high ← temperature → low

slow   adsorb   quick

SO₂   **Mineral dust**

quick   reaction   slow

high ← temperature → low

CONTENTS

Knudsen cell and smog chamber study of the heterogeneous uptake of sulfur dioxide on Chinese mineral dust

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ABSTRACT

The heterogeneous uptake processes of sulfur dioxide on two types of Chinese mineral dust (Inner Mongolia desert dust and Xinjiang sierozem) were investigated using both Knudsen cell and smog chamber system. The temperature dependence of the uptake coefficients was studied over a range from 253 to 313 K using the Knudsen cell reactor, the initial uptake coefficients decreased with the increasing of temperature for these two mineral dust samples, whereas the steady state uptake coefficients of the Xinjiang sierozem increased with the temperature increasing, and these temperature dependence functions were obtained for the first time. In the smog chamber experiments at room temperature, the steady state uptake coefficients of SO_2 decreased evidently with the increasing of sulfur dioxide initial concentration from 1.72×10^{12} to 6.15×10^{12} mol/cm^3. Humid air had effect on the steady state uptake coefficients of SO_2 onto Inner Mongolia desert dust. Consequences about the understanding of the uptake processes onto mineral dust samples and the environmental implication were also discussed.

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Introduction

Mineral dust is recognized as one of the major aerosols in the troposphere. Every year about 1000–3000 Tg mineral dust has been emitted into the atmosphere (Dentener et al., 1996; Harrison et al., 2001; Usher et al., 2003). Because of the transport distances and long atmospheric lifetime, mineral dust can provide reactive sites for surface-mediated heterogeneous reactions and influence the balance of atmospheric species by reacting with various trace gases (Prospero, 1999). Meanwhile, the thermodynamic and optical properties of mineral dust will also be altered (Lack et al., 2009).

As a predominating sulfur-containing gas, sulfur dioxide is one such critical pollutant, influencing the pH of rainwater and leading to the formation of secondary sulfate aerosol. The typical emitted SO_2 concentrations are about 10 pptv in remote regions, rising to several hundred ppb in polluted urban areas (Seinfeld and Pandis, 1998). The lifetime of SO_2 in the free troposphere is up to 15 days (Hanke et al., 2003).

Dust plumes that originate in Saharan Africa or central Asian can transport through or mix with air from more urbanized environment, so the chemical interactions between mineral dust aerosol and pollutants are important in atmospheric processing (Sullivan et al., 2007; Tang et al., 2004). From the already performed observations, it is apparent that mineral dust affects the local gas-phase concentration of sulfur dioxide, either by physical adsorption or by heterogeneous reaction. Many laboratory studies have focused on SO_2–dust interactions (Adams et al., 2005; Al-Hosney and Grassian, 2005; Baltrusaitis et al., 2007a,2007b; Goodman et al., 2001; Li et al., 2006; Ma et al., 2008; Santschi and Rossi, 2006; Seisel et al., 2006; Ullerstam et al., 2003). These series of results have important implications for improving the treatment of dust in global chemistry models and highlight many key processes that merit further investigation through laboratory and field studies. Whereas the experimental determination of rate constants for important atmospheric reactions and how these rate constants vary with temperature is still a crucial part of atmospheric science.

The temperature in the atmosphere varies with latitude, longitude, and altitude above the earth's surface, as well as with season and time of day. Therefore, the temperature dependence of the uptake coefficients of sulfur dioxide on mineral dust was further investigated over the temperature region of 253–313 K. In this study, we have investigated the heterogeneous uptake of SO_2 on two different types of powder samples which consist of <75 μm diameter fractions representative of mineral dust from the Inner Mongolia desert and Xinjiang arid region which are in the northwest of China. The concentration and relative humidity dependences of the steady state uptake coefficients of SO_2 on mineral dust have also been discussed.

1. Experimental section

1.1. Reactants

Inner Mongolia desert dust and Xinjiang sierozem used in this laboratory study were purchased from Chinese Stander Substance Center. The surface areas of these powders were measured with a Quantachrome Autosob-1-C BET apparatus (Quantachrome Instruments, autosorb-iQ, USA) that used a multipoint Brunauer–Emmett–Teller (BET) analysis. The BET areas were determined to be 5.06 m^2/g for Inner Mongolia desert dust, and 20.98 m^2/g for Xinjiang sierozem. X-ray experiments were carried out using Rigaku D/max-2500 diffractometer (Japan) with Cu K-radiation at 50 kV and 100 mA. Scans were performed from 2.6° to 50° (2θ) at a rate of 1° (2θ) per minute (Shen et al., 2009). The major peaks were indexed to permit recognition of the minerals. The main fractions of these mineral dusts are listed in Fig. 1.

Gaseous sulfur dioxide (99.9%) purchased from Beijing Huayuan Gas Chemical Industry Co., Ltd. was used directly without any purification.

1.2. Knudsen cell experiments

The uptake coefficient of sulfur dioxide on the mineral dust samples was measured by a Knudsen cell reactor coupled with an EI quadrupole mass spectrometer (Hiden, HAL 3F 501, UK). The detail of this experimental apparatus has been described elsewhere (Wang et al., 2011; Zhou et al., 2012).

Briefly, the Knudsen cell reactor consists of a chamber with four isolated sample compartments and a small escape aperture linking to the quadrupole mass spectrometer. The characteristics of the reactor are summarized in Table 1. The uptake of sulfur dioxide on mineral dust samples are monitored by m/z = 64 and 34 channels. In a blank experiment, there was no remarkable uptake due to the sample holder and the sample cover, with the gas phase reactant passing through the reactor. In addition, the parallel experiment using the four sample cells to assure the repeatability of the kinetic results was performed by loading the same weight of the mineral dust and entering the same concentration of SO_2. The effective area of the escape aperture was about 0.211 mm^2 in these experiments. The powdered samples were prepared in the Teflon-coated metal sample holders and the chamber can be either heated or cooled from 253 to 313 K by a circulator.

