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Heterogeneous uptake of nitrogen dioxide on Chinese mineral dust

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ABSTRACT

Mineral dust is one of the major aerosols in the atmosphere. To assess its impact on trace atmospheric gases, in this work we present a laboratory study of the effect of temperature on the heterogeneous reaction of NO₂ on the surface of ambient Chinese dust over the temperature range from 258 to 313 K. The results suggest that nitrogen dioxide could mainly be adsorbed on these types of Chinese mineral dust reversibly with little temperature dependence. Similar to a previous study on NO₂ uptake on mineral aerosols, the uptake coefficients are mainly on the order of 10⁻⁶ for the Chinese dust, when BET areas are taken into account. HONO was observed as a product, and its formation and decomposition on Chinese mineral dust during the uptake processes were also studied. The complete dataset from this study was compiled with previous literature determinations. Atmospheric implications of the heterogeneous reaction between NO₂ and mineral dust are also discussed, in an effort to understand this important heterogeneous process.

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Introduction

Mineral particulate matter, constituting 36% of total primary aerosol emissions, has been recognized as one of the major aerosols in the troposphere (Ooki and Uematsu, 2005; Sullivan et al., 2007). Annually, about 1000–3000 Tg mineral dust is emitted into the atmosphere (Dentener et al., 1996; Harrison et al., 2001; Usher et al., 2003). Mineral dust can react with various trace gases, and the lifetimes of the various trace gases may change via heterogeneous interactions with dust, which can provide reactive sites for surface-mediated heterogeneous reactions (Prospero, 1999; Wagner et al., 2008).

The chemical interactions between mineral dust and pollutants are significant contributors to atmospheric processes; dust plumes that originate from Saharan Africa or central Asia can be

transported several thousands of kilometers and mix with air from urban areas (Carmichael et al., 1997; Song and Carmichael, 2001; Tang et al., 2004). As one of the predominant polluting gases, nitrogen dioxide can influence the pH of rainwater and lead to the formation of secondary nitrate aerosols. A typical concentration of NO₂ in the photochemical smog may reach 70 ppb, but in emission sources, such as coal power plant stations and motor engines, the NO₂ concentration may reach as high as 400 ppm (Zamaraev et al., 1994; Lisachenko et al., 2006). With increasing NO₂ concentrations in the troposphere, the importance of NO₂ reactions with mineral dust in the atmosphere needs to be evaluated. From field observation results, it is apparent that mineral dust can affect the local gas-phase concentration of nitrogen dioxide, either by physical adsorption or by heterogeneous reaction. These results have important

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implications for improving the treatment of dust in global chemistry models and highlight a number of key processes that merit further investigation through laboratory and field studies (Guan et al., 2014; Nie et al., 2012; Li et al., 2010; Li and Han, 2010; Sullivan et al., 2007).

Heterogeneous reactions of NO₂ with atmospheric mineral particulates are thought to be a source of atmospheric HONO (Febo et al., 1996). Studies show that high levels of hygroscopic nitrate are generated by the heterogeneous conversion of NO₂ on the surface of particulates in the atmosphere (Al-Abadleh et al., 2003). Heterogeneous processes are thought to be the major source of HONO in the atmosphere. They have been intensively studied in the laboratory, and several mechanisms of HONO formation on aerosols and the ground surface have been proposed (Cwiertny et al., 2008). The enhanced NO₂ conversion could be an important HONO, and therefore also OH, source in regions where pollution and dust storms coincide (Kleffmann, 2007; Wang et al., 2003), while the contribution of mineral aerosol to the HONO loss in the atmosphere is limited (El Zein et al., 2013).

In this study, we investigated the heterogeneous uptake of NO₂ on two different solid particles representative of mineral dust from the Inner Mongolia desert and Xinjiang arid region. 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 (Smith, 2003). Therefore, the temperature dependence of the uptake coefficients of nitrogen dioxide on mineral dust was further investigated over the temperature range of 258–313 K, which covers the range of observed global temperatures, and can represent the common effects of temperature on these reactions. The potential of atmospheric production of HONO during these heterogeneous reactions was also investigated. The present studies provide useful information to understand the temperature dependent mechanism of the uptake and reaction processes of nitrogen dioxide on mineral dust, which is a critical factor in evaluating mineral dust environmental and climate impacts.

