Comments on ACP-2021-564

In this work, Liu et al. studied the formation of sulfate on mixed mineral dust particles and found a synergistic effect between TiO_2 and carbonate in promoting sulfate formation upon illumination. They proposed a novel mechanism in which carbonate radical ($\bullet CO_3^-$) was considered as an important intermediate. This $\bullet CO_3^-$ was assumed to oxidize SO_3^{2-} to $\bullet SO_3^-$ and then promote sulfate formation. Lots of methods were used to prove the existence of $\bullet CO_3^-$ and its interaction with other species in this reaction system. Furthermore, analysis of samples collected in field observation and quantum chemical calculation were also used to show this synergistic effect between TiO_2 and carbonate in promoting sulfate formation in the atmosphere. The formation mechanism of sulfate is an important research topic in atmospheric chemistry as well as the occurrence of high concentration of fine particles during haze episodes. This work provided a new and interesting perspective for synergistic effect in the formation of atmospheric sulfate aerosol. However, the flaws in the hypothesis of reaction mechanism make its scientific and environmental significance questionable. In addition, the manuscript is not well organized and a little hard to read. So, I think it may not be accepted in current version.

Main concerns.

1. It is not reasonable to exclude the buffering effect of carbonate in promoting the formation of sulfate. The results that $CaCO_3$ did not promote the formation of sulfate under dark conditions (Page 6 line 155) can not extend to confirm its effect in promoting sulfate formation under illumination. It has been well known that the conversion of SO_2 to S(VI) hardly happen under ambient conditions without strong oxidants or illumination. On the other hand, several recent studies reported that mineral dust photochemistry can induce the formation of H_2SO_4 (PNAS, 2012, 109, 20842–20847; EST, 2021, 55, 14, 9784-9793). In the present study, it seems the increase in sulfate concentration under illumination condition is most likely due to the enhanced condensation or neutralization of H_2SO_4 in the presence of $CaCO_3$ or carbonates. I think

the CO_2+SO_2 experiments may not rule out the buffering effect of carbonate effect in TiO_2+$CaCO_3$ system since the enhancement effect of CO_2 is significantly lower than that on $CaCO_3$. Moreover, why SO_2 concentration in Figure 2 is quite lower than those in Figure 1? And could you show the IR peaks due to CO_2 adsorption? Did their intensities change during the photooxidation of SO_2?

2. Consistency and comparability of experimental system. The heterogeneous reactions of SO_2 were studied on mineral particles while some characterization experiments for supporting evidences were conducted in solutions. Although some water layers may be formed on mineral dust particle surface at 30%RH, however, this situation may far from the liquid state. So, it is unreasonable to assume that all reaction mechanisms are ionic reactions in liquid phase.

3. mechanism: Firstly, only hole was consumed which resulted in the formation of •OH and •CO_3^- (eq 2 and 3). However, the consumption of photogenerated electron is not mentioned. According to eq 5-8, O_2 is the key oxidant for the oxidation of SO_3^{2-} to sulfate. However, the content of O_2 in solution is limited due to its low solubility if aqueous reactions were assumed. In addition, O_2 can react with photogenerated electron to form O_2^- and then oxidize SO_3^{2-} on particles surface. The authors need to compare the effect of these two processes on the formation of sulfate. Secondly, according to eq 6-8 (in eq 7, SO_4 should be SO_4^{2-}?), it seems that the oxidation of SO_3^{2-} by O_2 could be a catalytic reaction while •SO_3^- acted as catalyst. If so, the amounts of sulfate formed through photooxidation on TiO_2 should be the same (at least close to) in the presence of carbonates and CO_2 since •CO_3^- only contribute to the formation of •SO_3^-. Is it? Thirdly, what's the pH effect on the reaction? As seen in eq 3 and 4, only the reaction of •OH with HCO_3^-/CO_3^{2-} was considered. What's about the reactions between H^+ and HCO_3^-/CO_3^{2-}? As the oxidation of SO_2 or sulfite increased, the pH should decrease and then affect HCO_3^-/CO_3^{2-}.

Other concerns:

1. The concentrations of SO_2 used are much higher than the ambient atmospheric concentration.

2. Line 228: it is difficult to understand this sentence “ESR data (Fig. 3d) further confirms the increase of $SO_3^{\cdot-}$ after 2 min UV irradiation in the presence of carbonate ion” since the change is not very obvious.

3. sampling in field observation. The samples collected in daytime and nighttime did not mean they are always in dark and illuminated conditions. The samples collected in nighttime may also have undergone multiple daytime photochemical processes. In addition, as proposed by Sullivan et al. (Atmos. Chem. Phys., 7, 1213–1236, 2007), oxidation of S(IV) to S(VI) by iron in the aluminosilicate dust is a possible explanation for the enrichment of sulphate in Asian mineral dust. So, how to exclude the effect of Fe in this study?

4. Conclusion and atmospheric implications: this study only found the enhanced sulfate formation in mixed TiO_2 and $CaCO_3$ particles compared to individual TiO_2 or $CaCO_3$ particles. However, the hypotheses of CO_2-derived carbonate species and carbonate salt works as the precursor of $\bullet CO_3^-$ is exaggerated. As seen in this study, TiO_2 is necessary but its content in atmospheric particulate matter is very low. Considering the unclear role of $\bullet CO_3^-$, as well as the high concentration of SO_2 used, its implications even on sulfate formation is limited. Consequently, the extension of its atmospheric implications to fine PM concentration, human health, and climate is not meaningful.