

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

Heterogeneous uptake of gaseous hydrogen peroxide on mineral dust

Li Zhou, Weigang Wang*, Maofa Ge*, Shengrui Tong

Beijing National Laboratory for Molecular Science (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: zhouli@iccas.ac.cn

ARTICLE INFO

Article history:

Received 31 May 2015

Revised 6 August 2015

Accepted 17 August 2015

Available online 17 December 2015

Keywords:

Hydrogen peroxide

Mineral dust

Heterogeneous uptake

Uptake coefficients

ABSTRACT

The heterogeneous uptake processes of hydrogen peroxide on Arizona test dust and two types of authentic Chinese mineral dusts, i.e., Inner Mongolia desert dust and Xinjiang calciferous dust, were investigated using a Knudsen cell reactor coupled with a quadrupole mass spectrometer. The uptake coefficients were measured as a function of the initial concentration of H_2O_2 from 2.6×10^{11} to 1.2×10^{12} molecules/ cm^3 , and the temperature dependence of the uptake coefficients was investigated over a range from 253 to 313 K. The concentration of H_2O_2 showed little effect on the uptake coefficients of these heterogeneous processes. As a function of temperature, the initial uptake coefficients decrease with increasing temperature, whereas the steady state uptake coefficients of Arizona test dust and Inner Mongolia desert dust increase with increasing temperature. Implications for the understanding of the uptake processes onto mineral dust samples were also discussed.

© 2015 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

Mineral dust plays an important role as particulate matter in the troposphere. The amount of mineral dust injected into the atmosphere is about 1000–3000 Tg/year (Dentener et al., 1996; Usher et al., 2003). As one of the largest arid regions in the world, the Taklimakan Desert, Gobi Desert and loess areas are the main source of mineral dust in Asia. Mineral aerosols (at ~35%) in most circumstances are major components of the total aerosols in China (Zhang et al., 2012). Because wind-blown dust can transport long distances and has a long atmospheric lifetime, anthropogenic gas pollutants such as SO_2 , NO_x and O_3 can react over East Asia by interacting with mineral dust and producing secondary pollutants in this region.

In the atmosphere, as the precursor of odd-oxygen and reservoir of odd-hydrogen radicals (Lee et al., 2000), hydrogen

peroxide is an important secondary photochemical product, which is related to the bimolecular recombination of hydroperoxyl (HO_2) radicals (Hua et al., 2008; Jackson and Hewitt, 1999; Reeves and Penkett, 2003). The self-reaction of two hydroperoxyl radicals to form hydrogen peroxide has a particularly high reaction rate in photochemical smog. In the cloud aqueous phase, hydrogen peroxide is an important oxidant, which can oxidize sulfur dioxide to sulfuric acid (Husain et al., 2000). Hydrogen peroxide has also been used in the manufacturing industry field, for example as an antiseptic, disinfectant, or detergent (Vione et al., 2003). Normally, photolysis, reaction with OH, wet or dry deposition can remove the hydroperoxide radicals and lower the oxidizing capacity of the atmosphere (Rubio et al., 2006). However, in field measurement studies, gaseous H_2O_2 can be observed, which means that hydrogen peroxide is more stable in the gas phase (Bales et al., 1995; Jacobi et al., 2002). Field studies have

* Corresponding author. E-mail: wangwg@iccas.ac.cn (Weigang Wang), gemaofa@iccas.ac.cn (Maofa Ge).

also shown that gaseous H_2O_2 can react with ambient aerosols through heterogeneous reactions, which may be an important sink for H_2O_2 (de Reus et al., 2005; He et al., 2010).

Therefore, recently several laboratory studies have investigated the kinetics and mechanisms of H_2O_2 interactions with mineral aerosol surfaces, making it possible to reduce the discrepancies between field-measured and modeled H_2O_2 concentrations (El Zein et al., 2013, 2014; Pradhan et al., 2010a, 2010b; Romanias et al., 2012, 2013; Wang et al., 2011; Zhao et al., 2011, 2013; Zhou et al., 2012). However, most of the available data concern the reactions of H_2O_2 with model mineral oxides. Study on the reactivity of realistic mineral dust toward gaseous H_2O_2 is rather scarce and laboratory investigation on the combined action of hydrogen peroxide and other contaminants in the gas phase on aerosol surfaces is also very limited (Chu et al., 2000; Clegg and Abbatt, 2001a, 2001b).

Due to the scarcity of experimental measurements of kinetic data for important atmospheric processes and how these data vary with temperature, much uncertainty still remains in atmosphere science. This work presents a detailed investigation of the uptake coefficients of hydrogen peroxide on three types of mineral dust particles (Arizona Test Dust, Inner Mongolia desert dust and Xinjiang sioezem), which was motivated by a desire to mimic the behavior of mineral aerosol particles that are generally present in the atmosphere, over the temperature region from 253 to 313 K. The temperature dependence of these uptake processes and atmospheric implications of these reactions are discussed in detail in the following section. Through these series of experiments, we have been able to probe the effects of H_2O_2 as an important oxidant on mineral dust particles. The present studies provide useful information to understand the mechanisms of heterogeneous processes of hydrogen peroxide on these mineral particles. The experimentally determined data will also contribute to model studies of the atmosphere.

