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Comparative study of the effect of water on the heterogeneous reactions of carbonyl sulfide on the surface of α-Al_2O_3 and MgO

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Abstract. Here we compared the heterogeneous reactions of carbonyl sulfide (OCS) on the surface of α-Al_2O_3 and MgO and the effect of water on the reactions at 300 K using Knudsen cell – mass spectrometry, diffuse reflectance infrared Fourier transform spectroscopy, and temperature programmed reactions. H_2S and CO_2 were found to be hydrolysis products of OCS on both α–Al_2O_3 and MgO at ambient temperature. At low water vapor pressure ($<6.8\times10^{-6}$ Torr), when water vapor pressure in the Knudsen cell reactor increased from 2.3×10^{-6} to 6.8×10^{-6} Torr, the initial true uptake coefficient of OCS on α-Al_2O_3 decreased from $4.70\pm0.45\times10^{-7}$ to $3.59\pm0.34\times10^{-7}$; while it increased from $5.19\pm0.49\times10^{-7}$ to $6.48\pm0.62\times10^{-7}$ on MgO under the same conditions. At high relative humidity (0.07–0.67), the observed uptake coefficients of OCS on α-Al_2O_3 and MgO, which were measured using an in situ DRIFTS, decreased from $4.63\pm0.22\times10^{-6}$ to $1.00\pm0.47\times10^{-6}$ and from $9.72\pm0.46\times10^{-5}$ to $7.68\pm0.36\times10^{-5}$, respectively, when RH increased from 0.07 to 0.67 corresponding to 1.7–15.9 Torr of water vapor pressure. In the RH region of 0.17–0.67, the average observed uptake coefficient of OCS on α-Al_2O_3 and MgO was equal to $8.34\pm2.19\times10^{-7}$ and $8.19\pm0.48\times10^{-5}$, respectively. The restrictive effect of water on the heterogeneous reaction of OCS on the surface of α-Al_2O_3 and MgO was found to be related to competitive adsorption between water and OCS molecules; while the promotive effect of water on the heterogeneous reaction of OCS on the surface of MgO at low coverage was ascribed to the formation of surface hydroxyl groups. When the environmental RH was greater than the RH of the monolayer, which occurred readily at the atmospherically relevant humidity in the troposphere, thick water layer formed on the mineral dusts, especially, the basic thick water layer formed on the basic component of mineral dusts may be the primary contributor to the heterogeneous hydrolysis of OCS in the troposphere.

1 Introduction

Carbonyl sulfide (OCS) is the most abundant sulfur compound in the atmosphere and, in the troposphere, has a rather uniform mixing ratio of approximately 500 pptv (Watts, 2000). The oxidation of OCS in the stratosphere is an important source of stratospheric sulfate aerosol (SSA) during non-volcanic periods (Crutzen, 1976; Engel and Schmidt, 1994; Turco et al., 1980). SSA plays an important role in the Earth's radiation balance (Andreae et al., 1997; Craf, 2004; Turco et al., 1980) and stratospheric ozone chemistry (Solomon et al., 1993). Therefore, much interest has been drawn to the sources and sinks of OCS. In particular, it is important to investigate the tropospheric sinks of OCS because these sinks are not only related to the source of SSA but also to the global chemical cycle of OCS in the atmosphere.

Oxic soils, vegetation, photolysis, and oxidation by ·OH and ·O are the primary sinks of OCS in the atmosphere (Kettle et al., 2002; Montzka et al., 2007; Watts, 2000). In past decades, heterogeneous reactions of trace gases on atmospheric particulate matter (APM) have received much attention. Several atmospheric modeling studies have shown that APM often acts as a sink for certain species (Dentener et al., 1996; Jacob, 2000; Usher, 2003b). Mineral dust, which mainly originates from arid and semi-arid regions having a

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global source strength of ∼1000–3000 Tg year^{-1} (Dentener et al., 1996), is one of the most important contributors to the loading of APM. Recently, a few studies demonstrated that heterogeneous reactions of OCS can occur on APM, and on mineral oxides including Al_2O_3, SiO_2, Fe_2O_3, CaO, MgO, MnO_2 and the mixture of Fe_2O_3 and NaCl under ambient conditions (Chen et al., 2007; He et al., 2005; Liu et al., 2006, 2007a, b; Wu et al., 2004, 2005). Although the same intermediate (i.e. hydrogen thiocarbonate, $HSCO_2^-$) was observed, the pathways of heterogeneous reactions of OCS still require further study. For example, some researchers have proposed a heterogeneous oxidation mechanism (Chen et al., 2007; He et al., 2005; Liu et al., 2006; Wu et al., 2004, 2005), while recently we found that heterogeneous hydrolysis of OCS can also occur on MgO (Liu et al., 2007a). Nonetheless, information on the kinetics of the heterogeneous reaction of OCS on mineral oxides is limited. We recently reported uptake coefficients of OCS on MgO (Liu et al., 2008a), α-Al_2O_3 and γ-Al_2O_3 (Liu et al., 2008b). All of these studies were performed under dry conditions. However, the atmospherically relevant relative humidity ($RH=P/P_0$, where P_0 is the saturated vapor pressure of liquid water) in the troposphere is between 0.20 and 0.90. The presence of adsorbed water undoubtedly plays a vital role in the heterogeneous reaction of trace gases, such as HNO_3, O_3 and SO_2 etc., on mineral dust (Al-Abadleh et al., 2005; Roscoe and Abbatt, 2005). Nevertheless, the affect of water on the reaction mechanism and kinetics of OCS on mineral dust remains uncertain.

$\alpha-Al_2O_3$ and MgO are typical constituents of mineral dust and are widely used as model oxides for the study of trace gas heterogeneous reactions. In this work, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Knudsen cell mass spectrometry (KCMS), and temperature-programmed reactions (TPR) were used to investigate the effect of water on the heterogeneous reactions of OCS on α-Al_2O_3 and MgO. Our results demonstrate that catalytic hydrolysis of OCS can take place on the surface of both α-Al_2O_3 and MgO under ambient conditions and that adsorbed water on mineral dust influences this reaction greatly. The mechanism and the atmospheric implications for the effect of water on the heterogeneous reactions of OCS on mineral oxides are also discussed.

2 Experimental methods and data evaluation

2.1 Materials

The α-Al_2O_3 sample was prepared from boehmite (AlOOH, supplied by Shandong Alumina Corporation) by calcining at 1473 K. The MgO sample (A. R.) used in this experiment was supplied by the Haizhong Chemical Plant in Tianjin. All other chemicals were used without further purification. These included: Carbonyl sulfide (OCS, 2%, OCS/N_2, Scott Specialty Gases Inc.), N_2 and O_2 (99.999% purity, Beijing AP BEIFEN Gases Inc.), and C_2H_5OH (99.7%, Beijing Chemicals Factory).

2.2 Characterization of samples

The X-ray powder diffraction pattern was collected from 10 to 90° 2θ on a D/max-RB automatic powder X-ray diffractometer using Cu Kα irradiation. The Al_2O_3 sample calcined at 1473 K was identified as α-Al_2O_3 with the three main peaks at 35.0°, 43.0°, 57.0°, and the MgO sample was identified to be periclase with the three main 2θ peaks at 42.9°, 62.3°, and 78.6°.

Nitrogen Brunauer-Emmett-Teller (BET) physisorption measurement was performed using a Micromeritics ASAP 2000 automatic instrument. The specific surface area of α-Al_2O_3 and MgO samples was measured to be 12.0 $m^2\,g^{-1}$ and 14.6 $m^2\,g^{-1}$, respectively.

2.3 Experimental methods

2.3.1 KCMS experiments

A homemade Knudsen cell–mass spectrometer, described in detail elsewhere (Liu et al., 2008a, b), was used to measure the uptake coefficients of OCS at low water vapor pressures in the reactor. Briefly, the particle samples were dispersed evenly on a sample holder with alcohol and then dried at 393 K for 2 h. The pretreated samples and reactor chamber were evacuated at 323 K for 6 h to reach a base pressure of approximately 5.0×10^{-7} Torr. The sample cover was closed after the system was cooled to 300 K. OCS (1.51%) balanced with simulated air (21% O_2 and wet 79% N_2) in which the water vapor was introduced through a saturated water generator by a N_2 stream, was introduced into the reactor chamber through a leak valve. The RH in the feed gas was controlled by the ratio of dry air to wet N_2 and was measured using a hygrometer (Center 314) with a relative error of ±1.5%. Prior to the uptake experiments, the system was passivated with the feed gas for 150 min until a steady-state of quadrupole mass spectrometer (QMS) signal of OCS (m/z=60) established as the sample was isolated from the gas by the sample cover. Uptake of OCS on all samples was performed with an average OCS partial pressure of $5.3\pm0.3\times10^{-6}$ Torr, which is equivalent to $1.7\pm0.2\times10^{11}$ molecules cm^{-3} or 7.0 ± 0.3 ppb.

