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Heterogeneous reactivity of carbonyl sulfide on α -Al₂O₃ and γ -Al₂O₃

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Abstract

The heterogeneous reactions of trace gases in the atmosphere on atmospheric particles could greatly affect the nitrogen, sulfur, ozone, and photochemical oxidant cycles. The uptake coefficient is an important kinetic parameter for atmospheric models to assess the role of heterogeneous reaction in the global cycles of trace gases. In this study, the heterogeneous uptake coefficients of carbonyl sulfide (OCS) on Al₂O₃ have been measured using a Knudsen cell reactor at 300 K. Hydrogen sulfide (H₂S) and carbon dioxide (CO₂) were found to be the gaseous products. The reaction mechanism of OCS on Al₂O₃ was confirmed based on previous work and this study. The true initial uptake coefficient and steady-state uptake coefficient of OCS on α -Al₂O₃ were $(3.8 \pm 0.8) \times 10^{-7}$ and $(6.5 \pm 2.49) \times 10^{-8}$, and the corresponding uptake coefficients on γ -Al₂O₃ were $(7.0 \pm 0.7) \times 10^{-8}$ and $(1.8 \pm 0.4) \times 10^{-8}$, respectively. The annual flux of OCS due to heterogeneous reaction on α -Al₂O₃ was calculated to be 0.11–0.63 Tg yr⁻¹ based on the initial uptake coefficient and the steady-state uptake coefficient. When the fraction of Al₂O₃ in authentic atmospheric particles is taken into account, the annual flux of OCS due to heterogeneous reaction on atmospheric particles in the troposphere should be 0.02–0.10 Tg yr⁻¹.

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Keywords: Heterogeneous reactivity; Carbonyl sulfide; Al₂O₃; Global flux; Knudsen cell

1. Introduction

Over the past decade, the heterogeneous reaction of trace gases in the troposphere on atmospheric particles has attracted much attention (Ravishankara, 1997) because it not only affects the sources and sinks of trace gases but also accounts for the alteration of the particulate composition and surface properties (Jacob, 2000; Katrib et al., 2005)

which is closely related to the Earth's direct and indirect radiation balance (Anderson et al., 2003). It is estimated that the annual flux of atmospheric particles in the form of mineral dust, sea salt, organics, sulfate as well as soot is between 3000 and 5000 Tg (Dentener et al., 1996). A major contribution to the tropospheric particulate matter budget is mineral dust that mainly originates from arid and semi-arid areas with a global source strength of about 1000–3000 Tg yr⁻¹ (Grassian, 2002). Mineral dust in the troposphere providing reactive surfaces for heterogeneous chemistry could greatly affect the nitrogen, sulfur, ozone, and photochemical oxidant

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cycles (Andreae and Crutzen, 1997; Dentener et al., 1996; Jacob, 2000; Li et al., 2006). Many studies have been performed on the heterogeneous reactions of NO, NO₂, HNO₃, SO₂, H₂S, O₃, carbonyl compounds, alcohols, and organic acids on the model oxides of mineral dust including SiO₂, α -Al₂O₃, γ -Al₂O₃, α -Fe₂O₃, Fe₃O₄, CaO, MgO, ZnO, TiO₂, CeO₂, ZrO₂, kaolinite, etc. (Usher et al., 2003).

Carbonyl sulfide (OCS) is the most abundant sulfur compound in the atmosphere with a rather uniform mixing ratio of about 500 pptv in the troposphere (Watts, 2000). It contributes to the formation of stratospheric sulfate aerosol, which has an important influence on the Earth's radiation balance (Crutzen, 1976; Turco et al., 1980) and stratospheric ozone chemistry (Simmons et al., 1999). Therefore, much interest has been focused on the sources and sinks of OCS. Numerous sinks have been identified to date, such as oxic soils, vegetation, homogeneous reaction with OH and O as well as photolysis (Watts, 2000). Recently, a few studies have also reported the reaction mechanism of OCS on atmospheric particles, Al₂O₃, SiO₂, Fe₂O₃, CaO, and MnO₂ (He et al., 2005; Liu et al., 2006; Wu et al., 2004a, b). Hydrogen thiocarbonate (HSCO₂⁻) was observed as a key intermediate (He et al., 2005; Liu et al., 2006). CO₂ and SO₄²⁻ were found to be the gaseous and surface products, respectively. Surface sulfite (He et al., 2005; Liu et al., 2006) and elemental sulfur (Wu et al., 2004a, b) were also observed. However, very little is known about the heterogeneous reactivity of OCS on mineral oxides or atmospheric particles. Al₂O₃ is one of the most important components of atmospheric particles in the troposphere (Usher et al., 2003) and is often used as a model oxide for the study of heterogeneous reactions. In this paper, the uptake coefficients, γ , for OCS on α -Al₂O₃ and γ -Al₂O₃ were measured using a Knudsen cell reactor coupled to a mass spectrometer. The contribution of heterogeneous reaction to the global sinks of OCS is also discussed.

2. Experiment

2.1. Materials

The α -Al₂O₃ and γ -Al₂O₃ samples were prepared from boehmite (AlOOH, supplied by Shandong Alumina Corporation) by calcining at 873 and 1473 K, respectively.

