

ARTICLE

Heterogeneous Uptake of Hydrogen Peroxide on Mineral Oxides[†]

Wei-gang Wang, Mao-fa Ge*, Qiao Sun

Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

(Dated: Received on July 15, 2011; Accepted on August 31, 2011)

The interaction of mineral oxides (α -Al₂O₃, MgO, Fe₂O₃, and SiO₂) with hydrogen peroxide was investigated using the Knudsen cell reactor. The initial reactive uptake coefficients for the commercially available powders are measured as $(1.00 \pm 0.11) \times 10^{-4}$ for α -Al₂O₃, $(1.66 \pm 0.23) \times 10^{-4}$ for MgO, $(9.70 \pm 1.95) \times 10^{-5}$ for Fe₂O₃, and $(5.22 \pm 0.9) \times 10^{-5}$ for SiO₂. These metal oxide powders exhibit some catalytic behavior toward the decomposition of hydrogen peroxide excluding SiO₂. H₂O₂ can be destroyed on Fe₂O₃ surface and O₂ is formed. The experimental results suggest that the heterogeneous loss on mineral surface can represent an important sink of hydrogen peroxide.

Key words: Kinetics, Hydrogen peroxide, Heterogeneous uptake, Atmospheric lifetime**I. INTRODUCTION**

As one of the major aerosols in the atmosphere, mineral dust is now recognized for its potential impact on climate [1]. The troposphere contains plenty of mineral dust, which is emitted into the atmosphere from arid and semiarid regions such like Saharan desert and Central Asian. Every year 1000–3000 Tg mineral dust is injected into the atmosphere. Because of the long transport distances and atmospheric lifetime, mineral dust can interact with various trace gases and influence chemical balance of these atmospheric species. As a result, the thermodynamic and optical properties of mineral dust may also be altered [2]. Meanwhile, the lifetimes of the various trace gases may change because of the heterogeneous interaction. In all, climate forcing may be influenced by these processes.

Hydrogen peroxide has been widely used in industry, such as disinfectant, antiseptic, oxidizer, and so on [3, 4]. In the atmosphere, hydrogen peroxide is normally thought as secondary photochemical product [5]. The reaction rate of formation hydrogen peroxide by self-reaction of two hydroperoxyl radicals is particularly high in photochemical smog where the steady-state concentration of hydroperoxyl radicals is considerably higher than that in the unpolluted air. As reservoir of odd-oxygen radicals, hydrogen peroxide and organic hydroperoxide can reflect the radical levels of the troposphere. The removal of hydroperoxide by wet or dry

deposition will lower the oxidizing capacity of the atmosphere [6]. However, in the gas phase, due to its low photolysis rate and relatively slow reaction rate with other contaminants, hydrogen peroxide is relatively stable.

Because of the significant effect of hydrogen peroxide on atmospheric chemistry, various reaction of hydrogen peroxide, such as its aqueous phase reaction and dissociation of hydrogen peroxide have been widely investigated [7, 8]. Due to the high solubility and oxidizing property of hydrogen peroxide, hydrogen peroxide acts as oxidant in the droplets which is particularly important in the oxidation of sulfur dioxide to produce sulfuric acid in the aqueous phase. Hydrogen peroxide can effectively remove the contaminants, the catalytic decomposition of hydrogen peroxide using metal oxides in the aqueous phase have been widely investigated [9, 10]. Since the first measurement of H₂O₂, hydroperoxide has been observed by many field measurements [11, 12]. However, the laboratory investigation of the reaction of hydrogen peroxide on aerosol surface is very limited [13–15], particularly on mineral dust particles. Recently, Pradhan *et al.* firstly reported the uptake coefficient of gaseous H₂O₂ on TiO₂ aerosol and mineral dust [16, 17]. Zhao *et al.* investigated the heterogeneous reactions of H₂O₂ on SiO₂ and α -Al₂O₃ particles [18].