For steady-state uptake, the uptake coefficients at different water vapor pressures were calculated using the Knudsen cell equation (Underwood, 2000):

$$\gamma_{obs}=\frac{A_h}{A_g}\frac{(I_0-I)}{I} \tag{1}$$

where γ_{obs} is the observed uptake coefficient, A_h is the effective area of the escape aperture (m^2), A_g is the geometric area of the sample holder (m^2), and I_0 and I are the mass spectral intensities with the sample holder closed and open, respectively. The effective area of escape aperture, A_h, was measured according to previously described methodology (Liu et al., 2008a, b). As for multilayer powder samples, to consider the contribution of underlying layers of sample to the uptake coefficient, the true uptake coefficient, γ_t, was calculated from:

$$\gamma_t = slope \cdot \left(\frac{A_s}{S_{\mathrm{BET}}}\right) \tag{2}$$

where *slope* is the slope of the plot of γ_{obs} versus the sample mass in the linear region (kg^{-1}), A_s is the geometric area of the sample holder (m^2), and S_{BET} is the specific surface area of the particle sample ($\mathrm{m}^2\,\mathrm{kg}^{-1}$) (Liu et al., 2008a, b; Underwood et al., 2000, 2001). 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 to be 0–100 mg on MgO (Liu et al., 2008a). In this study, we kept the sample mass to be 70.0 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, and BET area of sample was used to calculate γ_t. The relative standard derivation (RSD) for the uptake coefficients was measured to be 9.50% for repeated experiments. In the Knudsen-cell reactor, all exposed interior surfaces 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.

2.3.2 TPR experiments

The instantaneous experiments for the heterogeneous reaction of OCS on mineral oxides were performed with a TPR apparatus. This apparatus consists of a temperature-programmed tube oven and a QMS (Hiden HPR20). One quartz tube was used as a sample tube, and another was used as a by-pass tube. The powder samples with 20–40 meshes (0.5 g) in the sample tube were pretreated in 100 mL min^{-1} of simulated air at 573 K for 1 h. After the sample cooled to room temperature (r. t.), the two ends of the sample tube were closed, and 1000 ppmv of OCS in simulated air with a total flow rate of 100 mL min^{-1} was introduced into the by-pass tube. The mass channels including *m/z*=60 (OCS), 44 (CO_2), and 34 (H_2S) were monitored online with the QMS. Until the steady-state of QMS signal intensity was established, the feed gas was shifted between the sample and by-pass tubes several times. Then, the TPR experiment was performed at 20 K min^{-1} from r. t. to 430 K as the feed gas passed through the sample tube.

2.3.3 DRIFTS experiments

The apparent reaction rate constants at high RH for the heterogeneous reactions of OCS on α-Al_2O_3 and MgO were measured with a DRIFTS reactor in a closed system. In situ DRIFTS spectra were recorded on a NEXUS 670 (Thermo Nicolet Instrument Corporation) Fourier transform infrared spectrometer (FTIR) equipped with an in situ diffuse reflection chamber and a high sensitivity mercury cadmium telluride (MCT) detector cooled by liquid N_2. The infrared spectra were collected and analyzed by a computer with OMNIC 6.0 software. All spectra reported here were recorded at a resolution of 4 cm^{-1} for 100 scans. The volume of the reactor chamber in the closed system was 30 mL.

The oxide sample (~10 mg) was finely ground and placed into a ceramic crucible in the in situ chamber. Before the DRIFTS measurement, the sample was pretreated in the in situ chamber at 573 K in 100 mL min^{-1} of simulated air (79% N_2 and 21% O_2) for 2 h. After the pretreated sample cooled to 300 K, the reference spectrum was collected. The oxide sample was then exposed to wet air with different RH for 20 min. The RH in the feed gas was controlled and measured as described for the KCMS experiment. After 1000 ppmv of OCS balanced with simulated wet air was introduced into the reactor for 3 min, the inlet and outlet of the reactor chamber were closed promptly. The infrared spectra in the closed system were collected automatically by a computer. The concentration of OCS in the reactor was calibrated with standard OCS gas as described in our previous work (He et al., 2005). From the decrease in concentration of gaseous OCS in the closed system, the apparent quasi first-order reaction rate constants were obtained:

$$\ln \frac{c_{\mathrm{OCS},t}}{c_{\mathrm{OCS},0}} = kt \tag{3}$$

where $c_{\mathrm{OCS},t}$ and $c_{\mathrm{OCS},0}$ are the concentrations of OCS at t s and 0 s, respectively, k is the apparent reaction rate constant (s^{-1}), and t is the reaction time (s). Based on the repeated experiments, the RSD of k was measured to be 4.69%. The observed uptake coefficients were calculated by Eqs. (4) and (5) (Li et al., 2006; Ullerstam et al., 2003):

$$\gamma_{\mathrm{obs}} = \frac{k}{Z \cdot A_s} \tag{4}$$

$$Z = \sqrt{\frac{8\,R \cdot T}{\pi \cdot M}} \cdot \frac{1}{4\,V} \tag{5}$$

where γ_{obs} is the observed uptake coefficient, k is the apparent reaction rate constant (s^{-1}), V is the reactor chamber volume (m^3), Z is the collision frequency, A_s is the reactive surface area (m^2), T is the temperature (K), R is the ideal gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$), and M is the molecular weight of the OCS molecule ($\mathrm{kg\,mol^{-1}}$).

To investigate the adsorption behavior of water on the model oxides, the infrared spectra and adsorptive isothermal curves of water on oxides were also measured using DRIFTS. Pretreated samples were exposed to wet air with different RH at 300 K for 20 min to establish an adsorption equilibrium. The infrared spectra at equilibrium were collected, and the original spectra were converted using the Kubelka-Munk function (Sirita et al., 2007). The K-M value

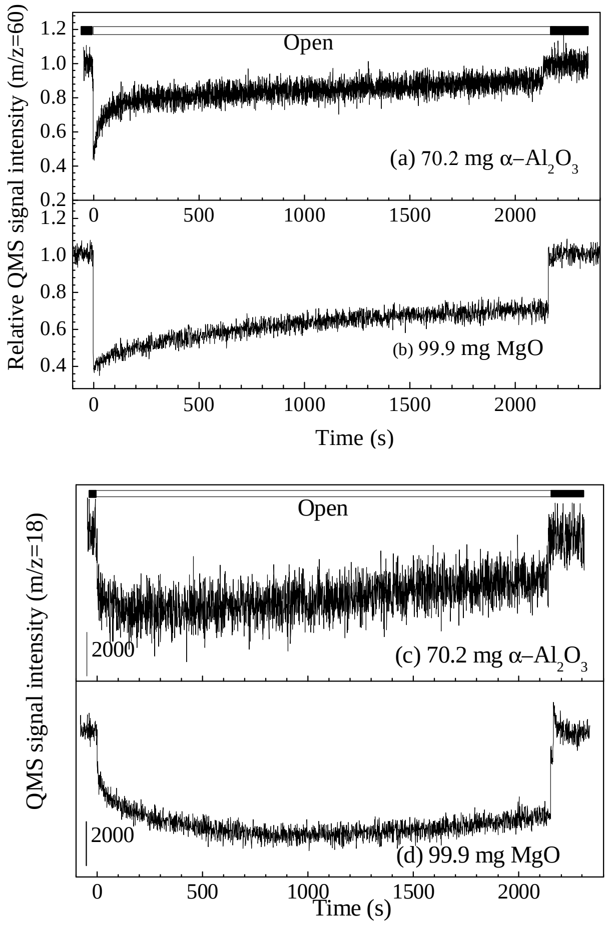

Fig. 1. Typical uptake profiles of OCS and water on α-Al_2O_3 and MgO at 300 K. **(a)** and **(b)** for OCS; **(c)** and **(d)** for water measured by Knudsen cell – mass spectrometry. The partial pressures of OCS and water in the Knudsen cell reactor were 5.3×10^{-6} and 5.8×10^{-6} Torr, respectively.

of OH vibrational stretch (3700–2500 cm^{-1}) was used to denote the adsorptive capacity of water on mineral oxides.