All of the other chemicals were used as received without further treatment: carbonyl sulfide (OCS, 1.98%, OCS/N₂, Beijing Huayuan Gases Inc.); N₂ and O₂ (99.99% purity, Beijing AP BEIFEN Gases Inc.); C₂H₅OH (99.7%, Beijing Chemicals Factory).

2.2. Characterization of samples

The X-ray powder diffraction pattern was collected from 10° to 90° 2 θ on a D/max-RB automatic powder X-ray diffractometer using Cu K α irradiation. The Al₂O₃ sample calcined at 873 K was identified as γ -Al₂O₃ with the three main peaks at 37.0°, 47.0°, and 66.7°. The Al₂O₃ sample calcined at 1473 K was identified as α -Al₂O₃ with the three main peaks at 35.0°, 43.0°, and 57.0°. Nitrogen BET physisorption measurement was performed using a Micromeritics ASAP 2000 analyzer, and the specific surface areas for γ -Al₂O₃ and α -Al₂O₃ were 257 and 12 m² g⁻¹, respectively.

2.3. Methods

A Knudsen cell reactor coupled to a quadrupole mass spectrometer (Hiden, HAL 3F PIC) was used to determine the uptake coefficients of OCS on particle surfaces. The mass spectrometer was housed in a vacuum chamber equipped with a 300 L s⁻¹ turbomolecular pump (Pfeiffer) and an ion gauge (BOC Edward). The vacuum chamber between the quadrupole mass spectrometer (QMS) and the Knudsen cell reactor was pumped by a 60 L s⁻¹ turbomolecular pump for differential pumping of the mass spectrometer and an ion gauge (both from BOC Edward).

The Knudsen cell reactor consisted of a stainless steel chamber with a gas inlet controlled by a leak valve, an escape aperture whose area could be adjusted with an adjustable iris, and a sample holder attached to the top ceiling of a circulating fluid bath. The geometric area of the sample holder, A_s , was 5.26 cm². A blank flange, serving as sample cover, attached to a linear translator made it possible to either isolate or expose the sample to reactant gas. No corrections were needed because the volume change upon opening the sample cover was <0.52 cm³ and the total volume of the reactor chamber was 94.0 cm³. The seal between the cover and sample holder was made with a Teflon O-ring. All exposed interior surfaces including 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 due to the sample holder. The temperature of the sample holder was measured by an embedded Pt resistance thermometer and could also be controlled from 233 to 373 K within ± 0.10 K using a super thermostat and a cryofluid pump (DFY-5/80, Henan Yuhua Laboratory Instrument Co, Ltd.).

The particle samples were dispersed evenly on the sample holder with alcohol and then dried at 393 K for 2 h. The pre-treated samples and reactor chamber were evacuated at 323 K for 6 h to reach a base pressure of approximately 5.0×10^{-7} Torr. After the system was cooled to 300 K, the sample cover was closed. The 1.51% OCS gas balanced with simulated air (21% O₂ and 79% N₂) was introduced into the reactor chamber through a leak valve. The pressure in the reactor was measured using an absolute pressure transducer (BOC Edward). Prior to the experiments, the system was passivated with OCS in air for 150 min to a steady QMS signal as the samples were isolated from the gas by the sample cover. Uptake measurements on all samples were obtained with an average OCS partial pressure of $(5.3 \pm 0.3) \times 10^{-6}$ Torr, equivalent to $(1.7 \pm 0.2) \times 10^{11}$ molecules cm⁻³ or 7.0 ± 0.3 ppb.

The effective area of the escape aperture, A_h , was measured in each independent experiment with N₂ which was taken as the ideal gas under experimental conditions. In this case, there is no residence time on the reactor walls. A_h can be calculated from

$$A_h = \frac{4Vk_{\text{esc}}^{\text{ideal}}}{\bar{v}}, \quad (1)$$

where $k_{\text{esc}}^{\text{ideal}}$, the inverse of residence time τ (s), is the first-order escape constant for ideal gas (s⁻¹), V is the volume of the reactor chamber (m³), and \bar{v} is the mean molecular speed (m s⁻¹) (Li et al., 2002). $k_{\text{esc}}^{\text{ideal}}$ was also determined through suddenly changing the molecule flow into the chamber from one steady state to a new steady state, thus

$$\ln\left(\frac{I - I'}{I_0 - I'}\right) = -k_{\text{esc}}^{\text{ideal}} t, \quad (2)$$

where I_0 and I' are the QMS signal intensities of N₂ for the first steady state and the second one, respectively, I is the QMS signal intensity of N₂ between the two steady states, and t is time (s). Therefore, $k_{\text{esc}}^{\text{ideal}}$ can be obtained from the slope of the plot of $\ln((I - I')/(I_0 - I'))$ versus t . The effective area of the escape hole was around 0.40 mm² in all of the experiments with a relative error of 6%

measured in reproducible experiments, and the residence time was approximately 1.8 s.

