mediated heterogeneous chemistry can be calculated by:

225
$$\gamma = \left[\frac{1}{\alpha} + \frac{v}{4H^*RT\sqrt{D_a k_{chem}}} \times \frac{1}{f_r}\right]^{-1} \tag{5}$$

$$k_{chem} = \frac{R_a}{\sum S_{(IV)}} \tag{6}$$

$$f_r = \coth\frac{r_p}{l} - \frac{l}{r_p} \tag{7}$$

$$l = \sqrt{\frac{D_a}{k_{chem}}} \tag{8}$$

Where k_{chem} is the first-order reaction rate constant of the studied $S_{(IV)}$ specie(s) (s^{-1}) that produce in the rate of R_a ($M\ s^{-1}$), f_r is

230   the diffusive correction term comparing the radius of natural dust r_p (m) with the diffuse-reactive length l (m), α is the mass accommodation coefficient (dimensionless), D_a is the aqueous-phase diffusion coefficient of SO_2 ($1.78 \times 10^{-5}\ m^2\ s^{-1}$ at 296.8 K) (Himmelblau, 1964; Haynes, 2014), H^* is the effective Henry's law constant for the studied $S_{(IV)}$ specie(s) ($M\ atm^{-1}$), and R is gas constant ($L\ atm\ mol^{-1}\ K^{-1}$).

The sulfate formation rate in the atmosphere can be calculated by the following equations (Jacob, 2000; Li et al., 2020a).

235
$$\frac{d[SO_4^{2-}]}{dt} = \left(\frac{r_p}{D_g} + \frac{4}{v\gamma}\right)^{-1} S_p[SO_2] \tag{9}$$

$$S_P = C \times F \times S_{BET} \tag{10}$$

Where $d[SO_4^{2-}]/dt$ is the atmospheric sulfate formation rate ($\mu g\ m^{-3}\ h^{-1}$), r_p is the particle radius (m), D_g is the gas-phase diffusion coefficient of SO_2 ($m^2\ h^{-1}$), v is the molecular velocity of SO_2 ($m\ s^{-1}$), γ is the reactive uptake coefficient

(dimensionless), S_p is the particle surface area density ($m^2\ m^{-3}$), [SO_2] is the atmospheric SO_2 concentration ($\mu g\ m^{-3}$), C is the dust concentration of 55 $\mu g\ m^{-3}$ in representative of the common atmospheric condition of China (Zhang et al., 2012), F is the mass fraction of clay mineral in the natural dust community (%), S_{BET} is the BET specific surface area ($m^2\ g^{-1}$).

2.6 Atmospheric lifetime of SO₂

For the gas- and aqueous-phase pathways, the lifetime of SO_2 (τ) can be calculated by Eq. (11) (Jacob, 2000).

$$\tau = \frac{1}{k_{chem}} \qquad (11)$$

Where k_{chem} is the assumed first-order reaction rate constant of the studied $S_{(IV)}$ specie(s) (s^{-1}).

For the heterogeneous pathways, the τ can be calculated by Eq. (12) (Clegg and Abbatt, 2001b).

$$\tau = \frac{4}{\gamma v S_p} \qquad (12)$$

Where γ is the reactive uptake coefficient (dimensionless), v is the molecular velocity of SO_2 ($m\ s^{-1}$), S_p is the particle surface area density ($m^2\ m^{-3}$), as described by Eq. (10).

The atmospheric lifetime caused by the multiple pathways (τ_{total}) can be estimated by Eq. (13) (Seinfeld and Pandis, 2016).

$$\tau_{total} = \left(\sum \frac{1}{\tau}\right)^{-1} \qquad (13)$$

3 Results and discussion

3.1 Driving factors of dust surface

Correlation analysis was performed at first to explore the dominant surface drivers that affect the heterogeneous sulfate production on different clay minerals (Fig. 1a). Under dark condition, the sulfate production rate corrects positively with Fe, while presents negative dependence against Al. By means of aerosol mass spectrometer, airborne sulfate was reported to be highly associated with the iron-rich dusts, and the heterogeneous reaction of SO_2 was regarded as a plausible explanation (Sullivan et al., 2007). Conversely, Al_2O_3 presents weaker heterogeneous reactivity than Fe_2O_3 (Zhang et al., 2006; Yang et al., 2018b; Xu et al., 2021), and was proved to suppress the nocturnal heterogeneous reaction by blocking the reactive sites on other components (Wang et al., 2018b). Accordingly, Fe-bearing component plays a crucial role in the heterogeneous SO_2 oxidation, while the presence of Al-bearing component directly weakens the dust's reactivity or indirectly decreases the proportion of other active mineral constituents.

Recent studies proposed that transition metal oxides in dust act as photocatalyst that yields electron-hole pairs (Chen et al., 2012; Abou-Ghanem et al., 2020; Wang et al., 2020c; Sakata et al., 2021), followed by the formation of reactive oxygen species (ROS) including hydroxyl radical ($^\bullet OH$), superoxide ($O_2^{\bullet-}$), hydroperoxyl radical ($HO_2^\bullet$) and dissociated active oxygen species (O^*). Sulfate radical ($SO_4^{\bullet-}$) is generated by the presence of abundant $^\bullet OH$ and participates into the oxidation events (Antoniou et al., 2018; Kim et al., 2019; Li et al., 2020b). Hence, there is positive correlation between the content of Ti and the sulfate production enhanced by solar irradiation. The abundance of Al associates positively with the photoinduced sulfate enhancement as well. Physically, Al-bearing components disperse other efficient mineralogical constituents in case of agglomeration (Darif et al., 2016). Chemically, sunlight was found to alter the electronic configuration of α-Al_2O_3, which presented photoactivity in the reported heterogeneous process (Guan et al., 2014). Hence, the discrepancy between the nocturnal and diurnal sulfate formation rates is primarily related to the existence of Ti- and Al-bearing mineral constituents.

No correlation can be observed between the abundance of element and the sulfate production rate of photoreaction. The dust sample with higher proportion of elemental Ti was reported to exhibit greater reactivity toward SO_2 (Park et al., 2017), or NO_2 (Ndour et al., 2009), or O_3 (Abou-Ghanem et al., 2020) in the photochemistry processes. However, these results were derived from the qualitative comparison rather than the quantitative analysis as performed in this work. Analogous to the Al_2O_3 discussed above, semi-conductive metal exhibits dual behaviors in dark and light reactions. For instance, the iron oxide under dark condition owns great reactivity toward SO_2, whereas that under solar irradiation may present impaired heterogeneous kinetics due to its dissolution process (Fu et al., 2009). In addition, the heterogeneous reaction on the surface of TiO_2 or Ti-bearing mineral is thermodynamically favored during nighttime but largely dependent on photocatalysis under solar irradiation (Chen et al., 2012). Due to the complexity of photoreaction that involves both of the dark and light reaction mechanisms, the sulfate formation rate of photoreaction may not be directly linked to particle chemical compositions.

Some water-soluble ions (Na^+, Cl^-) are observed to present positive impacts on the production of surface sulfate under dark

condition. The presence of halite (NaCl) has positive implications for the dust's hydroscopic property and may facilitate its heterogeneous reactivity (Wang et al., 2014; Tang et al., 2019). Moreover, there are negative associations between the photoinduced sulfate enhancement and the abundances of Na^+, K^+, Ca^{2+}. These cations can be hydrolyzed by adsorbed water to produce H^+, thereby elevating the particle acidity. The increased acidity retards the hydrolysis and dissociation of SO_2 (Park et al., 2008; Huang et al., 2015), and inhibits the production of OH by the irradiated dust surfaces (Zheng et al., 1997; Yang et al., 2008; Liu et al., 2017a). Urupina et al. (2022) recently reported the positive correlations between secondary dust sulfate and the amount of elemental Na. The results here provide additional insights into the heterogeneous effects of the water-soluble constituents on dust surface.

The correlation analysis helps to quantitatively identify the dust surface drivers and better understand the reaction mechanism of dust heterogeneous chemistry. Regression analysis can be further performed to predict the surface kinetics by the chemical compositions of dust. Referring to the publication of Zhang et al. (2020), we derived an exponential parameterization for the production rate of particle-phase sulfate:

$$SF_{dark} = M[A]^a[B]^b[C]^c[D]^d[E]^e[F]^f + N \tag{14}$$

Where SF_{dark} is the yield of SO_4^{2-} on the particle sample of per unit mass within per unit time (ions g^{-1} s^{-1}); [A], [B], [C], [D], [E] and [F] are the mass fractions of element and ion (%); M and N are the constant parameters (dimensionless). After the statistical procedures by SPSS (version 22.0), we obtained the regression equation for the nocturnal heterogeneous reaction:

$$SF_{dark}(\times 10^{15}) = 22.858 \ [Al]^{-0.001}[Fe]^{0.111}[Cl^-]^{0.001}[Na^+]^{0.001} - 13.404 \tag{15}$$

Analogously, the discrepancy between the nocturnal and diurnal sulfate production rates, denoted as $R_{light/dark}$, can be described by:

$$R_{light/dark} = SF_{light}/SF_{dark} = 14.539 \ [Al]^{0.073}[Ti]^{0.167}[Cl^-]^{-0.001}[Na^+]^{-0.001}[K^+]^{-0.001}[Mg^{2+}]^{-0.001} - 3.186 \tag{16}$$