1.3. Smog chamber experiments

The experimental setup consisted of a 360-L Teflon bag located in a steel box to achieve a chemically inert environment. An inlet and an outlet made of Teflon are used for the introduction of reactants and sampling. The reactor and the analytical instruments are linked via Teflon tubes. In order to reduce the interference from the wall effect, the reactor was deactivated with SO_2 for more than 24 hr beforehand. Then the reactor was purged with purified zero-air. The relative humidity (RH) of the stream was controlled by the addition of a flow of humidified zero-air and the RH was recorded by a hygrometer. Powdered dust samples were rapidly introduced into the chamber through a pressurized sample line. A nozzle and enough pressure in the flow path ensure efficient deagglomeration of the sample and the mixing time of the chamber contents is less than 30 sec. The concentrations of sulfur dioxide in the entire chamber and the varying processes
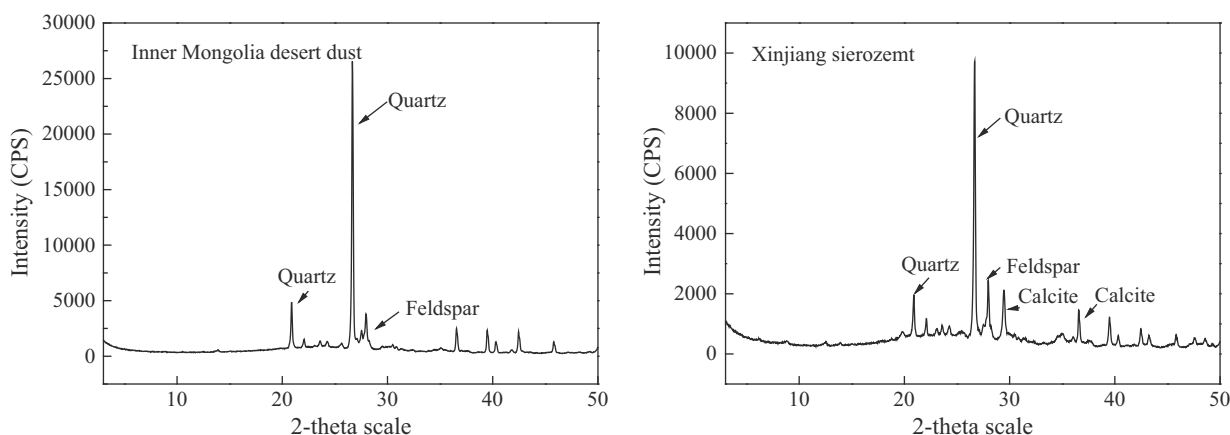
Fig. 1 – The main fractions of mineral dust samples from Inner Mongolia desert dust and Xinjiang sierozem carried out by the X-ray experiments.

during the reactions were monitored by SO$_2$–H$_2$S analyzer (Model 450i, Thermo Electron Corporation, USA). Its flow rate and precision were 0.7 L/min and 1 ppb, respectively. The measurement lasted for about 30 min to make sure the volume change less than 6%.

The absolute rate constant was governed by monitoring the sulfur dioxide decay rates in the presence of known concentrations of mineral dust. Under these conditions, the overall sulfur dioxide decay was caused by its wall decay and reaction with mineral dust. Before the dust was introduced into the chamber, the subsequent loss of SO$_2$ was less than 5%, and the wall losses can be neglected. The kinetics of sulfur dioxide loss can be modeled as a simple adsorption and reaction process with a rate constant, k (Mogili et al., 2006).

$$SO_2 + S \xrightarrow{\ k\ } P$$
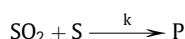
where, S represents the available surface sites in the reactor volume, and P represents reaction product species, either adsorption or reaction of gas phase.

2. Results and discussion

2.1. Knudsen cell experimental results

When one sample was exposed to sulfur dioxide, the signal of sulfur dioxide parent ion monitored at $m/z = 64$ dropped below its original value suddenly. An observed uptake coefficient, γ_{obs}, can be derived from the Knudsen cell (Eq. (1)):

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

where, A_h represents the effective area of the escape hole, A_s represents the geometric area of the sample holder, I_0 and I represent the QMS intensity detected when sample holder was covered and exposed. From this equation the initial uptake coefficients, $\gamma_{init,obs}$, are obtained.

Fig. 2 shows a typical QMS signal response of mineral dust exposed to sulfur dioxide. The mass spectral intensity of sulfur dioxide ($m/z = 64$) decreased immediately when the

sample holder was opened, then after a certain exposure time the uptake was irreversible at a single value.

When assuming that the total number of the gas–surface collisions is only with the top layer, the uptake coefficient γ_{obs} can be determined using the geometric surface area of the sample. The observed mass dependence depicted in Fig. 3 showed that the diffusion of the reactant gas to underlying layers was also involved, resulting in an increase in the number of collisions with the total surface area. These experiments were done to ensure that flowing experiments were conducted in the linear mass regime where the entire sample participates in the reaction correlated with the BET surface area (Underwood et al., 2000). Fig. 3 shows the region where γ_{obs} is linearly dependent on the mass of samples. From the plot, a mass independent uptake coefficient can be derived as

$$\gamma_{BET} = \frac{A_h}{A_{BET}}\left(\frac{I_0 - I}{I}\right) = \gamma_{obs}\frac{A_s}{A_{BET}} \tag{2}$$

where, A_{BET} represents the surface area of the sample, taken as the BET area, which is equal to the specific BET area of the powder times the sample mass (Underwood et al., 2001). The results in Table 2 are derived from the experiments done in this linear regime.

