Interactive comment on "Comparative study of the effect of water on the heterogeneous reactions of carbonyl sulfide on the surface of α-Al_2O_3 and MgO" by Y. Liu et al.

Y. Liu et al.

We thank Referee #2 for the comments on our manuscript and for the positive overall evaluation. Our point-to-point responses to the individual comments are as follows.

1) Abstract, 1st sentence: the authors indicate that they consider OCS uptake on minerals as a "new" sink to OCS in the troposphere. However, this theory is not new, because it has been shown by this group in the past to be a potential sink for OCS, even under dry conditions. This is misleading and I recommend leaving this first sentence in the abstract out.

Response: According to your suggestion, the first sentence in the abstract (Page 12484, lines 1-2) was deleted to avoid the misunderstanding.

2) I am not completely convinced that there are trends in the gamma values obtained using the KCMS with RH. There are only very small increases/decreases in gamma upon increasing RH and there is no indication of the uncertainty in these measurements to prove that the trends do indeed occur. For example, the gamma for

OCS on Al_2O_3 decreases from $4.70x10^{-7}$ to $3.59x10^{-7}$. These values differ only by $1.11x10^{-7}$. Thus, a very careful evaluation of measurement uncertainty is warranted. In addition, there should be some mention regarding the detection limits of the two methods and how they were determined.

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 α-Al_2O_3 at initial state under one condition are: 4.77×10^{-7}, 3.81×10^{-7}, 5.08×10^{-7}, 4.16×10^{-7}, 4.43×10^{-7}, 4.25×10^{-7} and 4.39×10^{-7}.) The RSD for DRIFTS measurements is 4.69 % (γ_{obs} measured by blank experiment is: 2.78×10^{-6}, 2.63×10^{-6}, 2.75×10^{-6}, 2.71×10^{-6}, 2.73×10^{-6}, 2.98×10^{-6}, and 2.58×10^{-6}). The uncertainties for these two methods were added in our revised manuscript. (Page 12488, line 19, and Page 12490, line 5). The detection limit of γ_t is estimated by the 2σ of blank experiment. However, the detection limit of γ_t depends on the specific surface area of particle samples and the probe depth of OCS. The detection limit for γ_t on α-Al_2O_3 and MgO used in this study are 4.2×10^{-8} and 3.7×10^{-8}, respectively. The detection limit of γ_{obs} for DRIFTS is also determined by the 2σ of blank experiment and is 2.57×10^{-8}. Therefore, although the decrease of γ with vapor pressure is very small, the difference (1.11×10^{-7}) is larger than the uncertainty for KCMS measurements.

3) I agree with Reviewer 1, in that the discussion of results as well as the summary of results in the abstract is often vague as to which method was used. Please clarify in

the abstract as well as throughout the manuscript precisely what method was used to determine the uptake coefficients discussed.

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

4) The authors indicate that they used the BET surface area of the minerals to account for adsorption on the underlying sample layers and microstructure in the KCMS studies. However, they did not perform a mass study. Considering that the sample masses used in the KCMS studies were rather large, I suggest performing a mass study that will allow for a more accurate determination of whether the OCS does indeed access all of the mineral surfaces within the time scale of the KCMS measurement, or if it only accesses the top most layers. In any case, the use of the BET surface area may over estimate the amount of accessible surfaces and thus the gamma determined this way should be considered a lower limit. Additionally, for the DRIFTS gamma measurements, the authors use the geometric surface area of the sample holder because they do not know if the OCS accesses the entire surface area of the sample. However, there is no discussion about the implications of the use of this surface area on their results. For example, even if only the top layer of particles were available for reaction, the microstructure of the particles in the top layer may give a higher surface area than just assuming a flat layer (SAgeom). Thus, the gamma obtained using this SA should be considered an upper limit. Some discussion regarding the choice of surface area and implications of that choice should be

included in the manuscript.