In this work, the heterogeneous uptake of hydrogen peroxide on a variety of mineral oxide particles including α -Al₂O₃, MgO, Fe₂O₃, and SiO₂ was investigated using the Knudsen cell reactor. These particles represent the most abundant elements in the atmosphere. The atmospheric implications of these reactions have been discussed in the following section. The present studies provide useful information of understanding the mechanism of uptake and decomposition processes of

[†]Part of the special issue for “the Chinese Chemical Society’s 12th National Chemical Dynamics Symposium”.

*Author to whom correspondence should be addressed. E-mail: gemaofa@iccas.ac.cn, FAX: +86-10-62559373

TABLE I Knudsen reactor parameters.

Value volume V/cm^3	461
Temperature T/K	298
Surface-to-volume ratio	0.57
Total pressure $p/\mu\text{Pa}$	1.4
Escape orifice #1 diameter/mm	3
Escape orifice #2 diameter/mm	8
Escape orifice #1 escape rate/ $((T/M)^{1/2}/\text{s})$	0.297
Escape orifice #2 escape rate/ $((T/M)^{1/2}/\text{s})$	1.8
Sample surface area A_s/cm^2	5.3
Sample collision frequency ω/s^{-1}	124.2

hydrogen peroxide on these particles.

II. EXPERIMENTS

Heterogeneous uptake coefficients were measured using Knudsen cell reactor with the volume of 461 cm^3 . The reactor consisted of a chamber with four isolated sample compartments and a small escape aperture through which reactant and product gases could be detected by a quadrupole mass spectrometer (Hiden, HAL 3F 501). The mass spectrometer was housed in a vacuum chamber equipped with a 600 L/s turbo molecular pump. In the Knudsen cell reactor, the pressure used was low enough (1 mPa) to ensure that the mean free path of the molecules exceeded the dimensions of the cell. The inner chamber and sample holders were coated with Teflon to reduce the wall effect. All powdered samples were prepared by gently heating a hydrosol of the powder until a dry and evenly dispersed coating of the sample remained in the bottom of the holder. Before every experiment, the chamber and samples were evacuated for 24 h to a base pressure of approximately 0.1 mPa. The relevant Knudsen reactor parameters were given in Table I. In our experiment, we used the continuum molecular flow sampler and the pressure of the mass spectrometer chamber was about 0.05 mPa. In order to research the background influence of the kinetic results, we designed the parallel experiment using the four sample cells. By using the similar weight of the mineral oxides and same H_2O_2 concentration, the uptake coefficient didn't obviously change in the experiment lasting 2 h. The background signal intensity at $m/z=34$ when turning off the H_2O_2 supply was lower than 5% of the MS signal of H_2O_2 at $m/z=34$.

Aqueous solutions of H_2O_2 (30%) were first concentrated to 75% by distillation under 2.1–3.2 kPa, which were then concentrated by bubbling dry nitrogen through the sample for approximate 5 days. Density measurements indicated that more than 95% H_2O_2 samples were prepared. H_2O_2 was introduced through a leak valve and the pressure was measured by a pres-

TABLE II The properties of the powdered mineral oxide.

Powder	Diameter/ μm	$S_{\text{BET}}/(\text{m}^2/\text{g})$
$\alpha\text{-Al}_2\text{O}_3$	1	9.24
MgO	1	7.33
Fe_2O_3	0.69	5.59
SiO_2	0.5	7.21

sure transducer (MKS 627 B). The sensitivity of H_2O_2 at mass 34 channel was relatively low. Uptakes of H_2O_2 on mineral oxides were performed by this channel because of the influence of water on other channels. The signal at $m/z=32$ is about ten times as large as that of $m/z=34$ and the natural abundance of the $^{34}\text{O}_2$ isotopic component of oxygen is only about 0.2%. So, the influence of oxygen isotope could be neglected.

Al_2O_3 ($\alpha\text{-Al}_2\text{O}_3$), MgO, and SiO_2 were purchased from Alfa Aesar. Fe_2O_3 was purchased from Sigma-Aldrich. 30% H_2O_2 was provided by Beijing Chemical Works. The specific surface area was measured using a Quantachrome Autosorb-1-C instrument, and the specific areas and other properties are listed in Table II.

