

## ***Interactive comment on “Comparative study of the effect of water on the heterogeneous reactions of carbonyl sulfide on the surface of $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and MgO” by Y. Liu et al.***

**Y. Liu et al.**

ycliu@rcees.ac.cn

Received and published: 10 August 2009

Y. Liu et al.

We thank Referee #1 for the comments on our manuscript and for the positive overall evaluation. In order to make it easy to understand, the questions in Major issues were answered individually. Our point-to-point responses to the individual comments are as follows.

Major issues: 1) I frequently was confused as to what data was being discussed – Knudsen cell or DRIFTS. Please be sure to make it clear which experimental technique was used to measure the data under discussion, particularly when data from both

C3727

techniques are discussed in the same sentence.

Response: It was improved in our revised manuscript. The methods used in experiment were added in abstract, text and Table 2 (added).

2) On a related note, the authors seem to assume, without any discussion, that the Knudsen cell and DRIFTS data are directly comparable. However, the two instruments operate under widely different pressure ranges, and also extremely different OCS reactant concentrations were used in the two experiments. [OCS] = 7 ppb for KCMS and 1000 ppm for DRIFTS yet there is NO discussion of this dramatic difference or the effect it might have on the uptake kinetics. This is really rather shocking. I realize that different concentrations are required for the two techniques, but the possible ramifications must be discussed. Reactant concentration has frequently been found to affect the uptake kinetics of reactant gases on mineral dust surfaces due to saturation effects (e.g. Hanisch and Crowley 2003; Sullivan et al. 2004). Furthermore, there should be a discussion of the comparability of the observed reaction probability between the two experiments for as similar as possible reaction conditions (e.g. zero water vapor). If such reactions have not been conducted they should and be included in the revised manuscript.

Response: We also have measured the effect of reactant concentration on the uptake coefficient using KCMS, and found that the lower concentration of OCS, the higher uptake coefficient (shown in follow). This can be ascribed to the saturation effect of reactive site by adsorption at higher concentration.

Figure. Effect of concentration of OCS on the observed uptake coefficients on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

However, in order to ensure a good signal-to-noise ratio (SNR), the concentration of OCS in KCMS experiment was chosen to be 7.0 ppb. In DRIFTS experiment, because the optical length in the reactor chamber was very short (~4 cm), 1000 ppm of OCS was chosen to gain a good SNR. In this paper, our purpose is to investigate the effect of water on the heterogeneous reaction of OCS on MgO and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. In KCMS

C3728

experiment, the concentration of OCS was kept to be 7.0 ppb, while it was kept to be 1000 ppm in DRIFTS measurement, and only the concentration of water (pressure or RH) was varied. Therefore, it is comparable between MgO and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for the effect of water on the reaction of OCS investigated with the same method. In our revised manuscript (Page 12503, line 21), we added a paragraph "It should be pointed out that in order to gain a good SNR, the concentration of OCS used in this study is higher than that in the troposphere. However, the concentration of OCS in KCMS or DRIFTS measurements was kept as a constant, and only the concentration of water (pressure or RH) was varied. Therefore, it is still comparable between MgO and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for the effect of water on the reaction of OCS with the same method. The results of this study will help for understanding the chemical cycle of OCS in the troposphere." to discuss this question.

On the other hand, we think it is very hard to compare the data obtained from different methods because of the different reaction conditions. Especially, even though no water was added into the reaction system, the uptake coefficient measured by KCMS was based on the reactive surface area of particle sample, while it was based on the geometric area for DRIFTS. Therefore, in our manuscript, we only compared the OCS uptake kinetics versus water concentration measured by the same method and did not directly compare the data obtained by KCMS and DRIFTS. The paragraph "On the other hand, it is very hard to compare the data obtained by KCMS and DRIFTS because of the different reaction conditions and different methods. Especially, even though no water was added into the reaction system, the uptake coefficient measured by KCMS was based on the reactive surface area of particle sample, while it was based on the geometric area for DRIFTS. However, it is comparable between MgO and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for the effect of water on the reaction of OCS with the same method and under the same reaction conditions." was added in our revised manuscript (Page 12495, line 23).

3) Only four water vapor mixing ratios were used to test the effect of water vapor on the

C3729

uptake kinetics measured by KCMS. Four conditions is the bare minimum to observe any significant trend. Given the shallow slope (Fig. 4) and scatter in the data more experiments at different conditions, over a wider range of water vapor (if possible) should be included.

Response: Because we must consider the concentration of OCS (diluted by 2.0 % OCS/N<sub>2</sub> with simulated air) to gain a good SNR, the portion of O<sub>2</sub>/N<sub>2</sub>, and the total pressure in the reactor ( $3.5 \times 10^{-4}$  Torr) to ensure a molecular flow state for Knudsen-cell reactor, the water vapor we used in Fig. 4 was the highest limit. Therefore, we can not perform the experiment at higher water vapor. As shown in Fig. 4, the trend is prominent even the uncertainty was considered.

