

Interactive comment on “Heterogeneous reactions of carbonyl sulfide on mineral oxides: mechanism and kinetics study” by Y. Liu et al.

Anonymous Referee #2

Received and published: 8 July 2010

Liu et al. report on a series of laboratory experiments to investigate kinetics and mechanism of carbonyl sulfide (OCS) interaction with mineral oxides. Carbonyl sulfide is an important air constituent and understanding of its heterogeneous reactions is necessary to assess atmospheric OCS budget. While the subject of this manuscript is relevant to ACP journal audience there are several concerns about the content. Some of the data plots present in this paper were compiled from the plots published earlier by the authors. For example, Fig.1 seems to be the product of Fig.1+Fig.2 from Liu et al. (Atmos. Environ, 2008). The authors do mention that previously reported results are given to facilitate comparison but including a very similar figure seems to be redundant.

Another concern is a significant inconsistency between the results from this study and previous work Liu et al. (Chinese Sci. Bull. 2007). For instance, reactivity of TiO_2

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was reported earlier to be higher (four times) than that of $\alpha - \text{Al}_2\text{O}_3$, while in this work OCS interaction with TiO_2 is negligible compared to $\alpha - \text{Al}_2\text{O}_3$ (P.12330 Tab.1). This is somewhat surprising since the samples were very similar; at least they had identical BET surface areas. The authors explain the discrepancy by the difference between KCMS and DRIFT techniques but this argument seems to be insufficient.

The authors claim that steady state coefficients are very small for ZnO and CaO and the sulfide or sulphur species could hardly desorb from the surface (P.12323 L.15-18). This seems to be the case for ZnO but not for CaO. H_2S signal increase at m/e34 for CaO is similar to that of $\alpha - \text{Al}_2\text{O}_3$ (Fig.3F and 1F) when scale difference is taken into account. Also statement about OCS irreversible adsorption on ZnO and reversible on $\alpha - \text{Fe}_2\text{O}_3$ (P.12324 L.21-23) seems to be questionable as one may see very similar signal patterns in Fig. 4A and 5A.

One of the weakest part of the manuscript is the estimate of atmospheric OCS removal by mineral dust (P.12324-12325). Due to lack of kinetic data on more realistic dust surrogates (such as Sahara dust, Arizona Test dust or other authentic dust samples) the authors make several assumptions without proper discussion of caveats. While the authors acknowledge the complexity of air-dust interaction they use a very speculative approach (Eq.4) to estimate the true uptake coefficient of authentic dust. Another point that I have a serious concern with is using “globally-averaged dust surface area” to global OCS flux calculation. The value of $150 \mu\text{m}^2\text{cm}^{-3}$ is taken from one flight airplane study (de Reus et al. 2000) and it is more representative of a regional dust layer rather than global average.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 12309, 2010.

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