The influence of the sulfur dioxide concentration to the uptake coefficient was also taken into account over the range from 2.6×10^{11} to 7.4×10^{11} mol/cm^3. By varying the initial concentration of sulfur dioxide, there was no distinct dependence of initial uptake coefficient on this range of sulfur dioxide concentration. After a long time exposure, the uptake

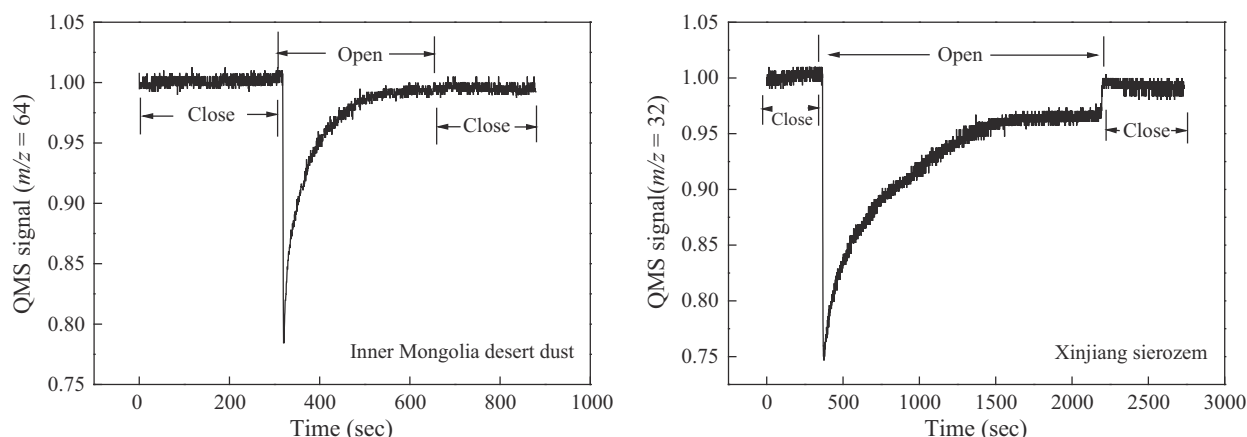| Table 1 – Knudsen reactor parameters.	
Knudsen reactor parameter	Value
Volume	461 cm^3
Temperature	253–313 K
Surface-to-volume ratio	0.57
Total pressure	1.5×10^{-3} Pa
Escape orifice diameter	3 mm
Escape orifice escape rate	0.297(T/M)$^{1/2}$ sec^{-1}
Sample surface area	5.3 cm^2
Sample collision frequency	91.3 sec^{-1}

Fig. 2 – Uptake curves of SO₂ on Inner Mongolia desert dust and Xinjiang sierozem at 283 K in Knudsen cell reactor.

of sulfur dioxide on mineral dust surface showed a saturated state and became inactive to further SO$_2$ decomposition; the sulfur dioxide signal intensity could recover to a steady state especially for Xinjiang sierozem.

The temperature dependence for the uptake coefficients of heterogeneous reactions on these mineral dust samples was further investigated over the temperature range of 253–313 K. As shown in Table 2, the initial uptake coefficients of Inner Mongolia desert dust are in the range of 4.71×10^{-5}–1.64×10^{-5}, and the ones of Xinjiang sierozem are in the range of 1.39×10^{-5}–5.66×10^{-6}. It was obvious that the initial uptake coefficients of sulfur dioxide on the mineral dust decreased with the increasing of temperature. This trend of the initial uptake coefficients with temperature agrees well with the physical adsorption process. However, the steady state uptake coefficients of Xinjiang sierozem are in the range of 0.75×10^{-6}–1.75×10^{-6}, which increased with the increasing of temperature and meant that the reaction exists.

Now that the initial uptake coefficients showed negative temperature dependence, the changes of observed enthalpy (ΔH_{obs}) and entropy (ΔS_{obs}) for SO$_2$ adsorption on mineral dust and the reactive energy (Ea) for Xinjiang sierozem can be

obtained by the following equation (Hudson et al., 2002; Jayne et al., 1991)

$$\ln\left(\frac{\gamma_{BET}}{1-\gamma_{BET}}\right) = -\frac{\Delta H_{obs}}{RT} + \frac{\Delta S_{obs}}{R} \tag{3}$$

$$\ln\left(\frac{\gamma_{ss}}{1-\gamma_{ss}}\right) = -\frac{Ea}{RT} + A \tag{4}$$

consequently, from the plot of the left side of Eq. (3) *versus* inverse temperature, as shown in Fig. 4, the enthalpy (ΔH_{obs}) and entropy (ΔS_{obs}) were determined to be –(10.9 ± 2.2) kJ/mol and –(125.6 ± 25.1) J K/mol for Inner Mongolia desert dust; –(9.3 ± 1.9) kJ/mol and –(129.4 ± 25.9) kJ/mol for Xinjiang sierozem. The reactive energy (Ea) for Xinjiang sierozem is 12.87 kJ/mol. Usually, for a given reaction in the atmosphere, when the activation energy is lower than 20 kJ/mol, the importance of the reaction in atmospheric chemistry cannot be ignored (Liu et al., 2008; Smith, 2003). The ΔH_{obs} value can demonstrate that SO$_2$ adsorbs on mineral dust in a similar capacity. The empirical formula between γ_{BET} of sulfur dioxide uptake on mineral dust and temperature can be calculated as:
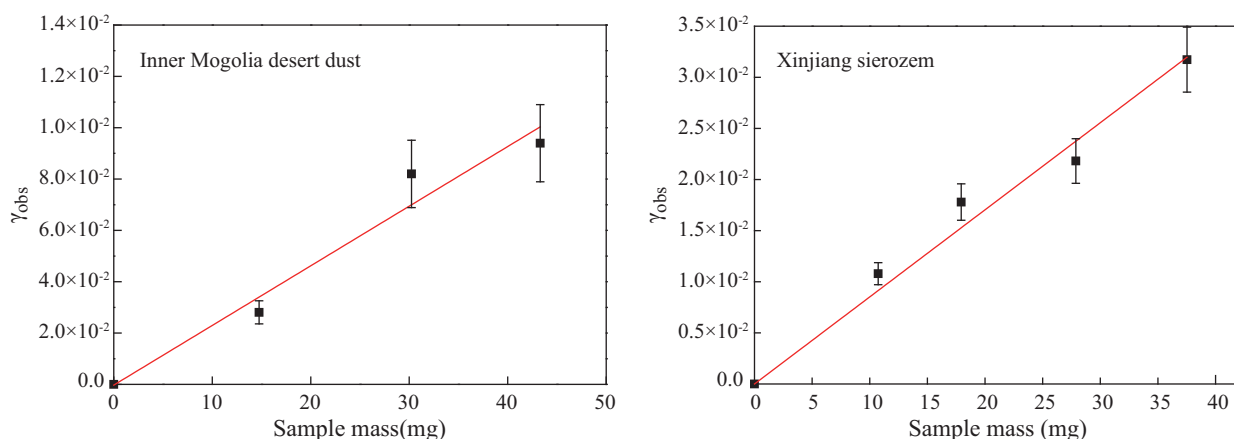

Fig. 3 – Uptake coefficient for SO2 on Inner Mongolia desert dust and Xinjiang sierozem calculated using the geometric surface area as the effective surface area as a function of sample mass.