4) It also does not appear that any of the experiments were ever repeated so there is no sense of the variability or reproducibility in the experimental data. Similarly, I did not see a discussion of how the measurement uncertainties were derived. Since the effect of water on the KCMS kinetics was small, the reaction probabilities should always be stated with their associated uncertainties, in the Abstract for example.

Response: The repeated experiments were performed and the relative standard derivation (RSD) for KCMS measurements is 9.50 %. (For example, the true uptake coefficients of OCS on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at initial state under one condition are:  $4.77 \times 10^{-7}$ ,  $3.81 \times 10^{-7}$ ,  $5.08 \times 10^{-7}$ ,  $4.16 \times 10^{-7}$ ,  $4.43 \times 10^{-7}$ ,  $4.25 \times 10^{-7}$  and  $4.39 \times 10^{-7}$ .) The RSD for DRIFTS measurements is 4.69 % ( $\gamma_{\text{obs}}$  measured by blank experiment is:  $2.78 \times 10^{-6}$ ,  $2.63 \times 10^{-6}$ ,  $2.75 \times 10^{-6}$ ,  $2.71 \times 10^{-6}$ ,  $2.73 \times 10^{-6}$ ,  $2.98 \times 10^{-6}$ , and  $2.58 \times 10^{-6}$ ). The uncertainties for these two methods were added in our revised manuscript. (Page 12488, line 19, and Page 12490, line 7). The uncertainties of these data were also added in revised manuscript.

5) Given the controversy and large differences in kinetics derived based on which surface area available for reaction is assumed, it is important that the authors always clearly state which surface area (geometric, BET, pore diffusion, etc.) they have used

C3730

to calculate the given reaction probability for a particular set of experiments.

Response: In KCMS experiments, BET area was used to calculate  $\gamma_t$ . A sentence “and BET area of sample was used to calculate  $\gamma_t$ .” was added in revised manuscript. (Page 12488, line 19) In DRITS experiments, geometric area of sample holder was used to calculate  $\gamma_{obs}$  because the probe depth of OCS into the particle samples is unknown. It was pointed out in Page 12495, lines 6-8. Additionally, according to the suggestions of reviewers, a table including uptake coefficients, vapor pressure, and methods was added in revised manuscript.

6) Different terms to discuss the water vapor mixing ratios used in the KCMS and DRIFTS experiments than “low” and “high” relative humidity should be used. These do not accurately reflect the several orders of magnitude difference in water vapor partial pressure used in the two experiments.

Response: The corresponding range of vapor pressure or RH were added in revised manuscript (Page 12484, line 8; Page 12498, lines 7-8; Page 12499, line 9; 12502, line 19, etc.)

7) The different effects of water on the kinetics for MgO and Al<sub>2</sub>O<sub>3</sub> in the KCMS and DRIFTS experiments need to be made clear. In KCMS gamma increased as water vapor partial pressure increased, while gamma decreased for Al<sub>2</sub>O<sub>3</sub>. However, at the high RH used in DRIFTS, gamma decreased with increasing RH for both surfaces, albeit by different degrees. I don't think that “liquid membrane” is the appropriate term for mineral particles surrounded by water. Membrane usually refers to a specific structure. Perhaps water coating or thick water layer could be used.

Response: Our results revealed that water restricts the heterogeneous reaction of OCS on Al<sub>2</sub>O<sub>3</sub>, while it promotes the reaction on MgO at low vapor pressure ( $<6.8 \times 10^{-6}$  Torr) (KCMS); and it restricts the reaction of OCS on both Al<sub>2</sub>O<sub>3</sub> and MgO at high water pressure (RH=0.07-0.67). The promoting effect was ascribed to the formation of surface hydroxyl on MgO, while the restrictive effect was found to be related to the

C3731

competitive adsorption between water and OCS on surface hydroxyl. In section 4.2, we discussed the reason in detail. The words “liquid membrane” was replaced with “thick water layer” in revised manuscript (Page 12502, lines 8-10; Page 12503, lines 3, 19).

8) A brief Table listing the reaction probabilities (instantaneous and steady-state) obtained from the two experiments and two surfaces for various conditions would be very useful.

Response: A table (shown as follow) was added in our revised manuscript. Table 2. Summary of uptake coefficients of OCS on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and MgO.