Response: It is correct that the observed uptake coefficient depends on the sample mass in a certain range. In our previous work, we have measured the linear range for the observed uptake coefficient of OCS on α-Al_2O_3 to be 0-70 mg (Liu et al., 2008b), and 0-100 mg on MgO (Liu et al, 2008a). In this study, we kept the sample mass to be 70 mg for α-Al_2O_3 and 90.0 mg for MgO to ensure OCS molecules accessing all of the layers of particle samples within the time scale of the KCMS measurement. We added this paragraph (blue color) in our revised manuscript (Page 12488, line 19). As for the surface area for γ_{obs} calculations in the DRIFTS experiments, we also added a few sentences to discuss the limit of our results in our revised manuscript (Page 12495, line 8). It is "As mentioned in 2.3.1, OCS molecules can access the sub-layers for the multi-layer particle samples. However, because the probe depth for OCS molecules in the powder samples could not be obtained in the DRIFTS experiments, the geometric area of the sample holder (0.20 cm^2) was used. Thus, the γ_{obs} obtained using this geometric area should be considered as an upper limit. It should be pointed out that the trend between γ_{obs} and *RH* should be the same as that between γ_t and *RH*."

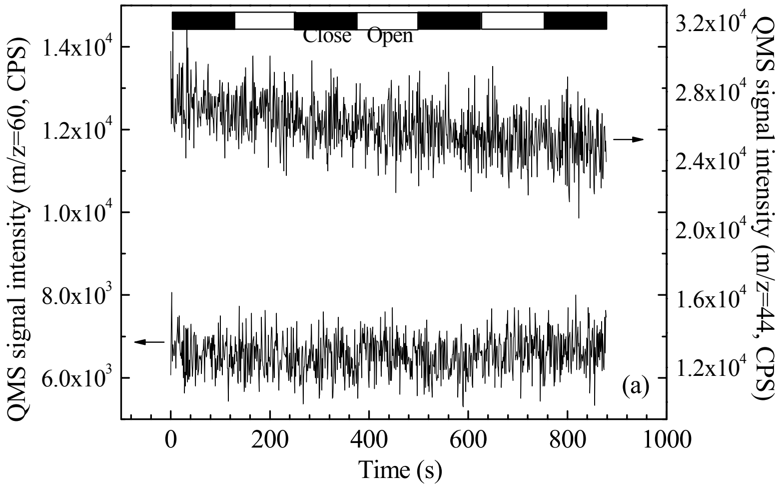
5) 67

Response: We do not understand the meaning of this number. So, no response for this question.

6) I do not see any comments regarding a correction for wall loss of OCS on the

KCMS and DRIFTS measurements. Was this accounted for, and if so, was it negligible? Please include a discussion of the detection limits based on blank measurements.

Response: In KCMS experiment, all exposed interior surfaces of the Knudsen-cell chamber and the surface of the sample holder were coated with Teflon to provide a chemically inert surface. A blank experiment revealed that there was no uptake of OCS by the sample holder under our experiment conditions. Therefore, the wall loss of OCS on the KCMS measurements is negligible. This paraphrase was added in the revised manuscript (Page 12488, line 19).



Blank experiment for Knudsen-cell reactor.

However, in DRIFTS experiment, as shown in Figure 5b and 6b, the γ_{obs} for OCS on the surface of blank reactor is $2.74\pm0.13\times10^{-6}$, it can not be neglected. The quasi first-order reaction can be described as,

$$-\frac{dc}{dt}=k_r c+k_s c=k_{obs} c \quad (1)$$

where k_r and k_s is the first-order rate constant on the surface of blank reactor and samples, respectively; k_{obs} is the observed first-order rate constant. Therefore, k_s can be obtained by subtracting k_r from k_{obs}. The observed uptake coefficients on the sample can also be obtained like this. We have accounted for this in our manuscript (Page 12495, lines 18-21). The detection limit of γ_{obs} for KCMS is 1×10^{-4} which is estimated by the 2σ of blank experiment. The detection limit for γ_t on α-Al_2O_3 and MgO used in this study are 4.2×10^{-8} and 3.7×10^{-8}, respectively. The detection limit of γ_{obs} for DRIFTS is also determined by the 2σ of blank experiment and is 2.57×10^{-8}.