Then,

$$SF_{light} = SF_{dark} \times R_{light/dark} \tag{17}$$

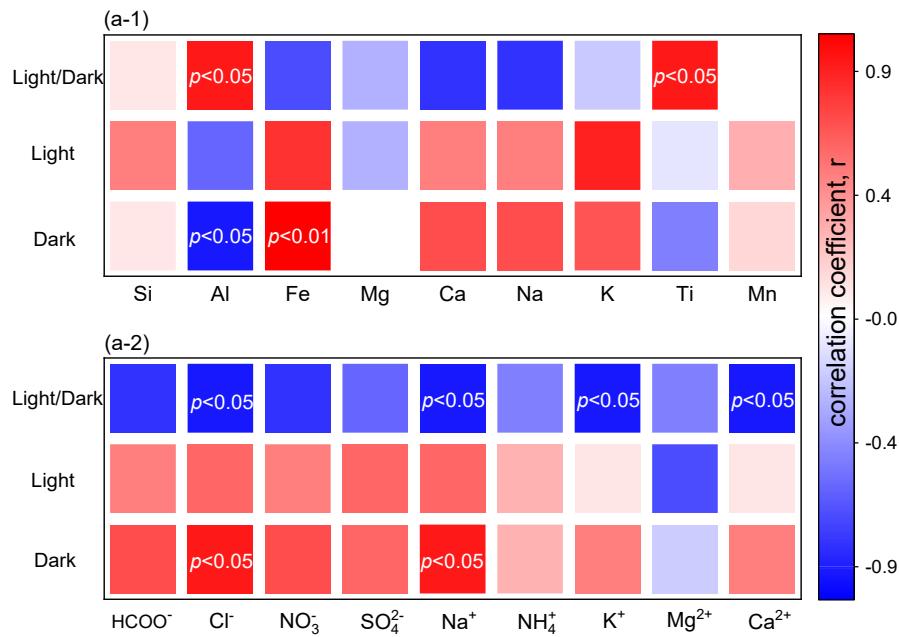
Because the abundance variation of water-soluble ion presents significantly less influence on the prediction result relative to the elemental transition metal, the complete regression models can be simplified by merely considering the mineral element abundances:

$$SF_{dark}(\times 10^{15}) = 30.880 \ [Fe]^{0.077} - 21.679 \tag{18}$$

$$R_{light/dark} = 15.581[Al]^{0.062}[Ti]^{0.141} - 4.277 \tag{19}$$

$$SF_{light} = SF_{dark} \times R_{light/dark} \tag{20}$$

Both of the complete and simplified regression models accurately simulate the experimental data with all of the linear slopes approaching 1.0 and all of the R^2 values larger than 0.995 (Fig. 1b and c). The simplified regression model can be considered as the preferred recommendation due to the fewer parameters needed and its greater performance in the photoreaction prediction. Shang et al. (2010) found that the heterogeneous sulfate production on pristine TiO_2 (Degussa P25) can be accelerated by 8.4 times by the presence of ultraviolet light (365 nm, 350 μW cm^{-2}). Such photoinduced enhancement is

comparable with the prediction result (10.2 times) derived from the simplified regression model developed by this study. Additionally, because the chemical composition of bulk sample may not fully explain the sulfate formation over dust surface, further study to discuss the model uncertainty is warranted.

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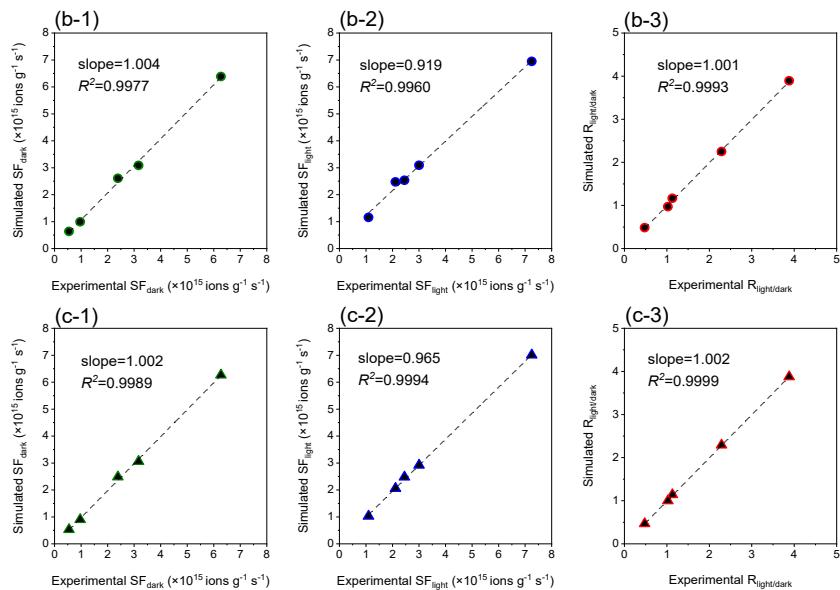
Figure 1. Correlation and regression analysis on the sulfate production rate of dust surface.

Correlation analysis bridging the rate of sulfate production and the abundance of (a-1) mineral element and (a-2) water-soluble ion. Linear relationships between the experimental SF_{dark}, SF_{light}, $R_{light/dark}$ and those simulated by the (b) complete and (c) simplified regression models. The unit of SF (ions g^{-1} s^{-1}) indicates the number of SO_4^{2-} formed on the particle sample of per unit mass within per unit time, and $R_{light/dark}$ indicates the ratio of SF values in presence and absence of simulated solar irradiation.

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3.2 Driving force of dust surface

The driving force of dust surface can be characterized by reactive uptake coefficient and particle acidity (Fig. 2, Table S8). Under dark condition, the reactive uptake coefficients are highest for SWy and NAu, followed by IMt and CCa, with that of KGa being the lowest. The presence of simulated solar irradiation causes a different rank: IMt>SWy>CCa>NAu>KGa. The diurnal uptake coefficients of CCa, SWy, KGa, IMt are respectively 1.52, 1.01, 2.94, 2.30 times greater than the corresponding nocturnal ones, reflecting the distinct photocatalytic performances of the clay minerals. Conversely, NAu presents the decreased heterogeneous uptake capacity under light irradiation than dark condition due to its rich abundance of Fe, whose oxide species may occur photoreductive dissolution in acidic media (Fu et al., 2010; Shi et al., 2012). Comparing the studies performed by the same experimental approach and assessment procedures, the studied clay minerals are more efficient than the previously concerned mineral dust proxies, including $CaCO_3$ (Li et al., 2006; Wu et al., 2011; Zhang et al., 2018), Al_2O_3 (Liu et al., 2017b), TiO_2 (He and Zhang, 2019) and manganese oxides (Wang et al., 2020d), in the heterogeneous production of sulfate under the parallel conditions.

The reactive uptake coefficients for the natural-dust-driven heterogeneous chemistry were calculated to be 6.08×10^{-6} during nighttime and 1.14×10^{-5} during daytime (Fig. 2a). Within the data set of authentic dust, the nocturnal value is lower than those of China loess (3.0×10^{-5}), Inner Mongolia desert dust (2.41×10^{-5}), Xinjiang sierozem (8.34×10^{-5}), Saharan dust (6.6×10^{-5}), Asian mineral dust (2.54×10^{-5}), Tengger desert dust (4.48×10^{-5}) and ATD (1.92×10^{-5}) under the similar experimental conditions (Usher et al., 2002; Adams et al., 2005; Zhou et al., 2014; Huang et al., 2015). It should be noted that, the previous studies measured net uptake coefficient that quantifies all of the heterogeneously adsorbed SO_2, and some of them assessed the oxidation events accelerated by the surface adsorbed oxidants (e.g. NO_2, O_3, H_2O_2). In order to quantify the driving force of dust surface drivers in the contribution of particle-phase sulfate, S(IV) species were not considered for the kinetics calculation in this study. Quantitatively, the dust surface drivers are responsible for the atmospheric sulfate formation rates of 0.195 and 0.365 $\mu g\ m^{-3}\ h^{-1}$ during nighttime and daytime, respectively.

Particle acidity is another important index reflecting the impacts of dust heterogeneous chemistry. After the exposure to SO_2, CCa is the most acidic, followed by IMt, KGa and NAu, leaving SWy being more neutral. Because no significant correlations can be found between γ and pH, the absolute acidity level is largely dependent on the basic nature of dust. The lowest pH assigned to CCa can be explained by its highest content of elemental Mg relative to the other clays (see Table S6). The Mg-bearing constituents dissolve to be Mg^{2+} that can be further hydrolyzed by water to produce H^+, thus accelerating the acidification of particle (Park et al., 2008; Huang et al., 2015). For one clay mineral, its different acidities after dark and light reactions reflect the distinct heterogeneous kinetics. All of the studied clays, with the exception of NAu, become more acidic after the photoreaction than the dark reaction, which can be explained by the photoinduced SO_2 adsorption and sulfate production on these samples. The opposite situation of NAu coincides to the decreased heterogeneous kinetics over its surface by the presence of solar irradiation. Generally, the natural dust presents the particle acidity (pH) of 4.177 after dark reaction and 4.405 after photoreaction (Fig. 2b). Such results locate within the acidity ranges of dust seeds (3.0-7.0) (Ault, 2020; Pye

et al., 2020) and haze aerosols (3.5-4.8) (Ding et al., 2019; Song et al., 2019), suggesting that the dust-driven heterogeneous process could affect aerosol acidity by a certain extent.