Table 2 – Summary of the uptake coefficients of SO$_2$ on mineral dust at different temperatures.

Temperature (K)	$\gamma_{BET,int}$ ($\times 10^{-5}$) [a] of Inner Mongolia desert dust	$\gamma_{BET,int}$ ($\times 10^{-6}$) [a] of Xinjiang sierozem	$\gamma_{BET,ss}$ ($\times 10^{-6}$) [a] of Xinjiang sierozem
253	4.71 ± 0.95	13.9 ± 2.8	
268	3.54 ± 0.71	12.0 ± 2.4	0.75 ± 0.15
283	2.95 ± 0.59	9.65 ± 1.93	1.06 ± 0.21
298	2.41 ± 0.48	8.34 ± 1.67	1.33 ± 0.27
313	1.64 ± 0.33	5.66 ± 1.13	1.75 ± 0.35

[a] Each value is the average of at least three measurements, and the error corresponds to one standard deviation (σ).

For Inner Mongolia desert dust:

$$\gamma_{BET} = \frac{\exp(1309.0/T - 15.1)}{1 + \exp(1309.0/T - 15.1)} \qquad (5)$$

For Xinjiang calciferous dust:

$$\gamma_{BET,\,int} = \frac{\exp(1123.8/T - 15.6)}{1 + \exp(1123.8/T - 15.6)} \qquad (6)$$

For Xinjiang calciderous dust:

$$\gamma_{BET,\,ss} = e^{\left(-\frac{1548.0}{T} - 8.3\right)} \qquad (7)$$

where, T is the temperature (K). Thus, the γ_{BET} at other temperature can be obtained using these equations. At 253 K, the initial uptake coefficients of mineral dust were approximately two times larger than those at 298 K.

For Xinjiang sierozem, desorption rate constants (k_{des}) at different temperature can be calculated using the following equations (Liu et al., 2010; Seisel et al., 2004), based on the uptake profiles as shown in Fig. 1.

$$F(t) = A_h \left[P/(2\pi MRT)^{1/2} \right] \qquad (8)$$

$$F_{des}(t) = F(t)(1 + k_{ini}/k_{esc}) - F_0 \qquad (9)$$

$$F_{des}(t) = k_{des} N_{ads}(t) \qquad (10)$$

where, $F(t)$ (mol/sec) represents the flux out of the reactor at time t; P (mTorr) represents the pressure of the gas; T (K) represents the absolute temperature, $F_{des}(t)$ represents the desorption flux of SO$_2$ from the surface at time t (molecules·s^{-1}); k_{ini} represents the initial rate constant and equal to k_{ads} (sec^{-1}); k_{esc} represents the escape rate constant of the Knudsen cell (sec^{-1}), and $k_{esc} = \omega \cdot A_h$, ω represents the collision frequency of SO$_2$ with mineral oxide. k_{des} represents the desorption rate constant (sec^{-1}); F_0 represents the flux into the reactor (mol/sec^{-1}); $N_{ads}(t)$ represents the number of molecules adsorbed on the surface at time t, $N_{ads}(t)$ can be determined by integrating the QMS-signal between $t = 0$ and the desired time t. The temperature dependence of k_{des} is shown in Fig. 5. According to the slope of this plot, the activation energy for desorption (E_{des}) of SO$_2$ on Xinjiang sierozem was calculated to be (6.9 ± 1.0) KJ/mol.

2.2. Smog chamber experimental results

The smog chamber experiments were performed to monitor the kinetics of sulfur dioxide uptake at atmospheric pressure and room temperature, in a concentration range from 1.7×10^{12} to 6.15×10^{12} mol/cm^3.