3. Results

3.1. Heterogeneous reaction of OCS on Al₂O₃

To investigate the heterogeneous reaction of OCS on Al₂O₃, a sample was exposed to a steady-state flow of OCS (1.51%) balanced with air (21% O₂ + 79% N₂) in the Knudsen cell. A representative QMS signal response of α -Al₂O₃ exposed to OCS is shown in Fig. 1. The observed uptake coefficient in Fig. 1C will be discussed in the following section. In this particular experiment, 50.2 mg of α -Al₂O₃ was exposed to 7.0 ppb of OCS/air for 30 min at 300 K. An immediate decrease in the mass spectral intensity for OCS ($m/z = 60$) was observed when the sample cover was opened. The initial drop in mass spectral intensity for OCS was 47.3%, and then the intensity of the mass signal increased gradually with time to a steady state with a steady drop of 11.6%. When the sample cover is opened, the QMS signal of reactant gases from the Knudsen cell usually responds in three ways: (i) recovery to the baseline intensity which indicates saturation coverage with increasing exposure time; (ii) indefinite continuation of the initial signal intensity which represents catalytic reactions; (iii) a combination of the previous two scenarios (Michel et al., 2003). Obviously, a heterogeneous reaction occurred for OCS on α -Al₂O₃ as shown in Fig. 1A. In our previous work (He et al., 2005; Liu et al., 2006), surface hydrogen thiocarbonate (HSCO₂⁻) was observed as the key intermediate, and gaseous carbon dioxide (CO₂), surface hydrogen carbonate (HCO₃⁻) and sulfate (SO₄²⁻), etc. were also identified with *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ*-DRIFTS) for heterogeneous reaction of OCS on Al₂O₃. This is in good agreement with the Knudsen cell study.

In all of the experiments, mass channels including m/z 44 (CO₂ and OCS-O), m/z 34 (H₂S), m/z 18 (H₂O), and m/z 64 (SO₂) were also monitored. As shown in Fig. 1B, the signal intensity of 44 also decreased intermediately with a maximal drop of 16.6% when the sample cover was opened, and then increased with time to a steady state. However, the intensity of 44 at the steady state exceeded the baseline slightly. If the mass channel at 44 only originates from the fragment of OCS (OCS-O), the change in mass spectra at 44 should be similar to its

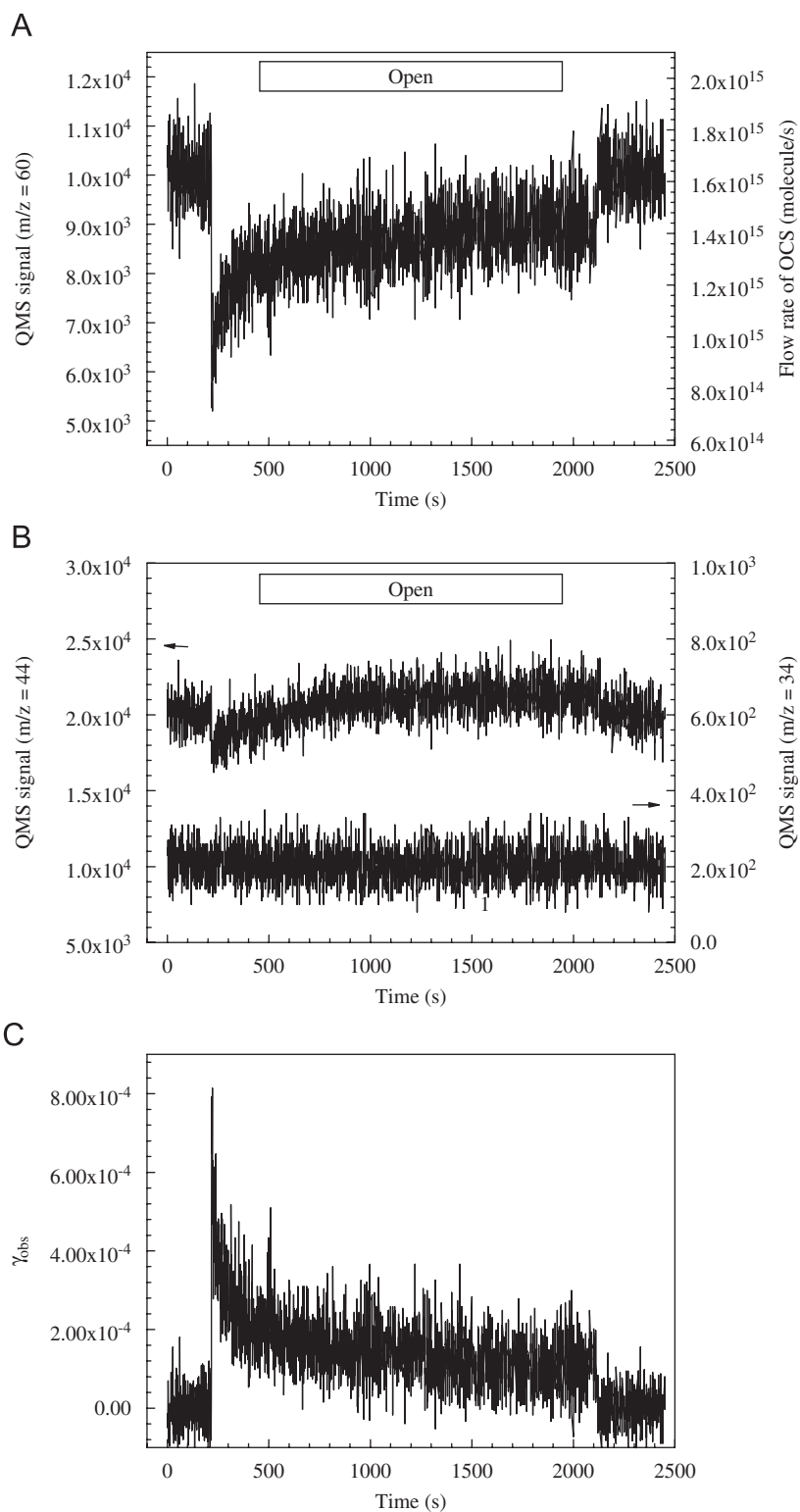
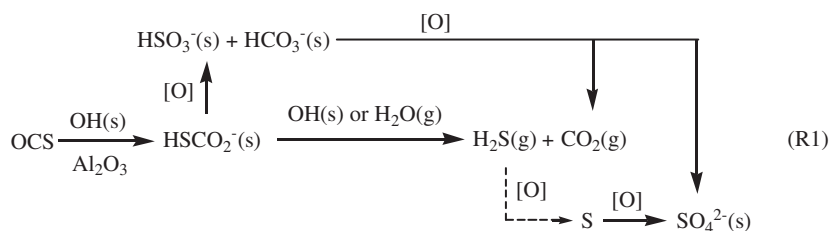