Figure 3 presents the pH-dependent reactive uptake coefficients for the natural-dust-mediated heterogeneous chemistry, accompanied with the experimental data of dust-driven heterogeneous chemistry. The sulfate formation mediated by dust surface is primarily affected by the surface adsorbed H_2O_2 below the nocturnal pH of 5.5 or the diurnal pH of 5.3. When the dust acidity exceeds the thresholds, dust-mediated chemistry would be kinetically dominated by NO_2 and O_3 during nighttime, or HOBr and HOCl during daytime. The γ of NO_2, O_3, HOCl, HOBr and CH_3COOOH presents positive dependence toward pH, in accordance with the evolution of the effective Henry's law constant for the studied sulfur species, as theoretically illustrated by Eq. (5). Generally, the dust-driven chemistry appears to be more efficient than the dust-mediated chemistry over the estimated pH range, and thus could account for more secondary sulfate aerosols. In the following sections, the oxidation of SO_2 mediated or driven by the surfaces of natural dust would be set as the typical examples of dust-mediated and dust-driven heterogeneous chemistries to compare with the widely reported gas- and aqueous-phase processes.
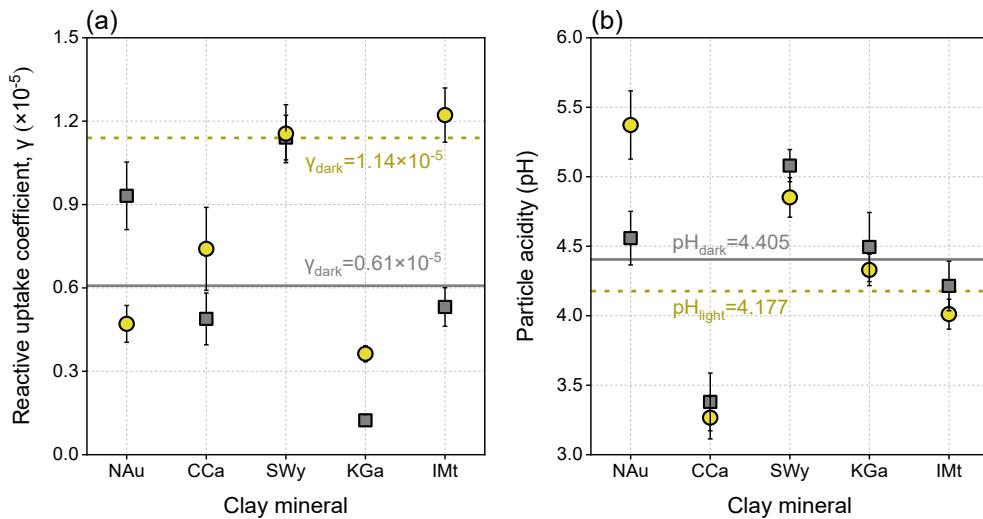
Figure 2. Analysis results of the *in-situ* infrared spectra recorded for the heterogeneous reaction of SO_2 on the clay minerals and natural dust.

(a) Reactive uptake coefficients (γ) for the heterogeneous production of sulfate. (b) Particle acidity (pH) after the heterogeneous reaction. Both of the dark (grey square) and light (yellow circle) conditions were considered. Dots represent the results of clay minerals, and those of natural dust are showed by the lines. All error bars represent 1 SD.
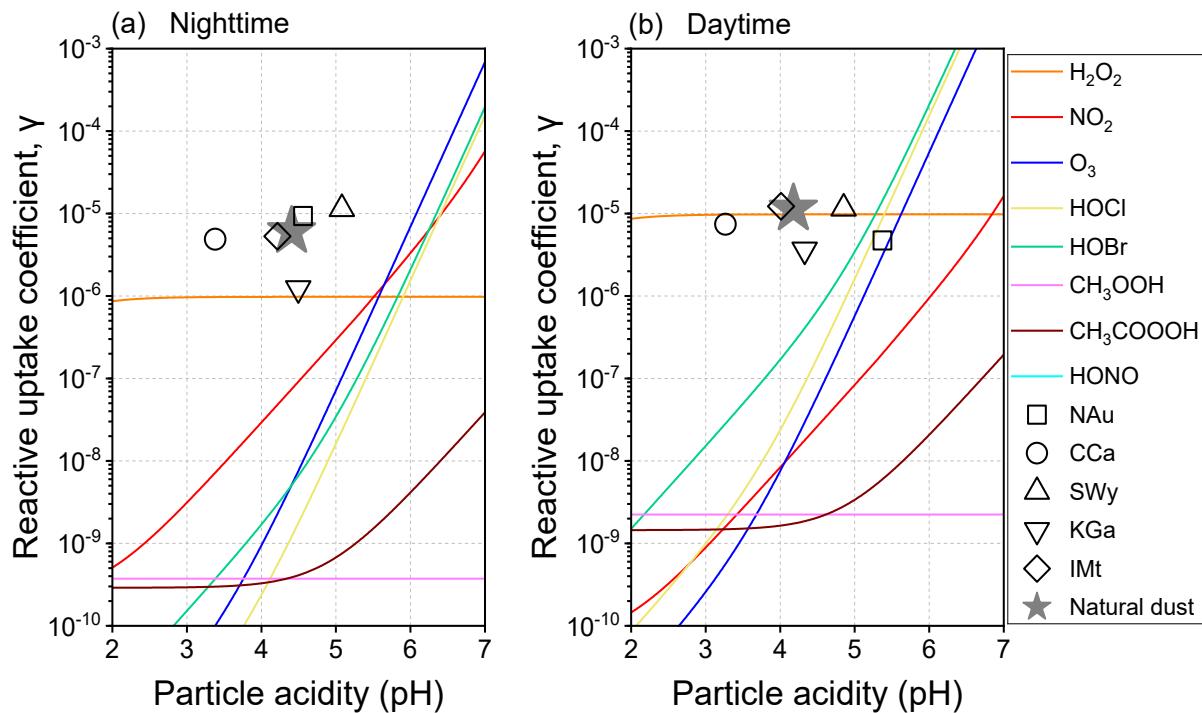
Figure 3. Particle-acidity-dependent reactive uptake coefficients for the dust-mediated and dust-driven heterogeneous sulfate formation.

The dust-mediated chemistry is induced by the surface oxidants co-adsorbed with SO_2, including hydrogen peroxide (H_2O_2), nitrogen oxide (NO_2), ozone (O_3), hypochlorous acid (HOCl), hypobromous acid (HOBr), methyl hydroperoxide (CH_3OOH), peroxyacetic acid (CH_3COOOH) and dissolved nitrous acid (HONO). The dust-driven chemistry is induced by the heterogeneous drivers (transition-metal-bearing components and water-soluble ions) on the surfaces of natural dust and clay minerals [Nontronite (NAu), Chlorite (CCa), Montmorillonite (SWy), Kaolin (KGa), Illite (IMt)].

3.3 Comparison of atmospheric oxidation pathways

Figure 4 compares dust heterogeneous chemistry with the gas- and aqueous-phase pathways in terms of the atmospheric sulfate formation rate. The clay minerals are kinetically comparable with other reactive species (Fig. 4a and e), indicating that the dust-driven chemistry makes considerable contributions to secondary sulfate aerosols. For instance, during nighttime, the heterogeneous reactivity of IMt is only next to those of OH and TMI-O_2. The sulfate formation rates are summed to be 0.795 $\mu g\ m^{-3}\ h^{-1}$ during nighttime and 5.179 $\mu g\ m^{-3}\ h^{-1}$ during daytime by the parameterization scheme of this study. The elevated sulfate formation rate during daytime can be explained by the photo-increased oxidation channels, oxidant concentrations, heterogeneous reactivity, and the elevated particle acidity that facilitates the TMI catalysis. It is worthwhile to mention that, in the real atmosphere, the observed sulfate concentration during nighttime may be comparable to or exceed that during daytime, which can be explained by the higher nocturnal humidity facilitating the liquid oxidations or the lower boundary layer causing the adverse diffusion conditions (Liu et al., 2017c; Tutsak and Koçak, 2019; Li et al., 2020c). The relevant meteorological factors were not considered by this comparison model, and the current results emphasized the different sulfate formation potentials through kinetic regime. The sulfate fluxes here are generally lower than some published data calculated by the same concentration of SO_2 (40 ppb) because the gas- and aqueous-phase parameters in this work were corrected by the experimental temperature (296.8K) rather than the standard temperature (271 K) used previously (Cheng et al., 2016; Gen et al., 2019; Liu et al., 2020; Su et al., 2020; Wang et al., 2020a; Liu et al., 2021a). Considering that part of the relevant parameters were experimentally determined under room temperature with the lack of temperature dependence, uncertainties may exist in the discussions on cold environments. The sulfate formation in this work was assessed near room temperature that is pertinent to the nature of sandstorm occurring during late spring and early summer in East Asia (Wu et al., 2020; Ren et al., 2021).

During nighttime, the gas-phase, aqueous-phase and heterogeneous chemistries explain 31.6, 39.8 and 28.6% of the secondary sulfate aerosols, respectively (Fig. 4b). The diurnal contribution proportions of gas-phase chemistry (45.5%) and aqueous-phase chemistry (41.4%) exceed their nocturnal levels, thus lowering the heterogeneous proportion to 13.1% during daytime (Fig. 4f). In other words, although the heterogeneous sulfate production during nighttime is quantitatively lower than that during daytime (see Sect. 3.2), the nocturnal heterogeneous chemistry accounts for the higher proportion of secondary sulfate. In the regime of gas-phase chemistry, OH is the predominant oxidant, followed by CIs, while NO_3 contributes little. In liquid phase, TMI-O_2 and H_2O_2 play crucial roles in the oxidation of SO_2, coinciding to the reported results (Fan et al., 2020; Song et al., 2021). Besides, there are lower contributions attributed to the NO_2 during nighttime, as well as the HOBr, photosensitization, nitrate photolysis during daytime. The heterogeneously formed sulfate is mostly ascribed to the dust-driven chemistry rather than the dust-mediated chemistry. The sulfate formation rates of gas-phase, aqueous-phase and heterogeneous chemistries under solar irradiation are respectively 9.4, 6.8 and 3.0 times greater than the corresponding nocturnal results, indicating that the oxidations in gaseous and liquid media could be more kinetically susceptible to the occurrence of sunlight than those relevant to the gas-solid interface. The sulfate contribution proportions of dust heterogeneous chemistry are comparable with those obtained by the OBM model (30.6% for nighttime and 19.4% for daytime) (Xue et al., 2016), as well

as the revised GEOS-Chem model (20-30%) (Tian et al., 2021) and WRF-CMAQ model (up to 12%) (Wang et al., 2012). While the kinetic uptake coefficients used in the previous studies are generally greater than the present experimental results, more pathways were implemented in the current comparison model, thereby causing the parallel comparison results. By contrast, the AMAR model highlighted the dust's photocatalytic surface that contributes remarkable secondary sulfate (>50%) under the constraint simulation conditions (Yu et al., 2017).

