

Interactive comment on “Heterogeneous Reactions of Carbonyl Sulfide on Mineral Oxides: Mechanism and Kinetics Study” by Y. Liu et al.

Y. Liu et al.

Referee #1

This manuscript reports mechanistic and kinetic study of interactions between OCS on various mineral oxides using two experimental methods (KCMS and UV-Vis). The results provide some insights into the reaction pathways for OCS on these oxides. The study also estimated uptake coefficients of OCS on mineral oxides, which can provide an estimate of the global flux of the OCS due to the heterogeneous reactions on atmospheric mineral oxides based on these kinetic parameters. The authors found a comparable flux of OCS to that of OCS with OH radicals. The topic is quite interesting and worthy of further investigation. However, the authors/coauthors have published a series of papers in several other journals on the heterogeneous reactions of OCS on several similar oxides using different experimental methods (e.g. DRIFTS) and drew similar conclusions for the same reactions [e.g., Liu LF et al. 2006; Liu YC et al., 2008a,b, 2007a,b, 2009 a,b]. The only new information reported in this study is the uptake coefficient of OCS on various mineral oxides, which is not worthy of a long paper (about 30 pages). Except for this piece of information, the reviewer feels that the authors would like to mainly confirm the previous experimental results rather than make a significant contribution to this research area. The reviewer also recommends that a shorter paper on the kinetic uptake coefficients of OCS on these mineral oxides might be publishable in other journal such as Journal of Physical Chemistry A/B. It should be pointed out that the reviewer doesn't agree with the authors that the uptake of OCS on ZnO is irreversible (page 12317) since Figure 5 show clearly no any sign of irreversible uptake behavior.

Response: We thank Referee #1 for the comments and suggestions on our manuscript. As you mentioned, we have published a series of papers in several other journals on the heterogeneous reactions of OCS on mineral oxides. We also cited these work on our manuscript. As for the reaction mechanism on Al₂O₃ and MgO, we have proposed the heterogeneous oxidation and hydrolysis pathways via hydrogen thiocarbonate (HSCO₂⁻) as a key intermediate (*J. Phys. Chem. A*, 113, 3387–3394, 2009; *J. Phys. Chem. A*, 111, 4333–4339, 2007; *J. Phys. Chem. B*, 110, 3225–3230, 2006; *Environ. Sci. Technol.*, 39, 9637–9642, 2005). We also have reported the uptake coefficients of OCS on Al₂O₃ and MgO (*Atmos. Chem. Phys.*, 9, 6273–6286, 2009; *Atmos. Environ.*, 42, 960–969, 2008; *J. Phys. Chem. A*, 112, 2820–2826, 2008). However, there still are many questions need to be answered for this issue. For example, besides Al₂O₃ and MgO, mineral dust also contains other components such as SiO₂, CaO, ZnO, Fe₂O₃ and TiO₂ etc. Is the reaction mechanism of OCS on these oxides the same as that on Al₂O₃ and MgO? What is the crucial factor determining the reaction pathway? As for the kinetics studies, except for Al₂O₃ and MgO, the reactions on all of the other oxides were investigated using infrared spectroscopy with a high OCS concentration (*Chinese Sci. Bull.*, 52, 2063–2071, 2007; *Sci. China. Ser. B Chem.*, 48, 31–37, 2005; *Chinese Sci. Bull.*, 49, 1231–1235, 2004). Because the effect of the background (reactive surface of reactor) and the diffusion limit of OCS in the reactor can not be avoided, apparent rate constants measured by IR method usually have large uncertainties. On the other hand, the effective diffuse depths of OCS in the powder layers were undetectable using IR method, thus the true uptake coefficients of OCS on these oxides were unavailable. Knudsen cell reactor can overcome these shortcomings. Therefore, the reaction mechanism and kinetics of OCS on other oxides were further investigated using a Knudsen cell reactor for comprehensive understanding the heterogeneous reactions of OCS in the atmosphere. These open questions were also pointed out in the introduction section in our manuscript. Therefore, we think one of the highlight of this work is the comprehensive reaction pathway of OCS on the main mineral oxides presenting in mineral dust (Scheme 1, [page 12339](#)). We also proposed two factors, i.e. the basicity of oxides and the decomposition ability of oxides for H₂S,

determining the reactivity of OCS on these oxides (Section 3.3, [pages 12318-12321](#)). Additionally, using these true uptake coefficients, we comprehensively estimated and renewed the contribution of heterogeneous reactions on mineral dust to the sink of OCS in the troposphere.