In the wall effect experiment, SO$_2$ decay rate constant was quite small, so the SO$_2$ loss caused by background decay in this work is negligible. Fig. 6 represents the sulfur dioxide concentration decay as a function of time for different mineral dust samples. The plot shows that sulfur dioxide concentration decreases significantly, when the samples are injected, and then reactive losses due to the presence of the mineral dust continued. After logarithmic conversion, the logarithms of the ratios of the concentrations in the presence of reactants were plotted for different reaction time. The
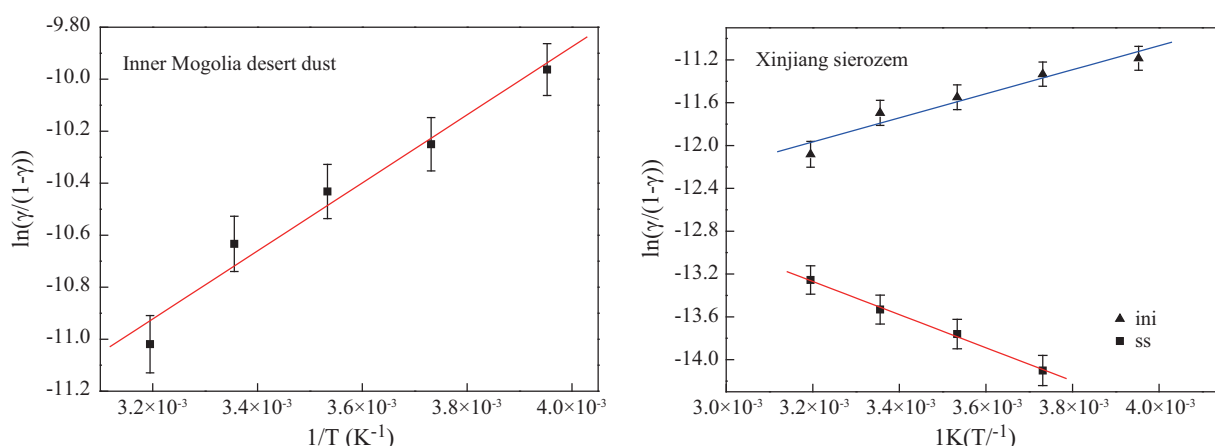
Fig. 4 – Plot to determine the temperature dependence of SO$_2$ on the panel of Inner Mongolia desert dust and Xinjiang sierozem, using the uptake coefficients.
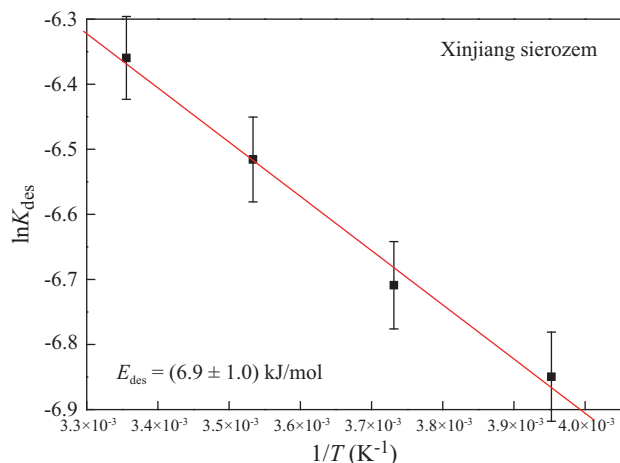
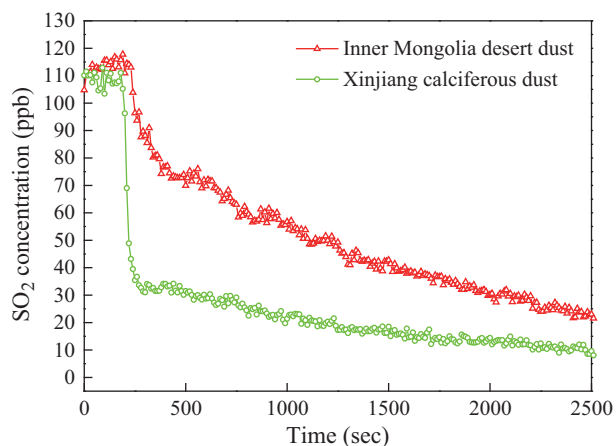**Fig. 5 – Plot to determine the dependence of desorption rate constant (K_{des}) of Xinjiang sierozem on temperature.**

Fig. 7 – The pseudo first-order plots for SO_2 with different mineral dust samples of Inner Mongolia desert dust and Xinjiang sierozem. The slope of such plots yields the pseudo first-order rate constant.

straight lines obtained on the time scale are represented in Fig. 7, which shows the typical plots obtained for reaction at 298 K. The slope of such plots yields the pseudo-first-order rate constant. The data shows that the concentration of SO_2 got from the analyzer had come to a steady state.

From the results above, the kinetics of sulfur dioxide loss can be modeled as a simple adsorption/reaction process with a rate constant, k_1 and k_2 (Prince et al., 2002).
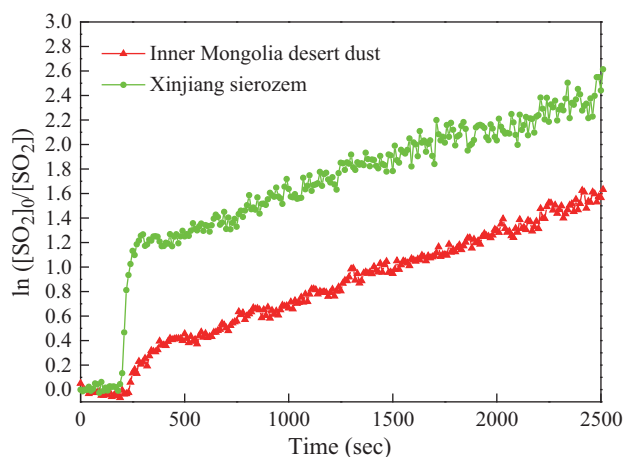
$$SO_{2(g)} + S \xrightleftharpoons[k_{-1}]{k_1} [SO_2 \cdot S] \tag{11}$$

$$[SO_2 \cdot S] \xrightarrow{k_2} product \tag{12}$$

When the system got a balance, the rate constants can be calculated by the equations below:

$$\frac{d[SO_2 \cdot S]}{dt} = k_1 [SO_{2(g)}][S] - k_{-1}[SO_2 \cdot S] - k_2[SO_2 \cdot S] = 0 \tag{13}$$

$$r_2 = k_2[SO_2 \cdot S] = \frac{k_1 k_2}{k_{-1} + k_2}[SO_{2(g)}][S] = k[SO_{2(g)}] \tag{14}$$

$$k = \frac{k_1 k_2}{k_{-1} + k_2}[S] \tag{15}$$

where, S represents the available surface sites in the reactor volume, which is correlated to the mass of dust loadings. These processes can be characterized in terms of a heterogeneous uptake coefficient γ which is the fraction of gas–surface collisions that lead to successful reaction. Assuming pseudo first-order conditions, γ can be determined from the following Eq. (16) (Mogili et al., 2006).

$$\gamma = \frac{4k}{\overline{c}S_{BET}v[C_{mass}]} \tag{16}$$

where, $\overline{c}$ is the mean speed of sulfur dioxide, C_{mass} is the mass concentration of the mineral dust sample, and S_{BET} is the specific surface area of the mineral dust, preciously measured by a BET analysis. The characteristic decay time, $\tau = 1/k$, k (sec^{-1}) can be determined by correcting k_{obs} for diffusion. $1/k = 1/k_{obs} - 1/k_{diff}$, k_{obs} is determined from the fit of an exponential function to the sulfur dioxide time course data. Fig. 8 shows the slope of which plots yield the pseudo-first-order rate constant k_{obs}. Assuming that the K_2CO_3 powder was a perfectly depositing surface for SO_2 (Sorimachi and Sakamoto, 2007; Sorimachi et al., 2004), the quick rate constant has been measured as 0.049 sec^{-1}.

