Dear editor

Please find the enclosed revision of our manuscript "Significant formation of sulfate aerosols contributed by the heterogeneous drivers of dust surface" (Manuscript Number: acp-2022-227). We thank the valuable comments from the reviewers and editor, which have greatly improved the manuscript. The point-by-point replies to the comments are attached on the following pages.

Thank you for your consideration.

Sincerely yours,

Liwu Zhang

Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science and Engineering, Fudan University

Shanghai, 200433, China

E: zhanglw@fudan.edu.cn

Referee #2

Reviewer comment: Is chemistries a real word?

Original author response: As a real word, it was widely utilized in the research papers of this field (e.g. doi.org/10.1021/cr500501m; doi.org/10.1021/cr5003485).

Editor comment: 'Chemistry' is defined as a branch of science that studies the composition and transformation of molecules and materials (cf e.g. Wikipedia). Therefore, in this context, it should not be used at all, but should be replaced by 'chemical processes' (or 'chemical composition' where appropriate) throughout the manuscript.

Revised author response:

Thanks for your comments.

We have replaced "chemistries" by the more appropriate words including "chemical processes", "processes", "pathways", and "reactions" throughout the revised manuscript. The following sentences are listed as examples:

Line 115-117: "*Hereby, upon understanding the driving factors and driving force of the airborne dust surface, this work compared dust heterogeneous pathways with the gas- and aqueous-phase ones with respect to the formation rate of sulfate and atmospheric lifetime of SO_2.*"

Line 446-447: "*During nighttime, the gas-phase, aqueous-phase and heterogeneous processes explain 31.6, 39.8 and 28.6% of secondary sulfate, respectively (Fig. 5b).*"

Reviewer comment: Figure 3: why does the reactive uptake coefficient drastically increases after particle acidity reached ~4.5/5?

Original author response: Figure 3 displays the particle acidity-dependent reactive uptake coefficients (γ) for the dust-mediated heterogeneous chemistry. We have discussed the dramatically increased γ when pH exceeds 4.5 or 5.0, in the revised manuscript (line 367-369). "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)."

Editor comment: I do not understand this response. A few lines above you state that "the dust mediated heterogeneous oxidation can be assumed to primarily proceed in the surface water layers" but yet you ascribe a significant impact on g by the term that describes the aqueous phase diffusion, i.e. the second term in the right-hand side in Eq. -5. What are the contributions to the total γ of the mass accommodation term ($1/\alpha$) and the aqueous

phase diffusion and reaction term [v/(4HRT(D$_a$k$_{chem}$)$^{-1}$)/f$_r$]? A figure should be included to demonstrate that indeed the second term increases significantly at increasing pH.

Revised author response:

We have explained the evaluation methodology for dust-mediated heterogeneous processes, and then discussed the absolute level and pH dependence of dust-mediated heterogeneous γ. The revisions are shown in detail as follows.

First, Eq. (5) quantitatively describes the heterogeneous sulfate formation mediated by dust surface. We have added its definition into the revised manuscript (line 246-248). *"The terms on the right-hand side (RHS) of Eq. (5) show the two contributions to the overall resistance to dust-mediated heterogeneous uptake: mass accommodation at surface, diffusion and reaction in surface liquid water layers."*

Second, in contrast to the Henry's law constant for SO$_2$ that quantifies its gas-liquid equilibrium, the H* in Eq. (5) refers to the effective Henry's law constant for the studied S$_{(IV)}$ specie(s). In other words, H* is considered to quantify the total dissolved sulfur species in the water layers of dust surface. We have emphasized the definition of H* in the revised manuscript (line 244-245, line 248). *"H* is the effective Henry's law constant for the studied S$_{(IV)}$ specie(s) (M atm^{-1}), and is jointly determined by the gas-liquid equilibrium of SO$_2$ and the ionization equilibriums of dissolved sulfur species" "The S$_{(IV)}$ species include SO$_2$·H$_2$O, HSO$_3^-$ and SO$_3^{2-}$."*

Last, the first term of the RHS of Eq. (5), mass accommodation (α), is several orders of magnitude higher than the calculated dust-mediated γ and no pH dependence has been reported for it. Thus, the absolute level and pH dependence of the dust-mediated heterogeneous γ is largely associated with the second term of the RHS of Eq. (5). We have rewritten the relevant paragraph in the revised manuscript (line 399-409). *"Figure 4 presents the pH-dependent γ for natural dust-mediated heterogeneous pathway, along with the experimental data of natural dust-driven heterogeneous pathway. The dust-mediated γ is orders of magnitude lower than the α of SO$_2$ (~ 0.14 under the experimental temperature of 296.8 K). By definition, α is the probability that a SO$_2$ molecule striking a liquid surface finally enters into the liquid phase, whereas γ is the sulfate formation rate normalized by the total surface collision rate of SO$_2$ (Jacob, 2000; Davidovits et al., 2006). That is, γ involves all the uptake processes, including the mass accommodation at surface (Seinfeld and Pandis, 2016). Moreover, unlike the pH-independent α, γ varies with pH, somewhat coinciding to the evolution of dissolved sulfur species that can be quantitatively described by the H* of SO$_2$. The γ values of H$_2$O$_2$, CH$_3$OOH and CH$_3$COOOH are pH-independent under specific conditions, in relation to the acid-catalyzed rate-limiting steps relevant to these peroxides (Lind et al., 1987; Liu et al., 2021a). Generally, the dust-mediated heterogeneous γ is largely determined by the diffusion and reaction processes in the water layers of dust surface, as characterized by the second item on the RHS of Eq. (5)."*

Reviewer comment: For daytime chemistry, did you consider the possibility of the formation of sulfate radicals on surfaces with high Ti content?