As for the paper length, we moved Figs. 1 and 2 to the SI section. The corresponding description ([pages 12315-12316](#)) was also simplified in our revised manuscript.

As can be seen in Fig. 5, when ZnO was exposed to OCS, uptake of OCS was very prominent while desorption of CO₂ and H₂S was not observed. Even with the largest iris area in the end of uptake experiment, no desorption of OCS, CO₂, and H₂S were observed. These behaviors were different from that on α -Al₂O₃, MgO, CaO and α -Fe₂O₃. Therefore, it implied that irreversible adsorption took place on ZnO. In order to confirm this process, the repeated uptake experiments were carried out on ZnO and α -Fe₂O₃. After the uptake experiment finished, the samples were out-gassed at $3.0 \pm 1.0 \times 10^{-7}$ Torr and at 300 K for 18 h. Repeated uptake experiments were performed at 300 K. As can be seen from the following figures (Fig. 1R), adsorption of OCS on ZnO was very clear in the 1st run, while it almost did not occur in the 2nd and the 3rd runs. For the comparison experiment, OCS can reversibly adsorb on α -Fe₂O₃. These results were also added in our revised manuscript.

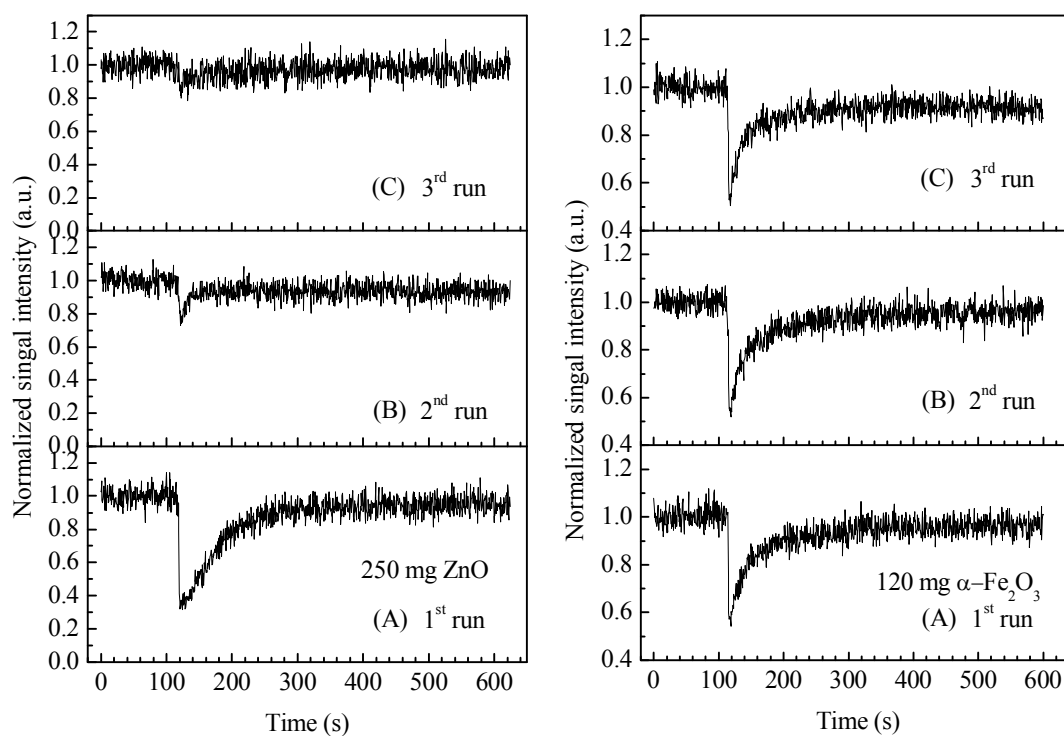


Fig. 1R. Repeated uptake experiments of OCS on ZnO and α -Fe₂O₃. After the uptake experiment finished, the sample were out-gassed at $3.0 \pm 1.0 \times 10^{-7}$ Torr and at 300 K for 18 h. Uptake experiments were performed at 300 K.