In the regime of dust-mediated heterogeneous chemistry, H_2O_2 is the most efficient oxidant, followed by the nocturnal NO_2 and diurnal hypohalous acids (HOBr, HOCl) responsible for less secondary sulfate (Fig. 4c, g). The dust-driven heterogeneous sulfate formation is mainly attributed to IMt that owns the largest proportion in dust community, followed by NAu and SWy with relatively great heterogeneous performances (Fig. 4d and h). The nocturnal and diurnal secondary sulfate fluxes of the dust-driven chemistry are respectively 5.8 and 1.2 times greater than those of the dust-mediated chemistry. In other words, the heterogeneous sulfate formation is primarily ascribed to the dust surface drivers rather than the surface adsorbed oxidants, as experimentally proved by the laboratory studies concerning the heterogeneous SO_2 oxidation on authentic dusts accelerated by the presence of NO_2 (Park et al., 2017), or O_3 (Park et al., 2017), or H_2O_2 (Huang et al., 2015). The kinetic discrepancy between the dust-mediated and dust-driven chemistries is more significant during nighttime than daytime. In the estimation, H_2O_2 is the predominant dust-mediated oxidant and its concentration becomes lower under weaker solar irradiation. During nighttime, the dust-mediated contribution is thus relatively small by the presence of the relatively low H_2O_2 concentration. When investigating the heterogeneous chemistry on dust particles, particle variables are thus more important than gas variables in elucidating the reaction characteristics and atmospheric implications.

The sulfate formation rates of diverse chemistry modes are summarized as a function of particle acidity as presented in Fig. 5. Relative to the pH-independent gas-phase chemistry, the aqueous-phase oxidation of SO_2 becomes relatively productive under the extremely acidic and near-neutral situations, while fails to support the rapid sulfate formation within the pH range of 4-5 (minimums at 4.85 for nighttime and 4.55 for daytime), which overlaps the acidity range of the weak dust-mediated heterogeneous chemistry. Noticeably, such selected range includes the acidity of the aged natural dust and overlaps that of the common haze aerosols, suggesting that the heterogeneous drivers of dust surface have profound impacts on the secondary sulfate burst in highly polluted environment (Ding et al., 2019; Song et al., 2019). As proved by the atmospheric observation research, secondary sulfate was discovered to accumulate on the dust-dominant super-micron particles collected in the North China Plain, and this pollution on coarse particles dramatically got worse during the evolutionary stages of haze episodes (Xu et al., 2020). In more detail, the significant sulfate formation in the acidic environment is primarily contributed by the TMI-O_2 pathway where the concentrations of TMIs and H^+ keep increasing as the aerosol water becomes more acidic. When pH>5.0, the formation rate of sulfate increases with the elevated pH, in step with the evolution of the concentration of dissolved sulfur species. Within the entire pH range, the aqueous-phase chemistry is more efficient than the dust-mediated heterogeneous chemistry in contributing to secondary sulfate.

Apart from sulfate formation rate, SO_2 lifetime is another index evaluating the atmospheric significance of certain oxidation pathway. Calculations of lifetimes can be useful in estimating how long the SO_2 is likely to remain airborne before it is removed

from the atmosphere (Seinfeld and Pandis, 2016). Under dark condition, IMt causes the shortest SO_2 lifetime, followed by NAu and SWy, with those ascribed to KGa and CCa being much longer. IMt owns the largest mass proportion in dust community and thus causes the shortest lifetime. The relatively great reactivities of NAu and SWy link to the second and third shortest SO_2 lifetimes. On the other hand, the weakest reactivity of KGa leads to the second longest lifetime, and the longest

460   result caused by CCa can be partly interpreted by its lowest S_p. The occurrence of solar irradiation alters the lifetime ranking (IMt<SWy<NAu<KGa<CCa), as influenced by the different photoactivities of the clay minerals. The heterogeneous drivers of natural dust surface are comparable with TMI-O_2 in the loss of SO_2, and both of them function as the most important lifespan influencers in the absence of sunlight (Fig. S9a). During daytime, the natural-dust-driven process is only next to the oxidations induced by OH, TMI-O_2 and H_2O_2 (Fig. S9b). The results of SO_2 lifetime agree well with those of sulfate formation rate (Fig.

465   4), illustrating that the heterogeneous drivers of dust surface are responsible for altering the concentrations of gas-phase and particulate sulfur species.

In summary, gas- and aqueous-phase chemistries function as the most significant influencers of the diurnal lifespan of SO_2, followed by dust-driven heterogeneous chemistry, while during nighttime these three chemistries present closer impacts (Fig. S10). The atmospheric lifetimes of SO_2 induced by all of the studied oxidation pathways are calculated to be 6.17 days during

470   nighttime and 0.99 days during daytime as presented in Fig. 6. Neglecting the dust heterogeneous chemistry may lengthen the SO_2 lifespans to 10.27 and 1.12 days in the absence and presence of solar irradiation, respectively. Analogously, scientists obtained the shorter lifetime of SO_2 from climate model after considering the heterogeneous reaction occurring on volcanic ash particles (Zhu et al., 2020). Clay minerals are more concentrated in the troposphere than volcanic ash and thus have more significant impacts on the removal of atmospheric SO_2.

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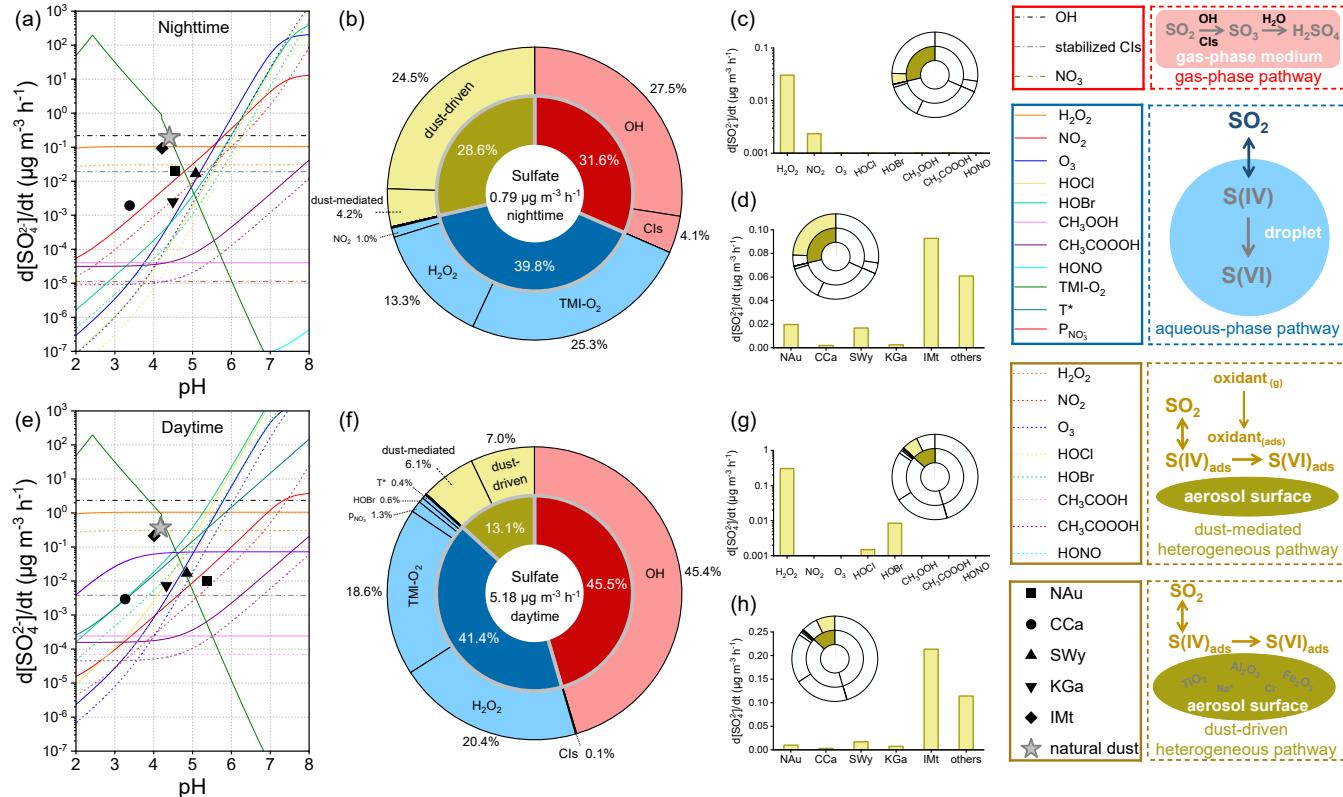
Figure 4. Contributions of diverse oxidation pathways to secondary sulfate aerosols.