3 Results

3.1 Comparative study of the heterogeneous reaction of OCS on the surface of α-Al_2O_3 and MgO

Figure 1 shows typical uptake profiles of OCS and water on α-Al_2O_3 and MgO at 300 K, as measured by KCMS. The partial pressures of OCS and water vapor in the Knudsen cell reactor were 5.3×10^{-6} Torr (7.0 ppb) and 5.8×10^{-6} Torr, respectively. As shown in Fig. 1a, when the pretreated samples were exposed to the feed gas, the QMS signal intensity of OCS (m/z=60) decreased dramatically and was followed by a quick saturation process within 100 s on α-Al_2O_3. An apparent steady-state of uptake on the time scale of this experiment was then quickly reached. However, the QMS signal intensity of OCS (m/z=60) on MgO came to a steady-state gradually within 1000 s (Fig. 1b). The quick saturation was ascribed to desorption of adsorbed OCS, while the steady-state uptake was related to the consumption of OCS by the heterogeneous reaction. Therefore, it can be deduced from Fig. 1a and b that desorption of OCS on the surface of α-Al_2O_3 was prominent while the heterogeneous reaction was weak. As shown in Fig. 1c and d, the signal intensity of water vapor also decreased when the same sample was exposed to the feed gas. The signal intensity of water vapor on α-Al_2O_3 increased gradually with exposure time, while continuous uptake of water was observed on MgO. These results demonstrate that α-Al_2O_3 and MgO can take up OCS and water simultaneously by adsorption and heterogeneous reaction at ambient temperature.

To investigate the surface and gaseous products during the heterogeneous processes of OCS on α-Al_2O_3 and MgO, DRIFTS and TPR experiments were performed. As described in Sect. 2.3, the sample was pretreated in the in situ chamber at 573 K in 100 mL min^{-1} of simulated air (79% N_2 and 21% O_2) for 2 h. The RH in the feed gas was measured to be 0.07. Figure 2 shows the surface species formed on α-Al_2O_3 and MgO at 300 K after 10 min in the closed system after the pretreated samples were exposed to 1000 ppmv of OCS balanced with air. The cutoffs below 1200 cm^{-1} in Fig. 2a and 900 cm^{-1} in Fig. 2b were not shown because of the strong lattice vibrational absorption of the samples. The absorption bands shown in Fig. 2 were assigned based on values found in the literature (Table 1). As shown in Fig. 2a, surface hydroxyl ($-$OH) was consumed and gaseous carbon dioxide (CO_2), surface carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), thiocarbonate ($HSCO_3^-$), carbonate (CO_3^{2-}) and sulfate (SO_4^{2-}) were formed on α-Al_2O_3. These results are similar to the previously described heterogeneous oxidation of OCS on γ-Al_2O_3 (He et al., 2005; Liu et al., 2006), suggesting that the heterogeneous oxidation of OCS may also occur on α-Al_2O_3. In Fig. 2b, apart from the above species, sulfur species including physisorbed sulfur dioxide (SO_2), surface sulfite or bisulfite (SO_3^{2-}/HSO_3^-), and surface hydrogen sulfide ($-$SH) were also observed. A band at 2578 cm^{-1} caused by adsorption of surface $-$SH was also observed and is shown enlarged in the insert graph in Fig. 2b. The formation of surface $-$SH implies that gaseous hydrogen sulfide (H_2S) may be formed during the heterogeneous reaction of OCS on the surface of MgO. However, this hypothesis needs to be further tested. It should be noted that the relative intensity between gaseous CO_2 and surface HCO_3^- in Fig. 2a is much higher than that in Fig. 2b. This could be due to the fact that the basicity of MgO is stronger than that of α-Al_2O_3, which leads to low gaseous concentrations of CO_2 and high surface concentrations of HCO_3^-.

Table 1. Assignment of the absorbance bands shown in Fig. 2.

Species	Absorbance bands	Oxides	Ref.
OCS(g)	2071, 2052	$\alpha-Al_2O_3$ and MgO	Tubergen et al. (2000)
CO_2(g)	2363, 2338	$\alpha-Al_2O_3$ and MgO	He et al. (2005)
−OH(a)	3737	$\alpha-Al_2O_3$	Peri and Hannan. (1960)
	3755	MgO	
H_2CO_3(a)	1683	$\alpha-Al_2O_3$	Al-Hosney et al. (2004)
	1681	MgO	
HCO_3^-(a)	3623, 1635	$\alpha-Al_2O_3$	Lavalley (1996)
	3618, 1659, 1409, 1225	MgO	
CO_3^{2-}(a)	1534	$\alpha-Al_2O_3$	Baltrusaitis et al. (2006)
	1584, 1545	MgO	
−SH(a)	2578	MgO	Datta and Cavell (1985)
SO_2(a)	1333	MgO	Ullerstam et al. (2003)
$HSCO_2^-$(a)	1578	$\alpha-Al_2O_3$	He et al. (2005)
	1273	MgO	Liu et al. (2007a)
SO_4^{2-}(a)	1384	$\alpha-Al_2O_3$	Li et al. (2006)
	1138	MgO	
SO_3^{2-}/HSO_3^-(a)	1084, 1030, 950	MgO	

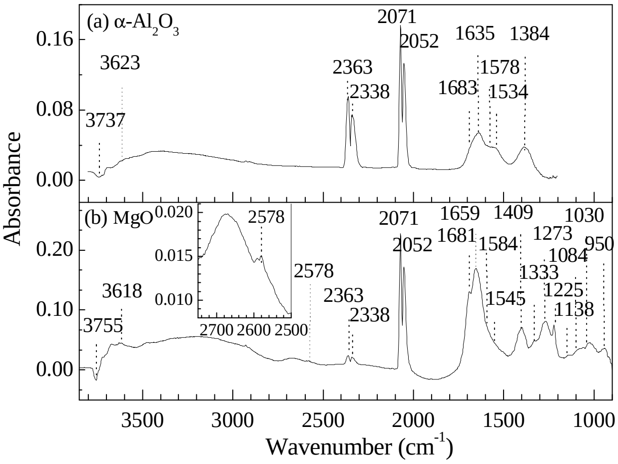

Fig. 2. DRIFTS spetra of the surface species for the heterogeneous reactions of OCS on the surface of α-Al_2O_3 and MgO at 300 K. The spectra were collected at 10 min in closed system after the samples were exposed to 1000 ppmv of OCS balanced with simulated air.

Figure 3a illustrates the change in QMS signal intensity in the heterogeneous reaction of OCS on MgO at 300 K. When the MgO sample was exposed to 1000 ppmv of OCS balanced with air, the signal intensity of OCS (*m/z*=60) decreased initially, and then quickly came to a steady-state due to saturation of adsorption. At the same time, the signal intensities of CO_2 (*m/z*=44) and H_2S (*m/z*=34) increased. When the feed gas was shifted to the by-pass tube (background), the QMS signals of these compounds quickly returned to their corresponding baselines. This indicates that H_2S is also one of the gaseous products of the heterogeneous reaction of OCS on MgO, which supports the spectroscopic results presented in Fig. 2b and is also consistent with the results of the Knudsen cell study (Liu et al., 2008a). However, for the heterogeneous reaction of OCS on α-Al_2O_3, no changes in the QMS signals of OCS, CO_2, or H_2S in the flow system were apparent under the same reaction conditions, although the formation of gaseous CO_2 and surface HCO_3^- were easily measured in the closed system (Fig. 2a). 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 α-Al_2O_3. These results imply that the reaction of OCS on α-Al_2O_3 may differ from that on MgO. It should be noted that the uptake of OCS by α-Al_2O_3 at steady-state was much lower than that by MgO (see Fig. 1), indicating a lower reaction rate. The lack of gaseous H_2S or surface −SH could be ascribed to the low yield of H_2S on α-Al_2O_3 at r. t., which was lower than the detectable limit of our apparatus. Therefore, TPR experiments were performed to increase the reaction rate and to confirm whether H_2S was formed during the heterogeneous reaction of OCS on the surface of α-Al_2O_3.

When 1000 ppmv of OCS in air passed through 0.5 g of α-Al_2O_3 or MgO samples and the temperature was increased, the concentration of OCS decreased, and the concentration of CO_2 and H_2S increased (Fig. 3c and d). However, the concentration of OCS (*m/z*=60), CO_2 (*m/z*=44), and H_2S (*m/z*=34) did not change with temperature when the feed gas passed through the by-pass tube. These data suggest that the

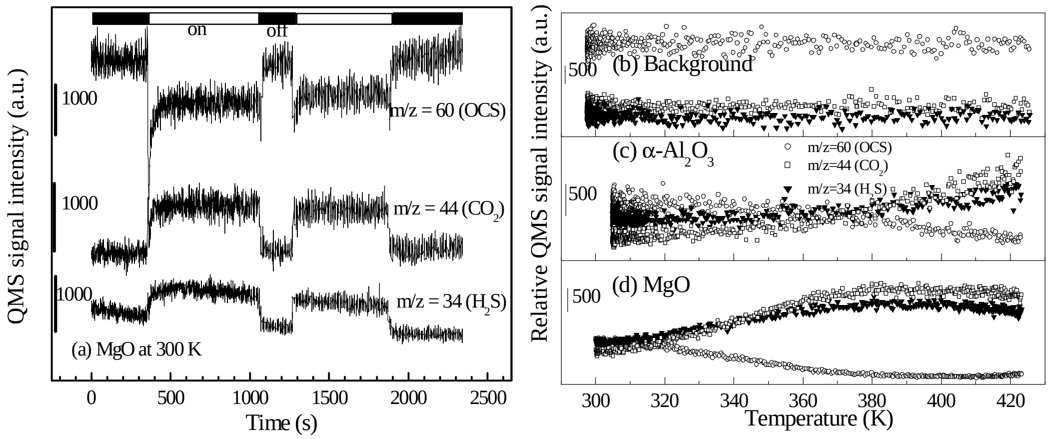

Fig. 3. Gaseous products for the heterogeneous reactions of OCS on the surface of α-Al_2O_3 and MgO measured by temperature programmed reaction. **(a)** 1000 ppmv of OCS balanced with simulated air passing through 0.5 g MgO at 300 K; **(b–d)** temperature-programmed reaction of 1000 ppmv of OCS balanced with simulated air on back ground, α-Al_2O_3 and MgO, respectively. The temperature rate was 20 K min^{-1}.