1. Experimental section

1.1. Materials

Arizona test dust with a nominal 0–5 μm size used in this study was purchased from Powder Technology Inc. (Powder Technology Inc., USA). Inner Mongolia desert dust and Xinjiang sioezem were purchased from the Chinese standard material center (the Chinese standard material center, China), consisting of <75 μm diameter fractions representative of mineral dust from the Inner Mongolia desert and Xinjiang arid region in the northwest of China. A Quantachrome Autosorb-1-C BET apparatus (autosorb-iQ, Quantachrome Instruments, USA) using multipoint Brunauer–Emmett–Teller (BET) analysis was applied to measure the surface areas of these powders. The BET areas were determined to be 5.30 m^2/g for Arizona test dust, 5.06 m^2/g for Inner Mongolia desert dust, and 20.98 m^2/g for Xinjiang sioezem. The main fractions of the mineral dust samples are quartz and feldspar. The certified chemical compositions of the mineral dust reference materials are listed in Table 1.

Aqueous solutions of H_2O_2 (35 wt.%, Alfa Aesar, China) were prepared as described in our previous work (Zhou et al., 2012). Before using, solutions were concentrated to greater than 95% by weight percentage by drying.

Table 1 – Certified reference materials for the chemical composition of mineral dusts.

Main composition	Arizona test dust (%)	Inner Mongolia desert dust (%)	Xinjiang calciferous dust (%)
SiO_2	68–76	78.30 ± 0.33	60.3 ± 0.41
Al_2O_3	10–15	9.65 ± 0.09	11.96 ± 0.09
Fe_2O_3	2.0–5.0	2.07 ± 0.03	4.07 ± 0.06
Na_2O	2.0–4.0	2.31 ± 0.04	2.02 ± 0.04
CaO	2.0–5.0	1.83 ± 0.05	7.40 ± 0.09
MgO	2.0–5.0	0.78 ± 0.08	2.04 ± 0.04
K_2O	2.0–5.0	2.56 ± 0.03	2.43 ± 0.04
TiO_2	0.5–1.0	<0.2	<0.2

1.2. Knudsen cell reactor

The measurements of the uptake coefficients of H_2O_2 on the mineral dust particles were conducted in a Knudsen cell reactor, and the signals of reactants were monitored by a quadrupole mass spectrometer (HAL 3F 501, Hiden, UK). The details of our experimental apparatus have been described in our previous publication (Wang et al., 2011). The characteristics of the reactor used in this work are summarized in Table 2. The uptake of hydrogen peroxide on mineral dust was monitored by mass charge ratio $m/z = 34$ (H_2O_2^+) channel as in our previous work (Zhou et al., 2012), and the temperature of the reaction cell was heated or cooled by a refrigerated circulator.

2. Results and discussion

2.1. Kinetics of hydrogen peroxide uptake on mineral dust at 298 K

The Knudsen cell reactor has been commonly used to measure heterogeneous reaction kinetics (Hanisch and Crowley, 2003; Li et al., 2002). In this study, both the initial and steady state uptake coefficients of H_2O_2 on three different kinds of mineral dust samples were measured at 298 K first. The typical quadrupole

Table 2 – Knudsen reactor parameters.

Knudsen reactor parameter	Value
Volume (V) (cm^3)	461
Temperature (T) (K)	253–313
Surface-to-volume ratio	0.57
Total pressure (P) (Pa)	1.5×10^{-3}
Escape orifice diameter (mm)	3
Escape orifice escape rate (sec^{-1})	$0.297(T/M)^{1/2}$
Effective area for the escape aperture (cm^2)	0.161
Sample surface area (A_s) (cm^2)	5.3
Sample collision frequency (ω) (sec^{-1})	124.2

The effective area of the escape aperture was measured in each independent experiment according to the attenuation of the N_2 signal from one steady state to another (Li et al., 2002). M: Relative molecular mass of the gas molecular in the knudsen cell.