The observed mass dependence involves the diffusion of the reactant gas, resulting in an increase in the number of collisions with the total surface area. Thus, it is an important factor in determining the reaction constants, which was done to ensure that experimental results were calculated in the linear mass regime where the entire sample participates in the reaction in the BET surface area. The calculated uptake coefficients when the concentrations of sulfur dioxides were fixed at about 3.44×10^{12} molecule cm^{-3} are shown in Fig. 8.

Fig. 6 – Sulfur dioxide concentration decay as a function of time for different mineral dust samples of Inner Mongolia desert dust and Xinjiang sierozem.
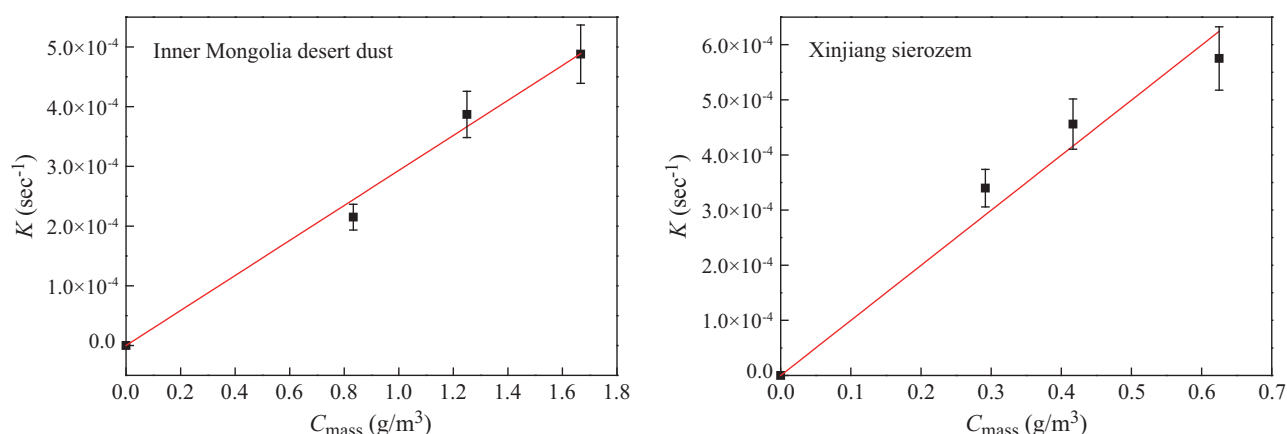
Fig. 8 – Linear mass-dependent regions of the uptake coefficients for SO₂ on Inner Mongolia desert dust and Xinjiang sierozem.

Several experiments were conducted to make a comparison among these two types of mineral dust in a range of initial concentration 1.72×10^{12}–6.15×10^{12} mol/cm^3. The uptake coefficients reported in Table 3 are the result of fits to the data with a single exponential function. The uptake coefficients of these two mineral dust samples were obviously correlated with the initial concentrations of the sulfur dioxide. As shown in Fig. 9, the higher initial sulfur dioxide concentration leads to a smaller steady state uptake coefficient. From the trend plots, the steady state uptake coefficients of each mineral dust could be calculated in the following equations.

Inner Mongolia desert dust:

$$\gamma_{BET} = 1.26 \times 10^{14} \times [SO_2]_0^{-1.70} \tag{17}$$

Xinjiang calciferous dust:

$$\gamma_{BET} = 1.15 \times 10^{8} \times [SO_2]_0^{-1.15}. \tag{18}$$

When the initial concentration of SO₂ is approximately 6.15×10^{11} mol/cm^3, the steady state uptake coefficients derived from the above equations for the Inner Mongolia desert dust and Xinjiang sierozem are 1.60×10^{-6} and 3.66×10^{-6} respectively, which can be comparable to the results got from the Knudsen cell experiments.

In the ambient atmospheric condition high relative humidity might have an influence on these reactions, which cause more complex processes in the atmosphere. Al-Hosney et al. have found that adsorbed water significantly influences

the uptake of most pollutant gases onto carbonate component of mineral dust aerosols (Al-Hosney and Grassian, 2005). However, the uptake coefficient of SO₂ on Saharan dust was not affected by an increase in relative humidity from 0% to 27%. (Adams et al., 2005). In the study of Ma et al. (2012), adsorbed water molecules have little enhancement effect for the conversion of SO₂ to sulfate species on the dust storm particles. In our smog chamber system, the relative humidity (RH) dependence of uptake coefficients of SO₂ onto mineral dust was also investigated. During the experiments, SO₂ (2.46×10^{12} mol/cm^3) with different RH (20%–80%) was preadjusted well in the chamber, and then 450 mg dust was sprayed into the chamber to start the reaction. As shown in Fig. 10, the steady state uptake coefficients of SO₂ onto Inner Mongolia desert dust have obvious dependence with RH. At RH = 40% the uptake coefficients of SO₂ are about five times larger than in dry condition. But the influence of RH to Xinjiang sierozem is little. The various structures of the dust samples may provide the different active sites and hygroscopic properties for the samples. Al-Hosney and Grassian have found that the adsorbed water film assists in the enhanced uptake of sulfur dioxide on CaCO₃ (Al-Hosney and Grassian, 2005). However, the uptake process is not influenced by the presence of humidity for Saharan dust (Adams et al., 2005). Depending on the size of the mineral dust inclusion and the mineralogy of the inclusion, sulfate coatings on mineral dust undergo efflorescence (crystallization) at different relative humidity (Usher et al., 2003). These reasons may lead to the different effects on uptake coefficients onto mineral dust.