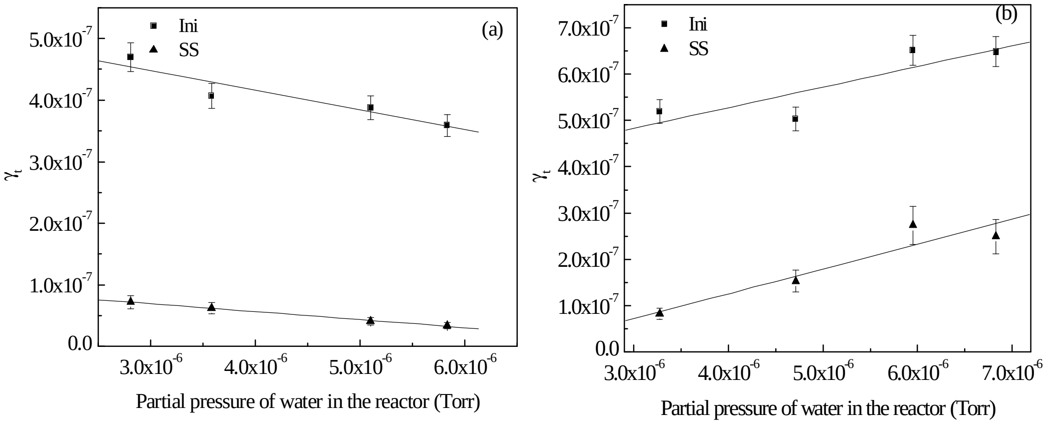

Fig. 4. Effect of water on heterogeneous reactions of OCS at low water vapor pressure. **(a)** on α-Al_2O_3; **(b)** on MgO measured by Knudsen cell – mass spectrometry. The average partial pressure of OCS in the Knudsen cell reactor was kept at $5.3\pm0.3\times10^{-6}$ Torr, and that of water vapor was 2.5×10^{-6}–6.8×10^{-6} Torr. The RSD is 9.50%.

quartz tube did not catalyze the oxidation or hydrolysis of OCS and that OCS did not decompose under our experimental conditions. These results clearly demonstrate that H_2S is a gaseous product of the heterogeneous reaction of OCS on α-Al_2O_3 and that hydrolysis of OCS also occurs on α-Al_2O_3. The heterogeneous reaction of OCS on the surface of α-Al_2O_3 and MgO is be described by Reaction (R1).

$$OCS+H_2O \rightarrow H_2S+CO_2 \qquad \text{(R1)}$$

3.2 Effect of water on the heterogeneous hydrolysis of OCS on the surface of α-Al_2O_3 and MgO

As shown in Fig. 1, the uptake of water and OCS occurred synchronously when the samples were exposed to the feed gas, followed by hydrolysis reactions of OCS on the surface of α-Al_2O_3 and MgO. Because water is one of the reactants, it should have a fundamental effect on the reaction kinetics. Therefore, the reaction kinetics at different water vapor pressures was studied using KCMS and DRIFTS. Figure 4 shows the true uptake coefficient (γ_t) of OCS on α-Al_2O_3 and MgO measured by KCMS under different water vapor pressures at 300 K. The partial pressure of water vapor in the Knudsen cell reactor was in the range of 2.5×10^{-6}–6.8×10^{-6} Torr. The uptake coefficients under different conditions are shown in Table 2. Chen et al. (2007) measured the γ_t (BET) OCS on Fe_2O_3 to be $1.87\pm0.21\times10^{-11}$ by DRIFTS with the assumption that OCS accesses all of the layers of particle sample. This value should be the lowest limit and is much lower than our results due to the different samples and different methods. As shown in Fig. 4, the γ_t of OCS on α-Al_2O_3 at

Table 2. Summary of uptake coefficients of OCS on α-Al_2 O_3 and MgO.

	$\alpha-Al_2O_3$			MgO		
Method	$P(H_2O)$(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	

[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}.

both the initial (Ini) and steady-states (SS) decreased under conditions of increased water vapor pressure in the Knudsen cell reactor; diametrically opposed effects occurred on MgO. This suggests that water significantly suppressed the adsorption and heterogeneous reaction of OCS on the surface of α-Al_2O_3 under these experimental conditions. However, water promoted the adsorption and heterogeneous reaction of OCS on the surface of MgO. The linear regression between γ_t and water vapor pressure (P_{H_2O}) can be expressed as follows:
for α-Al_2O_3,

$$\gamma_t(\mathrm{Ini})=5.4\times10^{-7}-0.032\times P_{H_2O},\quad R=0.937 \tag{6}$$

$$\gamma_t(SS)=1.1\times10^{-7}-0.013\times P_{H_2O},\quad R=0.999 \tag{7}$$

for MgO,

$$\gamma_t(\mathrm{Ini})=3.5\times10^{-7}+0.044\times P_{H_2O},\quad R=0.858 \tag{8}$$

$$\gamma_t(SS)=-8.9\times10^{-8}+0.054\times P_{H_2O},\quad R=0.939 \tag{9}$$

In the Knudsen cell reactor, low pressure must be maintained to avoid molecular collisions between gases (Underwood et al., 2000, 2001); the maximal value in our system was 3.5×10^{-4} Torr. Even though pure water vapor was introduced into the reactor chamber, the pressure achieved was still much lower than the water vapor pressure found in the atmosphere. Therefore, the effect of water on the heterogeneous reactions of OCS on the surface of α-Al_2O_3 and MgO at relative humidity values representative of the troposphere was investigated using DRIFTS. The initial concentration of OCS in the feed gas was held at 1000 ppmv. The relative humidity in the feed gas was in the range of 0.07–0.67, which corresponds to 1.7–15.9 Torr of water vapor pressure. Figures 5a and 6a show the time-dependent logarithmic decline in the concentration of OCS on α-Al_2O_3 and MgO at 300 K in the closed system. The apparent reaction rate constants were calculated according to Eq. (3); all correlation coefficients were greater than 0.99. Subsequently, the corresponding γ_{obs} were calculated using Eqs. (4) and (5). 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. However, the trend between γ_{obs} and RH should be the same as that between γ_t and RH. The relationship between the γ_{obs} and the RH in the feed gas is shown in Figs. 5b and 6b.

As shown in Fig. 5b, the γ_{obs} of OCS on α-Al_2O_3 decreased sharply with the increase of RH in the region of 0.07–0.17. The maximal γ_{obs} was $7.38\pm0.35\times10^{-6}$ at a RH of 0.07. When the RH increased to 0.17, γ_{obs} remained at a constant value ($3.58\pm0.19\times10^{-6}$), which was slightly higher than the background value ($2.74\pm0.13\times10^{-6}$) caused by adsorption or reaction on the surface of the reactor chamber. However, as shown in Fig. 6b, the γ_{obs} of OCS on MgO decreased slowly from $9.99\pm0.47\times10^{-5}$ at a RH of 0.07 to $7.95\pm0.37\times10^{-5}$ at a RH of 0.67. The average value of γ_{obs} between the RH values of 0.17 and 0.67 was $8.46\pm0.42\times10^{-5}$, which was ~30 times higher than the background value. When the contribution of the background to the uptake coefficients was subtracted, the observed uptake coefficients of OCS on α-Al_2O_3 and MgO decreased from $4.63\pm0.22\times10^{-6}$ to $1.00\pm0.47\times10^{-6}$ and from $9.72\pm0.46\times10^{-5}$ to $7.68\pm0.36\times10^{-5}$, respectively. The average observed uptake coefficient of OCS on α-Al_2O_3 and MgO was equal to $8.34\pm2.19\times10^{-7}$ and

