**Atmospheric
Chemistry
and Physics
Discussions**

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

**Y. Liu et al.**

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Referee #2

1. 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 TiO2 was reported earlier to be higher (four times) than that of a-Al2O3, while in this work OCS interaction with TiO2 is negligible compared to a-Al2O3 (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.

Response: Thank you for your comments and suggestions on our manuscript. According to your suggestions, we moved the Figs. 1 and 2 to the SI section in our revised manuscript. The corresponding description was also simplified.

In our previous work (Chinese Sci. Bull., 2007), the apparent rate constants were measured based on the loss of gaseous OCS (2071 and 2052 cm-1) using DRIFTS. The structure of the reactor is shown in Fig. 1R.

The powder sample was placed in the crucible (corundum) with a geometric area of about 0.20 cm2. The inner surface of the reactor, which including corundum, steel (the base of the reactor) and ZnSe (window material) surface, was quite large compared with the sample area. The large reactive inner surface of the reactor contributed large uncertainties to the apparent rate constant. In this work, the uptake coefficients were measured by a Knudsen cell reactor. The particle sample was placed in a Teflon coated sample holder, and the inner surface of the Knudsen cell reactor was inert to reactants by coating with Teflon film and was also passivated by reactants before the uptake experiment. Thus, the contribution of the inner surface can be avoided in experiment. The uptake coefficients measured in this work were more precise than that measured by DRIFTS. Therefore, we think the kinetic parameters determined by this work were more credible.

2. 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. H2S signal increase at m/e34 for CaO is similar to that of a-Al2O3 (Fig.3F and 1F) when scale difference is taken into account. Also statement about OCS irreversible adsorption on ZnO and reversible on of a-Fe2O3 (P.12324 L.21-23) seems to be questionable as one may see very similar signal patterns in Fig. 4A and 5A.

Response: Thank you very much. As shown in Table 1, the true uptake coefficient at steady state of OCS was measured to be 8.89±2.02E-7 on CaO, while it was 1.62±0.27E-6 on a-Al2O3 and 4.67±1.14E-6 on MgO, respectively. It also indicates a weak uptake of OCS on CaO at steady state. On the other hand, the normalized signal intensity of OCS at steady state (shown in Figs. 1-3, and 5), was 0.89±0.02 (a-Al2O3), 0.69±0.01 (MgO), 0.95±0.03 (CaO), and 0.99±0.02 (ZnO), respectively. Therefore, when compared with a-Al2O3 and MgO, the steady state uptake of OCS on CaO was very weak. Although the H2S signal at m/e=34 for CaO is somewhat similar to that of a-Al2O3, the increase amplitude is not so obvious when the signal-to-noise ratio was taken into account.

As you mentioned, signal patterns for the uptake of OCS on ZnO and a-Fe2O3 (Figs. 4A and 5A) were very similar. It means OCS can adsorb onto these two kinds of oxide. The irreversible adsorption on ZnO and reversible on a-Fe2O3, however, were distinguished by the different desorption signal patterns in the end of uptake experiment (Figs. 4D and 5D). On a-Fe2O3, desorption of OCS was observed, which indicates reversible adsorption taking place on a-Fe2O3, while no desorption of OCS on ZnO was observed, which indicates an irreversible adsorption process.

In order to confirm this process, the repeated uptake experiments were carried out on ZnO and a-Fe2O3. After the uptake experiment finished, the samples were outgassed at 3.0±1.0E10-7 Torr and at 300 K for 18 h. Repeated uptake experiments were performed at 300 K. As can be seen from Fig. 2R, adsorption of OCS on ZnO was very clear in the 1st run, while it was very weak in the 2nd and the 3rd runs. In the comparison experiments, OCS can reversibly adsorb on a-Fe2O3. These results were

also added in our revised manuscript.

3. 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 $\mu$m2âĂćcm-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.

Response: Thank you very much for your comment. We did not have realistic dust samples, thus the uptake coefficient of mineral dust in the troposphere was estimated by using the uptake coefficients of OCS on the individual components and their mass fraction in the mineral dust (Eq.4). This method was also used for estimating the uptake coefficient of SO2 on mineral dust by Usher et al (J. Geophys. Res., 107, 4713–4721, 2002). We also estimated the contribution of heterogeneous reaction of OCS on a-Al2O3 to the sink of OCS in the troposphere (Atmos. Environ. 42, 960–969, 2008). Although it contains an uncertainty, we think it is still meaningful for coarsely estimating the sink of OCS due to heterogeneous reaction. In our revised manuscript, we added the uncertainty analysis about this method as "Of course, the uptake coefficient of OCS on mineral dust estimated by using the uptake coefficients of OCS on the individual components and their mass fraction in the mineral dust (Eq.4) contains a considerable uncertainty. Therefore, in the future work, the uptake of OCS on realistic dust samples such as Sahara dust, Arizona Test dust or other authentic dust samples should be considered."

As you pointed out, the value of 150 $\mu$m2âĂćcm-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. Unfortunately, the global mean dust loading can not be obtained in published literatures. Therefore, in these published literatures (J. Phys. Chem. A, 108, 1560-1566, 2004; J. Geophy. Res. 107, 4713–4722, 2002.), the value of 150 $\mu$m2âĂćcm-3 was widely used for estimating the sinks of gases (SO2 and HNO3) on mineral dust. According to your suggestion, we also added the uncertainty analysis using this value in our revised manuscript as follows: On the other hand, the value of 150 $\mu$m2âĂćcm-3 was 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. Unfortunately, the global mean dust loading is unobtainable in published literatures. The estimating method for the sink of OCS due to heterogeneous reaction on mineral dust, therefore, is also a middle course of action.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C6582/2010/acpd-10-C6582-2010-supplement.pdf

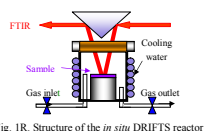Interactive comment on Atmos. Chem. Phys. Discuss., 10, 12309, 2010.

Fig. 1R. Structure of the *in situ* DRIFTS reactor
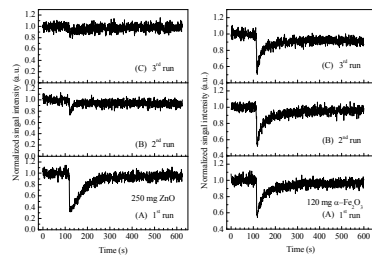
**Fig. 1.**

Fig. 2R. Repeated uptake experiments of OCS on ZnO and $\alpha$-Fe$_2$O$_3$. After the uptake experiment finished, the sample were out-gassed at $3.0\pm1.0\times10^{-7}$ Torr and at 300 K for 18 h. Uptake experiments were performed at 300 K.

**Fig. 2.**

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