Table 3 – Summary of the uptake coefficients of SO₂ on mineral dust with different [SO₂]₀ in smog chamber.			
Inner Mongolia desert dust		Xinjiang sierozem	
$[SO_2]_0 (10^{12}$ mol/cm^3)	$\gamma_{BET,ss} (\times 10^{-7})$ [a]	$[SO_2]_0 (\times 10^{12}$ mol/cm^3)	$\gamma_{BET,ss} (\times 10^{-7})$ [a]
1.72	1.99 ± 0.10	2.71	5.59 ± 0.28
2.46	1.17 ± 0.06	3.44	4.91 ± 0.25
3.44	0.69 ± 0.03	4.92	2.96 ± 0.15
4.92	0.33 ± 0.02	6.15	2.25 ± 0.11

[a] Each value is the average of at least three measurements, and the error corresponds to one standard deviation (σ).

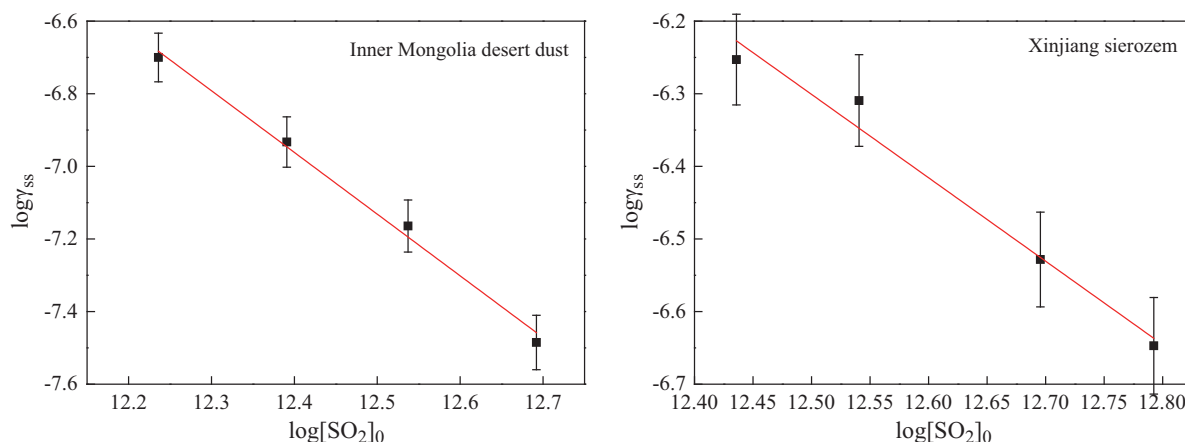**Fig. 9 – Plots to determine the concentration dependence of SO$_2$ on Inner Mongolia desert dust and Xinjiang sierozem using the uptake coefficient.**

2.3. Uptakes onto different mineral dust

Compared with the experimental data of sulfur dioxide uptake on different mineral dusts, the results presented that the uptake processes of these two Chinese mineral dust samples had a similar phenomenon. For the two dusts, sulfur dioxide was firstly major absorbed on the surface of the dust and then performed a further reaction. The initial absorbable trend was closely correlated with the BET areas of each mineral dust. In Knudsen cell or in smog chamber experiments, Xinjiang sierozem shows an apparently quicker initial uptake for sulfur dioxide because of a larger BET area. However, the continued reactions were tightly related to the active sites on the mineral dust.

In this study the experiments were mostly performed under dry condition. Nevertheless, some adsorbed water will be still present in the dust sample. Different types of water-related-reactive sites are present on the surface in form of O^- or OH group. The surface adsorbed water present during the experiment has not been quantified. The formation of absorbed

sulfate/bisulfate on the oxide particles is consistent with the reaction of gas-phase SO$_2$ with surface (Usher et al., 2002)

$$SO_2(g) \ + \ O^{2-}(s) \rightarrow SO_3{}^{2-}$$

$$SO_2(g) \ + \ OH^-(s) \rightarrow HSO_3{}^-.$$
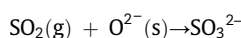
A previous study of the uptake of SO$_2$ proposed a two step mechanism for the oxidation of SO$_2$ where the first step is a reversible adsorption of SO$_2$ onto the surface followed by a second, irreversible reaction in which adsorbed SO$_2$ is oxidized to sulfate (Ullerstam et al., 2002).

$$OH * + SO_2 \rightleftharpoons OH * \cdots SO_2(ads)$$
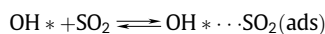
This mechanism was also well proved by the smog chamber experimental results. Uptake coefficient of SO$_2$ on mineral is an important parameter on understanding heterogeneous process of SO$_2$ in the atmosphere. Many works were taken using different methods such as Knudsen cell, DRIFTS and flow tube with FT-IR. In the last decades, a series of experiments have been done to get the uptake coefficients of sulfur dioxide on mineral dust surfaces, the preferred value is assumed to be 4×10^{-5} (Crowley et al., 2010). Goodman et al. and Usher et al. have got the uptake coefficients of SO$_2$ on a series of mineral oxides. The values of $\gamma_{BET,int}$ were determined to be $(9.5 \pm 0.3) \times 10^{-5}$ and $(2.6 \pm 0.2) \times 10^{-4}$ for SO$_2$ uptake on α-Al$_2$O$_3$ and MgO, $<1 \times 10^{-7}$ for SiO$_2$ with a Knudsen cell reactor 2. Usher et al. (2002) also calculated the value of 3×10^{-5} for Chinese loess. Ullerstam et al. (2002) have used DRIFTS to study on mineral dust samples from the Cape Verde Islands, where the main contents of the samples are quartz and potassic feldspars. The values of $\gamma_{BET,int}$ were in the order of 10^{-3} using the geometric surface area, or 10^{-7} using the BET surface area (Ullerstam et al., 2002). The values of $\gamma_{BET,int} = (6.6 \pm 0.8) \times 10^{-5}$ for Saharan dust were measured at 298 K by Adams et al. using a flow tube (Adams et al., 2005). Compared with the initial uptake coefficients of SO$_2$ on real mineral, they agreed well with our results. These results mostly concentrate on the initial part, but neglect the steady state, which is a thorough depletion of the sulfur dioxide in the atmosphere. Although the steady state uptake coefficients of SO$_2$ on mineral dust are not big enough,
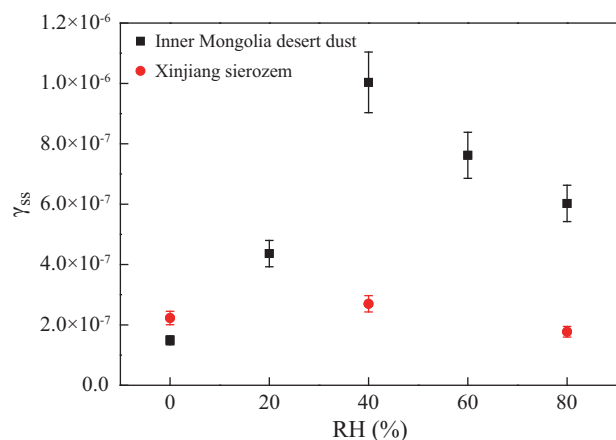