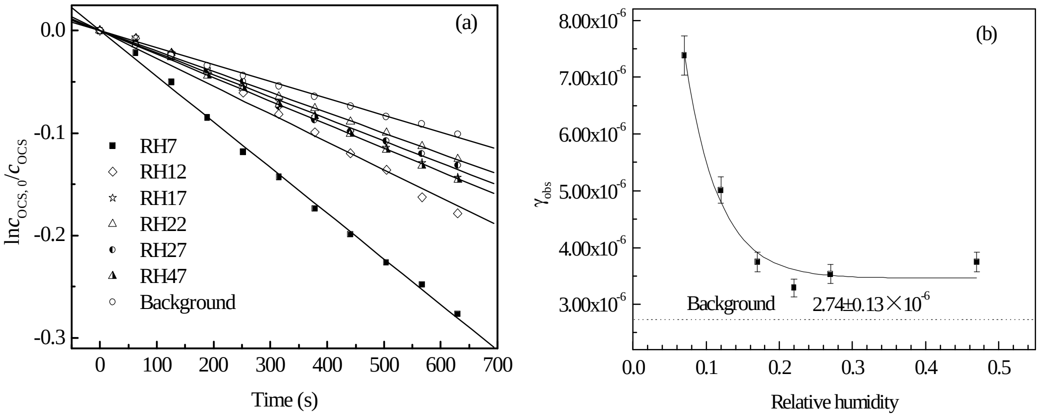

Fig. 5. Effect of water on the heterogeneous reaction of OCS on α-Al_2O_3 at high relative humidity calculated from the data of DRIFTS. The initial concentration of OCS in the feed gas was kept at 1000 ppmv. The RSD is 4.69%.

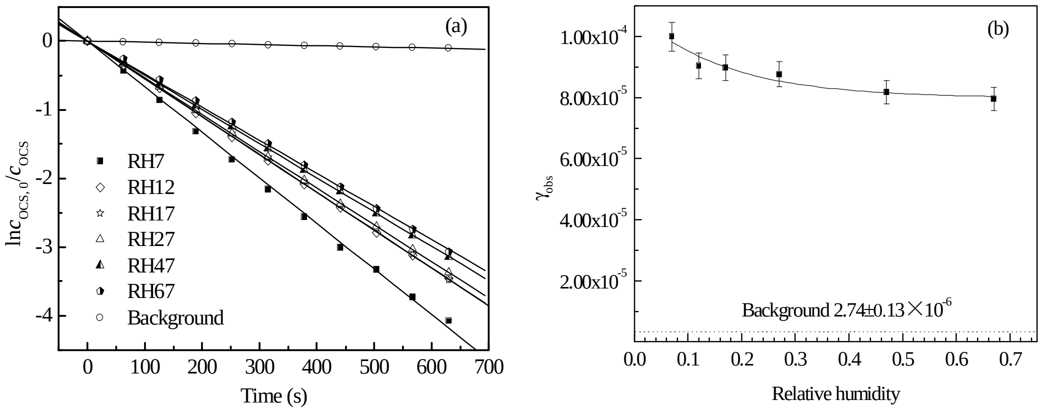

Fig. 6. Effect of water on the heterogeneous reaction of OCS on MgO at high relative humidity calculated from the data of DRIFTS. The initial concentration of OCS in the feed gas was kept at 1000 ppmv. The RSD is 4.69%.

$8.19\pm0.48\times10^{-5}$ between the RH values of 0.17 and 0.67, respectively. It should be noted that 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. 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 α-Al_2O_3 for the effect of water on the reaction of OCS with the same method and under the same reaction conditions.

4 Discussion

4.1 Catalytic hydrolysis of OCS on the surface of α-Al_2O_3 and MgO

Most studies of OCS reactions in the troposphere have focused on the heterogeneous oxidation of OCS on the surface of alumina etc. (Chen et al., 2007; He et al., 2005; Liu et al., 2006; Wu et al., 2004, 2005), and the hydrolysis pathway has not been elucidated because previous measurements have not measured H_2S as a reaction product. In those studies, FTIR was mainly used to investigate the reaction process; however, the sensitivity of infrared absorbance for surface $-SH$ or gaseous H_2S is much lower than that for CO_2. In our studies, the slope of the increased signal intensity of H_2S with temperature was smaller than that of CO_2 (Fig. 3c and d). This could be ascribed to the oxidation of gaseous H_2S or surface $-SH$ to other sulfur species with high oxidation states including gaseous SO_2, surface SO_3^{2-}/HSO_3^- and

SO_4^{2-}. These oxidized species were observed in this study (Fig. 2) and in previous works (Chen et al., 2007; He et al., 2005; Liu et al., 2006; Wu et al., 2004, 2005). Therefore, gaseous CO_2 is more easily observed than gaseous H_2S or surface $-SH$ when using FTIR. In our previous work, we reported the production of H_2S for the reaction of OCS on the surface of MgO using DRIFTS (Liu et al., 2007a) and KCMS (Liu et al., 2008a). Desorption of H_2S was also observed after the heterogeneous reaction of OCS on the surface of α-Al_2O_3 using KCMS (Liu et al., 2008b). Therefore, we conclude that, similar to reaction on the surface of MgO, heterogeneous hydrolysis of OCS on the surface of α-Al_2O_3 also occurs at ambient temperature.

In Fig. 1, the uptake profiles of OCS on α-Al_2O_3 and MgO can be classified into two stages – the quick recover stage and the steady-state stage. Because the uptake experiments were performed under steady-state conditions, the change in OCS intensity can be described according to the conservation of mass by Eq. (10) when the sample was exposed to the reactant gas:

$$-\frac{dn_g}{dt}=-k'dI=k_{\text{ads}}n_g(1-\theta)-k_{\text{des}}N_a+k_hN_a \qquad (10)$$

where n_g is the number of gaseous molecules of OCS in the Knudsen cell reactor (molecule), t is time (s), k' is a constant, I is the signal intensity of OCS measured by mass spectrometer (a. u.), k_{ads} is the apparent rate constant for adsorption of OCS (s^{-1}), k_{des} is the apparent rate constant for desorption of OCS (s^{-1}), k_h is the apparent rate constant for the heterogeneous reaction of OCS (s^{-1}), θ is the coverage of OCS on oxide samples ($=N/N_a^*$), N_a^* is the saturated coverage of OCS on oxide samples (molecules), and N_a is the number of OCS molecule adsorbed on the oxide samples at a given time (molecules).

Therefore, because θ was almost equal to zero at the initial time, the OCS signal decreased to its lowest intensity when the sample cover was removed. The signal intensity of OCS then gradually recovered because the contribution of desorption became prominent with the increase of θ (Fig. 1). If there was no catalytic reaction (k_h=0), the OCS signal would eventually recover to baseline due to the balance between adsorption and desorption. However, as shown in Fig. 1, a steady-state consumption of OCS was observed. As discussed above, gaseous and surface products were also detected. Therefore, it can be concluded that the hydrolysis of OCS on the surface of α-Al_2O_3 and MgO is a catalytic reaction. In Fig. 1, the steady-state consumption of OCS on MgO (Fig. 1b) was much larger than that on α-Al_2O_3 (Fig. 1a). The apparent reaction rate constant (k_h) of OCS on MgO is $0.21\,s^{-1}$, while k_h on α-Al_2O_3 is $0.080\,s^{-1}$. Therefore, compared to α-Al_2O_3, the slow recovery rate of the OCS signal on MgO (Fig. 1b) can be ascribed to the compensatory effect of the catalytic reaction to desorption of OCS. This relationship is well described by Eq. (10).

4.2 Mechanism for the effect of water on the heterogeneous reactions of OCS on the surface of α-Al_2O_3 and MgO

As shown in Figs. 4a and 5b, adsorbed water on α-Al_2O_3 prominently restricted the adsorption and heterogeneous reaction of OCS at low water vapor pressures and at high relative humidity. These data indicate that water and OCS compete for the same adsorption site on α-Al_2O_3. On the surface of MgO, adsorbed water promoted the adsorption and heterogeneous reaction of OCS at low water pressures ($<6.8\times10^{-6}$ Torr) (Fig. 4b), but had the opposite effect at high relative humidity (0.07–0.67) (Fig. 6). Therefore, the effect of water on the heterogeneous reaction or adsorption of OCS on the surface of MgO appears to utilize different reaction mechanisms under conditions of low water vapor pressures versus high humidity conditions.

In previous work, hydrogen thiocarbonate ($HSCO_2^-$) was determined to be the crucial intermediate for the heterogeneous oxidation and hydrolysis of OCS on mineral oxides; $HSCO_2^-$ is formed via the reaction of OCS with surface $-OH$ on mineral oxides (He et al., 2005; Hoggan et al., 1994; Liu et al., 2006, 2007a). Additionally, we found that surface $-OH$ contributes to not only the formation of $HSCO_2^-$ but also to the decomposition of $HSCO_2^-$ (Liu et al., 2007a). In Fig. 2, the consumption of hydroxyl was also observed. Therefore, the content and properties of surface hydroxyl groups of mineral oxides should be important in these reactions.