Gas-phase chemistry is induced by hydroxyl radical (OH), stabilized Criegee intermediates (CIs), as well as the nitrate radical (NO₃) only for nighttime. Aqueous-phase chemistry is induced by hydrogen peroxide (H_2O_2), nitrogen oxide (NO_2), ozone (O_3), hypochlorous acid (HOCl), hypobromous acid (HOBr), methyl hydroperoxide (CH_3OOH), peroxyacetic acid (CH_3COOOH), dissolved nitrous acid (HONO), transition-metal ion-catalyzed oxygen (TMI-O_2), and the photosensitization (T*) and nitrate photolysis ($P_{NO_3^-}$) only for daytime. Dust-mediated heterogeneous chemistry is initiated by the surface oxidants co-adsorbed with SO_2 (H_2O_2, NO_2, O_3, HOCl, HOBr, CH_3OOH, CH_3COOOH, HONO). Dust-driven heterogeneous chemistry is ascribed to the heterogeneous drivers (transition-metal-bearing components and water-soluble ions) on the surfaces of natural dust and clay minerals [Nontronite (NAu), Chlorite (CCa), Montmorillonite (SWy), Kaolin (KGa), Illite (IMt)]. The (a-d) nighttime and (e-h) daytime conditions were distinguished by the different parameterizations. (a, e) Particle-acidity-dependent sulfate formation rate of the studied SO_2 oxidation pathways. (b, f) Quantified sulfate contribution proportions of the studied oxidation pathways. Sulfate formation rates of the dust-mediated and dust-driven pathways during (c-d) nighttime and (g-h) daytime. The effects of ionic strength on the aqueous-phase SO_2 oxidation were not taken into account. The dust concentration was set to be 55 μg m⁻³ to reflect the common atmospheric condition of China (Zhang et al., 2012). The panels right to the legends illustrate the primary physical-chemical processes of atmospheric sulfate formation. More parameterization and methodology details can be found in the Texts S2-S4 of Supporting Information and Sect. 2.1-2.5 of the main content.
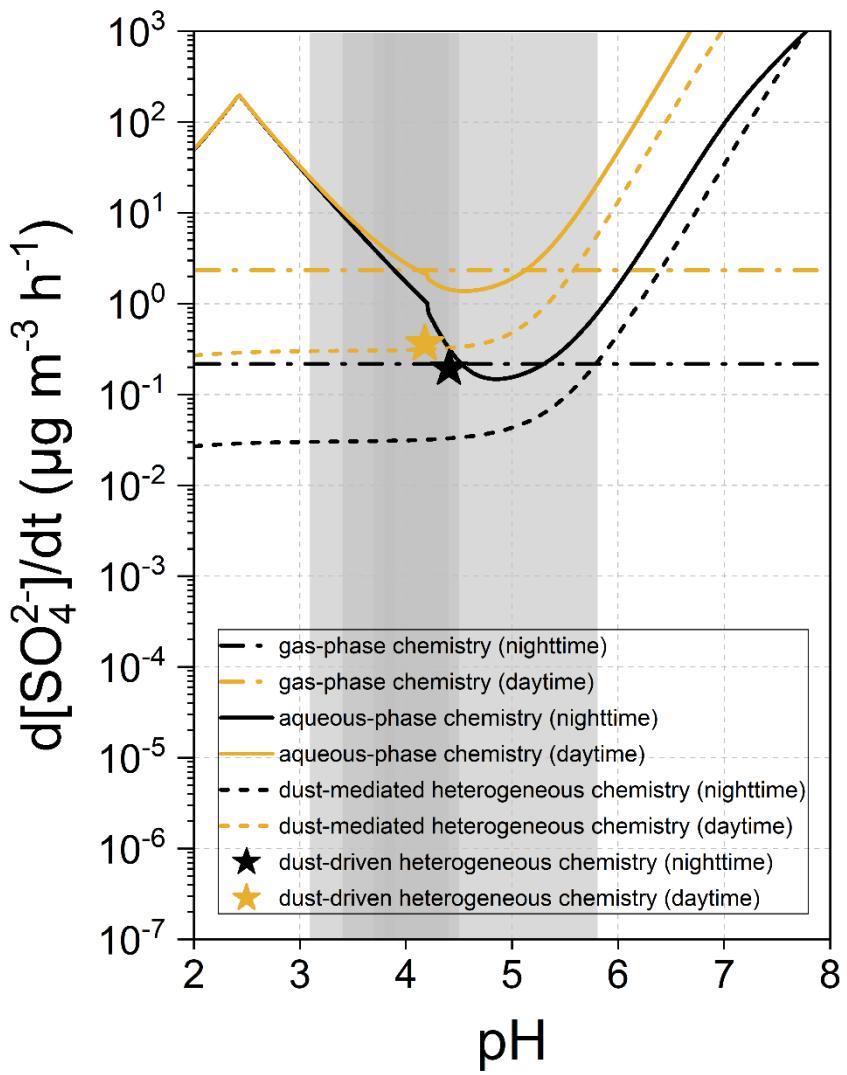
Figure 5. Formation rate of sulfate in the kinetic regimes of gas-phase chemistry, aqueous-phase chemistry and dust heterogeneous chemistry as a function of particle acidity (pH).

495   Grey areas indicate the pH ranges of the polluted particulate matters, with darker ones being more common (Ding et al., 2019).
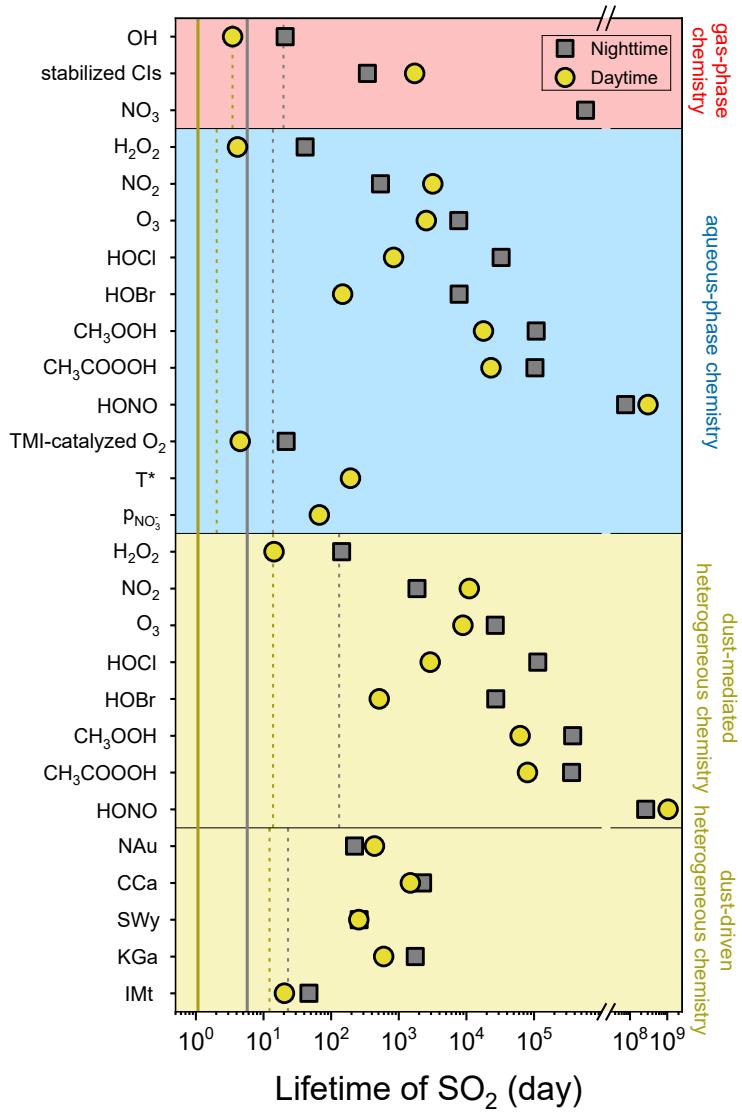
Figure 6. Atmospheric lifetimes of SO_2 induced by the diverse sulfate formation pathways.

Both of the nighttime (grey square) and daytime (yellow circle) conditions were considered. The lifetimes of SO_2 caused by gas-phase, aqueous-phase and dust heterogeneous chemistries are displayed by the dash lines. The atmospheric lifetimes of SO_2 induced by all of the studied oxidation pathways are presented by the solid lines. The effects of ionic strength on the aqueous-phase SO_2 oxidation were not taken into account. The dust concentration was set to be 55 µg m^{-3} to reflect the common atmospheric condition of China. More methodology details can be found in Sect. 2.6 of the main content.

3.4 Sensitivity analysis

505 The aforementioned calculations set the concentration of natural dust to be 55 µg m^{-3}. In contrast to the common atmospheric loading, the burst of sandstorm was normally accompanied by the quickly elevated dust concentration up to thousands of µg m^{-3} (Li et al., 2021; Yin et al., 2021; Filonchyk, 2022). It would be meaningful to estimate the heterogeneous contributions in the dust-rich environments. Theoretically, dust concentration within the ranges of 72-770 µg m^{-3} during nighttime and 24-260 µg m^{-3} during daytime could cause the extra sulfate formation of 0.3-3.0 µg m^{-3} h^{-1} (Fig. 7a), in line with the acknowledged

510 range of missing sulfate formation rate (Cheng et al., 2016; Liu et al., 2020), which was found to be positively correlated with PM concentration as well (Cheng et al., 2016). Therefore, the heterogeneous reaction of SO$_2$ on dust surface is a considerable sulfate formation pathway and may evolve into the missing sulfate source.

The occurrence of sandstorm, particularly during nighttime, aggravates the sulfate pollution in coarse aerosol mode (Fig. 7b). For instance, the dust concentration of 200 µg m^{-3}, which approaches the PM$_{10}$ level in North China on March 2021 (Yin et

515 al., 2021), could heterogeneously explain 44.9% of the secondary sulfate during nighttime, as well as 29.6% during daytime. It is worthwhile to note that, the heterogeneous contribution proportion is susceptible to the evolution of relatively low dust concentration, further increase of dust loading will not significantly elevate the heterogeneous proportion, resulting in a plateau (nighttime) or decrease (daytime) under severe dust pollution. The increased dust concentration facilitates the aqueous-phase TMI-O$_2$ pathway and the dust-mediated and dust-driven heterogeneous reactions, whereas presents negative impacts on the

520 others by the removal of gaseous oxidants over dust surface. The unsusceptible response to dust concentration, as shown by Fig. 7b, can be related to the increased sulfate contributions from the TMI-O$_2$ pathway. Unlike the TMI-O$_2$ pathway and dust-driven chemistry receiving constant positive feedbacks from the increased dust concentration, the dust-mediated chemistry is somewhat affected by the decreased oxidants adsorbed on dust surface. Since the importance of dust-mediated chemistry is more significant during daytime than nighttime, there is a negative correlation between the high dust concentration and

525 heterogeneous contribution proportion under solar irradiation.