Original author response: We have considered the impact of sulfate radical on the heterogeneous formation of sulfate. Necessary discussions are added into the revised manuscript (line 266-267). "Sulfate radical ($SO_4^{\cdot-}$) is generated by the presence of abundant •OH and participates into the oxidation events (Antoniou et al., 2018; Kim et al., 2019; Li et al., 2020b)."

Editor comment: This response and revision is not sufficient to discuss the potential role of sulfate radicals. A discussion on possible chemical mechanisms of the observed processes should be added including the possibility of oxidation by the sulfate radical. You can either add this to section 3.3. or dedicate a full new section to this discussion.

Revised author response:

We have provided more discussions on reaction mechanism, including the possible effects of sulfate radical.

In this manuscript, Sect. 3.1 identified the dominate dust surface drivers that influence the heterogeneous sulfate formation, whereas Sect. 3.3 performed comparison among diverse atmospheric oxidation pathways to figure out the predominate sulfate contributors. Relative to Sect. 3.3, Sect. 3.1 is believed to be more appropriate to display the reaction mechanism details. In order to make Sect. 3.1 more accessible to our readers, we enriched it by adding more knowledges on reaction mechanism. In addition, a scheme has been drawn to illustrate the possible chemical mechanism of dust-driven heterogeneous oxidation (Scheme 1 in manuscript, copied as follows).
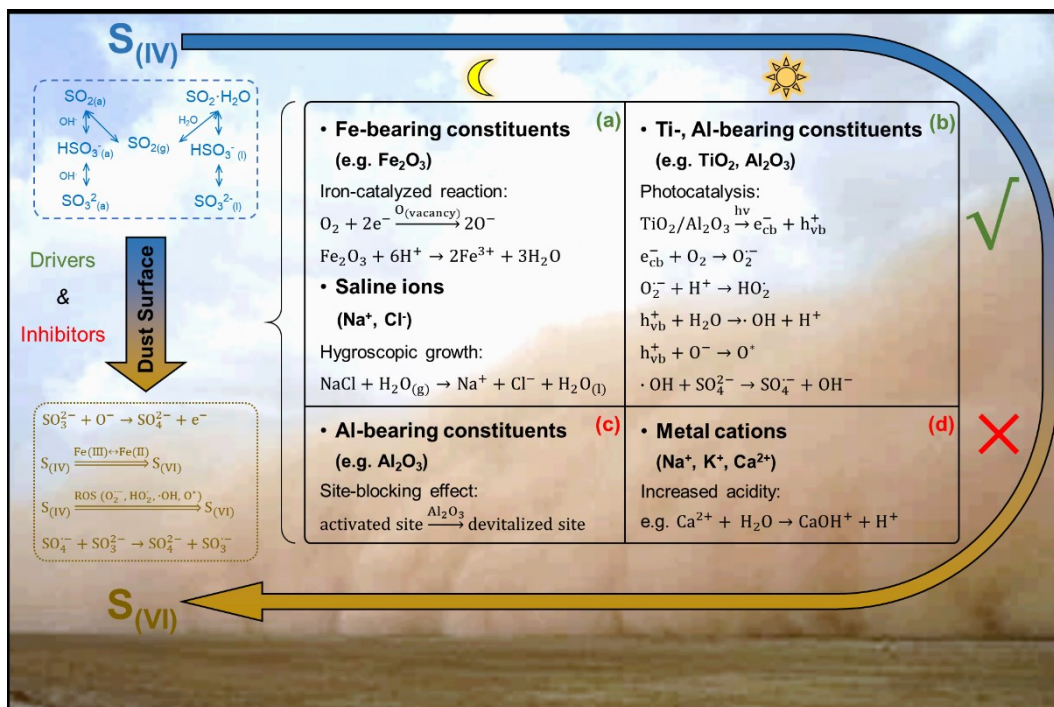
By the first paragraph of Sect. 3.1, we claimed the close association between correlation analysis and mechanism illustration (line 269-270). *"Correlation analysis is performed to identify the dust surface drivers (Fig. 1), based on which the reaction mechanism of dust heterogeneous pathway can be better understood (Scheme 1)."*

The following contents, some of which are newly organized, are displayed in Sect. 3.1 to illustrate the relevant reaction mechanism details.

(1) The reaction mechanism relevant to metal elements in dark reaction (line 273-278): *"Typical Fe-bearing minerals accelerate the oxidation of $S_{(IV)}$ species by either the surface active oxygen (O^-) derived from the adsorbed O_2 in oxygen vacancy or the iron redox cycling initiated by Fe^{3+} from surface acidic media, or both (Baltrusaitis et al., 2007; Fu et al., 2007; Yang et al., 2016). 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 may hinder heterogeneous reaction by blocking the active sites of other minerals (Wang et al., 2018b)."*

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(2) The reaction mechanism relevant to metal elements in photoreaction (line 281-288): *"Transition metal oxides in dust act as photocatalyst that yields electron-hole pairs, followed by the formation of reactive oxygen species (ROS) such as hydroxyl radical ($\cdot$OH), superoxide ($O_2^{\cdot-}$), hydroperoxyl radical ($HO_2^{\cdot}$) and dissociated active oxygen species (O*) (Chen et al., 2012; Abou-Ghanem et al., 2020; Wang et al., 2020c; Sakata et al., 2021). Apart from the site-blocking effect under dark condition, irradiated Al-bearing constituents additionally facilitate the sulfate formation. Physically, Al-bearing components disperse other efficient mineralogical constituents in case of agglomeration (Darif et al., 2016). Chemically, sunlight may alter the electronic configuration of α-Al_2O_3, which presented photoactivity in the reported heterogeneous process (Guan et al., 2014)."*