On the base of synchrotron-based photoemission spectroscopy, low energy electron diffraction studies and high-level theoretical simulations, it was found that water molecules could dissociate and react with a low concentration of defective sites on mineral surfaces at very low vapor pressures (Brown Jr., 2001; Eng et al., 2000; Hass et al., 1998; Liu et al., 1998a, b). For example, water molecules react relatively fast with surface defects (corners, edge-step sites, and point defects) on MgO to form surface $-OH$ when the water vapor pressure is less than 3×10^{-5} Torr. When the water vapor pressure is greater than 10^{-4} Torr, dissociative chemisorption of water on terrace sites occurs (Liu et al., 1998a, b). The formation of surface $-OH$ at $3700\,cm^{-1}$ on MgO at low water coverage was also confirmed using FTIR (Foster et al., 2002). Thus, below 0.05 RH, the reaction between water and MgO can be described by Reaction (R2) (Al-Abadleh et al., 2005):

$$MgO+H_2O \rightarrow Mg(OH)_2 \qquad (R2)$$

In our experiment, the water vapor pressures in the Knudsen cell reactor were lower than 3×10^{-5} Torr. The number of surface hydroxyl groups on MgO would likely increase with water vapor pressure due to the dissociative chemisorption of adsorbed water. As shown in Fig. 4b, adsorbed water promoted the adsorption and heterogeneous reaction of OCS

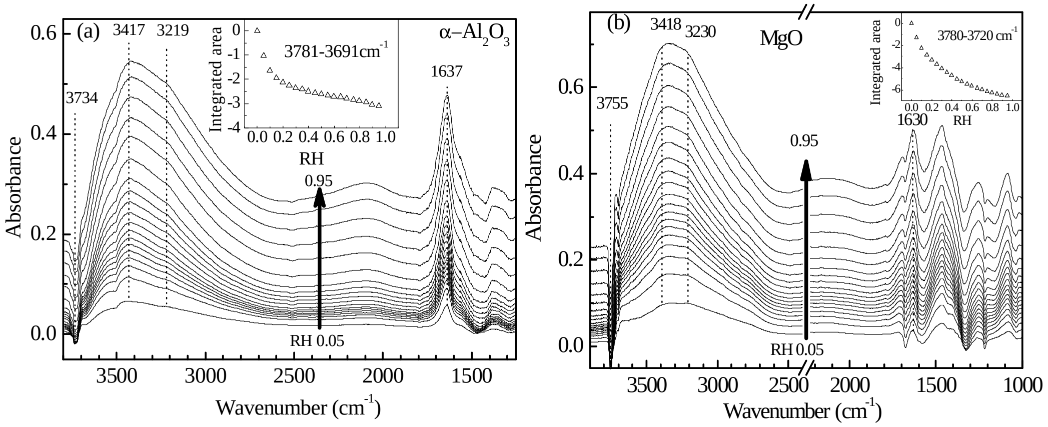

Fig. 7. Adsorption behavior of water at 300 K on **(a)** α-Al_2O_3 and **(b)** MgO measured by DRIFTS.

on the surface of MgO at low water pressures ($<6.8\times10^{-6}$ Torr).

As for α-Al_2O_3, it was also shown that hydroxylation occurred during the conversion of corundum to gibbsite ($Al(OH)_3$) according to Reaction (R3) (Al-Abadleh and Grassian, 2003; Eng et al., 2000; Hass et al., 1998):

$$Al_2O_3+3H_2O \rightarrow 2Al(OH)_3 \qquad \text{(R3)}$$

Although a rather high initial sticking coefficient of 0.1 has been measured for H_2O on α-Al_2O_3 at 300 K, the sticking coefficient was found to decrease exponentially with increasing water coverage (Elam et al., 1998). After the surface is fully hydroxylated, additional water can only be physisorbed on the hydroxyl layer on both α-Al_2O_3 and MgO (Elam et al., 1998; Liu et al., 1998b). Because surface $-$OH is the reactive site for the heterogeneous reaction of OCS, the formation of surface $-$OH should promote the reaction while the molecular adsorption of water on surface $-$OH should suppress this reaction. Theoretically, the uptake coefficients on both α-Al_2O_3 and MgO (shown in Fig. 4) should increase initially and then decrease with the increased water vapor pressures. However, this turning point was not observed, which may be due to limitations of our experiment conditions. It should be pointed out that the α-Al_2O_3 sample used in our experiment may have already been partially hydroxylated, which would lead to a turning point that occurs at low water vapor pressures. Therefore, in Figs. 4a, 5b and 6b, the decrease in the uptake coefficients of OCS on α-Al_2O_3 and MgO under conditions of increased water vapor pressure can be explained by competitive adsorption of H_2O and OCS on surface $-$OH. This assumption is well-supported by the consumption of surface $-$OH during the adsorption of pure water vapor on α-Al_2O_3 and MgO.

As shown in Fig. 7, when the pretreated samples were exposed to water vapor at different RH, negative bands of surface $-$OH at 3734 cm^{-1} on α-Al_2O_3 and 3755 cm^{-1} on MgO were observed. The bands at 3417, 3219, and 1637 cm^{-1} on α-Al_2O_3 (as well as 3418, 3230, and 1630 cm^{-1} on MgO) were assigned to the υ_{as}(HOH), υ_s(HOH) and δ(HOH) of adsorbed water, respectively (Al-Abadleh et al., 2005). Obviously, the frequencies of the hydroxyl groups consumed by water in Fig. 7 are the same as those consumed by the reaction of OCS in Fig. 2. This suggests that OCS and H_2O have the same adsorption site on both α-Al_2O_3 and MgO.

In Fig. 7, the insert graphs show the variations in the amount of surface $-$OH consumed by water at different RH. The consumption of surface $-$OH (A) with RH in Fig. 7 is directionally identical to the corresponding observed uptake coefficient of OCS with RH (Figs. 5b and 6b). At RH between 0.07 and 0.27, the observed uptake coefficient of OCS on α-Al_2O_3 and MgO decreased almost linearly with increased consumption of surface hydroxyl (A) by the adsorbed water (shown in Fig. 8). The linear equations are as follows:

$$\gamma_{\text{obs}}=8.10\times10^{-6}-4.86\times10^{-6}\times A,\ \ \alpha-Al_2O_3,\quad R=0.997; \qquad (11)$$

$$\gamma_{\text{obs}}=1.02\times10^{-4}-4.76\times10^{-6}\times A,\ \text{MgO},\quad R=0.866 \qquad (12)$$

Although the apparent activity of the heterogeneous reaction of OCS on MgO is much higher than that on α-Al_2O_3, the slope in Eq. (11) is almost equal to that in Eq. (12). This demonstrates that the decrease in γ_{obs} is quantitatively related to the amount of surface hydroxyl groups consumed by adsorbed water regardless of the type of mineral oxide.

It is well known that, depending on the RH value, monolayer and multilayers of water can adsorb to the surface of minerals. To measure the relative humidity of one monolayer (RH_{ML}) of water and to understand the effect of water on the heterogeneous reaction of OCS on the surface of α-Al_2O_3 and MgO at high RH, the adsorption isotherm curves of water on these oxides were investigated. The number of adsorbed water layers was assumed to be in direct proportion to the integrated K-M value of the stretch vibration (3700–2500 cm^{-1}) of surface adsorbed water (Sirita et al., 2007). Therefore, the coverage of adsorbed water on α-Al_2O_3 and MgO was quantified by generating adsorption isotherm curves according to a three-parameter Type III BET fit, as shown in Eq. (13) (Goodman et al., 2001):

$$\frac{KM}{KM_{\mathrm{ML}}}=\left(\frac{c\mathrm{RH}}{1-\mathrm{RH}}\right)\left(\frac{1-(n+1)\mathrm{RH}^{n}+n\mathrm{RH}^{n+1}}{1+(c+1)\mathrm{RH}-c\mathrm{RH}^{n+1}}\right) \qquad (13)$$

where *KM* is the integrated K-M value of adsorbed water in the region of 3700–2500 cm^{-1}, KM_{ML} is the integrated K-M value of adsorbed water at one monolayer, c is a temperature-dependent constant, n is the maximum number of layers of adsorbed water, and RH is the relative humidity. The adsorption isotherm curves of water on α-Al_2O_3 and MgO at 300 K are shown in Fig. 9.