III. RESULTS AND DISCUSSION

A. Reactive uptake determination

The uptake coefficient is defined as the ratio of number of gas phase molecules lost on the surface to the total number of gas surface collisions. The heterogeneous reaction kinetics was measured using Knudsen cell reactor similar to other reactors [19, 20]. For all of the kinetic experiments and the pressure dependence experiments, the temperature of chamber was kept at 298 K. The system was passivated with H_2O_2 for 1 h while the samples were isolated from the gas reagent before each experiment till the signal of hydrogen peroxide reached a steady state. Then one sample was exposed to gas reagent by a quick opening cover, the H_2O_2 signal of the parent ion monitored at $m/z=34$ dropped below its steady state value. An observed uptake coefficient, γ_{obs} , can be determined from the steady state derived Knudsen cell equation:

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

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 intensity measured with sample covered and exposed, respectively. The values in this work are the initial uptake coefficients, γ_{init} , representing the uptake coefficient that is observed at the initial stages of the reactions.

Figure 1 shows a typical QMS signal response of $\alpha\text{-Al}_2\text{O}_3$ exposed to hydrogen peroxide. In this example, 4.9 mg $\alpha\text{-Al}_2\text{O}_3$ was exposed to H_2O_2

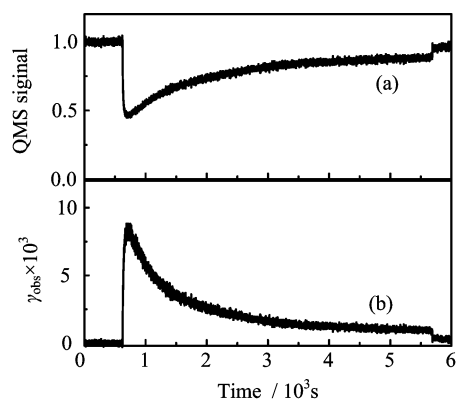


FIG. 1 Knudsen cell data for the uptake of hydrogen peroxide on 4.9 mg of α -Al₂O₃. (a) QMS signal ($m/z=34$) as a function of time. (b) γ_{obs} , calculated from the QMS data in (a) and Eq.(1), is plotted as a function of time.

(3.4×10^{11} molecules/cm³). We can see from Fig.1, the mass spectral intensity for hydrogen peroxide ($m/z=34$) decreases immediately on its first stage. Then the signal intensity recovers to a steady state, which have been reached at 5000 s. However, the signal intensity is still lower than that of the initial baseline intensity. When the sample holder is closed, the H₂O₂ signal return to the initial steady state baseline. Similar signal of the exposure of MgO to hydrogen peroxide is observed. When Fe₂O₃ is exposed to hydrogen peroxide, the H₂O₂ signal decreases immediately in intensity and could not recover toward the baseline during 10 min exposure. After that, the signal is relatively stable during several hours time scale. The uptake coefficients for SiO₂ are measured under the same conditions. The samples are not as reactive as either MgO or Fe₂O₃. The uptake curves for the SiO₂ are different from the other mineral oxides. The signal intensity for the hydrogen peroxide decreases immediately when the sample holder is opened, then the signal intensity recovers to the initial intensity.

The $\gamma_{\text{init,obs}}$ of H₂O₂ uptake depends on the sample mass, therefore upon the number of particle layers and total surface area. As Eq.(1) is derived assuming that the total number of the gas-surface collisions is with the top layer only, the uptake coefficient is calculated using the geometric surface area of the sample. The observed mass dependence involves the diffusion of the reactant gas to underlying layers, resulting in an increase in the number of collisions with the total surface area. Thus, it is an important factor in the determination of the true uptake coefficient. It can be seen in Fig.2, the observed uptake values are dependent on the mass of the samples. The plot in Fig.2 shows the region where $\gamma_{\text{init,obs}}$ is linearly dependent on the mass of samples. From the plot, a mass independent uptake coefficient

