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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

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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.

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).

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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 sierozem), 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 sierozem 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 sierozem. 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.