One monolayer of water adsorbed on α-Al_2O_3 and MgO occurred at a RH (RH_{ML}) of 0.37 and 0.30, respectively (Fig. 9). Goodman et al. (2001) measured the RH_{ML} of water on α-Al_2O_3 and MgO 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 RH_{ML} 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. As discussed above, when water vapor pressure exceeds the corresponding RH_{ML}, multilayer adsorption of water should take place on mineral oxides, and the surface –OH should be consumed completely. Therefore, uptake of OCS should not be observed at high relative humidity. However, as shown in Figs. 5b and 6b, when RH exceeded the corresponding RH_{ML}, the uptake coefficients of OCS on the samples remained higher than that measured in the background experiment. In particular, the average value of γ_{obs} on MgO in the RH region between 0.47 and 0.67 was 29 times as that of the background value. This indicates that the thick water layer on α-Al_2O_3 and MgO might also contribute to the heterogeneous hydrolysis of OCS. In our previous work, we found that the heterogeneous reaction of OCS on the surface of mineral oxides is related to the basicity of the oxide (Liu et al., 2007b). The base catalytic hydrolysis of OCS in aqueous solutions has also been widely investigated (Amararene and Bouallou, 2004). It is well known that the basicity of MgO is higher than that of α-Al_2O_3. The pH value of slurry for 1.0 g of MgO in 20.0 mL water was measured to be 10.7, while that for α-Al_2O_3 was 9.1. Therefore, the observed uptake coefficients of OCS on MgO at high RH (0.07–0.67) were much higher than that on α-Al_2O_3. At the atmospherically relevant humidity, water could not wet the oxides (Foster et al., 2002). Therefore, the surface basicity of the thick water layer formed on mineral dust would be higher than the value measured in slurry. Additionally, it should 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. Consequently, it is reasonable to deduce that both the thick water layer formed on atmospheric particulate matter, especially the basic components and the remained surface hydroxyl groups, should be the main contributors to heterogeneous reactions of OCS in the atmosphere.

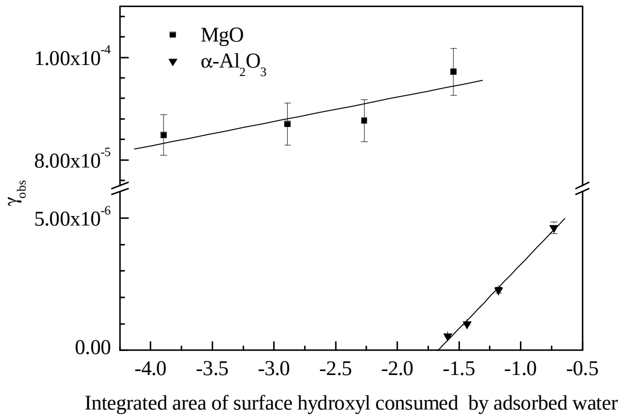

Fig. 8. Correlation between the observed uptake coefficients (measured by DRIFTS) and amount of surface hydroxyl (A) consumed by water at different RH in the region of 0.07–0.27. The RSD is 4.69%.

5 Conclusions and atmospheric implications

In this work, the heterogeneous reactions of OCS on the surface of α-Al_2O_3 and MgO were studied using KCMS, DRIFTS, and TPR. We found that hydrolysis of OCS leading to the formation of H_2S and CO_2 could occur on the surface of both α-Al_2O_3 and MgO at ambient temperature. The reaction kinetics was influenced significantly by adsorbed water on the surface of α-Al_2O_3 and MgO. At low water vapor pressure ($<6.8\times10^{-6}$ 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; these surface hydroxyl groups were confirmed to be the sites for the heterogeneous reaction of OCS on the surface of mineral oxides. However, at high coverage, adsorbed water on the surface hydroxyl groups led to a decrease in the uptake coefficients on MgO. For α-Al_2O_3, adsorbed water suppressed the heterogeneous hydrolysis of OCS at both low and high water vapor pressures due to the competitive adsorption of H_2O and OCS on surface hydroxyl groups. At

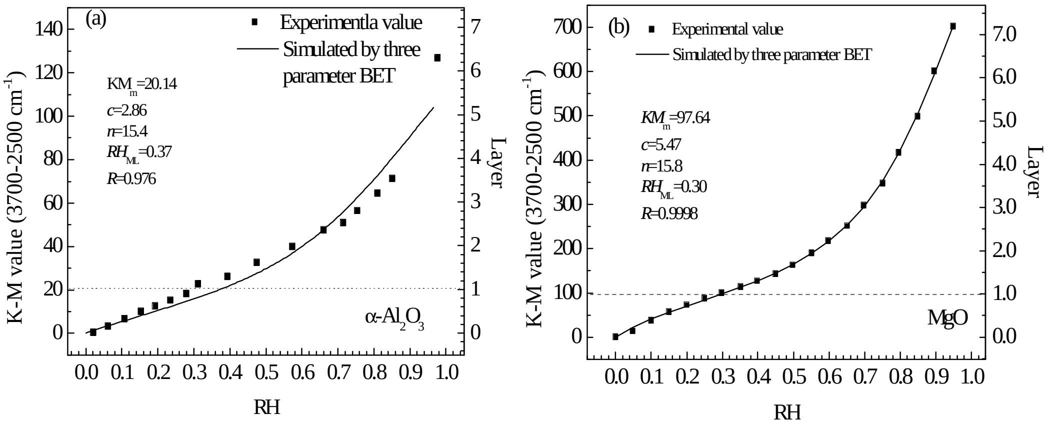

Fig. 9. Adsorptive isothermal curve of water at 300 K on **(a)** α-Al_2O_3 and **(b)** MgO calculated from the data of DRIFTS.

high relative humidity (0.07–0.67), the decrease in the uptake coefficients was in proportion to the amount of surface hydroxyl groups consumed by adsorbed water on α-Al_2O_3 and MgO. The uptake coefficients of OCS on MgO at high relative humidity remained higher than that of both α-Al_2O_3 and the background due to the contribution of basic thick water layer of water on MgO.

Hydrolysis is regarded as the most important universal reaction in the atmosphere (Ravishankara, 1997), and much work has been done regarding the hydrolysis of gaseous species on ice surfaces (Abbatt, 2003). Mineral dust has also been found to be an important constituent of atmospheric particulate matter (Dentener et al., 1996). The adsorption and oxidation of inorganic compounds including SO_2, NOx, O_3, and HNO_3 on the surface of mineral dust have been well investigated (Usher et al., 2003a). However, under typical atmospheric conditions (298 K and 0.50–0.60 RH), about 3–4 monolayers of water adsorb on mineral dust (Eng et al., 2000). This membrane of liquid formed on the surface of mineral dust imparts particulate matter with a capacity to heterogeneously hydrolyze trace gases. These studies mentioned above demonstrate that heterogeneous oxidation on mineral oxides may be a new sink of OCS in the troposphere. Here we found that mineral dust catalyzes the heterogeneous hydrolysis of OCS, which may be a tropospheric sink for OCS. However, water adsorbed on mineral dust appeared to restrict the heterogeneous hydrolysis of OCS at atmospherically relevant humidity in the troposphere. Nevertheless, the hydrolysis of OCS on mineral dust should not be ignored even if the RH is higher than RH_{ML}. Thick water layer of high basicity that formed on mineral dust are likely primary contributors to the heterogeneous hydrolysis of OCS and sinks for OCS in the troposphere. 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.

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References

Abbatt, J. P.: Interactions of atmospheric trace gases with ice surfaces: adsorption and reaction, Chem. Rev., 103, 4783–4800, 2003.

Al-Abadleh, H. A., Al-Hosney, H. A., and Grassian, V. H.: Oxide and carbonate surfaces as environmental interfaces: the importance of water in surface composition and surface reactivity, J. Mol. Catal. A-Chem., 228, 47–54, 2005.

Al-Abadleh, H. A. and Grassian, V. H.: FT-IR study of water adsorption on alumina oxide surfaces, Langmuir, 19, 341–347, 2003.

Al-Hosney, H. A. and Grassian, V. H.: Carbonic acid: an important intermediate in the surface chemistry of calcium carbonate, J. Am. Chem. Soc., 126, 8068–8069, 2004.

Amararene, F. and Bouallou, C.: Kinetics of carbonyl sulfide (COS) absorption with aqueous solutions of diethanolamine and methyldiethanolamine, Ind. Eng. Chem. Res., 43, 6136–6141, 2004.

Andreae, M. O. and Crutzen, P. J.: Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052–1058, 1997.

Baltrusaitis, J., Jensen, J. H., and Grassian, V. H.: FTIR spectroscopy combined with isotope labeling and quantum chemical calculations to investigate adsorbed bicarbonate formation following reaction of carbon dioxide with surface hydroxyl groups on Fe_2O_3 and Al_2O_3, J. Phys. Chem. B, 110, 12005–12016, 2006.