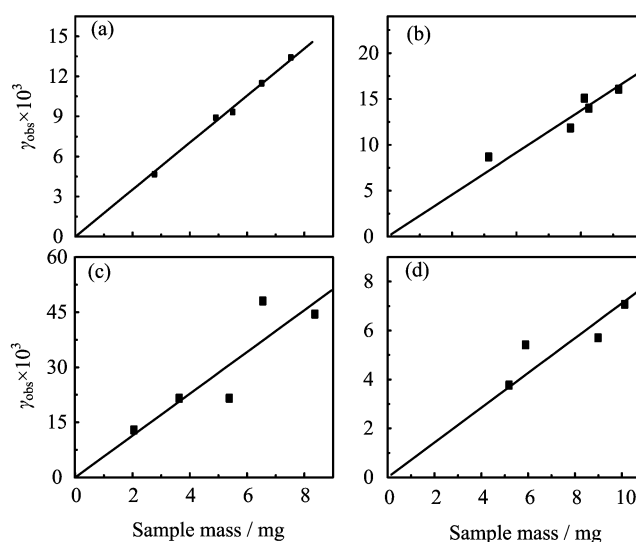


FIG. 2 Linear mass-dependent regions of the observed uptake coefficient for H₂O₂ on (a) α -Al₂O₃, (b) MgO, (c) Fe₂O₃, and (d) SiO₂.

TABLE III Initial uptake coefficients $\gamma_{\text{o,BET}}$ and steady state uptake coefficient $\gamma_{\text{ss,BET}}$ of hydrogen peroxide on mineral oxide particles.

Sample	$\gamma_{\text{o,BET}}$	$\gamma_{\text{ss,BET}} \times 10^5$
α -Al ₂ O ₃	$(1.00 \pm 0.11) \times 10^{-4}$	1.1
MgO	$(1.66 \pm 0.23) \times 10^{-4}$	1.6
Fe ₂ O ₃	$(9.70 \pm 1.95) \times 10^{-5}$	5.5
SiO ₂	$(5.22 \pm 0.90) \times 10^{-5}$	

can be derived as

$$\begin{aligned} \gamma_{\text{BET}} &= \frac{A_{\text{h}}}{A_{\text{BET}}} \left(\frac{I_0 - I}{I} \right) \\ &= \gamma_{\text{obs}} \frac{A_{\text{s}}}{A_{\text{BET}}} \end{aligned} \quad (2)$$

where A_{BET} is the surface area of the sample, taken as the BET area. This area is equal to that the specific BET area of the powder times the sample mass [21]. The results for each experiment which is done in the linear regime are given in Table III. The middle column gives the average value of the BET-area-corrected initial uptake coefficients determined from different mass samples. The steady state uptake coefficients are also given in Table III.

B. Pressure dependence

The pressure dependence of the reactivity may influence the uptake processes on aerosol surfaces, so we also considered the influence of the pressure on the uptake coefficient. Hydrogen peroxide partial pressure for pressure dependence studies varied from

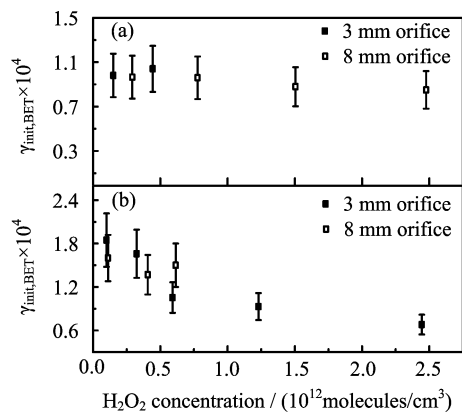


FIG. 3 Initial uptake coefficient for H_2O_2 on (a) $\alpha\text{-Al}_2\text{O}_3$ and (b) MgO as a function of initial H_2O_2 pressure.

1 mPa to 15 mPa, equivalent to concentrations of 10^{11} – 10^{12} molecules/ cm^3 .