(3) The reaction mechanism relevant to water-soluble ions in dark reaction (line 301-303): *"The presence of halite (NaCl) has positive implications for the dust's hydroscopic growth (Wang et al., 2014; Tang et al., 2019), and the moderate surface water provides an efficient medium for the adsorption of gas-phase SO_2 and the ionization of dissolved sulfur species (Rubasinghege and Grassian, 2013)."*

(4) The reaction mechanism relevant to water-soluble ions in photoreaction (line 304-307): *"These cations can be hydrolyzed by adsorbed water to produce H^+, thereby elevating the particle acidity. In the surface liquid medium, 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 irradiated dust surface (Zheng et al., 1997; Yang et al., 2008; Liu et al., 2017a)."*

After introducing the metal elements and water-soluble ions, a new paragraph is followed to illustrate the possible oxidation by $SO_4^{\cdot-}$ over dust surface (line 310-318). *"Apart from the dust surface drivers and inhibitors, sulfate radical ($SO_4^{\cdot-}$) may also participate into the heterogeneous event. In the absence of solar irradiation, laboratory studies discovered the uncatalyzed SO_2 autoxidation by $SO_4^{\cdot-}$ at the acidic droplet interface (Hung and Hoffmann, 2015; Hung et al., 2018; Chen et al., 2022). With an appropriate humidity and sufficient saline components, there could be an air-liquid interface occurring over the solid dust surface via water uptake (Gaston et al., 2017; Tang et al., 2019; Wu et al., 2020), then producing $SO_4^{\cdot-}$. Moreover, on the surface of iron oxide, the $\cdot$OH derived from Fenton reaction reacts with SO_4^{2-} to form $SO_4^{\cdot-}$ (Kim et al., 2019; Li et al., 2020b). The presence of solar irradiation would accelerate the formation of $SO_4^{\cdot-}$ due to the abundant $\cdot$OH produced via photocatalysis (Antoniou et al., 2018). Generally, the dust surface with higher proportion of saline components and transition metals may cause the more significant oxidation by $SO_4^{\cdot-}$, especially under solar irradiation with higher ambient humidity and particle acidity."*

S(IV)

$SO_{2(a)}$ $SO_2 \cdot H_2O$
OH^- H_2O
$HSO_3^-{}_{(a)}$ $SO_{2(g)}$ $HSO_3^-{}_{(l)}$
OH^-
$SO_3^{2-}{}_{(a)}$ $SO_3^{2-}{}_{(l)}$

Drivers & Inhibitors

Dust Surface

$SO_3^{2-} + O^- \rightarrow SO_4^{2-} + e^-$

$S_{(IV)} \xrightarrow{Fe(III) \leftrightarrow Fe(II)} S_{(VI)}$

$S_{(IV)} \xrightarrow{ROS\ (O_2^-,\ HO_2^\cdot,\ \cdot OH,\ O^\cdot)} S_{(VI)}$

$SO_4^- + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^-$

S(VI)

(a)
- **Fe-bearing constituents** (e.g. Fe_2O_3)

Iron-catalyzed reaction:

$O_2 + 2e^- \xrightarrow{O_{(vacancy)}} 2O^-$

$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O$

- **Saline ions** (Na^+, Cl^-)

Hygroscopic growth:

$NaCl + H_2O_{(g)} \rightarrow Na^+ + Cl^- + H_2O_{(l)}$

(b)
- **Ti-, Al-bearing constituents** (e.g. TiO_2, Al_2O_3)

Photocatalysis:

$TiO_2/Al_2O_3 \xrightarrow{hv} e_{cb}^- + h_{vb}^+$

$e_{cb}^- + O_2 \rightarrow O_2^{\cdot-}$

$O_2^{\cdot-} + H^+ \rightarrow HO_2^\cdot$

$h_{vb}^+ + H_2O \rightarrow \cdot OH + H^+$

$h_{vb}^+ + O^- \rightarrow O^\cdot$

$\cdot OH + SO_4^{2-} \rightarrow SO_4^{\cdot-} + OH^-$

(c)
- **Al-bearing constituents** (e.g. Al_2O_3)

Site-blocking effect:

activated site $\xrightarrow{Al_2O_3}$ devitalized site

(d)
- **Metal cations** (Na^+, K^+, Ca^{2+})

Increased acidity:

e.g. $Ca^{2+} + H_2O \rightarrow CaOH^+ + H^+$

Scheme 1. Mechanism illustration on the dust-driven heterogeneous conversion of SO_2.

The heterogeneous reaction of airborne SO_2 on natural dust surface includes the initial adsorption of gas-phase SO_2 and the later conversion of $S_{(IV)}$ species to $S_{(VI)}$ products. The formed $S_{(IV)}$ species include both adsorbed and dissolved SO_2, bisulfite and sulfite (dashed box in blue). The generation of $S_{(VI)}$ products can be attributed to the surface active oxygen (O^-), Fe(III)-Fe(II) redox cycling, reactive oxygen species (ROS), and sulfate radical ($SO_4^{\cdot-}$) (dotted box in deep yellow). Heterogeneous oxidation is largely influenced by the dust surface drivers and inhibitors, which promote and hinder the heterogeneous procedures, respectively (solid box in black). Dust surface drivers are determined as (a) the Fe-bearing constituents and saline ions (Na^+, Cl^-) under dark condition, and (b) the Ti- and Al-bearing constituents under solar irradiation. Dust surface inhibitors are identified as (c) the Al-bearing constituents under dark condition, and (d) the metal cations (Na^+, K^+, Ca^{2+}) under solar irradiation.