Fig. 1. Knudsen cell data for the uptake of OCS in air on 50.2 mg of α -Al₂O₃ at 300 K for (A) $m/z = 60$; (B) $m/z = 44$ and $m/z = 34$; (C) for observed uptake coefficient. Conditions of OCS flow: 1.51% OCS in air balance (21% O₂ + 79% N₂).

parent mass (OCS). However, the QMS signal intensity for OCS did not recover to the baseline within 30 min as shown in Fig. 1A. On the other hand, the maximal drop for 44 is only approximately one-third of that for OCS ($m/z = 60$). According to previous studies, CO_2 is one of the gaseous products for catalytic oxidation or hydrolysis of OCS on alumina at ambient temperature (He et al., 2005; Liu et al., 2006; Thomas et al., 2003; West et al., 2001; Wu et al., 2004a, b). Therefore, the discrepancy for

and H_2S desorbed noticeably at 300 K when the sample cover was opened. This suggests that H_2S is also one of the gaseous products of heterogeneous reaction of OCS on $\alpha\text{-Al}_2\text{O}_3$. The QMS data for the adsorption and reaction of OCS on $\gamma\text{-Al}_2\text{O}_3$ (not shown) resemble that on $\alpha\text{-Al}_2\text{O}_3$. On the basis of the results obtained in this study and previous work (He et al., 2005; Liu et al., 2006; Wu et al., 2004a, b), the reaction mechanism of OCS on Al_2O_3 can be confirmed as follows:



the QMS signal between 44 and 60 can be ascribed to the production of gaseous CO_2 that offsets the drop in the mass channel at 44. However, no change in QMS signal was observed for H_2S ($m/z = 34$), the same was also true for SO_2 (data not shown). It should be noted that the heterogeneous reaction of OCS under these experimental conditions is so slow that the amount of gaseous products should be very small. Meanwhile, the sulfur-products may be mainly absorbed on the surface (Datta and Cavell, 1985) or be oxidized to other species on the surface, such as S, SO_3^- , and SO_4^{2-} (He et al., 2005; Liu et al., 2006; Wu et al., 2004a, b). Apart from these reasons, in typical experiments, only 2.8% of gas molecules in the reactor flow into the QMS detector. This may be lower than the sensitivity of QMS for the concentration change of H_2S produced by heterogeneous reaction in the reactor upon opening the sample cover. In order to further identify the gaseous products, the following experiments were carried out with a larger escape aperture.

After OCS/air flow into the reactor had been stopped for the above sample, the reactor chamber was evacuated to 5.0×10^{-7} Torr with the sample cover closed. Then the escape aperture was increased to 300 from 0.40 mm^2 with the adjustable iris. The molecule flow into the QMS detector was increased from 2.8% to 56.4% in the reactor. The QMS data are shown in Fig. 2. Desorption of OCS and SO_2 (data not shown) was negligible while CO_2

where (s) is surface species; (g) is gaseous species; and [O] is gaseous or surface oxygen species.