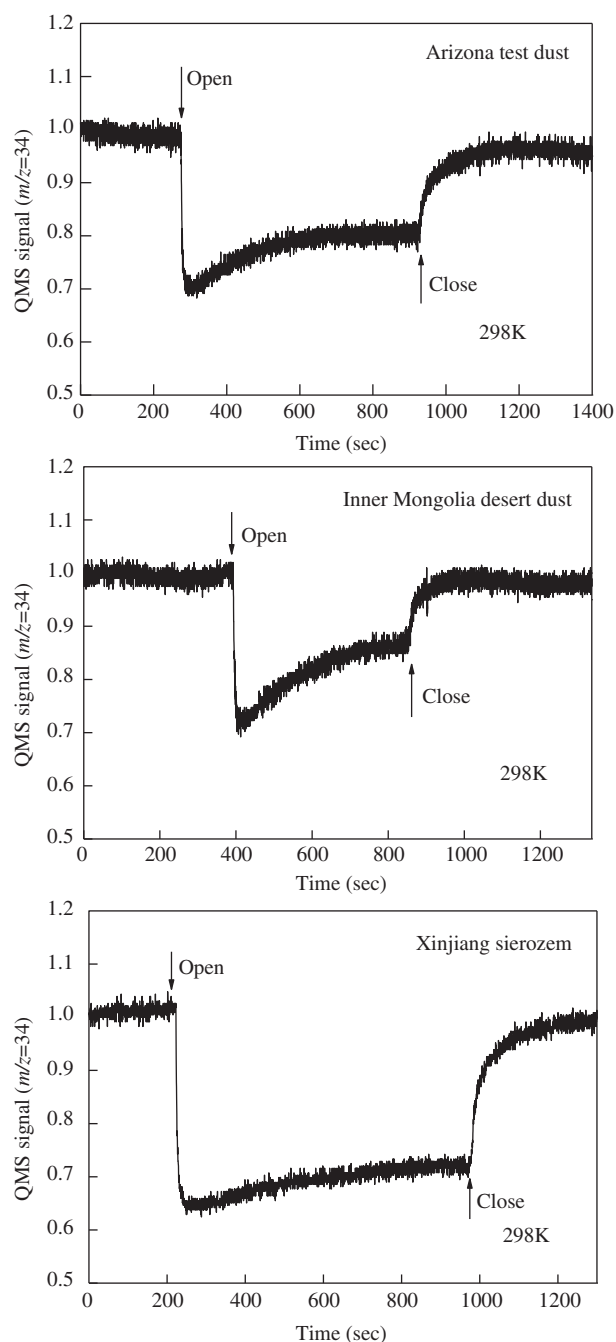


Fig. 1 – Uptake curves of hydrogen peroxide on Arizona test dust, Inner Mongolia desert dust, and Xinjiang sierozeem at 298 K in Knudsen cell reactor. QMS: quadrupole mass spectrometry.

mass spectrometry (QMS) signal response of each mineral dust samples exposed to gaseous hydrogen peroxide at 298 K is depicted in Fig. 1. The initial concentration of gaseous hydrogen peroxide was first established in the chamber, and then one powder sample was exposed to contact with the reactant. The signal of hydrogen peroxide ($m/z = 34$) dropped below its original value quickly initially, and then the signal intensity recovered gradually to a new steady state. An observed uptake coefficient

(γ_{obs}), can be derived from the Knudsen cell Eq. (1) (Usher et al., 2002):

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

where, A_h is the effective area of the escape hole, A_s is the geometric area of the sample holder, and I_0 and I are the QMS intensities detected when sample holder is covered and exposed, respectively. The values obtained from this equation were either the initial uptake coefficients ($\gamma_{\text{obs,int}}$) or the steady state uptake coefficients ($\gamma_{\text{obs,ss}}$) representing the uptake coefficient observed at the initial stages or the steady stages of the reactions.

During the experiments, the concentration of H_2O_2 is related to the pressure in the reactor, which was kept approximately at 3.0×10^{-3} Pa equal to 3.7×10^{11} molecules/ cm^3 . There were no remarkable variations of other monitored channels such as O_2 ($m/z = 32$) and CO_2 ($m/z = 44$), which meant that no catalytic oxidation reactions took place during the uptake experiments.

Eq. (1) is derived by assuming that gas–surface collisions only take place with the top layer of the dust. In order to determine the surface area of dust samples involved in the uptake processes, the uptake coefficients γ_{obs} were measured using the geometric surface area of the sample as a function of sample mass. As can be seen from Fig. 2, the observed uptake values are linearly dependent on the mass of these three types of dust. We determined the range of this mass dependence, and in this range the diffusion of the reactant gas can enter into the underlying layers of the dust, which can increase the collisions with the dust surface. In our study, the experiments were conducted in the linear mass regime. The entire surface area of the dust sample was accessible to H_2O_2 ; where the entire sample participates in the reaction, the BET surface area is applicable (Underwood et al., 2000). From Eq. (2), a mass independent uptake coefficient can be derived

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

where, A_{BET} is 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 of all of our experiments are given in Table 3.

At 298 K, the effect of the gaseous hydrogen peroxide concentration on the uptake coefficient was also considerable in the range of 2.6×10^{11} – 1.2×10^{12} molecules/ cm^3 . When the initial concentration of gaseous hydrogen peroxide was changed in this range, there was no distinct dependence of initial uptake coefficients on this explored range. This concentration independence observed for gaseous H_2O_2 initial uptake to mineral dust is very similar to the results reported by El Zein et al. (2014). They measured the heterogeneous interaction of H_2O_2 with solid films of Arizona test dust using a low pressure flow tube reactor. After long time exposure, the uptake of hydrogen peroxide on the mineral dust surface showed relative saturation and became inactive toward further H_2O_2 decomposition. There was clearly steady state uptake for all of the mineral dust samples. These phenomena suggest that the adsorption of H_2O_2 on these three types of mineral dust was the