7) Please note on Page 12488, line 1 what m/z values were monitored for OCS. In addition, it should be noted the time scale in which the initial gamma was determined from the KCMS and DRIFTS measurements. It is mentioned that 100 scans were collected for each DRIFTS measurement, which would take a very long time compared to the KCMS measurements. Some discussion regarding the use of the DRIFTS measured gamma for an initial uptake coefficient should be included based on the widely different timescales of the two measurements.

Response: For OCS, m/z=60 was monitored. This value was added in the revised manuscript (Page 12488, line 1). The timescale for every spectrum in DRIFTS measurement is 1 min, and the timescale for kinetic parameter evaluation is around 10 min. This value is much longer than that for KCMS measurement. Therefore, the observed uptake coefficient measured with DRIFTS represents the steady state, but not the initial state. This paraphrase was added in the revised manuscript (Page 12495, line 23).

8) It is also not mentioned within the manuscript about whether there was a calibration of OCS with the MS done. How did the authors perform this calibration?

Response: The cylinder gas (Standard gas, 2% OCS/N_2, Scott Specialty Gases Inc.) was used in this study. We have calibrated the MS signal of OCS in intensity with the partial pressure of OCS in the Knudsen-cell reactor. A good linear relationship was observed between the MS signal of OCS and its partial pressure.

9) Please include more detail as to how the OCS concentration was calibrated for the DRIFTS measurements (Page 12490, line 2).

Response: The concentration was diluted by the standard gas of OCS with simulated air (21 % O_2 and 79 N_2). The flow was precisely controlled by mass flow controller. The concentration of OCS in the mixture gas has been calibrated by the integrated area of gaseous OCS (He et al, Environ. Sci. Technol., 2005, 39, 9637-9642). The word "as described in our previous work (He et al, 2005)" was added in our revised manuscript (Page 12490, line 2).

10) When reporting the vapor pressure of water in the KCMS measurements, some idea of the resulting RH should be given as well. For example, what RH occurs at a water vapor pressure of $2.5\text{x}10^{-6}$ Torr?

Response: In the Knudsen cell chamber, we think it is more reasonable to directly give the partial pressure of water vapor because the low pressure must be kept. For example, the $RH(P/P_0)$ is 9.4 $\text{x}10^{-8}$ at a water vapor pressure of $2.5\text{x}10^{-6}$ Torr. If the molar fraction is considered, the molar fraction of water in KCMS reactor is 0.73 % -1.99 %, and is in the range of atmospheric value (0.70%-3.15%).

11) A table of gamma values determined using both methods would be very helpful in hashing out what values came from what method.

Response: A table was added in our revised manuscript.

Table 2. Summary of uptake coefficients of OCS on α-Al_2O_3 and MgO.

Method	α-Al_2O_3			MgO		
	$P(H_2O)$(Torr) or RH	γ_{Ini}	γ_{SS}	$P(H_2O)$(Torr) or RH	γ_{Ini}	γ_{SS}
KCMS [a]	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 γ_t in KCMS experiments; b, geometric area of sample holder was used to measure γ_{obs}.

12) Page 12495, Line 1: The authors state that the concentration of the feed gas was held at 1000 ppm OCS. Is this the concentration of OCS in the DRIFTS measurements? There is no mention of the concentration of OCS, besides the partial pressure, in the KCMS measurements. Please add the corresponding concentration of OCS to Page 12491, line 6 for comparison. Also, 1000 ppmv is very high compared to the concentration of OCS in the troposphere. Some discussion regarding the relevance

of the concentrations of OCS used in the KCMS and DRIFTS measurements should be included as well as the potential implications of measurements at these concentrations.