Baltrusaitis, J., Schuttlefield, J., Jensen, J. H., and 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., 9, 4970–4980, 2007.

Brown Jr., G. E.: How minerals react with water, Science, 294, 67–70, 2001.

Chen, H. H., Kong, L. D., Chen, J. M., Zhang, R. Y., and Wang, L.: Heterogeneous uptake of carbonyl sulifide on hematite and hematite-NaCl mixtures. Environ. Sci. Technol., 41, 6484–6490, 2007.

Craf, H. F.: The complex interaction of aerosols and clouds, Science, 303, 1309–1311, 2004.

Crutzen, P. J.: The possible importance of CSO for the sulfate layer of the stratosphere, Geophys. Res. Lett., 3, 73–76, 1976.

Datta, A. and Cavell, R. G.: Claus catalysis, 2, An FTIR study of the adsorption of H_2S on the alumina catalyst, J. Phys. Chem., 89, 450–454, 1985.

Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, J., and Crutzen, P. J.: Role of mineral aerosol as a reactive surface in the global troposphere, J. Geophys. Res., 101, 22869–22889, 1996.

Elam, J. W., Nelson, C. E., Cameron, M. A., Tolbert, M. A., and George, S. M.: Adsorption of H_2O on a single-crystal α-Al_2O_3 (0001) surface, J. Phys. Chem. B, 102, 7008–7015, 1998.

Eng, P. J., Trainor, T. P., Brown Jr., G. E., Waychunas, G. A., Newville, M., Sutton, S. R., and Rivers, M. L.: Structure of the hydrated α-Al_2O_3 (0001) surface, Science, 288, 1029–1033, 2000.

Engel, A. and Schmidt, U.: Vertical profile measurements of carbonyl sulfide in the stratosphere, Geophys. Res. Lett., 22(20), 2219–2222, 1994.

Foster, M., Furse, M., and Passno, D.: An FTIR study of water thin films on magnesium oxide, Surf. Sci., 502/503, 102–108, 2002.

Goodman, A. L., Bernard, E. T., and Grassian, V. H.: Spectroscopic study of nitric acid and water adsorption on Oxide particles: enhanced nitric acid uptake kinetics in the presence of adsorbed water, J. Phys. Chem. A, 105, 6443–6457, 2001.

Hass, K. C., Schneider, W. F., Curioni, A., and Andreoni, W.: The chemistry of water on alumina surfaces: reaction dynamics from first principles, Science, 282, 265–268, 1998.

He, H., Liu, J. F., Mu, Y. J., Yu, Y. B., and Chen, M. X.: Heterogeneous oxidation of carbonyl sulfide on atmospheric particles and alumina, Environ. Sci. Technol., 39, 9637–9642, 2005.

Hoggan, P. E., Aboulayt, A., Pieplu, A., and Lavalley, J. C.: Mechanism of COS hydrolysis on alumina, J. Catal., 149, 300–306, 1994.

Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmos. Environ., 34, 2131–2159, 2000.

Kettle, A. J., Kuhn, U., von Hobe, M., Kesselmeier, J., and Andreae, M. O.: Global budget of atmospheric carbonyl sulfide: temporal and spatial variations of the dominant sources and sinks, J. Geophys. Res., 107(D22), 4658, doi:10.1029/2002JD002187, 2002.

Lavalley, J. C.: Infrared spectrometric studies of the surface basicity of metal oxides and zeolites using adsorbed probe molecules, Catal. Today, 27, 377–401, 1996.

Li, L., Chen, Z. M., Zhang, Y. H., Zhu, T., Li, J. L., and Ding, J.: Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate, Atmos. Chem. Phys., 6, 2453–2464, 2006, http://www.atmos-chem-phys.net/6/2453/2006/.

Liu, J. F., Yu, Y. B., Mu, Y. J., and He, H.: Mechanism of heterogeneous oxidation of carbonyl sulfide on Al_2O_3: an in situ diffuse reflectance infrared Fourier transform spectroscopy investigation, J. Phys. Chem. B, 110, 3225–3230, 2006.

Liu, P., Kendelewicz, T., and Brown Jr., G. E.: Reaction of water with MgO (100) surfaces, Part II: synchrotron photoemission studies of defective surfaces, Surf. Sci., 412/413, 315–332, 1998a.

Liu, P., Kendelewicz, T., Brown Jr., G. E., and Parks, G. A.: Reaction of water with MgO (100) surfaces, Part I: synchrotron X-ray photoemission studies of low-defect surfaces, Surf. Sci., 412/413, 287–314, 1998b.

Liu, Y. C., He, H., and Ma, Q. X.: Temperature dependence of the heterogeneous reaction of carbonyl sulfide on magnesium oxide, J. Phys. Chem. A, 112, 2820–2826, 2008a.

Liu, Y. C., He, H., and Mu, Y. J.: Heterogeneous reactivity of carbonyl sulfide on α-Al_2O_3 and γ-Al_2O_3, Atmos. Environ., 42, 960–968, 2008b.

Liu, Y. C., He, H., Xu, W. Q., and Yu, Y. B.: Mechanism of heterogeneous reaction of carbonyl sulfide on magnesium oxide, J. Phys. Chem. A, 111, 4333–4339, 2007a.

Liu, Y. C., Liu, J. F., He, H., Yu, Y. B., and Xue, L.: Heterogeneous oxidation of carbonyl sulfide on mineral oxides, Chinese Sci. Bull., 52, 2063–2071, 2007b.

Montzka, S. A., Calvert, P., Hall, B. D., Elkins, J. W., Conway, T. J., Tans, P. P., and Sweeney, C.: On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2, J. Geophys. Res., 112, D09302, doi:10.1029/2006JD007665, 2007.

Peri, J. B. and Hannan, R. B.: Surface hydroxyl groups on γ-alumina, J. Phys. Chem., 64, 1526–1530, 1960.

Ravishankara, A. R.: Heterogeneous and multiphase chemistry in the troposphere, Scinece, 276, 1058–1065, 1997.

Roscoe, J. M. and Abbatt, J. P. D.: Diffuse reflectance FTIR study of the interaction of alumina surfaces with ozone and water Vapor, J. Phys. Chem. A, 109, 9028–9034, 2005.

Sirita, J., Phanichphant, S., and Meunier, F. C.: Quantitative analysis of adsorbate concentrations by diffuse reflectance FT-IR, Anal. Chem., 79, 3912-3918, 2007.

Solomon, S., Sanders, R. W., Garcia, R. R., and Keys, J. G.: Increased chlorine dioxide over Antarctica caused by volcanic aerosols form Mount Pinatubo, Nature, 363, 245-248, 1993.

Tubergen, M. J., Lavrich, R. J., and McCargar, J. W.: Infrared spectrum and group theoretical analysis of the vibrational modes of carbonyl sulfide, J. Chem. Educ., 77(12), 1637–1639, 2000.

Turco, R. P., Whitten, R. C., Toon, O. B., Pollack, J. B., and Hamill, P.: OCS, stratospheric aerosols and climate, Nature, 283, 283–286, 1980.

Ullerstam, M., Johnson, M. S., Vogt, R., and Ljungström, E.: DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO_2 and NO_2 on mineral dust, Atmos. Chem. Phys., 3, 2043–2051, 2003, http://www.atmos-chem-phys.net/3/2043/2003/.

Underwood, G. M., Li, P., Al-Abadleh, H. A., and Grassian, V. H.: A Knudsen cell study of the heterogeneous reactivity of nitric acid on oxide and mineral dust particles, J. Phys. Chem. A, 105, 6609–6620, 2001.

Underwood, G. M., Li, P., Usher, C. R., and Grassian, V. H.: Determining accurate kinetic parameters of potentially important heterogeneous atmospheric reactions on solid particle surfaces with a Knudsen cell reactor, J. Phys. Chem. A, 104, 819–829, 2000.

Usher, C. R., Michel, A. E., and Grassian, V. H.: Reactions on mineral dust, Chem. Rev., 103, 4883–4939, 2003a.

Usher, C. R., Michel, A. E., Stec, D., and Grassian, V. H.: Laboratory studies of ozone uptake on processed mineral dust, Atmos. Environ., 37, 5337–5347, 2003b.

Watts, S. F.: The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide, Atmos. Environ., 34, 761–779, 2000.

Wu, H. B., Wang, X., Cheng, J. M., Yu, H. K., Xue, H. X., Pan, X. X., and Hou, H. Q.: Mechanism of the heterogeneous reaction of carbonyl sulfide with typical components of atmospheric aerosol, Chinese Sci. Bull., 49, 1231–1235, 2004.

Wu, H. B., Wang, X., and Cheng, J. M.: Photooxidation of carbonyl sulfide in the presence of the typical oxides in atmospheric aerosol, Sci. China. Ser. B, 48, 31–37, 2005.