Referee #3:

Reviewer comment: Line 373-374: Earlier authors assert that the sulfate formation is more during nighttime and less during the daytime, but this statement is opposite and confusing. Can the author clarify this?

Original author response: In the real atmosphere, the sulfate concentration during nighttime could be comparable to or even exceed that during daytime, as normally explained by the different meteorological conditions. We have explained the relevant details in the revised manuscript (line 396-401) to make our calculation results more reasonable. "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."

Editor comment: I still got confused what you compare in this section vs to the discussion earlier in the manuscript. Please reorganize Section 3.3 such that it becomes clear that these are estimates based on a model for which you assume ambient conditions whereas previously you discussed experimental lab data. It might help if you refer in the discussion of your experimental data to 'illuminated' and 'dark' conditions only and in the discussion of model results for atmospheric conditions to 'day' and 'night'.

Revised author response:

We have revised the relevant contents to emphasize the addition of experimental data into the newly developed comparison model. And the results from laboratory research and modeling simulation have been distinguished in a better way.

   First, at the start of Sect. 3.3, we introduced the combination of laboratory and modeling works (line 430-433). *"Figure 5 compares the sulfate formation rates of diverse atmospheric oxidation pathways by a newly developed comparison model. Based on the parameterization scheme in model and the experimental results discussed above, the total sulfate formation rates are summed to be 0.795 µg m^{-3} h^{-1} during nighttime and 5.179 µg m^{-3} h^{-1} during daytime, under the acidity of natural dust (Fig. 5a and e)."* Moreover, we have reorganized Sect. 3.3 to make it clearer and more readable. More revisions are highlighted in blue in the revised manuscript.

   Second, the results obtained from laboratory experiments and modeling simulations have been described by different characteristic words. We have checked through the manuscript, exampled as follows.

(1) Description of experimental results (line 376-377): *"The γ values for the natural dust-driven heterogeneous reactions are calculated to be 6.08 × 10^{-6} under dark condition and 1.14 × 10^{-5} under illuminated condition (Fig. 3a).*

(2) Description of modeling results (line 450-453): *"The diurnal sulfate formation rates of gas-phase, aqueous-phase and heterogeneous processes are respectively 9.4, 6.8 and 3.0 times greater than the nocturnal levels, indicating that the oxidations in gaseous and liquid media could be more kinetically susceptible to the occurrence of sunlight than those relevant to the humidified gas-solid interface."*

Last, according to the question raised by the reviewer, we noticed some documented atmospheric observations where the sulfate concentrations during nighttime approach or even exceed those during daytime, in contrast to the modeling data herein. In order to better explain such discrepancy and emphasize the feature of the current comparison model, we rewrote the relevant sentences in the revised manuscript (line 434-438). *"It is worthwhile to mention that, the nocturnal sulfate concentration was reported to approach or exceed the subsequent diurnal level, as explained by the higher nocturnal humidity facilitating the liquid oxidations or the lower boundary layer at night causing the adverse diffusion conditions (Liu et al., 2017c; Tutsak and Koçak, 2019; Li et al., 2020c). Meteorological factors like humidity are not considered by the current model, which emphasizes the comparison of diverse pathways through kinetic regime."*

Reviewer comment: Line 380-390: In addition to the temperature dependence, did the authors consider the change of relative humidity during the day and night can also contribute to the heterogeneous chemistry reaction with sulfate?

Original author response: We attempted to carry out the heterogeneous laboratory experiments under the higher relative humidity (RH) relative to the current setting. However, the presence of surface adsorbed water makes the Gaussian/Lorentzian deconvolution difficult to be performed, as reflected by the large uncertainties in determining the relative abundance of $SO_2 \cdot H_2O$ and SO_3^{2-}. Accordingly, the RH of 50% was utilized for the experiments. In the revised manuscript (line 654-656), we have emphasized the importance of various meteorological factors when discussing the atmospheric relevance of heterogeneous chemistry, as shown follows. "In addition, the influence of meteorological factors, like temperature, humidity and irradiance, on the atmospheric relevance of heterogeneous chemistry warrants further research. "

Editor comment: I understand that you cannot do any quantitative estimates on the influence of humidity. However, a statement on the extent to which relative humidity would change particle radius and aqueous volume and therefore sulfate formation should be added.

Revised author response:

A new paragraph has been added into "Conclusions and implications" section to discuss the possible effects of ambient humidity on the atmospheric relevance of dust heterogeneous oxidation (line 692-701). The new paragraph is shown as follows.

"Meteorological factors impact the atmospheric relevance of dust heterogeneous pathway. Taking humidity as an example, on dust surface, the heterogeneous reaction of SO_2 is humidity-dependent, and the exact dependence varies with the type of dust and the condition of reaction (Huang et al., 2015; Park et al., 2017; Urupina et al., 2022). The uptake of gas-phase oxidants over dust surface is also influenced by humidity (Kumar et al., 2014). For aerosol droplet, increased humidity elevates its liquid volume and radius (Wu et al., 2018; Ding et al., 2019). Aerosol liquid water serves as an efficient medium for multiphase reactions (Wu et al., 2018; Yue et al., 2019), whereas radius is negatively associated with the sulfate formation at droplet interface (Hung et al., 2018; Wang et al., 2021a; Chen et al., 2022). Furthermore, droplet acidity decreases as the liquid volume increases, thereby increasing the ionization of dissolved sulfur species, followed by the increased sulfate formation rate (Yue et al., 2019; Jin et al., 2020; Gao et al., 2022). Overall, how meteorological factors influence the relative importance of gas-phase, aqueous-phase and heterogeneous processes warrants further research."