Response: Yes, 1000 ppm of OCS is the concentration of OCS in the DRIFTS measurements (Page 12489, line 27). In the KCMS measurements, the concentration of OCS is 7.0 ppb and was given in Page 12488, line 4. We also add this value in our revised manuscript (Page 12491, line 6). 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. Although the concentration of OCS used in this study is higher than that in the troposphere, the concentration is held at a constant value, and only the concentration of water (pressure or RH) was varied. Therefore, it is comparable between MgO and Al_2O_3 for the effect of water on the reaction of OCS with the same method. The 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 α-Al_2O_3 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." was added in our revised manuscript (Page 12503, line 21).

13) Page 12496, Line 5-6: The sentence stating "the hydrolysis pathway has not been

elucidated due to the absence of reaction products such as H_2S" is confusing. Are you trying to say that previous measurements have not measured H_2S as a reaction product? Please clarify.

Response: Yes, we mean that previous measurements have not measured H_2S as a reaction product. In our revised manuscript, we rewrote this sentence as "the hydrolysis pathway has not been elucidated because previous measurements have not measured H_2S as a reaction product." (Page 12496, line 6).

14) Page 12496, Lines 11-12: Did the authors scan the entire mass spectrum to see if any other reaction products occurred in the gas phase? That is, they mention that gaseous SO_2 could be a reaction product. Did you see SO_2 in the mass spectrum?

Response: In our previous work (Liu et al., J. Phys. Chem. A, 111, 4333-4339, 2007), we scanned the entire mass spectrum and detected the gaseous SO_2 as a reaction product using a mass spectrometer at high concentration of OCS. We added the reference in revised manuscript (Page 12496, line 12).

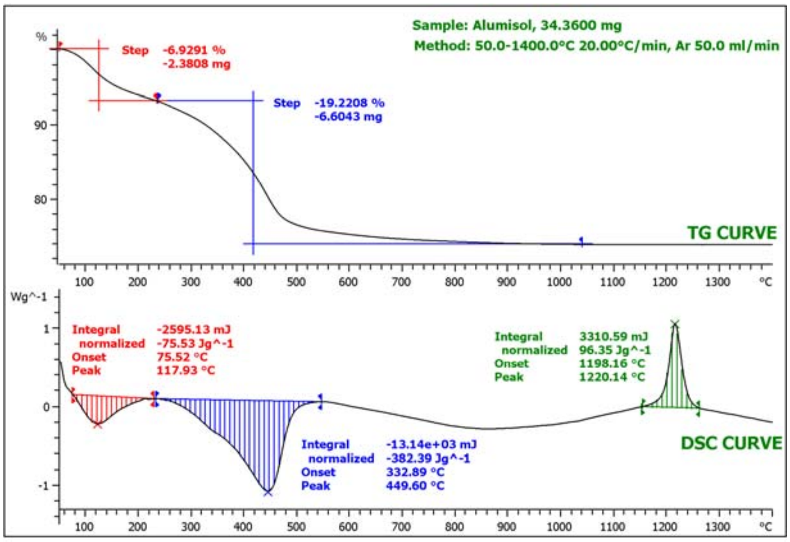
15) Page 12499: A clearer connection needs to be drawn between your work and the previously reported results.

Response: It was improved in revised manuscript (Section 4.2).

16) Does heating the sample have any effect on the uptake of OCS? Did the authors investigate the effects of sample heating? This could be important considering that the

samples were heated to rather high temperatures during "pretreatment". Was the sample completely dehydroxylated? If so, how does the reaction occur under dry conditions with no surface –OH groups? A closer investigation of the effects of pretreatment could help nail down the reaction pathway. On page 12501, the authors state that their ML coverages occurred at higher RH values than were previously reported. Could this also be due to pretreatment effects? Also, the authors indicate that significant uptake of OCS still occurred (higher than the background value) at RH values of 0.47 to 0.67 on Page 12501, Line 24. Some discussion regarding surface sites available for uptake should be discussed. For example, it could be that not all of the surface OH sites were consumed by adsorbed water. Instead, as some previous studies (Baltrusaitis et al., 2007) have found that there are adsorbed water islands. That is, water is not adsorbed according to they hypothetical ML, but rather in islands such that some surface adsorption sites are still available for reaction by OCS.