Uptake experiments of hydrogen peroxide on Al_2O_3 were systematically carried out by varying the initial concentration of hydrogen peroxide and its residence time (Fig.3(a)). For a given orifice, we observed that the rate constant was independent of H_2O_2 concentration within experimental uncertainty. As a case we presented data for the 3 mm orifice and for H_2O_2 concentration ranging between 2.0×10^{11} and 2.5×10^{12} molecules/ cm^3 , leading to the initial uptake coefficient $\gamma_{\text{init,BET}} = (1.00 \pm 0.11) \times 10^{-4}$ for $\alpha\text{-Al}_2\text{O}_3$ based on the BET area of the sample. From this series of measurements it was evident that the heterogeneous reaction of H_2O_2 on Al_2O_3 surface corresponds to a pseudo first-order rate constant. Then we increased the orifice size to 8 mm, thus decreasing residence time at different H_2O_2 concentration ranging between 1.0×10^{11} and 6.0×10^{11} molecules/ cm^3 . There is no obviously dependence of initial uptake coefficient on residence time, which suggests that the mechanism of hydrogen peroxide uptake corresponds to a simple first-order rate law for uptake.

The similar uptake experiments of hydrogen peroxide on MgO were carried out by varying the initial concentration of hydrogen peroxide and its residence time (Fig.3(b)). For 3 mm orifice we observed that the uptake coefficient was dependent on H_2O_2 concentration for H_2O_2 concentration ranging between 2.0×10^{11} and 2.5×10^{12} molecules/ cm^3 . Then we increased the orifice size to 8 mm at different H_2O_2 concentration ranging between 1.0×10^{11} and 6.0×10^{11} molecules/ cm^3 . There was no obviously dependence of initial uptake coefficient on residence time at different H_2O_2 concentration ranging between 1.0×10^{11} and 6.0×10^{11} molecules/ cm^3 . Because of experimental limitation, we couldn't measure the uptake coefficient with the H_2O_2 concentration higher than 6.0×10^{11} molecules/ cm^3 . The uptake coefficient did not follow a rate law pseudo first order in hydrogen peroxide, suggesting that the mechanism

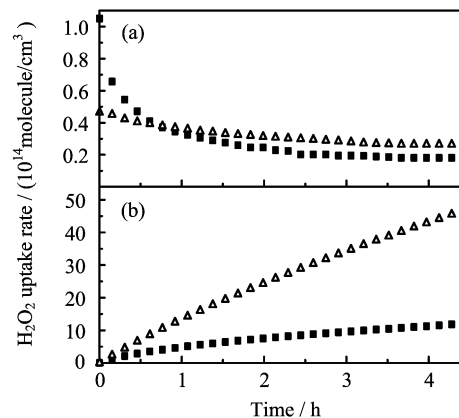


FIG. 4 5.2×10^{11} molecules/ cm^3 H_2O_2 uptake rate per second and H_2O_2 uptake rate per cm^2 of 5.14 mg MgO (square) and 3.51 mg Fe_2O_3 (triangle) as a function of time. (a) Al_2O_3 and (b) MgO .

of hydrogen peroxide uptake on MgO is complex. The similar dependence has been observed by Hanisch and Crowley in their work on ozone decomposition on Saharan dust [19] and by Sullivan and coworker in their study of ozone decomposition on alumina films [22]. The reason for the observed inverse dependence between the reaction probability and the hydrogen peroxide concentration is that the higher concentrations of hydrogen peroxide will lead to an increased blocking of reactive sites and an overall decrease in the reaction rates. This inhibition behavior was also observed for other free radicals interacting with the solid substrate [23, 24]. In contrast with MgO , the pressure dependences of the uptake of hydrogen peroxide on Fe_2O_3 surface were not observed. Because of the independence of uptake coefficient to escape rate, the uptake coefficient was measured with 3 mm orifice in other parts of this work.

C. Time dependent reactivity studies

Mineral oxides were exposed to H_2O_2 for 4.5 h, the time was enough long to test if the uptake of hydrogen peroxide on the mineral oxide was stoichiometric. If the adsorption of H_2O_2 on mineral oxides was the only process of the system, the maximum for surface coverage was often below 10^{15} molecules/ cm^2 and the hydrogen peroxide signal intensity could return toward the initial baseline. After a long time exposure, only the uptake of hydrogen peroxide on SiO_2 surface showed saturation.