3.2. Uptake coefficients of OCS on Al_2O_3

A heterogeneous uptake coefficient, γ , can be calculated using the Knudsen cell equation derived for steady-state uptake (Beichert and Finlayson-Pitts, 1996; Tabor et al., 1994; Ullerstam et al., 2003; Underwood et al., 2000):

$$\gamma_{\text{obs}} = \frac{A_h}{A_s} \times \frac{I_0 - I}{I}, \quad (3)$$

where A_h is the effective area of the escape aperture (cm^2); A_s is the geometric area of the sample holder (cm^2); and I_0 and I are the mass spectral intensities with the sample holder closed and open, respectively. Typical γ_{obs} values with exposure time are shown in Fig. 1C. For 50.2 mg of $\alpha\text{-Al}_2\text{O}_3$ sample, the initial observed uptake coefficient for the maximal value, $\gamma_{\text{obs}}(\text{MAX})$, was $(6.9 \pm 1.0) \times 10^{-4}$. The average initial observed uptake coefficient within the first 10 s, $\gamma_{\text{obs}}(\text{AVG})$, was calculated to be $(5.1 \pm 0.8) \times 10^{-4}$. The observed uptake coefficient for steady state, $\gamma_{\text{obs}}(\text{SS})$, was $(8.7 \pm 1.3) \times 10^{-5}$ which decreased to 12.8% of the maximal uptake coefficient. The relative errors in A_s ($\pm 1\%$), A_h ($\pm 6\%$), I ($\pm 5\%$, relative standard deviation), and I_0 ($\pm 5\%$, relative standard deviation) yielded a systematic relative error in γ_{obs} of $\pm 15\%$. The

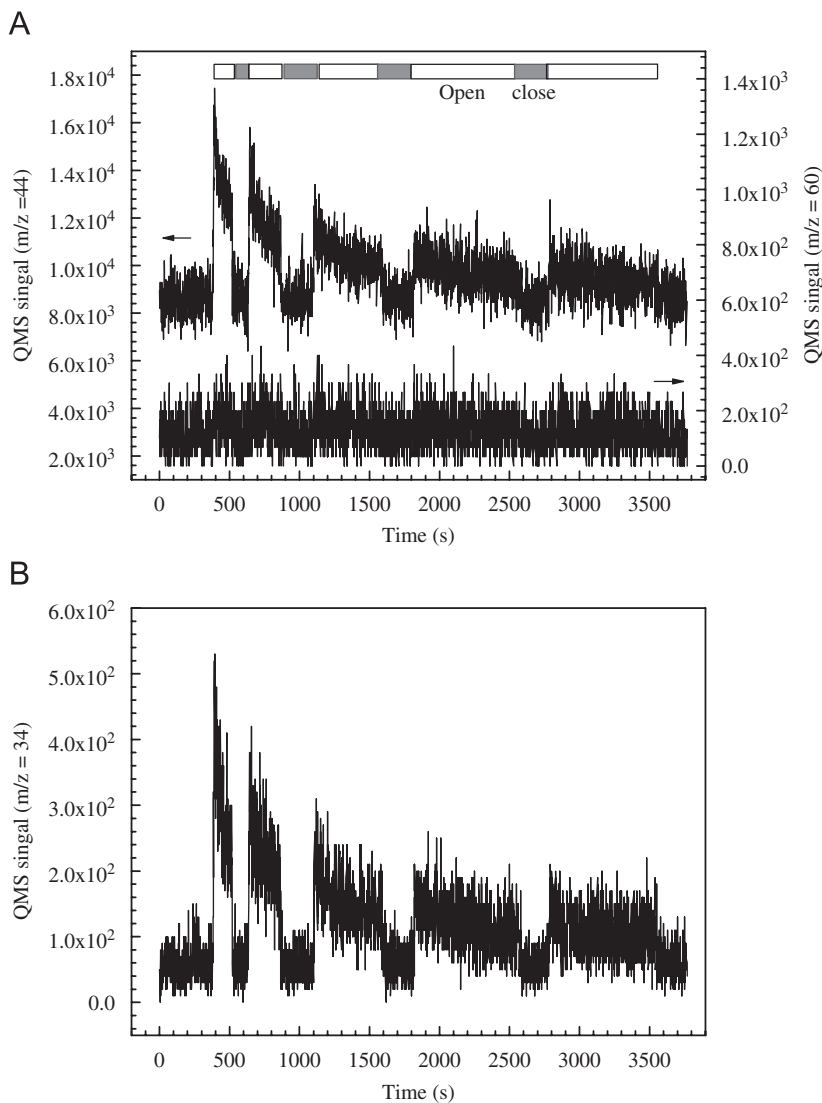


Fig. 2. QMS data for the desorption of surface species after reactant flow was stopped at a larger escape aperture (300 mm²) for (A) $m/z = 60$ and $m/z = 44$; (B) $m/z = 34$.

relative error for reproducible experiments was also $\pm 15\%$. Therefore, the relative errors for observed uptake coefficients were given by the reproducible experiments in Fig. 3.

It should be noted that the observed uptake coefficients decreased with exposure time corresponding to the increase in the QMS signal of OCS. Two stages can be classified in Fig. 1C. The first one is the sharp descending stage within 5 min which is due to the increase in coverage of surface OCS. The second one is the plateau region corresponding to the catalytic reaction. It can be deduced that the trend for observed uptake coefficients should decrease slowly with longer exposure times, because

the formed surface sulfate or sulfur (He et al., 2005; Liu et al., 2006; Wu et al., 2004a,b) blocked the active site for heterogeneous reaction.