Additional editor comments

I. 32: What do you mean by 'in mainstream'?

Response:

We have revised this description based on the recent publications (line 32-35), as shown follows.

"In addition, the reported oxidation channels were compared with each other by aerosol observations 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; Gao et al., 2022; Wang et al., 2022a; Ye et al., 2022)."

I. 35: What do you mean by 'aimed liquid reaction' as opposed to 'aqueous phase reaction'? Do you imply reactions in liquid non-aqueous phases?

Response:

The phrase "aimed liquid reaction" referred to the newly discovered aqueous-phase reaction that was ready for the comparison research. To avoid misconception, we have rewritten this sentence in the revised manuscript (line 35-36), as shown follows.

"In general, these studies emphasized the importance of certain newly discovered aqueous-phase process or compared the contributions from the documented gas- and aqueous-phase pathways."

I. 37: What do you mean by 'gas-solid interactions'? What solid phase are you referring to? In the lines above, you refer to reactions on or in liquid phases.

Response:

The purpose of this introduction paragraph is to emphasize the limited knowledges on the sulfate formation relevant to aerosol surface, including both gas-liquid and gas-solid (mostly humidified) interfaces. We have revised this sentence in the revised manuscript (line 36-38), as shown follows.

"Nevertheless, heterogeneous reaction was scarcely involved in discussion, thus hindering the deeper understanding of the atmospheric relevance of aerosol surfaces."

l. 64-66: This sentence is too convoluted and mixes multiple processes and effects. The study by Clegg and Abbatt was performed on ice, Wu et al explored uptake on calcium carbonate and Wang et al. reactivity on hematite. Either split this sentence into three describing the essential information from each study or remove.

Response:

In the revised manuscript (line 65-67), we attempted to explain the temperature effects by several sentences, as shown follows.

"The reversible adsorption of SO_2 is believed to be exothermic (Clegg and Abbatt, 2001a). In contrast, there were positive temperature dependences observed for $CaCO_3$ below 250 K over the entire reaction (Wu et al., 2011) and for Fe_2O_3 within 284-318 K during the initial reaction stage (Wang et al., 2018a)."

l. 68: What do you mean by 'negative light effect'?

Response:

The phrase "negative light effect" referred to the decreased heterogeneous reactivity of iron oxide by the presence of stimulated solar irradiation. We have performed revision to make the sentence clearer, as shown follows (line 67-70).

"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 thus exhibit weaker reactivity under sunlight (Fu et al., 2009)."

l. 73-74: 'In terms of...' – what does this sentence say?

Response:

The original sentence attempted to introduce the particle physical properties that influence the heterogeneous reaction of SO_2. We have rewritten this sentence to make the contents more readable (line 76-78), as shown follows.

"The particle physical properties, including size (Baltrusaitis et al., 2010; Zhang et al., 2016), morphology (Li et al., 2019) and crystal structure (Yang et al., 2017), display varied impacts on heterogeneous reaction."

l. 75: 'is more efficient' for what?

Response:

We have revised this sentence to highlight the higher heterogeneous reactivity of Fe_2O_3 than Al_2O_3 and SiO_2 (line 78-80), as shown follows.

"When considering the particle chemical properties, Fe_2O_3 is more active than Al_2O_3 and SiO_2 in the heterogeneous uptake of SO_2 and formation of sulfate (Chughtai et al., 1993; Zhang et al., 2006; He et al., 2014)."

I. 77: What do you mean by 'dust community'?

Response:

We have rewritten the sentence to explain that the addition of one certain atmospherically relevant constituent onto dust surface would accelerate the heterogeneous uptake of SO_2. More recent publications have been added into the content (line 80-82), as shown follows.

"Furthermore, the presence of moderate nitrate (Kong et al., 2014; Du et al., 2019), or Al_2O_3 (Wang et al., 2018b), or surfactant (Zhanzakova et al., 2019), or oxalate (Li et al., 2021b), or (bi)carbonate (Liu et al., 2022) on dust surfaces could favor the heterogeneous kinetics under specific conditions."

I. 108: correct 'derisble'

Response:

We have corrected the word to "desirable" (line 113).

I. 119: replace 'Technical Route' by 'Experimental methodology' or something similar.

Response:

The section title has been replaced by "Methodology overview".

I. 125: In the sentence starting 'In the dust-mediated...' is a verb missing.

Response:

We have revised this sentence in the manuscript (line 130-131), as shown follows.

"In dust-mediated mode, dust surface functions as a reaction medium that supports the interaction between adsorbed oxidants and SO_2."

l. 140: Please clarify this sentence. Why don't you state simply the relevant temperature range as being representative for the warm season?

Response:

We have provided an approximate temperature range concluded from the various temperature levels determined by the atmospheric observations (line 145-146), as shown follows.

"The measurements conducted in warm seasons were considered in priority to correspond the experimental temperature. The relevant temperature range is 293-303 K in representative of warm season."

l. 178/179: Which 'gas and aqueous phase parameters' are you referring here to?

Response:

We have rewritten this sentence to make it more readable (line 184-186), as shown follows.

"The kinetic parameters involved in the gas- and aqueous-phase oxidation pathways (listed by Sect. 2.2) were corrected by the experimental temperature as much as possible."

l. 195: The reference to Hennigan et al. 2015 would be much better placed in this context here than in l. 190 as it was shown in their study that HSO_4^- and SO_4^{2-} are not sufficient to calculate acidity.

Response:

We have read the publication by Hennigan and performed more discussions on the particle acidity determination, as shown follows.