The increased dust concentration, in fact, not merely facilitates the heterogeneous chemistry by providing more reactive surfaces, but also affects the gas- and aqueous-phase chemistries by altering the atmospheric abundances of the reactive species therein, as explained below. The evolution of dust pollution from slight to heavy conditions would cause the loss of various gaseous oxidants by heterogeneous uptake, and therefore the gas- and aqueous-phase sulfate fluxes, except that induced by

530 TMI-O$_2$, decrease against dust concentration (Bian and Zender, 2003; Tang et al., 2017). Moreover, the dissolution of mineral constituents produces TMIs in aerosol liquid media (Alexander et al., 2009; Shao et al., 2019), and the irradiated mineral dust was reported to emit gaseous ROS by surface photocatalysis (Dupart et al., 2012; Chen et al., 2021). Herein, the studied oxidation pathways are distinguished by their contribution proportions (Fig. 7c and d). The contribution proportions of OH and H$_2$O$_2$ decrease against dust loading, while the relative importance of TMI-derived oxidation and dust-driven chemistry

535 become more significant as the dust concentrates. The contribution proportion assigned to dust-mediated chemistry increases with dust concentration at first and then decreases. While the increased dust loading provides more physical space for the

occurrence of dust-mediated reactions, the simultaneously decreased gas-phase oxidants restrain the accumulation of particle-phase oxidants.

Atmospheric lifetime of SO_2 is also affected by the concentration of dust. As shown by Fig. 8a, the lifespan of airborne SO_2 during nighttime is higher than that during daytime, and both of them decrease against dust concentration. Analogous to the heterogeneous contribution proportion (Fig. 7b), the atmospheric lifetime of SO_2 is more susceptible to the variation of dust concentration in clean and slightly polluted environments than heavily polluted conditions. The mild dust pollution, especially its level variations, should be paid more attention. The heterogeneous loss of SO_2 by dust surface was normally evaluated against the gas-phase loss by OH (Ullerstam et al., 2003; Adams et al., 2005; Li et al., 2006; Huang et al., 2015; Ma et al., 2018). Current estimation indicates that the airborne dust with the concentration of 45 μg m^{-3} during nighttime, or 91 μg m^{-3} during daytime, can be regarded as comparable with OH in controlling the removal of SO_2 (Fig. 8b). Such dust concentrations could be common in the troposphere (Zhang et al., 2012), suggesting that under most atmospheric conditions, the heterogeneous loss of SO_2 by airborne dust surface has a similar magnitude as the main gas-phase loss process and can be taken as an important sink for SO_2.

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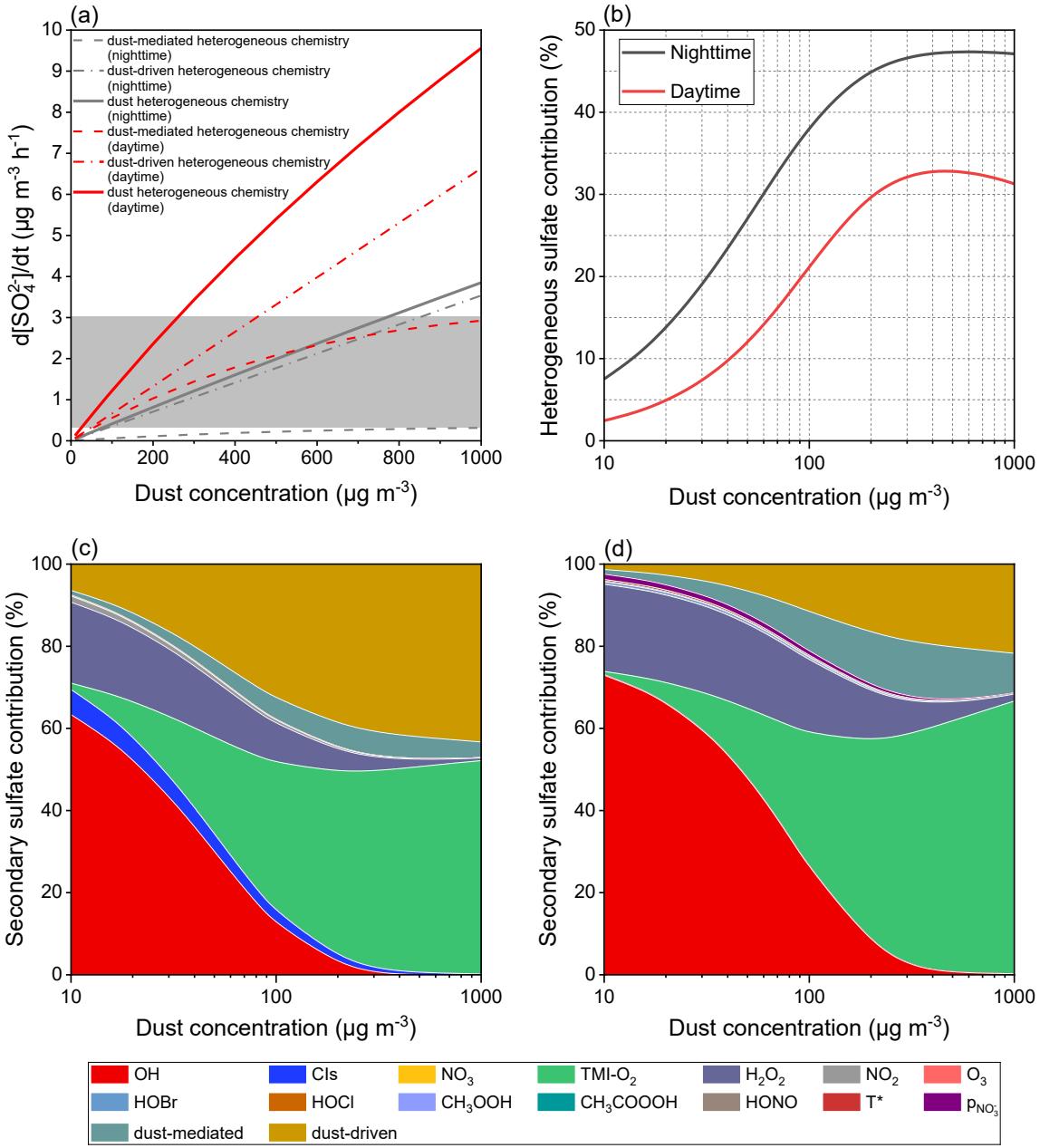
Figure 7. Sensitivity tests of sulfate formation rate on dust concentration.

(a) Sulfate formation rate of diverse dust-related heterogeneous chemistries as a function of dust concentration. The grey area suggests the missing sulfate formation rate ranging from 0.3 to 3 μg m^{-3} h^{-1} as a reference (Cheng et al., 2016; Liu et al., 2021a).

(b) Heterogeneous sulfate proportion varying with dust concentration. Secondary sulfate contributions attributed to the studied

555 oxidation pathways during (c) nighttime and (d) daytime.
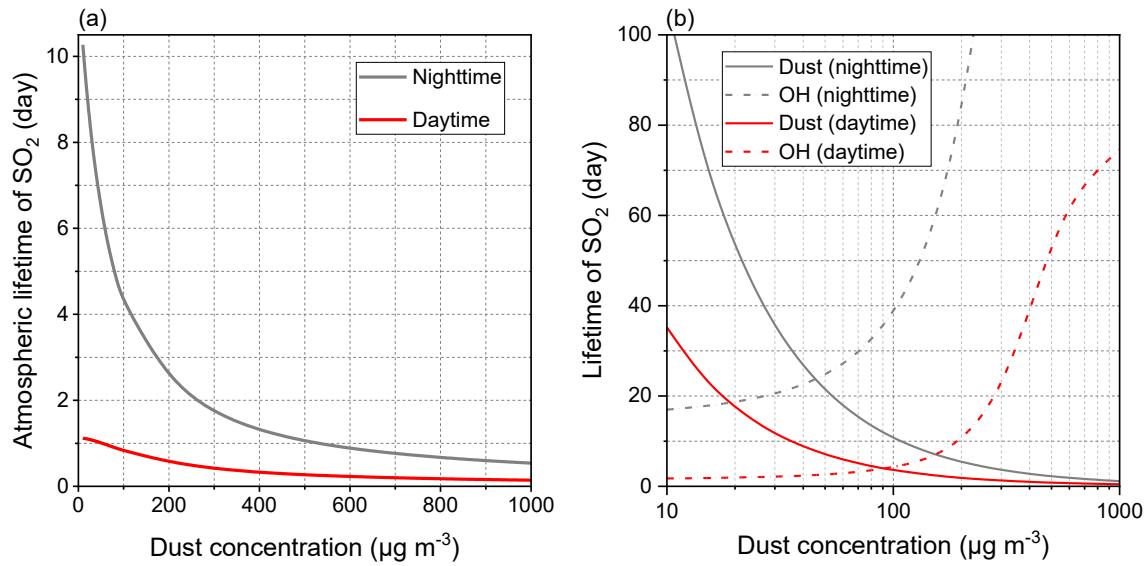
Figure 8. Sensitivity tests of SO$_2$ lifetime to dust concentration.

(a) Atmospheric lifetime of SO$_2$ induced by all of the studied pathways varying with dust concentration. (b) Comparison
between the SO$_2$ lifetimes induced by dust heterogeneous chemistry and OH-initiated gas-phase chemistry.