Response: In order to clean the surface of samples, the oxide samples were heated gently in air before experiment to desorb surface impurity such as water and organic compounds. The pretreatment temperature was kept at 323 K in KCMS experiment, and it was 573 K in DRIFTS experiment. In our previous work, we have investigated the effect of pretreatment temperature on the heterogeneous reaction of OCS on Al_2O_3 and found that higher pretreatment temperature leads to the lower reactivity (Liu et al., J. Phys. Chem. B, 2006, 110, 3225-3230). Therefore, we did not perform the effect of pretreatment temperature on the reaction in this study. As we known, even in DRIFTS experiments in this study, the pretreatment of sample at 573 K could only lead to partial dehydroxylation of the sample. For example, the following figure shows the thermal gravity (TG) of boehmite. When temperature is lower than 523 K, the loss of weight mainly originates from the desorption of water. At 573 K, only a part of surface hydroxyl lost and contributes to the weight loss. Therefore, the samples used in this study were not completely dehydroxylated. The consumption of surface hydroxyl (Fig. 2) during reaction also suggests that hydroxyl group remains on the surface.



The RH_{ML} measured in this study is higher than the value in literature. We think that pretreatment method may also contribute this difference. We have added this reason in our revised manuscript (Page 12501, lines 16-18). As for the surface sites available for uptake, a paragraph "Additionally, it could be noted that not all of the surface OH sites were consumed by adsorbed water. Instead, as some previous studies (Baltrusaitis et al., 2007) have found that there are adsorbed water islands. That is, water is not adsorbed according to the hypothetical monolayer, but rather in islands such that some surface adsorption sites are still available for reaction by OCS." was added in revised manuscript (Page 12502, line 9).

17) Page 12502, Line 7: What do you mean specifically by "At the typical relative humidity: : :"

Response: It means at atmospherically relevant humidity. It was revised in our manuscript. (Page 12502, line 7)

18) Page 12503, Atmospheric implications: Can you give some idea of what the lifetime of OCS is in the troposphere with respect to heterogeneous loss on mineral surfaces at different RH values and compare this lifetime to other loss processes in the troposphere. Your results should be considered more carefully with respect to whether it truly is significant loss mechanism in the troposphere. See Frinak et al., 2004 for the calculation.

Response: In our previous work (Liu et al, Atmos. Environ. 2008, 42, 960-969), we have estimated the consumption of OCS by mineral oxide should be 0.11-0.64 Tg/year based on the true uptake coefficient of α-Al_2O_3 and without considering the *RH*. The lifetime was estimated to be ~3 years in this case. However, the RH in Knudsen cell reactor in this study is $\sim 10^{-8}$ and much lower than the atmospherically relevant RH (0.20-0.90); on the other hand, the data obtained by DRIFTS was calculated by geometric area. Therefore, it is hard to estimate the variation of the lifetime of OCS with RH based on our current work. And in this paper, we only mainly discussed the effect of water on the heterogeneous reaction of OCS on mineral oxide.

19) Figure 3: Please label each according to what species is being monitored.

Response: According to this suggestion, the corresponding species were labeled in Figure 3.

20) Figures 4, 5, 6, 8, and 9: Please give some indication of the uncertainty in your measurements. Error determination is critical to interpretation of your results.

Response: In Figs. 4, 5, 6 and 8, the RSD was given in revised manuscript. And the figures with error bar were replaced in revised manuscript. However, in Fig. 9, the RSD can not be gained because these points were measured in a dynamic experiment for adsorption of water on oxides and it can not be repeated in one experiment.

One reference was added in page 12504, line 20.

Baltrusaitis, J., Schuttlefield, J., Jensen, J. H., Grassian, V. H. FTIR spectroscopy combined with quantum chemical calculations to investigate adsorbed nitrate on aluminum oxide surfaces in the presence and absence of co-adsorbed water, Phys. Chem. Chem. Phys., 2007, 9, 4970 – 4980.