First, considering that the proxy methods reviewed by Hennigan et al. (2015) may not accurately estimate the pH of clay mineral, we cited this publication at the beginning of paragraph.

Furthermore, we noted the contents illustrating the limitation of pH calculation by ion balance. Such disadvantage would not affect the results from this work because the relative abundance of $S_{(IV)}$ species were derived from the infrared measurements. We have added discussions into the revised manuscript (line 204-208).

"As noted by Keene et al. (2004) and Hennigan et al. (2015), estimating the pH of airborne aerosol by ion balance may be difficult because it is unable to distinguish between free and undissociated H^+ (e.g. protons associated with HSO_4^- and HSO_3^-). Herein, the relative abundance of $S_{(IV)}$ species is derived from the different infrared absorption

signals relevant to atomic sulfur. Thus, the current method is recommended for the pH determination of humidified gas-solid interface."

l. 212: what do you mean by 'standard item'? Is it the 'standard mixture' or 'standard solution'?

Response:

The "standard item" referred to the Na_2SO_4 powders that were mixed with the prepared clay mineral particles as sulfate standard. We have revised the sentence in the manuscript (line 223-224), as shown follows.

"Because Na_2SO_4 was thoroughly mixed with the particles, S_{BET} was used to calculate γ."

l. 255: replace 'corrects' with 'correlates'

Response:

We have revised the spelling error.

l. 259: Why only 'nocturnal heterogeneous reaction'? Why does this not happen during the day? Could 'nocturnal' be omitted in this sentence?

Response:

The Al-bearing mineral constituents, such as Al_2O_3, would block the active sites of other constituents under both dark and illuminated conditions. We have deleted "nocturnal" and rewritten the sentence (line 275-277), as shown follows.

"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 may hinder heterogeneous reaction by blocking the active sites of other mineral constituents (Wang et al., 2018b)."

l. 263 – 291: This text should not be in the result section but belongs in the introduction where it is partially already cited. Please condense this paragraph and either move relevant parts into the discussion of your results (which are not presented at this place of the paper yet) or to the introduction.

Response:

We have reorganized the relevant contents as suggested.

In Sect. 3.1, in the description contents relevant to Fig. 1, each paragraph introduces the results of correlation analysis at first, followed by the discussion on the possible reaction mechanisms. We combined the result and discussion contents due to their close associations in illustrating the dominate dust surface drivers. We have emphasized this attempt by the first paragraph of Sect. 3.1 in the revised manuscript (line 269-270). *"Correlation analysis is performed to identify the dust surface drivers (Fig. 1), based on which the reaction mechanism of dust heterogeneous processes can be better understood (Scheme 1)."*

Moreover, we have rewritten or shorten the sentences that read like those in introduction section. For instance, each paragraph is now started by the correlation analysis result rather than the cited knowledge, as shown follows. We believe that the current text is appropriate for better understanding the primary elements that influence the heterogeneous sulfate formation over dust surfaces.

Start of the second paragraph of Sect. 3.1: *"The mineral drivers are investigated at first (Fig. 1a). Under dark condition, the sulfate production rate correlates positively with Fe, while presents negative dependence against Al."*

Start of the third paragraph of Sect. 3.1: *"The sulfate yield enhanced by solar irradiation associates positively with the abundance of Ti or Al."*

Start of the fourth paragraph of Sect. 3.1: *"No correlation can be observed between the abundance of element and the sulfate production rate of photoreaction."*

Start of the fifth paragraph of Sect. 3.1: *"The driving effects of water-soluble ions are further studied (Fig. 1b). Herein, Na^+ and Cl^- are observed to present positive impacts on the sulfate formation under dark condition.",* followed by the illustration on the negative effects of water-soluble ions: *"Moreover, there are negative associations between the photoinduced sulfate enhancement and the abundances of Na^+, K^+, Ca^{2+}."*

Start of the sixth paragraph of Sect. 3.1 *"Apart from the dust surface drivers and inhibitors, sulfate radical (SO_4^{-}) may also participate into the heterogeneous event."*

l. 350: This sentence is not clear. Please clarify what you want to say here.

Response:

We have rewritten the sentence in the revised manuscript (line 285).

"Particle acidity is further calculated to discuss the driving force of dust surface for sulfate formation."

l. 350/351: 'no significant correlations can be found between γ and pH' contradicts your later discussion and findings in Figure 3. Please clarify.

Response:

The γ in Fig. 3 (previously denoted as Fig. 2) characterizes the kinetics of dust-driven heterogeneous pathway. Statistical analysis indicates that no significant correlation can be found between the dust-driven heterogeneous γ and particle acidity (pH). Thus, the absolute acidity of reacted dust may be primarily dependent on the dust's basic nature. To avoid misunderstanding, we have rewritten this sentence by emphasizing the dust-driven process (line 387-389), as shown follows.

"Because no significant correlation can be found between the γ for dust-driven sulfate formation and the pH of reacted clay mineral, the absolute acidity level depends largely on the basic nature of dust."

By contrast, the γ in Fig. 4 (previously denoted as Fig. 3) evaluates the kinetics of dust-mediated heterogeneous pathway. The γ for dust-mediated heterogeneous process is pH-dependent, which relates to the effective Henry's law constant for the studied $S_{(IV)}$ specie(s), as discussed above. We have emphasized this point in the revised manuscript (line 399), as shown follows.

"Figure 4 presents the pH-dependent γ for natural dust-mediated heterogeneous pathway"

l. 359/360: Are three digits of the pH value significant figures? What is the variability in this value?