Method	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	MgO	P(H <sub>2</sub> O)(Torr) or RH	$\gamma_{Ini}$	$\gamma_{SS}$	P(H <sub>2</sub> O)(Torr) or RH	$\gamma_{Ini}$	$\gamma_{SS}$	
KCMS	2.81E-6	4.70±0.45E-7	7.20±0.68E-8	3.27E-6	5.19±0.49E-7	8.20±0.78E-8	3.58 E-6	4.07±0.39E-7	
		6.23±0.59E-8	4.71E-6	5.03±0.68E-7	1.53±0.15E-7	5.10 E-6	3.88±0.37E-7	4.08±0.39E-8	
		5.95E-6	6.51±0.62E-7	2.73±0.26E-7	5.83 E-6	3.59±0.34E-7	3.35±0.32E-8	6.83E-6	
		6.48±0.62E-7	2.49±0.24E-7	DRIFTS	b	0.07	7.38±0.35E-6	0.07	9.99±0.47E-5
		0.12	5.01±0.23E-6	0.12	9.04±0.42E-5	0.17	3.75±0.18E-6	0.17	8.97±0.42E-5
		0.22	3.29±0.15E-6	0.27	8.76±0.41E-5	0.27	3.53±0.17E-6	0.47	8.17±0.38E-5
		0.47	3.75±0.18E-6	0.67	7.95±0.37E-5	Note: a, BET area of sample was used to measure $\gamma_t$ in KCMS experiments; b, geometric area of sample holder was used to measure $\gamma_{obs}$ .			

9) The Discussion could often benefit if the specific experimental values being discussed were stated, rather than discussing them in relative terms. I have noted just a few such occasions below. The uptake kinetics derived from these experiments should be compared to those obtained from other systems to put the potential significance of this reaction for the atmospheric sink of OCS in perspective.

Response: This has improved in our revised manuscript. The results obtained by this study were compared with that reported in literature (Chen et al., Environ. Sci. Technol. 2007, 41, 6484-6490) and it was added in Page 12494, line 5

C3732

Specific comments: 10) p. 12486 line 5: these References are not appropriate for typical tropospheric RH, but no Reference is really required for these values.

Response: These references were deleted in our revised manuscript. (Page 12486, line 5 and page 12504 lines 21-24)

11) p. 12493, line 2, this sentence is difficult to follow: "These contrary phenomena could be explained by the differential signals detected by QMS in the flow system and the integrated signal of DRIFTS in the closed system; however, the characteristic absorption band of -SH was also not observed."

Response: This paragraph was rewritten as "These contrary phenomena could be explained by the different ways for data collection. Differential signals were measured by QMS in the flow system; while integrated signal were measured by DRIFTS in the closed system. It should be pointed out that the characteristic absorption band of -SH was also not observed on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>" in our revised manuscript (Page 12493, lines 2-4).

12) p. 12493: How do the product concentrations differ for the two surfaces as a function of temperature? Does MgO produce more H<sub>2</sub>S per reactant?

Response: As shown in Figure 3c and 3d, the concentration of H<sub>2</sub>S produced by reaction of OCS over MgO is higher than that over Al<sub>2</sub>O<sub>3</sub> (the slope of H<sub>2</sub>S concentration with temperature on MgO is higher than that on Al<sub>2</sub>O<sub>3</sub>), while there is no difference for the yield of H<sub>2</sub>S (H<sub>2</sub>S produced per reactant) over these two oxides.

13) p. 12496: Additionally, H<sub>2</sub>S and CO<sub>2</sub> were observed as the gaseous products for the catalytic hydrolysis of OCS on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at ambient temperature (Rhodes et al., 2000; West et al., 2001). Therefore, we conclude that, similar to reaction on the surface of MgO, heterogeneous hydrolysis of OCS on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> also occurs at ambient temperature." This is confusing and misleading, it sounds as though you observed the H<sub>2</sub>S and CO<sub>2</sub> products from reactions on Al<sub>2</sub>O<sub>3</sub> but you are citing other work. Make it clear that these are not your results by saying "Work by Rhodes et al.

C3733

(2000) and West et al. (2001)..." or similar, and make it clear which products were observed in YOUR experiments.

Response: We deleted the sentence "Additionally, H<sub>2</sub>S and CO<sub>2</sub> were observed as the gaseous products for the catalytic hydrolysis of OCS on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at ambient temperature (Rhodes et al., 2000; West et al., 2001)" (Page 12496, lines 19-21) in our revised manuscript to avoid the misunderstanding. The corresponding references were also deleted (Page 12506, lines 25-27; Page 12507, lines 22-23).

14) p. 12497, lines 19-25: Give the rate constants when comparing the results. Could the desorption rate be determined?