The time dependent uptake of hydrogen peroxide on MgO over 4.5 h was determined. Figure 4 shows the hydrogen peroxide uptake rate *vs.* exposure time for MgO . During 4.5 h, it was about 4.65×10^{17} H_2O_2 molecules lost on the surface, taking into account the mass and the specific surface area of the sample, corresponding to 1.2×10^{15} molecules/ cm^2 . The uptake rate of hydrogen peroxide still remained 10% comparing with the initial

uptake rate. The surface coverage for Fe_2O_3 sample over 4.5 h was determined as well. In Fig.4, the line composed of white triangle shows the uptake rate per second for Fe_2O_3 and the uptake rate per square centimeter, which uses BET surface area as the denominator. About 5×10^{17} H_2O_2 molecules were lost to the surface over the duration of experiment. It was about 4.8×10^{15} molecules/ cm^2 , taking into account the mass and the BET surface area of the sample. Although the initial uptake rate of hydrogen peroxide on Fe_2O_3 surface was slower than that on MgO surface, the total number of H_2O_2 molecules lost per cm^2 of sample for Fe_2O_3 was more than that for MgO . The similar process was observed for the uptake of hydrogen peroxide on $\alpha\text{-Al}_2\text{O}_3$.

D. Mechanism

According to the results obtained from experimental measurement, we can deduce the mechanism of these uptake processes. When SiO_2 was exposed to the hydrogen peroxide, the mass spectral intensity for hydrogen peroxide ($m/z=34$) was decreased immediately, then it recovered to the initial baseline. After closing the sample valve, the signal of hydrogen peroxide could reach zero. Then the sample holder was opened, there were H_2O_2 desorbed from the sample. The reactivity of the sample could recover after 12 h evacuation. So the mechanism on SiO_2 surface can pass through the following scheme:



The absorption and desorption of the hydrogen peroxide on SiO_2 surface are reversible.

As can be seen from Fig.5, when Fe_2O_3 was exposed to hydrogen peroxide, the mass spectral intensity for hydrogen peroxide ($m/z=34$) decreased immediately. The mass spectral intensity for oxygen ($m/z=32$) increased with the decrease of the $m/z=34$ channel. By calibrating the mass spectrum of O_2 and H_2O_2 , at the steady state, one O_2 molecule was released after about average $2.5\text{H}_2\text{O}_2$ were adsorbed for Fe_2O_3 . The difference from the theoretical stoichiometry of 2 (1O_2 molecules released after $2\text{H}_2\text{O}_2$ molecules were taken up) can be explained by the chemisorption or that some of the active sites have been passivated. Our observations indicate that the uptake of H_2O_2 is time dependent and decreases with increased exposure time due to surface passivation. The uptake coefficient decreases from 9.7×10^{-5} with the increasing time. But the uptake coefficient could still remain half of the initial uptake coefficient after 4.5 h. Thus the Fe_2O_3 surfaces possess some of the catalytic character toward hydrogen peroxide destruction, although there are passivation effects simultaneously. Because of the high baseline signal of water and the obviously uptake of water on metal ox-

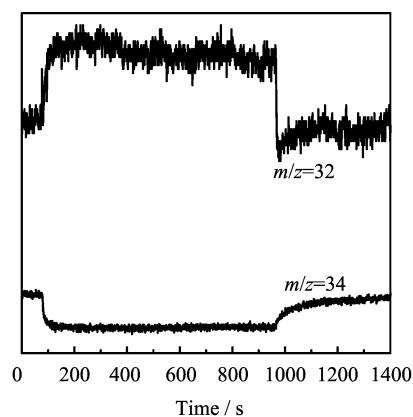


FIG. 5 The uptake of H_2O_2 and product on Fe_2O_3 at 298 K.

ides surface, it is difficult to observe the change of water in the uptake processes.