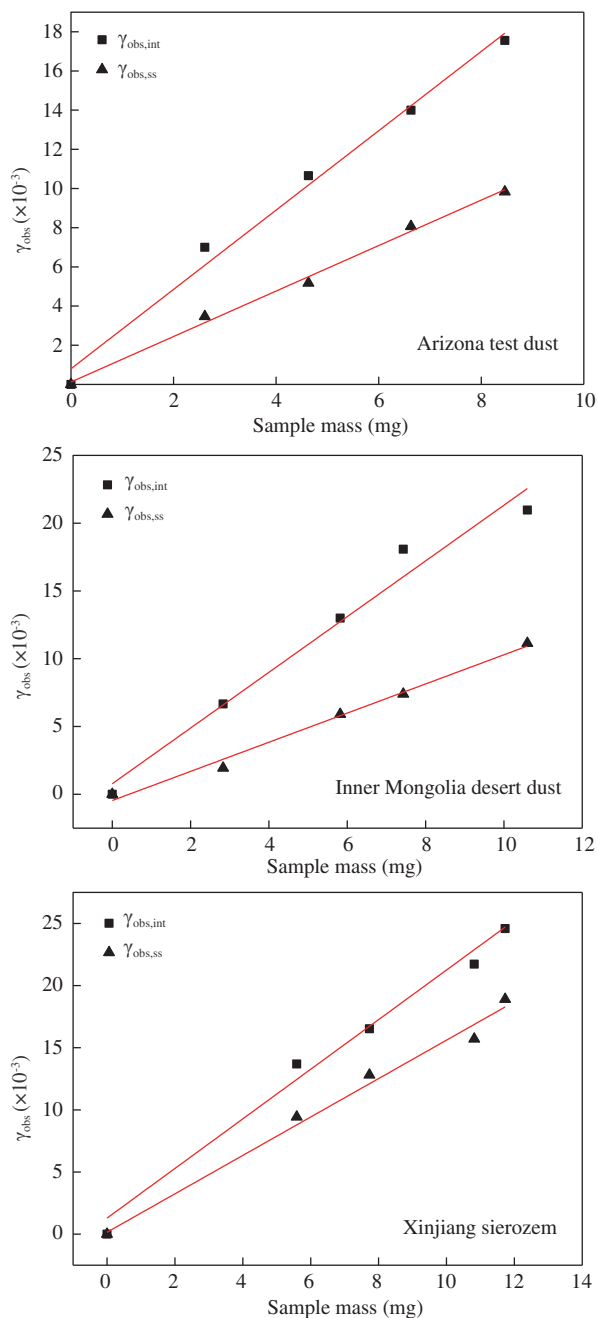


Fig. 2 – Linear mass-dependent regions of the observed initial and steady state uptake coefficients ($\gamma_{obs,int}$ and $\gamma_{obs,ss}$) for hydrogen peroxide on Arizona test dust, Inner Mongolia desert dust, and Xinjiang sierozeem.

first step of the uptake process, and then there were continuing surface reactions. From the results of the experimental measurement, we inferred that the heterogeneous uptake on mineral dust surface took place through two steps, physical adsorption and heterogeneous reactions. This phenomenon also supported the results of field studies showing that heterogeneous uptake on ambient mineral dust aerosol seems to be an important sink for H_2O_2 (de Reus et al., 2005; He et al., 2010).

2.2. Effects of temperature on uptake kinetics of hydrogen peroxide on mineral dust

The temperature dependence of the uptake coefficients of heterogeneous processes on these mineral dusts were further investigated with an initial concentration of H_2O_2 of about 3.7×10^{11} molecules/cm³ over the temperature region of 253–313 K.

Table 3 summarizes all the results from the experiments. The initial uptake coefficients of Arizona test dust changed from 1.47×10^{-4} to 2.71×10^{-4} , the initial uptake coefficients of Inner Mongolia desert dust changed from 2.19×10^{-4} to 3.56×10^{-4} , and those of Xinjiang sierozeem were in the range of 4.46×10^{-5} – 7.34×10^{-5} . From these results, it can be seen that the initial uptake coefficients of gas phase hydrogen peroxide uptake on these mineral dusts showed similar phenomena, in that they all decreased with increasing temperature. This phenomenon of the coefficient change trend with temperature conforms well to the physical adsorption process, which is the first main process in these systems. A similar temperature dependence of initial uptake coefficients was also observed in previous studies (El Zein et al., 2014; Romanias et al., 2013; Zhou et al., 2012). However, the steady state uptake coefficients of the mineral dust samples showed different phenomena. The γ_{ss} of Arizona test dust increased slowly with increasing temperature from 5.57×10^{-5} to 9.40×10^{-5} , the γ_{ss} of Inner Mongolia desert dust increased markedly in the range of 2.50×10^{-5} – 1.31×10^{-4} , and the steady state uptake coefficients of Xinjiang sierozeem had little correlation with temperature. El Zein et al. (2014) investigated the interaction of H_2O_2 with the Arizona test dust (0–3 μ m) surface over the temperature range from 268 to 320 K at initial concentration of H_2O_2 ($[H_2O_2]_0$) $\sim 1.0 \times 10^{12}$ molecules/cm³. They found that γ_{ss} was independent of temperature. The observed temperature dependence indicates that the structure or the components may influence the steady state uptake processes.

Since the initial uptake coefficients showed negative temperature dependence, the changes of observed enthalpy (ΔH_{obs}) and entropy (ΔS_{obs}) for H_2O_2 adsorption on mineral dust and the reactive energy (E_a) for Inner Mongolia desert dust could be calculated from the following equations (Hudson et al., 2002; Jayne et al., 1991).

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

$$\ln \left(\frac{\gamma_{BET,ss}}{1-\gamma_{BET,ss}} \right) = -\frac{E_a}{RT} + A \quad (4)$$

Consequently, as shown in Fig. 3, the enthalpy (ΔH_{obs}) and entropy (ΔS_{obs}) were determined to be $-(7.7 \pm 1.5)$ kJ/mol and $-(98.6 \pm 19.7)$ J K/mol for Arizona test dust, $-(5.4 \pm 1.1)$ kJ/mol and $-(87.2 \pm 17.4)$ J K/mol for Inner Mongolia desert dust, and $-(7.8 \pm 1.6)$ kJ/mol and $-(108.3 \pm 21.7)$ J K/mol for Xinjiang sierozeem. The activation energy (E_a) for Arizona test dust and Inner Mongolia desert dust is 8.64 and 18.4 kJ/mol respectively. In the atmosphere, when the activation energy of a given reaction is greater than 20 kJ/mol, the role of the reaction in atmospheric chemistry is regarded as unimportant

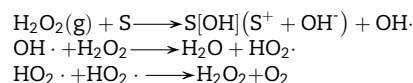
Table 3 – Summary of the uptake coefficients of H₂O₂ on mineral dust at different temperatures.