As for the powder sample, the linear mass dependent (LMD) region of the observed uptake coefficient has been reported by different groups in various reaction systems (Al-Abadleh and Grassian, 2000; Frinak et al., 2004; Gebel and Finlayson-Pitts, 2001; Ullerstam et al., 2003; Underwood et al., 2001), and has been ascribed to the diffusion of reactant molecules into the underlying layers of multilayer powder samples. This phenomenon was also observed in our experiments. As shown in Fig. 3A, there is initially a strong linear dependence

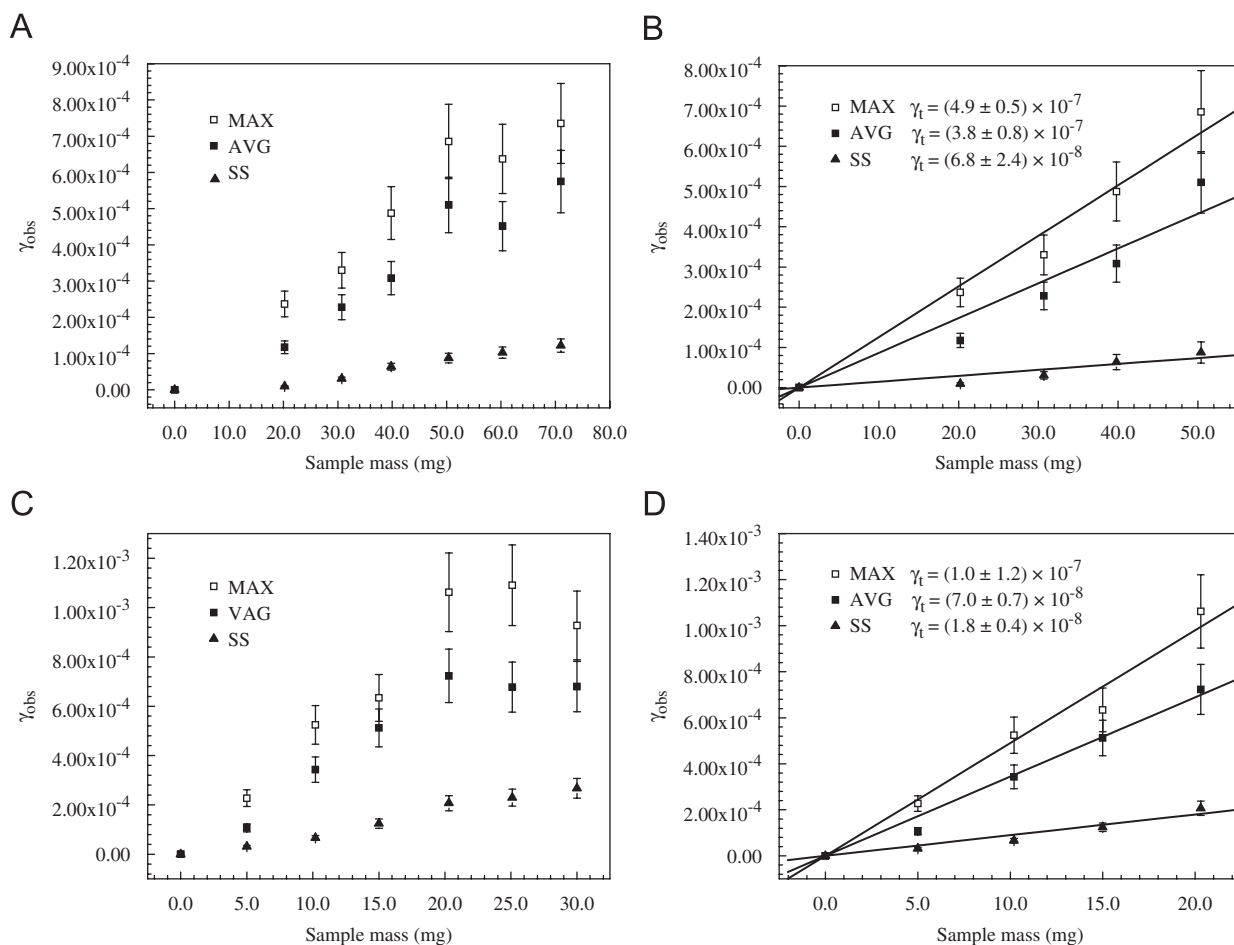


Fig. 3. Linear mass dependence of OCS on α -Al₂O₃ and γ -Al₂O₃ at 300 K. (A) and (B) for α -Al₂O₃; (C) and (D) for γ -Al₂O₃. Conditions of OCS flow: 1.51% OCS in air balance (21% O₂ + 79% N₂) (MAX is the maximal value, AVG is the average value in the initial 10 s, SS is the steady state value).