The process of H_2O_2 decomposition on alumina and magnesia is similar to that of Fe_2O_3 surface, however, the catalytic effect of $\alpha\text{-Al}_2\text{O}_3$ and MgO is relatively weaker than that of Fe_2O_3 . The steady state uptake coefficient of $\alpha\text{-Al}_2\text{O}_3$ and MgO is only 10% of the initial uptake coefficient. From the results of the long time exposure measurements, it can be seen that the surfaces haven't saturated toward hydrogen peroxide except SiO_2 . This phenomenon indicates that mineral oxides have some catalytic effects on the decomposition of hydrogen peroxide. So the surface can remove many more hydrogen peroxide than the total number of active sites present on the surface.

IV. TROPOSPHERIC IMPLICATIONS

The values of uptake coefficients for H_2O_2 were assumed in the range of $2.0 \times 10^{-4} - 1.0 \times 10^{-5}$ in Zhang *et al.* box model study [25]. They found that the presence of the dust resulted in the concentration decreases of H_xO_y by 11%–59%. Pradhan *et al.* recently measured the uptake coefficient of gaseous H_2O_2 on TiO_2 aerosol surface [16]. The uptake coefficient was calculated using the time-and aerosol area dependent loss rate of H_2O_2 under different humidity. As the uptake coefficient was based on the projected, geometric surface area of the dust sample, it represents an upper limit [26]. Zhao *et al.* researched the interaction between H_2O_2 and two major components of mineral dust aerosol, using transmission-Fourier Transform Infrared spectroscopy, and high-performance liquid chromatography [18]. Because the initial uptake processes were achieved on a few minutes time scale. Therefore, they observed uptake coefficients represent the steady state rather than the initial state [18]. The uptake coefficient can represent the lower limit.

The rate of removal of H_2O_2 by uptake onto mineral oxide can be approximated in a simple model. We as-

sume that the lifetime τ for removal of H_2O_2 by dust is given by

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

where A is the dust surface area density, \bar{c} is the mean molecular speed, and γ is the uptake coefficient. If we assume a conservatively low (*i.e.*, background) dust loading of $5 \mu\text{g}/\text{m}^3$ to a high dust loading of $150 \mu\text{g}/\text{m}^3$ [27], we obtained $A \approx 6 \times 10^{-7} \text{ cm}^2/\text{cm}^3$ to $1.8 \times 10^{-5} \text{ cm}^2/\text{cm}^3$. Our measured uptake coefficient are about 1.00×10^{-4} , 1.66×10^{-4} , 9.70×10^{-5} , and 5.22×10^{-5} for $\alpha\text{-Al}_2\text{O}_3$, MgO , Fe_2O_3 , and SiO_2 , respectively, which lead to the corresponding atmospheric lifetimes with respect to processing by dust of 14 h to 18 d, 9 h to 11 d, 15 h to 18 d, and 27 h to 34 d, respectively. The uptake coefficient calculated from our experiment was based on BET surface area of the dust sample, it represents a lower limit. Compared with the lifetime of 1 d for photolysis of H_2O_2 , the interaction between mineral aerosol and H_2O_2 can still significantly influence the concentration of H_2O_2 in the atmosphere and consequently contribute to variability in predicting the change of hydroperoxyl radicals in troposphere ozone formation.

V. ACKNOWLEDGMENTS

This work was supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (No.KJXC2-YW-N24, No.KZCX2-YW-Q02-03), the National Basic Research Program of China of Ministry of Science and Technology of China (No.2011CB403401), and the National Natural Science Foundation of China (No.40925016, No.40830101, No.21077109, and No.41005070).

- [1] C. R. Usher, A. E. Michel, and V. H. Grassian, *Chem. Rev.* **103**, 4883 (2003).
- [2] D. A. Lack, P. K. Quinn, P. Massoli, T. S. Bates, D. Coffman, D. S. Covert, B. Sierau, S. Tucker, T. Baynard, E. Lovejoy, D. M. Murphy, and A. R. Ravishankara, *Geophys. Res. Lett.* **36**, L24805 (2009).
- [3] B. J. Finlayson-Pitts and J. N. Pitts, *Chemistry of the Upper and Lower Atmosphere*, San Diego: Academic Press, (2000).