3.5 Uncertainty analysis

The contribution proportion of dust heterogeneous chemistry could be over- or underestimated if considering the uncertainty factors. Herein, the joint impacts of ionic strength (I) and aerosol liquid water content (ALWC) on the aqueous-phase oxidation of SO_2, as well as the comparison between microdroplet interfacial oxidation and dust-driven heterogeneous chemistry, are additionally discussed to further understand the atmospheric significance of the dust surface drivers under the complex atmospheric conditions.

The aqueous-phase oxidation of SO_2 by H_2O_2, O_3, NO_2 and TMI-O_2 was quantified under different I-ALWC parameterizations. At first, the sulfate formation rate was calculated as a function of ionic strength under the studied ALWC of 300 μg m^{-3} (Fig. S11). TMI-O_2 and H_2O_2 dominate the liquid oxidation, while the impacts of NO_2 and O_3 only slightly peak at ~ 1.0 M in the absence of solar irradiation. Specifically, during nighttime, TMI-O_2 dominates the sulfate formation under the relatively low ionic strength, while the contribution of H_2O_2 exceeds that of TMI-O_2 over the ionic strength of 0.028 M. During daytime, H_2O_2 becomes the dominant oxidant within the studied ionic strength range. Relative to the ionic strength-free calculations, the aqueous oxidation could be weakened by the ionic strength lower than 17.8 M during nighttime or 14.3 M during daytime. Such values can be taken as criteria to distinguish the over- or underestimation of the liquid kinetics under the ALWC of 300 μg cm^{-3}, which was widely used to characterize the haze events in North China (Cheng et al., 2016).

The joint influences of I and ALWC were further considered (Fig. 8). At each ionic strength, sulfate formation rate associates positively with ALWC. At each ALWC, the increase of ionic strength hinders the aqueous oxidation at first and then facilitates this process, as a consequence resulting in a threshold line distinguishing the negative or positive effects of ionic strength, as presented by Fig. 9a and b. Furthermore, the I-ALWC relationships of California, USA (Stelson and Seinfeld, 1981); Beijing, China (Song et al., 2021); Mexico City, Mexico (Volkamer et al., 2007; Hennigan et al., 2015); and the nine cities of Germany (Scheinhardt et al., 2013) were found to locate left to the thresholds, implying the negative effect of ionic strength under the investigated scenarios (Fig. 9c). Calculated by the reported I-ALWC relationships, the dust-mediated chemistry contributes 4.3%-20.1% of the secondary sulfate during nighttime and 6.8%-22.0% during daytime, and the dust-driven chemistry accounts for respectively 29.1%-41.6% and 9.9%-12.4% of the sulfate formation in the absence and presence of sunlight (Fig. 9d). Therefore, the heterogeneous contribution proportions in the complex atmospheric environments can be even higher than those estimated by the present study.

Besides the gas-solid interface, gas-liquid interface is another type of medium that supports the rapid formation of sulfate. The oxidation of SO_2 was found to proceed at the interfacial layer of a droplet with higher kinetics than the bulk process (Jayne and Davidovits, 1990). Recently, the interfacial roles of O_2 (Hung and Hoffmann, 2015; Hung et al., 2018; Chen et al., 2022), NO_2 (Liu and Abbatt, 2021; Yu, 2021) and Mn^{2+} (Zhang et al., 2021; Wang et al., 2021a; Wang et al., 2022c) have been quantitatively investigated. Figure 10 compares dust-driven heterogeneous chemistry with the documented gas-liquid interfacial oxidations. As reported by Hung et al. (2015, 2018), acidic droplet interface favors the noncatalyzed oxidation by the presence of sufficient $SO_3^{\cdot-}$ and $SO_4^{\cdot-}$ when pH<4.0, which can be further explained by the structure differences of water

at the interface versus the characteristic water structure in bulk-phase water. Recently, Chen et al. (2022) reevaluated the sulfate formation by interfacial O_2 within the pH range of 3.5-4.5 and discovered the positive dependence toward ionic strength. The oxidation of SO_2 by interfacial NO_2 was documented to display the similar pH dependence as that occurs in bulk solution. The sulfate contribution of interfacial Mn^{2+} is associated positively with particle acidity. Overall, the O_2 at acidic interface dominates the SO_2 oxidation over pH<4.0, whereas over pH>4.0 the interfacial oxidation is primarily controlled by Mn^{2+}. Comparing the sulfate formation rates under the same particle acidity, the dust surface drivers generally present greater reactivity than the interfacial NO_2 and O_2. Under the ionic strength of 40 M, the reactivity of interfacial O_2 can be regarded as equivalent to that of the dust surface drivers during nighttime. Interfacial Mn^{2+} kinetically exceeds the dust surface drivers through kinetic regime. For instance, the Mn^{2+}-catalyzed oxidation characterized by Wang et al. (2021a) is respectively 6.5 and 1.7 times more efficient than the dust-driven chemistry in forming sulfate aerosols during nighttime and daytime.

It is worthwhile to note that, the dust-driven heterogeneous chemistry was investigated by the infrared technique focusing on the bulk particle sample rather than air-suspended particles. Up to now, the micro-scale effects of dust particle have not been systematically studied. Suspended ATD was concerned in a smog chamber research and its reactivity toward SO_2 was characterized by the net uptake coefficient of 1.71×10^{-6} under dark condition (Park and Jang, 2016). Such kinetic constant is approximately one order of magnitude higher than those obtained from the film-based flow tube experiments ($\sim 1.75 \times 10^{-7}$) under the parallel experimental conditions (Zhang et al., 2019b). Therefore, the dust-driven heterogeneous chemistry in ambient atmosphere may approach the microdroplet interfacial reactivity in the removal of SO_2 and formation of sulfate.
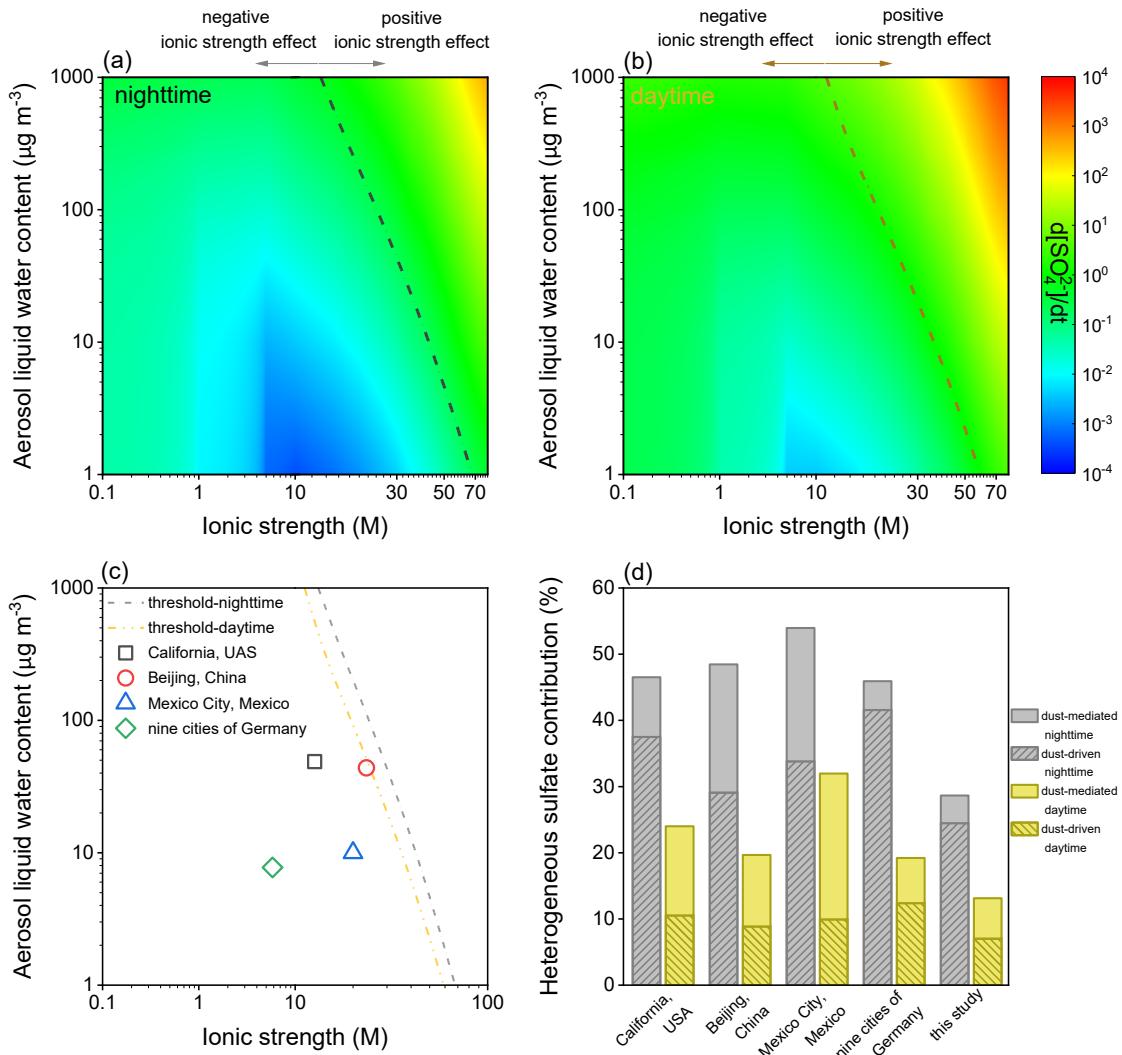
Figure 9. Joint influences of ionic strength (I) and aerosol liquid water content (ALWC) on the aqueous-phase oxidation of SO₂.