of $\gamma_{\text{obs}}(\text{MAX})$, $\gamma_{\text{obs}}(\text{AVG})$ as well as $\gamma_{\text{obs}}(\text{SS})$ versus sample mass with correlation coefficients of 0.990, 0.969, and 0.941, respectively. Along with the increase in sample mass, all of these observed uptake coefficients reached constant values. The diffusion depth of OCS on α -Al₂O₃ within the reaction time is approximately 136 μm corresponding to 50 mg. The true uptake coefficients, γ_t , can be calculated from

$$\gamma_t = \text{slope} \times \left(\frac{A_s}{S_{\text{BET}}} \right), \quad (4)$$

where slope is the slope of the plot of γ_{obs} versus sample mass in the linear regime (mg^{-1}); A_s is the geometric area (cm^2) of the sample holder, and S_{BET} is the specific surface area of the particle sample ($\text{cm}^2 \text{mg}^{-1}$) (Carlos-Cuellar et al., 2003). Therefore, $\gamma_t(\text{MAX})$, $\gamma_t(\text{AVG})$, and $\gamma_t(\text{SS})$ values for OCS on

α -Al₂O₃ are $(4.9 \pm 0.5) \times 10^{-7}$, $(3.8 \pm 0.8) \times 10^{-7}$, and $(4.7 \pm 2.4) \times 10^{-8}$, respectively. The relative errors for these true uptake coefficients are $\pm 11.0\%$, $\pm 20.4\%$, and $\pm 50.9\%$, respectively.

The Knudsen cell signal response of OCS on γ -Al₂O₃ resembles that on α -Al₂O₃. As shown in Fig. 3C and D, the LMD region is also clear in the range of 0–20 mg, which corresponds to a diffusion depth of about 148 μm . Usually, the probe depth of reactant molecules depends on γ_t , particle size, particle roughness, and the surface saturation coverage (Underwood et al., 2001). The diffusion depth for OCS into γ -Al₂O₃ is almost the same as that for α -Al₂O₃ (136 μm) in spite of the different linear ranges of the observed uptake coefficient and mass. The true uptake coefficients of OCS on γ -Al₂O₃ were calculated from Eq. (4) as follows: $\gamma_t(\text{MAX})$, $\gamma_t(\text{AVG})$, and $\gamma_t(\text{SS})$, are $(1.0 \pm 1.2) \times 10^{-7}$, $(7.0 \pm 0.7) \times 10^{-8}$, and

Table 1
True uptake coefficient and flux of OCS due to heterogeneous reaction

Sample	γ_t	k_{het} (s^{-1})	$t_{1/2}$ (years)	Conversion (1 year, %)	Flux (Tg yr^{-1})
$\alpha\text{-Al}_2\text{O}_3$					
MAX	$(4.9 \pm 0.5) \times 10^{-7}$	$(6.0 \pm 0.7) \times 10^{-9}$	3.9 ± 0.4	17.3 ± 1.7	0.80 ± 0.08
AVG	$(3.8 \pm 0.8) \times 10^{-7}$	$(4.6 \pm 0.9) \times 10^{-9}$	5.0 ± 1.0	13.6 ± 2.6	0.63 ± 0.12
SS	$(6.5 \pm 2.4) \times 10^{-8}$	$(7.9 \pm 0.3) \times 10^{-7}$	32.2 ± 11.8	2.5 ± 0.9	0.11 ± 0.04
$\gamma\text{-Al}_2\text{O}_3$					
MAX	$(1.0 \pm 1.2) \times 10^{-7}$	$(1.2 \pm 0.1) \times 10^{-9}$	19.5 ± 2.3	3.6 ± 0.4	0.16 ± 0.02
AVG	$(7.0 \pm 0.7) \times 10^{-8}$	$(8.1 \pm 0.8) \times 10^{-10}$	27.6 ± 2.8	2.5 ± 0.26	0.12 ± 0.01
SS	$(1.8 \pm 0.4) \times 10^{-8}$	$(2.9 \pm 0.5) \times 10^{-10}$	111.4 ± 24.8	0.7 ± 0.15	0.03 ± 0.01

$(1.8 \pm 0.4) \times 10^{-8}$, respectively. Wu et al. (2004b) reported the apparent reaction rate constants of OCS on Al_2O_3 at 295 K which were determined with a White cell (FTIR). The apparent rate constants for basic, neutral, and acidic alumina are 1.51×10^{-4} , 9.81×10^{-5} , and 3.06×10^{-6} , respectively. However, our results can not be compared with their data because different experimental methods, samples, and reaction conditions were used.

When the QMS signal intensity (I) was calibrated with molecular flow rate (F , molecule s^{-1}), the adsorption capacity could be calculated. It was 0.244 ± 0.106 molecule nm^2 and 0.041 ± 0.009 molecule nm^2 for $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$, respectively, when the contribution from the catalytic reaction was subtracted.