Response: The apparent reaction rate constant (k<sub>h</sub>) of OCS on MgO is 0.21 s<sup>-1</sup>, while k<sub>h</sub> on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is 0.080 s<sup>-1</sup>. This sentence was added in our revised manuscript (Page 12497, lines 20-22). At low temperature (< 250 K), we can determine the desorption rate and have published a paper on J. Phys. Chem. A (Liu et al., 2008, 112, 2820-2826). However, when the temperature is higher than 250 K using our system, the effect of heterogeneous reaction on desorption becomes very significant and leads to a very bad fitting results (see the paper J. Phys. Chem. A, 2008, 112, 2820-2826).

15) p. 12500, lines 22-25: Can you estimate the concentration of surface groups (A) on the two surfaces in your experiments?

Response: We want, but can not estimate the absolute concentration of surface hydroxyl group based on our current experiments.

16) p. 12501, lines 16-18: Give the values reported by Goodman et al. The differences between their and your results should not be discounted so quickly. The preparation and state of the surfaces used in these types of reactions has a large impact on the measured kinetics. If such a large difference for water adsorption exists between your and previous work, further investigation is required.

Response: Goodman et al.(2001) measured the RHML of water on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and MgO

C3734

to be 0.17 and 0.23, respectively. These values are lower than our results. The difference might be due to the different sample origins. It also should be pointed out that Goodman et al measured the RHML by using a vacuum reactor in which the sample can be cleaned under  $10^{-7}$  Torr, while it was performed under ambient pressure in this study. Therefore, the surface cleanliness of the samples may also contribute to this difference. The above paragraph was added in our revised manuscript (Page 12501, lines 16-18).

17) p. 12502, line 7: what does “typical relative humidity” mean, what RH value are you referring to? This term is frequently used later in the manuscript as well.

Response: It means “atmospherically relevant humidity”. In our revised manuscript, we have replaced it with atmospherically relevant humidity (Page 12502, line 7). It is 0.20-0.90. This value was mentioned in Page 12486, line 5.

18) p. 12502, lines 24-30: How did MgO behave at “low” RH?

Response: At low water vapor pressure ( $<6.8 \times 10^{-6}$  Torr), the uptake coefficients of OCS on MgO increased with increases in water vapor pressure in the feed gas due to the formation of surface hydroxyl groups. This paragraph was shown in Page 12502, lines 18-20.

19) p. 12503, line 19: state the RH(ML).

Response: It means the RH when one monolayer of water formed on the surface of the oxide. This symbol was defined in revised manuscript (Page 12501, line 15). 20) Technical corrections: There are several grammatical or syntax errors, including: p. 12484, line 14: “corresponding” not “which corresponding” p. 12486 line 11: “gas” not “gases” p. 12492 line 2: “literature” not “literatures” p. 12493, line 16: “data” not “date” p. 12503, line 4: atmosphere” not “atmospheric” Figure 3: List the ions being measured at the three m/z ratios. Figure 8: State what instrument the uptake coefficients were measured in.

C3735

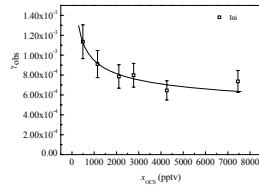
Response: These errors were corrected in revised manuscript. Figure 8: “measured by DRIFTS” was added in revised manuscript.

Please also note the Supplement to this comment.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 12483, 2009.

C3736



Effect of concentration of OCS on the observed uptake coefficients on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

1

**Fig. 1.** Effect of concentration of OCS on the observed uptake coefficients on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

C3737

Table 2. Summary of uptake coefficients of OCS on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and MgO.

Method	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>		MgO	
	$P(\text{H}_2\text{O})$ (Torr) or RH	$\gamma_{\text{obs}}$	$P(\text{H}_2\text{O})$ (Torr) or RH	$\gamma_{\text{obs}}$
KCMS <sup>a</sup>	2.81E-6	4.70±0.45E-7	3.27E-6	5.19±0.49E-7
	3.88 E-6	4.07±0.39E-7	4.71E-6	5.03±0.68E-7
	5.10 E-6	3.88±0.37E-7	4.08±0.39E-8	5.95E-6
	5.83 E-6	3.59±0.34E-7	3.35±0.32E-8	6.83E-6
	0.07	7.38±0.35E-6	0.07	9.99±0.47E-5
DRIFTS <sup>b</sup>	0.12	5.01±0.23E-6	0.12	9.04±0.42E-5
	0.17	3.75±0.18E-6	0.17	8.97±0.42E-5
	0.22	3.29±0.15E-6	0.27	8.76±0.41E-5
	0.27	3.53±0.17E-6	0.47	8.17±0.38E-5
	0.47	3.75±0.18E-6	0.67	7.95±0.37E-5

Note: a, BET area of sample was used to measure  $\gamma_i$  in KCMS experiments; b, geometric area of sample holder was used to measure  $\gamma_{\text{obs}}$ .

1

**Fig. 2.** Summary of uptake coefficients of OCS on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and MgO

C3738