Aqueous-phase sulfate formation rate varying with I and ALWC during (a) nighttime and (b) daytime. The dash-dot lines indicate the thresholds distinguishing the negative or positive effects of ionic strength. (c) Reported I-ALWC relationships versus the nocturnal and diurnal thresholds. The field-observed date were derived from the measurements in California, USA (Stelson and Seinfeld, 1981); Beijing, China (Song et al., 2021); Mexico City, Mexico (Volkamer et al., 2007; Hennigan et al., 2015); and the nine cities of Germany (Scheinhardt et al., 2013). (d) Heterogeneous contribution proportions calculated by the reported I-ALWC relationships and the parameterization of this study (ionic strength-free settings and an ALWC of 300 µg m⁻³ for aqueous-phase chemistry; dust concentration of 55 µg m⁻³ for heterogeneous chemistry).
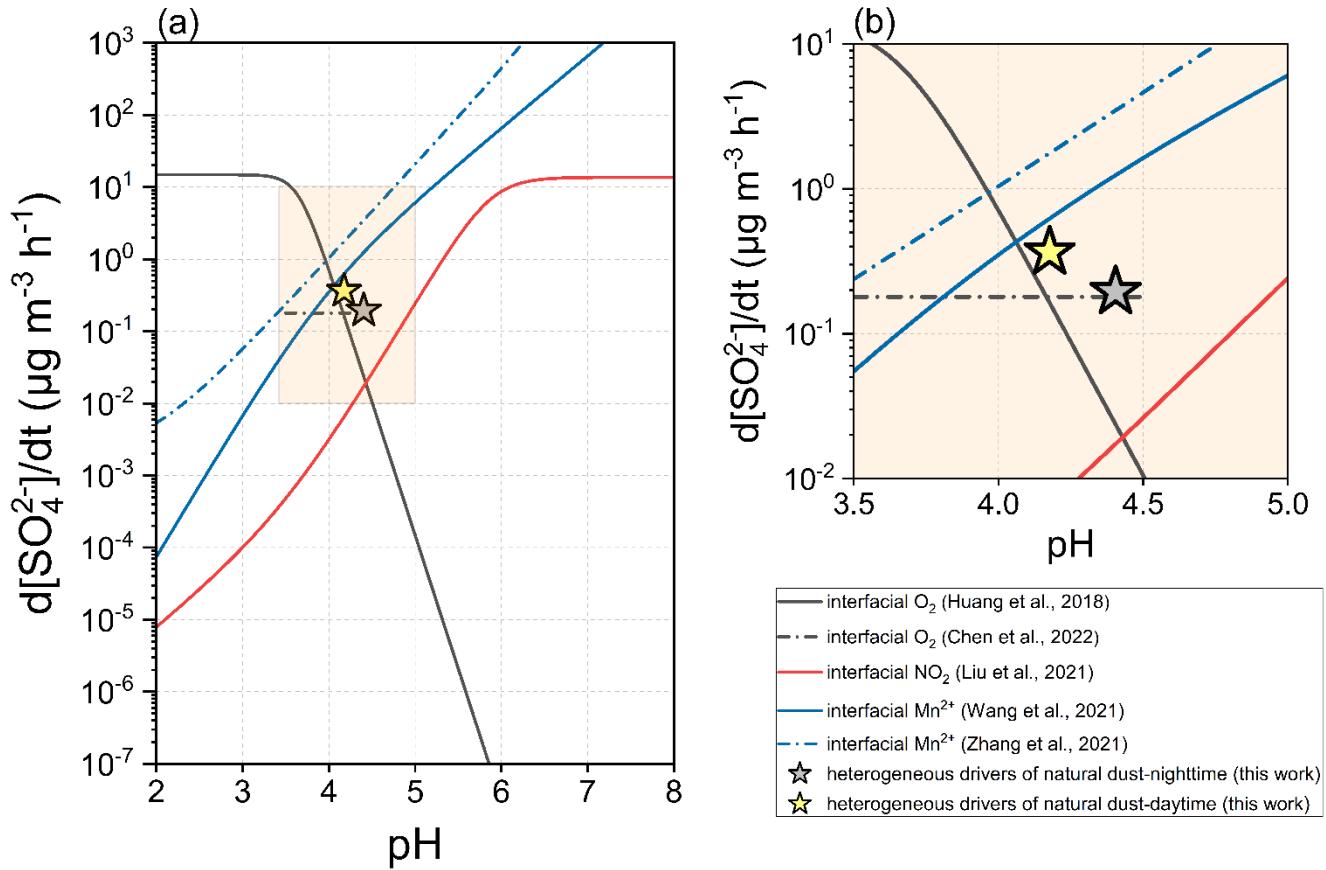
Figure 10. Kinetics comparison between microdroplet interfacial oxidation and dust-driven heterogeneous chemistry. The interfacial oxidation of SO_2 can be induced by the O_2, or NO_2, or Mn^{2+} at aerosol particle interfaces. The O_2-dominated oxidation can be assessed by the method concluded by Hung et al. (2018). Chen et al. (2022) refreshed the assessment method relevant to the interfacial O_2, and the result here was obtained under the ionic strength of 40 M. The NO_2-dominated oxidation was assessed based on the work of Liu and Abbatt (2021). The Mn^{2+}-dominated oxidation can be assessed by the methods from Wang et al. (2021a) and Zhang et al. (2021). More parameterization and methodology details can be found in the Text S5 of Supporting Information.

4 Conclusions and implications

This study attempted to deeply understand the importance of heterogeneous chemistry, particularly that induced by the dust surface drivers, in the loss of airborne SO_2 and formation of sulfate aerosols. Based on the correlation and regression analysis, transition metal elements, particularly Fe for dark condition, and Al and Ti for photoreaction, were determined to dominate the heterogeneous oxidation, while water-soluble ions present minor influences. A series of empirical equations were developed to kinetically predict the dust-driven process. The Al, Fe, Ti-bearing mineralogical components, as well as their mixtures, are thus recommended as appropriate proxies for the laboratory research. The reactive uptake coefficients for the dust-driven sulfate formation were calculated to be 6.08×10^{-6} during nighttime and 1.14×10^{-5} during daytime, corresponding respectively to the atmospheric sulfate formation rates of 0.195 and 0.365 μg m^{-3} h^{-1} in the presence of 55 μg m^{-3} natural dust. Dust heterogeneous chemistry is suggested to explain 28.6% of the secondary sulfate aerosols during nighttime and 13.1% during daytime, and the dust surface drivers act as the dominate contributors. Moreover, dust heterogeneous chemistry affects the atmospheric lifetime of SO_2. The increased dust concentration may aggravate the secondary sulfate pollution and has the potential to explain the acknowledged missing sulfate formation rate (0.3-3 μg m^{-3} h^{-1}). Ionic strength and aerosol liquid water content not merely influence the liquid kinetics, but further affect the assessment of heterogeneous contributions. The heterogeneous contribution proportions estimated by the reported I-ALWC relationships could be even greater than those calculated by this study. Additionally, dust heterogeneous chemistry in the atmosphere is believed to be kinetically comparable with the microdroplet interfacial SO_2 oxidation.

Overall, this study suggests that the implementation of heterogeneous processes into atmospheric models shall vastly improve the agreement between the modeled and observed sulfate concentrations. Dust heterogeneous chemistry should be treated as a significant contributor of secondary aerosols rather than a plausible influencer. More necessarily, the heterogeneous drivers of dust surface are needed to be viewed as an important research focus. Zheng et al. (2015) revised the CMAQ model by adding heterogeneous chemistry mechanism and observed the accurate simulation run upon determining the uptake coefficient to be 2.0×10^{-5}, which is higher than the reactive uptake coefficients of the dust heterogeneous chemistry discussed by this work (7.04×10^{-6} for nighttime and 1.55×10^{-5} for daytime). As a consequence, other solid aerosol surfaces, such as those of sea salts (Laskin et al., 2003; Rossi, 2003) and carbonaceous particles (He and He, 2020; Zhang et al., 2020), would better be taken into the following heterogeneous discussions together with the dust chemistry. In addition, the influence of meteorological factors, like temperature, humidity and irradiance, on the atmospheric relevance of heterogeneous chemistry warrants further research.

Heterogeneous laboratory results were scarcely discussed together with other SO_2 conversion routes. This study attempted to set an example for kinetically comparing the heterogeneous process characterized by laboratory work with the widely documented gas- and aqueous-phase data. Relative to the three-dimensional numerical models, the developed comparison model involves more oxidation pathways. Moreover, the aqueous-phase chemistry here is relevant to aerosol particle rather

than cloud/fog droplet, and the parameterization here could be more appropriate for simulating the fine particulate matters that were frequently collected by atmospheric observation campaigns and compared with modeling data. Further, the heterogeneous chemistry was classified into the dust-mediated and dust-driven modes to better distinguish the key surface impactors. Therefore, the dynamic comparison in this study has advantages over the traditional atmospheric chemistry models, and is thus recommended for the following heterogeneous laboratory research to systematically compare the experimental data with the acknowledged gas-phase/aqueous-phase/heterogeneous oxidation pathways.

This work also broadens the application of infrared technique in the atmospheric laboratory research. Apart from measuring the reactive uptake coefficient normally concerned, this study moved forward to bridge the relationship between particle acidity and sulfate formation rate by analyzing the shape and intensity of infrared spectrum, and further compared the dust heterogeneous chemistry with other sulfate formation pathways. This research not merely provides a promising methodology for the future heterogeneous research utilizing the classic *in-situ* DRIFTS approach, but also helps to take good advantages of the infrared technique in the laboratory studies in relation to atmospheric heterogeneous chemistry.

Data availability. The data that support the results are available from the corresponding author upon request.

Author Contributions. T.W. designed the experiments and processed the data, and wrote the paper together with Y.L; H.C. and Z.W. measured the physical and chemical properties of the particle samples; H.F., J.C., and L.Z. provided guidance in the data analysis and paper writing.

Competing interests. The authors declare no competing financial interest.

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