Fig. 10 – Relative humidity dependence of steady state of uptake coefficients of SO$_2$ on Chinese mineral dust of Inner Mongolia desert dust and Xinjiang sierozem.

the consumption of SO_2 on mineral dust is limited, but in the presence of O_3, NO_2 or H_2O_2 further oxidation of sulphite to SO_4^{2-} and HSO_4^- occurs (Li et al., 2006; Liu et al., 2012).

2.4. Decomposition measurement with different systems

Compared with the two types of experimental measurement system, both of them have advantages in ascertaining the uptake coefficients of sulfur dioxide on mineral dust. As a low pressure reactor, Knudsen cell can simplify the experimental condition to eliminate some other interference during measuring process. At the same time, the temperature of the experiments is easily controlled to investigate the temperature dependence of these uptake processes. Whereas the smog chamber system can provide an experimental condition more approaching to the actual environment and the results could be more close to the real one.

In this study, sulfur dioxide uptake onto mineral dust was measured using these two different systems. Using Eqs. (17) and (18), when the initial concentration of SO_2 is approximately 6.2×10^{11} molecule/cm^3, the steady state uptake coefficients derived from the above equations for the Inner Mongolia desert dust and Xinjiang sierozem are 1.60×10^{-6} and 3.66×10^{-6} respectively, which can be comparable to the results got from the Knudsen cell experiments, which is $(1.33 \pm 0.27) \times 10^{-6}$ for Xinjiang sierozem. Because of the different systems used in the experiments, the differences in the results can hardly be avoided. Although the results had some diversity, they were still comparable.

The discrepancy of the results may be caused by the differences of the systems. Knudsen cell is a low pressure reactor, which was used to investigate SO_2 uptake to mineral dust substrates and have concluded that pore diffusion is not important; sample surface morphology means that the BET area is the assumed area with which collisions are taking place. However, the smog chamber system is kept at atmospheric pressure; the diffuse effect cannot be neglected simply. It can be seen from Fig. 6 that there is a time dependence of the uptake coefficient which indicates surface saturation. Subjected to the volume of the chamber, the lower time resolutions during smog chamber experiments were inevitable.

3. Conclusions and atmospheric implications

At present, atmospheric modeling studies have shown that mineral aerosol has a potentially important role in the chemistry of the troposphere, by interacting with trace atmospheric gases such as NO_2 and SO_2. In this work, the uptake coefficients of sulfur dioxide on two types of mineral dust were investigated using both Knudsen cell reactor and smog chamber system. As a function of temperature, the initial uptake coefficients decrease with the increasing of temperature for these mineral dusts and the steady state uptake coefficients increase with the Xinjiang sierozem in the Knudsen cell study. While the initial uptake coefficients of mineral dust showed no observable dependence on the concentration of SO_2 in a range of 2.6×10^{11}–7.4×10^{11} molecule/cm^3. The initial uptake coefficient varied significantly with temperature. At 253 K, the initial uptake coefficients of mineral dust were approximately two

times larger than those at 298 K, and it can be expressed as Eqs. (5) and (6). Based on the temperature dependence of uptake coefficients, the activation energy for desorption (E_{des}) of SO_2 on Xinjiang sierozem was calculated to be (6.9 ± 1.0) kJ/mol. In the smog chamber, the uptake coefficients of mineral samples were achieved over the sulfur dioxide concentration range from 1.72×10^{12} to 6.15×10^{12} mol/cm^3, and the effect of relative humidity on the uptake processes was also studied.

In addition, owning to the diversity of measure methods, Knudsen cell reactor can detect lower concentration of oxidative gas approaching to the ambient one which was about 20 ppb in the atmosphere (Jackson, 1999). The rate of removal of sulfur dioxide by uptake onto mineral dust can be estimated in a simple model. The lifetime of sulfur dioxide due to uptake onto Inner Mongolia desert dust and Xinjiang sierozem can be estimated by

$$\tau = \frac{4}{\gamma \bar{c} A} \tag{19}$$

where, A is the dust surface area density in cm^2/cm^3, $\bar{c}$ is the mean molecular speed, and γ is the uptake coefficient. Supposing that a conservatively low dust loading is 5 μg/m^3 and a high dust loading is 600 μg/m^3 (Aymoz et al., 2004; Guo et al., 2013; Li et al., 2012), we obtained $A \approx 2.5 \times 10^{-5}$ to 3.0×10^{-3} m^2/m^3 for Inner Mongolia desert dust and $A \approx 1.05 \times 10^{-4}$ to 1.3×10^{-2} m^2/m^3 for Xinjiang sierozem. Our measured uptake coefficients are about 2.41×10^{-5} and 8.34×10^{-6} at 298 K for Inner Mongolia desert dust and Xinjiang sierozem, respectively, which lead to the corresponding atmospheric lifetimes with respect to processing by Inner Mongolia desert dust and Xinjiang sierozem of 2.1 to 246.3 days, 1.4 to 170.1 days, respectively. The uptake coefficients calculated from our experiments were based on BET surface area of the dust samples, which represent the lower limit. Compared with the lifetime of 15 days for mean atmospheric lifetime of sulfur dioxide, the interaction between mineral aerosol and sulfur dioxide can still influence the concentration of sulfur dioxide in the atmosphere, especially at low temperature and consequently contribute to variability in predicting the change of aerosols in troposphere sulfate formation.

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