4. Discussion

Although the observed uptake coefficient of OCS on $\gamma\text{-Al}_2\text{O}_3$ is much higher than that on $\alpha\text{-Al}_2\text{O}_3$, the true uptake coefficient is only about one-fifth of that on $\alpha\text{-Al}_2\text{O}_3$. It should be noted that $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ were obtained by calcining AlOOH at 873 and 1473 K, respectively. The specific surface area of $\gamma\text{-Al}_2\text{O}_3$ ($257 \text{ m}^2 \text{ g}^{-1}$) is approximately 21 times higher than that of $\alpha\text{-Al}_2\text{O}_3$ ($12 \text{ m}^2 \text{ g}^{-1}$). For samples such as $\gamma\text{-Al}_2\text{O}_3$ with high specific surface area, determined by N_2 adsorption, a large portion of the area contributed by internal pores may be invalid for the reaction of OCS, which was well supported by the adsorption capacity of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$. On the other hand, our previous work showed that surface hydroxyl was the key reactive site for the heterogeneous reaction of OCS on Al_2O_3 using *in situ*-DRIFTS (He et al., 2005; Liu et al., 2006, 2007). The higher true uptake coefficient of

OCS on $\alpha\text{-Al}_2\text{O}_3$ indicates the higher surface hydroxyl content in the unit area of $\alpha\text{-Al}_2\text{O}_3$ than that in $\gamma\text{-Al}_2\text{O}_3$. As discussed in the above section, the saturated adsorption capacity of OCS on $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ is 0.244 ± 0.106 and 0.041 ± 0.009 molecule nm^2 , respectively. This also demonstrates that the surface hydroxyl content in the unit area of $\alpha\text{-Al}_2\text{O}_3$ is higher than in $\gamma\text{-Al}_2\text{O}_3$.

The heterogeneous reaction rate coefficient, k_{het} , can be calculated using

$$k_{\text{het}} = \frac{\bar{v}}{4} \gamma_t \text{SA}, \quad (5)$$

where \bar{v} is the average velocity of OCS (m s^{-1}); γ_t is the true uptake coefficient at 300 K; and SA is the surface area of the dust event ($\text{m}^2 \text{ m}^{-3}$) (Frinak et al., 2004; Ravishankara, 1997; Sullivan et al., 2004). With the assumption of a dust loading of $150 \mu\text{m}^2 \text{ cm}^{-3}$ (de Reus et al., 2000; Frinak et al., 2004) and the true uptake coefficient of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ at 300 K, the heterogeneous reaction rate constant and half-life can be calculated. As shown in Table 1, the half-life of OCS for heterogeneous reaction varies from 3 to 111 years. When the reaction was treated as a pseudo-first-order reaction, the conversion of OCS on Al_2O_3 within 1 year can be calculated. The largest value for the conversion of OCS per year is $17.3 \pm 1.7\%$ originating from $\gamma_t(\text{MAX})$ on $\alpha\text{-Al}_2\text{O}_3$ and the lowest one is $0.7 \pm 0.2\%$ originating from $\gamma_t(\text{SS})$ on $\gamma\text{-Al}_2\text{O}_3$. As discussed in the previous section, the relative error for measurement of QMS signal intensity is approximately 5%, thus there is a large uncertainty for the maximal true uptake coefficient, $\gamma_t(\text{MAX})$. Therefore, the average value within 10 s, $\gamma_t(\text{AVG})$, should be used to represent the initial true uptake coefficient. In the troposphere, it is more reasonable

to take non-porous α -Al₂O₃ as the model oxide for authentic atmospheric particles. Therefore, the half-life and conversion based on α -Al₂O₃ are more credible. The half-life of OCS is 5.0 ± 1.0 years and the conversion of OCS per year on α -Al₂O₃ is $13.6 \pm 2.6\%$ based on the initial true uptake coefficient, γ_t (AVG). The corresponding half-life and conversion based on γ_t (SS) are 27.6 ± 2.8 years and $2.5 \pm 0.3\%$, respectively.

Assuming the total mass of OCS in the troposphere is 4.63 Tg (Chin and Davis, 1995), the flux of OCS due to heterogeneous reaction is about 0.64 ± 0.11 Tg yr⁻¹ based on γ_t (AVG) and 0.11 ± 0.04 Tg yr⁻¹ for γ_t (SS) of α -Al₂O₃, respectively. The calculated data are also shown in Table 1. When the fraction of Al₂O₃ (15%) in authentic atmospheric particles (He et al., 2005; Usher et al., 2003) is taken into account, the true uptake coefficient for atmospheric particles is calculated from

$$\gamma_{\text{APM}} = \sum f_i \gamma_i, \quad (6)$$

where γ_{APM} is the true uptake coefficient for atmospheric particulate matter, f_i is the fraction of oxide in atmospheric particles, and γ_i is the true uptake coefficient of corresponding oxide (Usher et al., 2002). The annual flux of OCS due to heterogeneous reaction should be 0.10 ± 0.02 and 0.02 ± 0.006 Tg yr⁻¹ based on γ_t (AVG) and γ_t (SS) of α -Al₂O₃, respectively. This value is equivalent to the annual flux of reaction with OH (Watts, 2000). It should be the low limit because atmospheric particles also consist of other reactive oxides for the heterogeneous reactions of OCS.

Although the kinetic parameters reported here were obtained under dry conditions at 300 K without considering the effect of temperature, relative humidity, pressure, and the reactivity of OCS on other oxides, the obtained results illustrate that the heterogeneous reactions of OCS on mineral oxides will have a strong bearing on the sinks of OCS in the atmosphere. The effect of temperature, relative humidity, pressure, and types of mineral oxides will be further investigated in future work.

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