1. Experimental section

1.1. Reactants

The samples used in our experiments were purchased from the Chinese Standard Substance Center (the Chinese Standard Substance Center, Beijing, China). In the Standard Substance Center, Inner Mongolia desert dust and Xinjiang sierozem were collected from Inner Mongolia Wulate and Xinjiang Shihezi, respectively. The dust samples were dried first and debris was removed by sieves (0.25 mm). Then the samples were heated to 120 °C for 24 hr, crushed by a jet mill to about 20 μm, and mixed by a ball grinding mill for 48 hr. The chemical compositions of the samples are listed in Table S1. Related information can be obtained from Reference Materials Information Center of China. In our previous work, we have used the X-ray diffraction method to measure and analyze the compositions of these two mineral dusts. The major peaks were indexed to determine the mineral phases present, which showed that the main fractions were quartz and feldspar (Zhou et al., 2014). The surface areas of these powders were measured with a

Quantachrome Autosorb-1-C BET apparatus (autosorb-iQ, Quantachrome Instruments, USA) using multipoint Brunauer–Emmett–Teller (BET) analysis. The BET areas were determined to be 5.06 m²/g for Inner Mongolia desert dust, and 20.98 m²/g for Xinjiang sierozem.

Gaseous nitrogen dioxide (99.9%) purchased (Beijing Huayuan Gas Chemical industry Co., Ltd., Beijing, China) was used directly without any purification.

1.2. Knudsen cell experiments

A Knudsen cell reactor coupled with a quadrupole mass spectrometer was used to measure the uptake coefficient of nitrogen dioxide on the Inner Mongolia desert dust and Xinjiang sierozem (Chinese Standard Substance Center). This experimental apparatus has been described in detail elsewhere (Wang et al., 2011; Zhou et al., 2012).

Briefly, the Knudsen cell reactor (volume of 461 cm³), with four isolated sample compartments and a small escape aperture, links to an electron impact ion source (EI) quadrupole mass spectrometer (HAL 3F 501, Hiden Analytical Ltd, Warrington, UK). The geometric area of the sample holder (*A_s*) was 5.3 cm². The effective area of the escape aperture was measured in each independent experiment according to the attenuation of the N₂ signal from one steady state to another (Li et al., 2002). It was about 0.173 cm² in our experiments. NO₂ was monitored by the *m/z* = 46 channel. The powdered samples were prepared in Teflon-coated metal sample holders, by heating a hydrosol of the powder until a dry coating of the sample remained on the bottom surface of the holder. In the Knudsen cell experiments, NO₂ gas was introduced through a leak valve to the desired pressure as measured with a wide range gauge (WRG-S-NW25, Edwards, UK). For the total uptake measurements, it was necessary to calibrate the flow out of the cell in terms of molecules per second. This was accomplished using the effective area of the escape aperture and the conversion of pressure to flux using the kinetic theory of gases. This gave the number of molecules per second escaping the cell as a function of pressure. Multiplying this value by the experimentally determined absolute pressure versus the quadrupole mass spectrometer (QMS) intensity data yields a conversion factor through which the NO₂ mass spectrometer signal is converted to molecular flow through the cell. Relative mass spectral sensitivities for NO₂ were determined from calibration with the pure gases. These sensitivity factors were then used in conjunction with the daily NO₂ calibration to convert the mass spectrometer signal to molecular concentration for NO₂.

When a sample was exposed to nitrogen dioxide, the signal of nitrogen dioxide molecular ion monitored at *m/z* = 46 dropped below its original value suddenly. An observed uptake coefficient (γ_{obs}) can be derived from the Knudsen cell Eq. (1):

$$\gamma_{\text{obs}} = \frac{A_{\text{h}}}{A_{\text{s}}} \left(\frac{I_0 - I}{I} \right) \quad (1)$$

where *A_h* is the effective area of the escape hole (cm², *A_h* = 0.1713 cm² in this study), *A_s* is the geometric area of the sample holder (cm², *A_s* = 5.3 cm² in this study), and *I*₀ and *I*

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