I have reviewed the manuscript “Significant formation of sulfate aerosols contributed by the heterogeneous drivers of dust surface” by Wang et al. Authors investigated the different metals and ions of the dust surface are associated with the heterogeneous formation of sulfate and used models to predict the heterogeneous reactivity. This study found that a significant amount of secondary sulfate aerosol was formed during nighttime and the heterogeneous drivers on the dust surface are more efficient to convert SO_2 to secondary sulfate. Given the importance of atmospheric secondary sulfate formation and heterogeneous chemistry of aerosols, this work is both significant and appropriate for this journal. However, there are some issues in this work that needs to be addressed before it can be published, as detailed below.

Introduction: authors should add some broad impacts of secondary sulfate aerosol as the motivation, such as the climate and health.

Answer:

Thanks for your comments.

We have discussed the relevant information at the start of Introduction section (line 25-27).

“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).”

Line 45: authors need to add relevant references “… mentioned in the previous works” and be more specific.

Answer:

We have rewritten the sentences to make the declaration more specific (line 47-49), as shown follows.

“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.”

The following references are added.

Wang, Y., Zhang, Q., Jiang, J., Zhou, W., Wang, B., He, K., Duan, F., Zhang, Q., Philip, S., and Xie, Y.: Enhanced sulfate formation during China's severe winter haze episode in January 2013 missing from current models, J. Geophys. Res., 119, 10425-10440, http://doi.org/10.1002/2013jd021426, 2014.

Zheng, B., Zhang, Q., Zhang, Y., He, K. B., Wang, K., Zheng, G. J., Duan, F. K., Ma, Y. L., and Kimoto, T.: Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China, Atmos. Chem. Phys., 15, 2031-2049, http://doi.org/10.5194/acp-15-2031-2015, 2015.

Xue, J., Yuan, Z., Griffith, S. M., Yu, X., Lau, A. K. H., and Yu, J. Z.: Sulfate formation enhanced by a cocktail of high NOx, SO2, particulate matter, and droplet pH during haze-fog events in megacities in China: an observation-based modeling investigation, Environ. Sci. Technol., 50, 7325-7334, http://doi.org/10.1021/acs.est.6b00768, 2016.

Method Line 118: Can authors briefly describe the “documented methodologies” and add references.

Answer:

In the revised manuscript (line 122-124), we have briefly described the utilized methodologies and parameterizations.

“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 Section 2.2 (more details in Supporting Information).”

The following references are added.

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, Sci. Adv., 2, e1601530, http://doi.org/10.1126/sciadv.1601530, 2016.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics, From Air Pollution to Climate Change, 3rd Edition, Wiley, New Jersey, USA, 2016.

Shao, J., Chen, Q., Wang, Y., Lu, X., He, P., Sun, Y., Shah, V., Martin, R. V., Philip, S., Song, S., Zhao, Y., Xie, Z., Zhang, L., and Alexander, B.: Heterogeneous sulfate aerosol formation mechanisms during wintertime Chinese haze events: air quality model assessment using observations of sulfate oxygen isotopes in Beijing, Atmos. Chem. Phys., 19, 6107-6123, http://doi.org/10.5194/acp-19-6107-2019, 2019.

Song, H., Lu, K., Ye, C., Dong, H., Li, S., Chen, S., Wu, Z., Zheng, M., Zeng, L., Hu, M., and Zhang, Y.: A comprehensive observation-based multiphase chemical model analysis of sulfur dioxide oxidations in both summer and winter, Atmos. Chem. Phys., 21, 13713-13727, http://doi.org/10.5194/acp-21-13713-2021, 2021.

Line 339-340: Can author provide more explanation about why the different clay minerals can affect the significant change of particle acidity?

Answer:

Firstly, the absolute acidity level varies with the type of clay mineral. The relevant discussions in the revised manuscript (line 350-355) is shown as follows.

"After the exposure to SO_2, CCa is the most acidic, followed by IMt and KGa, leaving SWy and NAu 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)."

In addition, we discussed the different particle acidities after the dark and light reactions (line 355-359).

"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."

Line 343-343: It is very interesting to see the difference in particle acidity between dark reaction and photoreaction, are they statistically different? Can author discuss why the CCa has the lowest pH among all the different types of clay minerals?

Answer:

For a certain clay mineral, the particle acidity after dark reaction is statistically different from that after photoreaction, as reflected by the Mean±SD data presented in Fig.2b. We have added more details in the data processing section (line 187-188).

"The consistent deconvolution procedure was performed for the infrared spectra derived from the repeated experiments."

We have provided an explanation for the lowest pH of CCa. The added text in the revised manuscript (line 352-355) is shown as follows.

"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)."

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?

Answer:

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."

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?

Answer:

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. "

Line 391-393: This sentence "Relative to … heterogeneous chemistries by …" does not make sense, please rephrase/refine the sentence.

Answer:

We have rewritten the sentences to make the relevant content more readable (line 417-420).

"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."

Figure 5: Can author provide some discussion about the trend shown in Figure 5? Why would it show a dip in sulfate formation rate at pH 5 and more sulfate at higher pH?

Answer:

The dip in sulfate formation rate around the pH of 5.0 is attributed to the significant sulfate formations under the extremely acidic and near-alkaline conditions. We have discussed the pH-dependent kinetics of the aqueous-phase and dust-mediated heterogeneous chemistries (line 449-452), as shown follows.

"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."

Figure 10 Line 558-559: Can author explain why the O_2 affects SO_2 oxidation over pH <4 and why is it starting to decrease after pH 4?

Answer:

We have explained the pH-dependent kinetics of the interfacial O_2 at acidic aerosol interface (line 592-594).

"As reported by Hung et al. (2015, 2018), acidic droplet interface favors the noncatalyzed oxidation by the presence of sufficient $SO_3^{\bullet-}$ and $SO_4^{\bullet-}$ 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."

Comments in the quick report

Can author provide more information about the particle acidity calculation and standard calibration? Rindelaub et al developed the direct pH measurement for single-particle using the ratio of bisulfate and sulfate peak.

Answer:

The calculation of particle acidity by the relative abundance of bisulfate and sulfate may not be applied for this study because the characteristic bisulfate signals cannot be determined in some of the recorded infrared spectra. We have discussed the report from Rindelaub et al. (2016) and provided more information on the calculation of particle acidity (line 195-197).

"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."

Line 336: Author mentioned that the more sulfate formation during the daytime than the nighttime, but later author suggests more secondary sulfate aerosol formation during nighttime than daytime, can author clarify this?

Answer:

As discussed in Section 3.2, the dust surface drivers are responsible for the atmospheric sulfate formation rate of 0.195 μg m^{-3} h^{-1} during nighttime and 0.365 μg m^{-3} h^{-1} during daytime. As discussed in Section 3.3, the dust heterogeneous chemistry is responsible for 28.6% and 13.1% of the secondary sulfate during nighttime and daytime, respectively. We have clarified the different dependences of absolute sulfate yield and relative sulfate contribution in the revised manuscript (line 411-413).

"In other words, although the heterogeneous sulfate production during nighttime is quantitatively lower than that during daytime (see Section 3.2), the nocturnal heterogeneous chemistry accounts for the higher proportion of secondary sulfate."

In figure 5, it is interesting to see the formation rate of sulfate increase after pH5, can author provide some discussion about this trend and the increasing sulfate formation with increasing pH?

Answer:

In the revised manuscript (line 450-452), we have explained the positive pH dependence when pH>5.0.

"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."