Temperature (K)	Arizona test dust		Inner Mongolia desert dust		Xinjiang sierozem	
	$\gamma_{\text{BET,int}} (10^{-4})$	$\gamma_{\text{BET,ss}} (10^{-5})$	$\gamma_{\text{BET,int}} (10^{-4})$	$\gamma_{\text{BET,ss}} (10^{-5})$	$\gamma_{\text{BET,int}} (10^{-5})$	$\gamma_{\text{BET,ss}} (10^{-5})$
253	2.71 ± 0.54	5.57 ± 1.11	3.56 ± 0.71	2.50 ± 0.50		
268	2.56 ± 0.51	6.58 ± 1.32	3.08 ± 0.62	4.72 ± 0.94	7.34 ± 1.47	3.84 ± 0.77
283	1.77 ± 0.35	9.09 ± 1.82	2.73 ± 0.55	7.97 ± 1.59	6.50 ± 1.30	4.31 ± 0.86
298	1.51 ± 0.30	9.95 ± 1.99	2.41 ± 0.48	10.8 ± 2.16	5.30 ± 1.06	4.23 ± 0.85
313	1.47 ± 0.29	9.40 ± 1.88	2.19 ± 0.44	13.1 ± 2.62	4.46 ± 0.89	3.77 ± 0.75

Each value is the average of at least three measurements, and the error corresponds to one standard deviation (σ). $\gamma_{\text{BET,int}}$: initial uptake coefficient; $\gamma_{\text{BET,ss}}$: steady state uptake coefficient.

(Liu et al., 2008; Smith, 2003). This suggests that the heterogeneous reaction of H₂O₂ on Inner Mongolia desert dust should not be neglected in the troposphere.

At low relative humidity conditions, the generally accepted mechanism for these uptake processes on oxide surfaces is as shown below (Lin and Gurol, 1998; Pradhan et al., 2010b; Zhao et al., 2011).



The ΔH_{obs} value can demonstrate that H₂O₂ adsorbs on mineral dust samples in a similar capacity. The empirical formula between $\gamma_{\text{BET,int}}$ of H₂O₂ on mineral dusts with temperature can be calculated as:

$$\gamma_{\text{BET,int}}(\text{Arizona test dust}) = \frac{\exp(931.0/T-11.9)}{1 + \exp(931.0/T-11.9)} \quad (5)$$

$$\gamma_{\text{BET,int}}(\text{Inner Mogolia desert dust}) = \frac{\exp(643.7/T-10.5)}{1 + \exp(643.7/T-10.5)} \quad (6)$$

$$\gamma_{\text{BET,int}}(\text{Xinjiang sierozem}) = \frac{\exp(941.3/T-13.0)}{1 + \exp(941.3/T-13.0)} \quad (7)$$

Thus using this equation, the γ_{BET} at other temperatures can be obtained. The initial uptake coefficients of hydrogen peroxide on these mineral dusts resembled those of other mineral aerosols.

3. Conclusions and atmospheric implications

To sum up, mineral dust plays an important role as particulate matter in the troposphere, and can act as a sink or reactive surface for a variety of atmospheric chemical species. In this study, we investigated heterogeneous uptake of H₂O₂ on three different mineral dust samples as a function of concentration of H₂O₂ over a temperature range from 253 to 313 K in a Knudsen cell reactor. Reactant concentrations were kept closer to ambient atmospheric levels compared to all previous studies of this reaction. The uptake coefficients showed little observable dependence on the concentration of hydrogen peroxide; while as a function of temperature, the initial uptake coefficients decreased with increasing

temperature for these mineral dust samples. The temperature dependences of these processes can be expressed by Eqs. (5)–(7) for each mineral dust. For these three different kinds of mineral dust, with increasing temperature, the gap between initial uptake coefficient and steady state uptake coefficient became smaller and smaller. This meant that increasing temperature can promote the uptake processes from adsorption to reaction. According to the temperature dependence of uptake coefficients, the enthalpy (ΔH_{obs}), entropy (ΔS_{obs}) and activation energy (E_a) for each mineral dust were also determined.