- [4] D. Vione, V. Maurino, C. Minero, and E. Pelizzetti, *Anal. Chim.* **93**, 477 (2003).
- [5] A. V. Jackson, *Crit. Rev. Env. Sci. Technol.* **29**, 175 (1999).
- [6] M. A. Rubio, M. J. Guerrero, G. Villena, and E. Lissi, *Atmos. Environ.* **40**, 6165 (2006).
- [7] S. H. Do, B. Batchelor, H. K. Lee, and S. H. Kong, *Chemosphere* **75**, 8 (2009).
- [8] M. A. Hasan, M. I. Zaki, L. Pasupulety, and K. Kumari, *Appl. Catal. A* **181**, 171 (1999).
- [9] E. Chevallier, R. D. Jolibois, N. Meunier, P. Carlier, and A. Monod, *Atmos. Environ.* **38**, 921 (2004).
- [10] J. J. Pignatello, E. Oliveros, and A. MacKay, *Crit. Rev. Env. Sci. Technol.* **36**, 1 (2006).
- [11] R. C. Bales, M. V. Losleben, J. R. McConnell, K. Fuhrer, and A. Neftel, *Geophys. Res. Lett.* **22**, 1261 (1995).
- [12] H. W. Jacobi, M. M. Frey, M. A. Hutterli, R. C. Bales, O. Schrems, N. J. Cullen, K. Steffen, and C. Koehler, *Atmos. Environ.* **36**, 2619 (2002).
- [13] L. Chu, G. W. Diao, and L. T. Chu, *J. Phys. Chem. A* **104**, 7565 (2000).
- [14] S. M. Clegg and J. P. D. Abbatt, *Atmos. Chem. Phys. Discuss.* **1**, 73 (2001).
- [15] S. M. Clegg and J. P. D. Abbatt, *J. Phys. Chem. A* **105**, 6630 (2001).
- [16] M. Pradhan, M. Kalberer, P. T. Griffiths, C. F. Braban, F. D. Pope, R. A. Cox, and R. M. Lambert, *Environ. Sci. Technol.* **44**, 1360 (2010).
- [17] M. Pradhan, G. Kyriakou, A. T. Archibald, A. C. Papanageorgiou, M. Kalberer, and R. M. Lambert, *Atmos. Chem. Phys. Discuss.* **10**, 11081 (2010).
- [18] Y. Zhao, Z. M. Chen, X. L. Shen, and X. Zhang, *Environ. Sci. Technol.* **45**, 3317 (2011).
- [19] F. Hanisch and J. N. Crowley, *Phys. Chem. Chem. Phys.* **5**, 883 (2003).
- [20] P. Li, H. A. Al-Abadleh, and V. H. Grassian, *J. Phys. Chem. A* **106**, 1210 (2002).
- [21] G. M. Underwood, P. Li, H. Al-Abadleh, and V. H. Grassian, *J. Phys. Chem. A* **105**, 6609 (2001).
- [22] R. C. Sullivan, T. Thornberry, and J. P. D. Abbatt, *Atmos. Chem. Phys. Discuss.* **4**, 1301 (2004).
- [23] K. Tabor, L. Gutzwiller, and M. J. Rossi, *J. Phys. Chem. A* **98**, 6172 (1994).
- [24] F. Karagulian and M. J. Rossi, *Phys. Chem. Chem. Phys.* **7**, 3150 (2005).
- [25] Y. Zhang and G. R. Carmichael, *J. Appl. Meteorol.* **38**, 353 (1999).
- [26] J. N. Crowley, M. Ammann, R. A. Cox, R. G. Hynes, M. E. Jenkin, A. Mellouki, M. J. Rossi, J. Troe, and T. J. Wallington, *Atmos. Chem. Phys. Discuss.* **10**, 5233 (2010).
- [27] G. Aymoz, J. L. Jaffrezo, V. Jacob, A. Colomb, and C. George, *Atmos. Chem. Phys. Discuss.* **4**, 2499 (2004).