Response:

The pH level was previously calculated with three significant digits. For consistency, two significant digits are shown for all pH values in the revised manuscript. Moreover, standard errors have been added into Fig. 3 to make it more accurate. The revised figure is shown as follows.
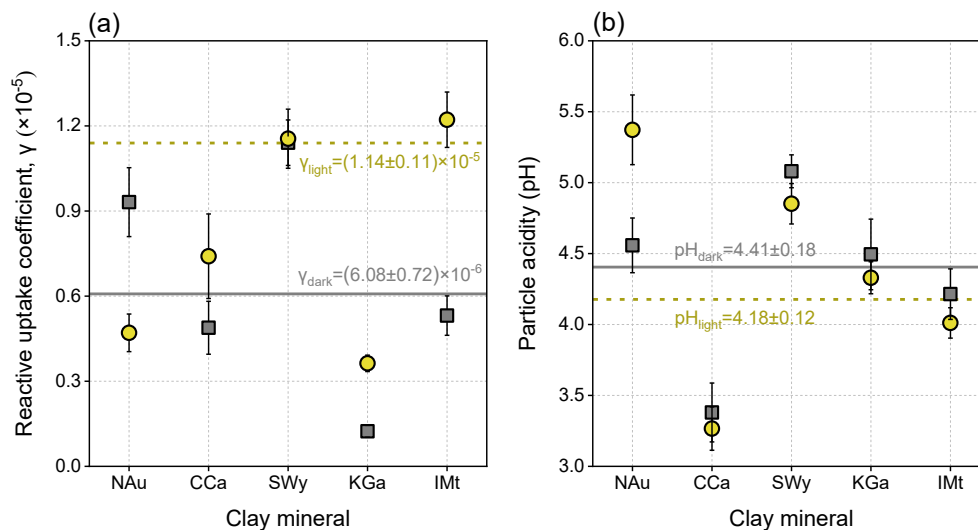
Figure 3. Analysis results of the *in-situ* infrared spectra recorded for the heterogeneous reaction of SO_2 on clay minerals and natural dust.

(a) Reactive uptake coefficients (γ) for the heterogeneous formation of sulfate. (b) Particle acidity (pH) of the reacted particle samples. The dark (grey square) and light (yellow circle) conditions were both considered. Dots represent the results of clay minerals, and those of natural dust are showed by the lines. All error bars represent 1 SD.

l. 430: replace 'great heterogeneous performances' by 'significant contributions by heterogeneous sulfate formation' (or similar)

Response:

We have revised the sentence (line 465-467), as shown follows.

   "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 significant contributions by heterogeneous sulfate formation (Fig. 5d and h)."

l. 446 – 448: The sentence starting 'As proved by ...' seems out of place here. Either remove or clarify its connection to the text in this paragraph.

Response:

We have rewritten this sentence in the revised manuscript (line 486-489), as shown follows.

"The important role of dust in sulfate formation was confirmed by atmospheric observation research. For example, secondary sulfate was observed to accumulate on the dust-dominant super-micron particles collected in the North China Plain, and the mass fraction of coarse-mode sulfate dramatically increased during the evolutionary stages of haze episode (Xu et al., 2020)."

l. 454-461: 1) Refer to Figure 6 at the beginning of this text , 2) Be more specific in the text, rather than just saying longest, second longest etc lifetime.

Response:

First, we have referred to Fig. 7 (previously numbered as Fig. 6) at the beginning of this paragraph (line 491), as shown follows.

"Figure 7 compares the lifetimes of SO_2 influenced by the diverse atmospheric oxidation pathways."

Furthermore, we have specified the discussions, and the revised content is shown as follows.

"Figure 7 compares the lifetimes of SO_2 influenced by the diverse atmospheric oxidation pathways. 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). Theoretically, the lifetime of SO_2 determined by heterogeneous reaction is negatively correlated with γ and S_p, and S_p is positively associated with the concentration and S_{BET} of dust, as respectively described by Eq. (12) and (10). As a result, the dust with greater heterogeneous reactivity, or higher atmospheric loading, or larger S_{BET} is prone to cause the shorter lifetime. During nighttime, IMt causes the shortest SO_2 lifetime (46.90 days) due to its highest concentration relative to the other clay minerals. The relatively large heterogeneous uptake capacity of NAu and SWy link to the second and third shortest SO_2 lifetimes (221.30 and 260.12 days, respectively). On the other hand, the weakest heterogeneous reactivity of KGa leads to the second longest lifetime (1758.65 days), and the longest result caused by CCa (2256.25 days) can be interpreted by its lowest S_{BET} that causes the lowest S_p. The presence of solar irradiation alters the lifetime ranking: IMt (20.39 days) < SWy (256.96 days) < NAu (437.85 days) < KGa (597.54 days) < CCa (1488.46 days), as influenced by the different photoactivities of the clay minerals."

Figure 4: 1) Make labels on panels b, c, d, f, g, h larger. 2) Explain the colors in panels a and e. Are they same as in panels b and f?