The lifetime of H₂O₂ due to uptake onto Arizona test dust, Inner Mongolia desert dust and Xinjiang sierozem can be estimated by Eq. (8).

$$\tau = \frac{4}{\gamma \bar{c} A} \quad (8)$$

where, A (cm²/cm³) is the dust surface area density, \bar{c} is the mean molecular speed, and γ is the uptake coefficient. Because BET areas are applicable for calculating the uptake coefficients, here we use them as dust surface areas. If we assume a conservatively lowest dust loading of 5 to a highest dust loading of 600 $\mu\text{g}/\text{m}^3$ (Aymoz et al., 2004; Guo et al., 2013; Li et al., 2012), our measured uptake coefficients at room temperature are about $(1.51 \pm 0.30) \times 10^{-4}$, $(2.41 \pm 0.48) \times 10^{-4}$ and $(5.30 \pm 1.06) \times 10^{-5}$ for Arizona test dust, Inner Mongolia desert dust and Xinjiang sierozem, which leads to the related atmospheric lifetimes of gaseous H₂O₂ consumed by heterogeneous on Arizona test dust, Inner Mongolia desert dust and Xinjiang sierozem of 2.3 hr to 11.9 day, 1.5 hr to 7.5 day and 6.5 hr to 43.2 day respectively. The lifetimes of H₂O₂ via uptake onto mineral dust samples at different temperatures are listed in Table 4. Because the uptake coefficients were calculated based on the BET surface areas of the dust samples, they represent the lower limit. Since for Arizona test dust the BET surface area is about 4 times larger than the geometric area, this may cause γ to be 4 times smaller than that calculated basing on the geometric surface area (Wagner et al., 2009). This gap should also be taken into account in box model studies, where it would cause an underestimation of H₂O₂ transformation. When sand storms occur, the surface mass aerosol concentrations may reach a peak at 3000 $\mu\text{g}/\text{m}^3$. Our results suggested that the heterogeneous uptake of H₂O₂ on mineral aerosol can significantly influence the concentration of H₂O₂ in the atmosphere.

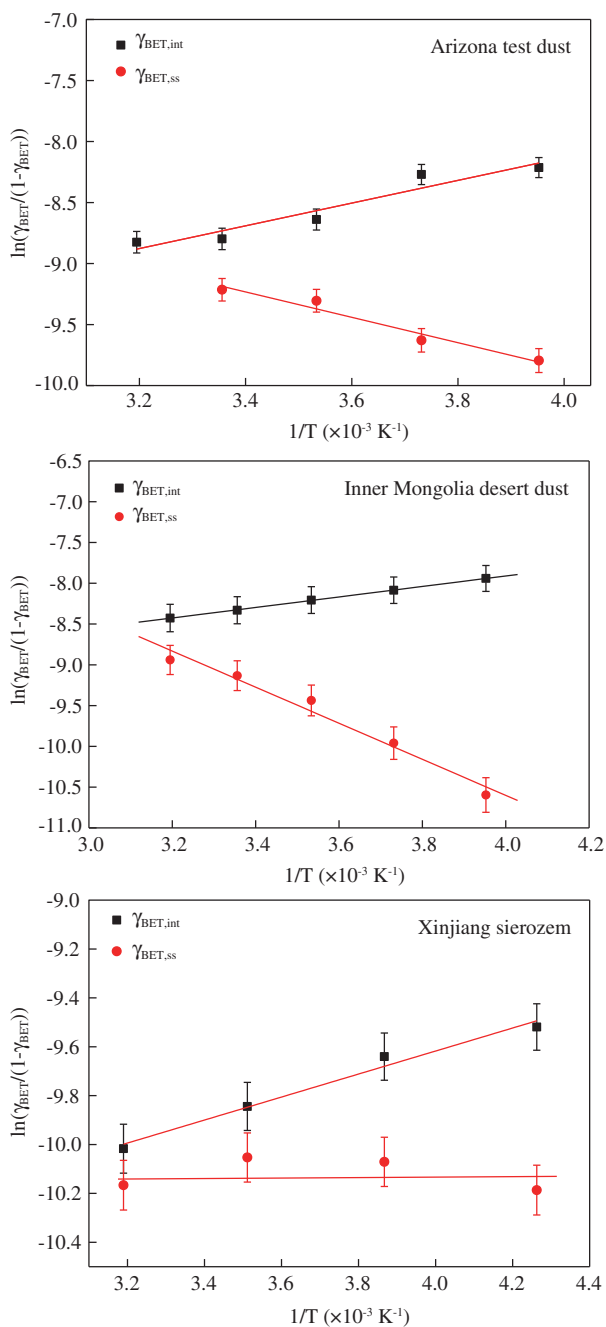


Fig. 3 – Plot to determine the temperature dependence of hydrogen peroxide uptake on Arizona test dust, Inner Mongolia desert dust, and Xinjiang sierozem. $\gamma_{BET,int}$: initial uptake coefficient; $\gamma_{BET,ss}$: steady state uptake coefficient; T: temperature.

Acknowledgments

This project was supported by the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (No. XDB05010400), the National Basic Research Program of China (973 Program) (No. 2011CB403401) of Ministry of Science and Technology of China, and the National Natural Science Foundation of China (Nos. 41173112, 21477134).

Table 4 – Atmospheric lifetime of hydrogen peroxide by uptake onto mineral dust samples.

Temperature (K)	Hydrogen peroxide atmospheric lifetime		
	Arizona test dust	Inner Mongolia desert dust	Xinjiang sierozem
253	1.3 hr–6.6 day	1.0 hr–5.1 day	
268	1.4 hr–7.0 day	1.1 hr–5.8 day	4.7 hr–24.7 day
283	2.0 hr–10.2 day	1.2 hr–6.6 day	5.3 hr–27.9 day
298	2.3 hr–11.9 day	1.5 hr–7.5 day	6.5 hr–34.2 day
313	2.4 hr–12.2 day	1.6 hr–8.2 day	7.8 hr–40.7 day

REFERENCES

Aymoz, G., Jaffrezo, J.L., Jacob, V., Colomb, A., George, C., 2004. Evolution of organic and inorganic components of aerosol during a Saharan dust episode observed in the French Alps. *Atmos. Chem. Phys.* 4 (11–12), 2499–2512.

Bales, R.C., Losleben, M.V., McConnell, J.R., Fuhrer, K., Neftel, A., 1995. H₂O₂ in snow, air and open pore-space in firn at Summit. *Greenl. Geophys. Res. Lett.* 22 (10), 1261–1264.

Chu, L., Diao, G.W., Chu, L.T., 2000. Heterogeneous interaction of SO₂ on H₂O₂-ice films at 190–210 K. *J. Phys. Chem. A* 104 (32), 7565–7573.

Clegg, S.M., Abbatt, J.P.D., 2001a. Uptake of gas-phase SO₂ and H₂O₂ by ice surfaces: dependence on partial pressure, temperature, and surface acidity. *J. Phys. Chem. A* 105 (27), 6630–6636.

Clegg, S.M., Abbatt, J.P.D., 2001b. Oxidation of SO₂ by H₂O₂ on ice surfaces at 228 K: a sink for SO₂ in ice clouds. *Atmos. Chem. Phys.* 1 (1), 73–78.

de Reus, M., Fischer, H., Sander, R., Gros, V., Kormann, R., Salisbury, G., et al., 2005. Observations and model calculations of trace gas scavenging in a dense Saharan dust plume during MINATROC. *Atmos. Chem. Phys.* 5 (7), 1787–1803.

Dentener, F.J., Carmichael, G.R., Zhang, Y., Lelieveld, J., Crutzen, P.J., 1996. Role of mineral aerosol as a reactive surface in the global troposphere. *J. Geophys. Res.-Atmos.* 101 (D17), 22869–22889.

El Zein, A., Bedjanian, Y., Romanias, M.N., 2013. Kinetics and products of HONO interaction with TiO₂ surface under UV irradiation. *Atmos. Environ.* 67, 203–210.

El Zein, A., Romanias, M.N., Bedjanian, Y., 2014. Heterogeneous interaction of H₂O₂ with Arizona test dust. *J. Phys. Chem. A* 118 (2), 441–448.

Guo, J.P., Niu, T., Wang, F., Deng, M.J., Wang, Y.Q., 2013. Integration of multi-source measurements to monitor sand-dust storms over North China: a case study. *Acta Meteor. Sin.* 27 (4), 566–576.

Hansch, F., Crowley, J.N., 2003. Heterogeneous reactivity of NO and HNO₃ on mineral dust in the presence of ozone. *Phys. Chem. Chem. Phys.* 5 (5), 883–887.

He, S.Z., Chen, Z.M., Zhang, X., Zhao, Y., Huang, D.M., Zhao, J.N., et al., 2010. Measurement of atmospheric hydrogen peroxide and organic peroxides in Beijing before and during the 2008 olympic games: chemical and physical factors influencing their concentrations. *J. Geophys. Res.-Atmos.* 115 (D17), D17307.

Hua, W., Chen, Z.M., Jie, C.Y., Kondo, Y., Hofzumahaus, A., Takegawa, N., et al., 2008. Atmospheric hydrogen peroxide and organic hydroperoxides during PRIDE-PRD’06, China: their concentration, formation mechanism and contribution to secondary aerosols. *Atmos. Chem. Phys.* 8 (22), 6755–6773.

Hudson, P.K., Shilling, J.E., Tolbert, M.A., Toon, O.B., 2002. Uptake of nitric acid on ice at tropospheric temperatures: implications for cirrus clouds. *J. Phys. Chem. A* 106 (42), 9874–9882.