Response:

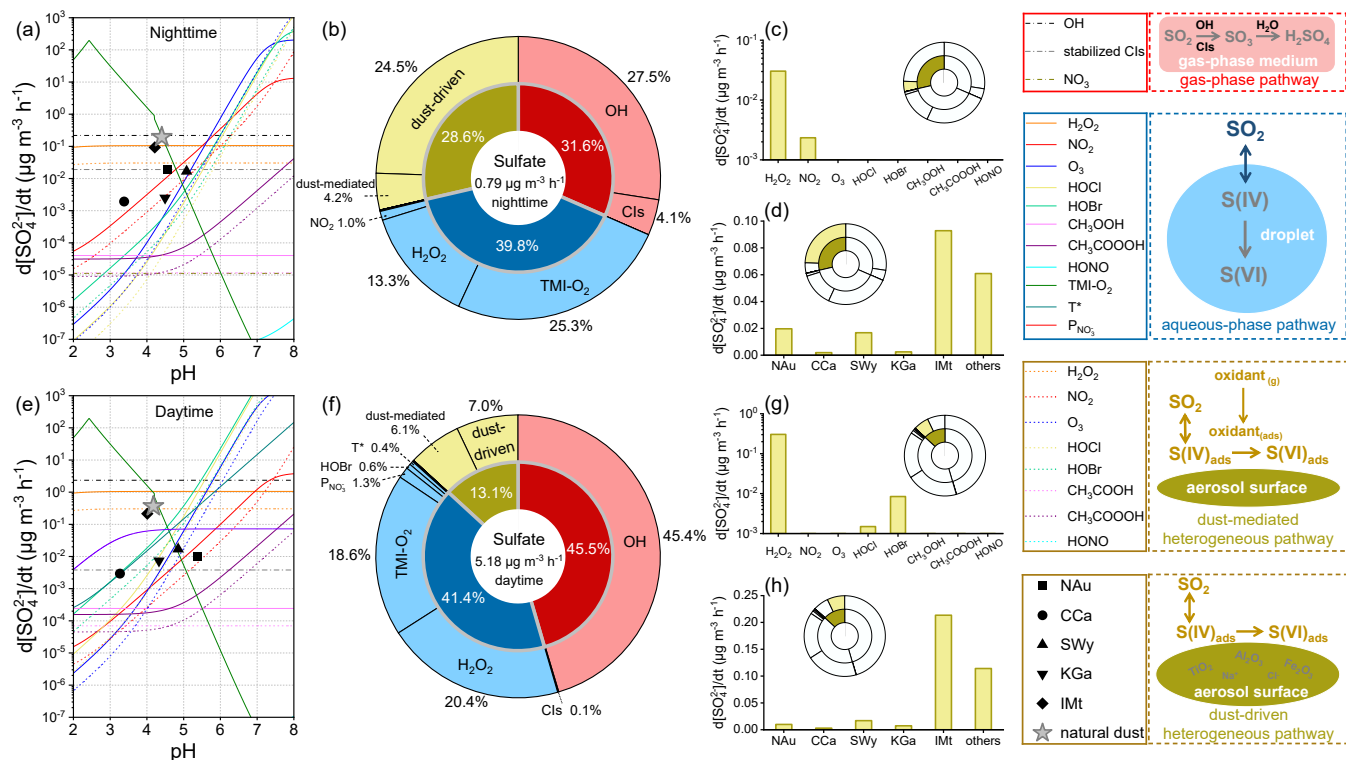We have revised this figure and its caption, as copied follows.

Figure 5. Contributions of diverse atmospheric oxidation pathways to secondary sulfate aerosols.

Gas-phase oxidation can be induced by hydroxyl radical (OH), stabilized Criegee intermediates (CIs), as well as the nitrate radical (NO_3) only for nighttime. Aqueous-phase oxidation can be 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 oxidation can be initiated by the surface oxidants (H_2O_2, NO_2, O_3, HOCl, HOBr, CH_3OOH, CH_3COOOH, HONO) co-adsorbed with SO_2. Dust-driven heterogeneous oxidation can be 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 rates of the diverse atmospheric oxidation pathways. The elements' colors and shapes are characterized by the legends in solid boxes. (b, f) Quantified sulfate contribution proportions of the studied gas-phase (red), aqueous-phase (blue), and heterogeneous (yellow) reaction 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 oxidation were not taken into account. The dust concentration was set to be 55 µg m^{-3}, in representative of the common atmospheric condition of North China (Zhang et al., 2012). The panels in dashed boxes 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.

l. 526: should 'merely' be 'only' here?

Response:

We have replaced "merely" by "only".

l. 547: These dust concentrations seem only representative for some regions of the globe (e.g. https://agupubs.onlinelibrary.wiley.com/doi/epdf/10.1029/2021MS002845). Please tone down your statement and state that your conclusions are only relevant for specific regions.

Response:

We have considered the uncertainties relevant to the concentration of dust (line 584-587). The revised sentences are shown as follows.

   "Such dust concentrations are sometimes common in the troposphere, especially during the dust storm periods (Li et al., 2021a; Yin et al., 2021; Filonchyk, 2022) or near the dust source regions (Ke et al., 2022). Therefore, the heterogeneous loss of SO_2 by airborne dust surface may have a similar magnitude as the main gas-phase loss process and can be taken as an important sink for SO_2."

l. 587: What do you mean by gas-solid interface? Aerosol particles are never completely dry and thus, gases are always exposed to aqueous surfaces.

Response:

We have replaced the "gas-solid interface" by "humidified gas-phase interface" to emphasize the surface of dust particles exposed to the humid atmospheric environments. The revision in manuscript (line 625-626) is shown as follows.

   "Besides the humidified gas-solid interface, gas-liquid interface of microdroplet is another type of medium that supports the heterogeneous formation of sulfate."

l. 648: I do not understand the expression 'plausible influencer'. I suggest removing it.

Response:

The expression of "plausible influencer" has been deleted.

l. 674: Please add all data into a suitable repository that can be accessed freely by the readers, corresponding to the journals' data policy https://www.atmospheric-chemistry-and physics.net/policies/data_policy.html.

Response:

We have added all data into a repository and introduced the data availability in the revised manuscript (line 719), as shown follows.

"Data availability. A dataset for this paper can be accessed at https://data.mendeley.com/datasets/hyvdz7khs6/1."