- Husain, L., Rattigan, O.V., Dutkiewicz, V., Das, M., Judd, C.D., Khan, A.R., et al., 2000. Case studies of the $\text{SO}_2 + \text{H}_2\text{O}_2$ reaction in clouds. *J. Geophys. Res.-Atmos.* 105 (D8), 9831–9841.
- Jackson, A.V., Hewitt, C.N., 1999. Atmosphere hydrogen peroxide and organic hydroperoxides: a review. *Crit. Rev. Environ. Sci. Technol.* 29 (2), 175–228.
- Jacobi, H.W., Frey, M.M., Hutterli, M.A., Bales, R.C., Schrems, O., Cullen, N.J., et al., 2002. Measurements of hydrogen peroxide and formaldehyde exchange between the atmosphere and surface snow at Summit. *Greenl. Atmos. Environ.* 36 (15–16), 2619–2628.
- Jayne, J.T., Duan, S.X., Davidovits, P., Worsnop, D.R., Zahniser, M.S., Kolb, C.E., 1991. Uptake of gas-phase alcohol and organic-acid molecules by water surfaces. *J. Phys. Chem.* 95 (16), 6329–6336.
- Lee, M., Heikes, B.G., O'Sullivan, D.W., 2000. Hydrogen peroxide and organic hydroperoxide in the troposphere: a review. *Atmos. Environ.* 34 (21), 3475–3494.
- Li, J., Wang, Z., Zhuang, G.S., Luo, G., Sun, Y.J., Wang, Q.X., 2012. Mixing of Asian mineral dust with anthropogenic pollutants over East Asia: a model case study of a super-duststorm in March 2010. *Atmos. Chem. Phys.* 12 (16), 7591–7607.
- Li, P., Al-Abadleh, H.A., Grassian, V.H., 2002. Measuring heterogeneous uptake coefficients of gases on solid particle surfaces with a Knudsen cell reactor: complications due to surface saturation and gas diffusion into underlying layers. *J. Phys. Chem. A* 106 (7), 1210–1219.
- Lin, S.S., Gurol, M.D., 1998. Catalytic decomposition of hydrogen peroxide on iron oxide: kinetics, mechanism, and implications. *Environ. Sci. Technol.* 32 (10), 1417–1423.
- Liu, Y.C., He, H., Ma, Q.X., 2008. Temperature dependence of the heterogeneous reaction of carbonyl sulfide on magnesium oxide. *J. Phys. Chem. A* 112 (13), 2820–2826.
- Pradhan, M., Kalberer, M., Griffiths, P.T., Braban, C.F., Pope, F.D., Cox, R.A., et al., 2010a. Uptake of gaseous hydrogen peroxide by submicrometer titanium dioxide aerosol as a function of relative humidity. *Environ. Sci. Technol.* 44 (4), 1360–1365.
- Pradhan, M., Kyriakou, G., Archibald, A.T., Papageorgiou, A.C., Kalberer, M., Lambert, R.M., 2010b. Heterogeneous uptake of gaseous hydrogen peroxide by Gobi and Saharan dust aerosols: a potential missing sink for H_2O_2 in the troposphere. *Atmos. Chem. Phys.* 10 (15), 7127–7136.
- Reeves, C.E., Penkett, S.A., 2003. Measurements of peroxides and what they tell us. *Chem. Rev.* 103 (12), 5199–5218.
- Romanias, M.N., El Zein, A., Bedjanian, Y., 2012. Heterogeneous interaction of H_2O_2 with TiO_2 surface under dark and UV light irradiation conditions. *J. Phys. Chem. A* 116 (31), 8191–8200.
- Romanias, M.N., El Zein, A., Bedjanian, Y., 2013. Uptake of hydrogen peroxide on the surface of Al_2O_3 and Fe_2O_3 . *Atmos. Environ.* 77, 1–8.
- Rubio, M.A., Guerrero, M.J., Villena, G., Lissi, E., 2006. Hydroperoxides in dew water in downtown Santiago, Chile. A comparison with gas-phase values. *Atmos. Environ.* 40 (32), 6165–6172.
- Smith, I.W.M., 2003. Laboratory studies of atmospheric reactions at low temperatures. *Chem. Rev.* 103 (12), 4549–4564.
- Underwood, G.M., Li, P., Al-Abadleh, H., Grassian, V.H., 2001. A Knudsen cell study of the heterogeneous reactivity of nitric acid on oxide and mineral dust particles. *J. Phys. Chem. A* 105 (27), 6609–6620.
- Underwood, G.M., Li, P., Usher, C.R., Grassian, V.H., 2000. Determining accurate kinetic parameters of potentially important heterogeneous atmospheric reactions on solid particle surfaces with a Knudsen cell reactor. *J. Phys. Chem. A* 104 (4), 819–829.
- Usher, C.R., Al-Hosney, H., Carlos-Cuellar, S., Grassian, V.H., 2002. A laboratory study of the heterogeneous uptake and oxidation of sulfur dioxide on mineral dust particles. *J. Geophys. Res.-Atmos.* 107 (D23) (ACH 16-1-ACH 16-9).
- Usher, C.R., Michel, A.E., Grassian, V.H., 2003. Reactions on mineral dust. *Chem. Rev.* 103 (12), 4883–4939.
- Vione, D., Maurino, V., Minero, C., Pelizzetti, E., 2003. The atmospheric chemistry of hydrogen peroxide: a review. *Ann. Chim.* 93 (4), 477–488.
- Wagner, C., Schuster, G., Crowley, J.N., 2009. An aerosol flow tube study of the interaction of N_2O_5 with calcite, Arizona dust and quartz. *Atmos. Environ.* 43 (32), 5001–5008.
- Wang, W.G., Ge, M.F., Sun, Q., 2011. Heterogeneous uptake of hydrogen peroxide on mineral oxides. *Chin. J. Chem. Phys.* 24 (5), 515–520.
- Zhang, X.Y., Wang, Y.Q., Niu, T., Zhang, X.C., Gong, S.L., Zhang, Y.M., et al., 2012. Atmospheric aerosol compositions in China: spatial/temporal variability, chemical signature, regional haze distribution and comparisons with global aerosols. *Atmos. Chem. Phys.* 12 (2), 779–799.
- Zhao, Y., Chen, Z.M., Shen, X.L., Huang, D., 2013. Heterogeneous reactions of gaseous hydrogen peroxide on pristine and acidic gas-processed calcium carbonate particles: effects of relative humidity and surface coverage of coating. *Atmos. Environ.* 67, 63–72.
- Zhao, Y., Chen, Z.M., Shen, X.L., Zhang, X., 2011. Kinetics and mechanisms of heterogeneous reaction of gaseous hydrogen peroxide on mineral oxide particles. *Environ. Sci. Technol.* 45 (8), 3317–3324.
- Zhou, L., Wang, W.G., Ge, M.F., 2012. Temperature dependence of heterogeneous uptake of hydrogen peroxide on silicon dioxide and calcium carbonate. *J. Phys. Chem. A* 116 (30), 7959–7964.