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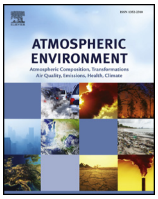

Adsorption of SO_2 on mineral dust particles influenced by atmospheric moisture

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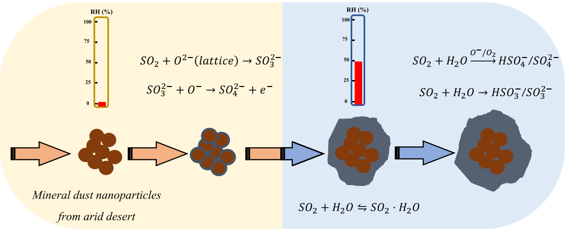
GRAPHICAL ABSTRACT



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ABSTRACT

Moisture plays a crucial role in the heterogeneous formation of sulfur compounds on mineral dust particles. The heterogeneous uptake of SO_2 under various humidity conditions, however, is not well explained. In this study, heterogeneous reaction of SO_2 on hematite particles are investigated using an in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The interaction of SO_2 with H_2O is divided into the initial moisture absorption stage and the subsequent heterogeneous oxidation stage, indicating physical adsorption and chemical conversion of SO_2, respectively. Uptake coefficients were estimated by Brunauer-Emmett-Teller (BET) surface area and geometric surface area. For unreacted (fresh) particles, the coefficients peak at 33% RH and then decline with increasing RH in both stages, implying the competition between SO_2 and large amount of adsorbed H_2O besides the promoting effect of water. For hematite after in-situ exposure to SO_2 (sulfated particles), the coefficients increase as a function of RH in moisture absorption stage, indicating SO_2 adsorption with particle hygroscopic growth. Nevertheless, the coefficients exhibit similar variation with that for fresh particles in heterogeneous oxidation stage, highlighting the competition effect after H_2O accumulation. Generally, H_2O plays both positive and negative roles in the adsorption of SO_2. Reaction on sulfated hematite is significantly influenced by previously formed sulfate compounds with low hygroscopicity. Moreover, sulfate products may influence particle acidity after H_2O introduction, and further result in diverse existence forms of S(IV) species. The extremely great uptake capacity of sulfated particles in moisture absorption stage may offer opportunities to explain the severe haze in high RH.

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1. Introduction

Mineral dust particles, emitted mainly from arid and semiarid regions with a maximal flux of 3000 Tg per year, act as one of the most important aerosols in mass terms in the troposphere (Zhao et al., 2015). Nanoscale particles have lifetimes of up to several days and can be transported over thousands of kilometers, and thus have global impacts (Tang et al., 2016). In the journey, these particles act as sinks for many trace gases, leading to the formation of various inorganic/organic compounds on the efficient surfaces (Tan et al., 2017; Tang et al., 2017). This process could be important in East Asia, because dust/soil occupies a great share in fine particles in spring due to the frequent occurrence of dust storms (Zhang et al., 2015). As chief constituents in the upper continental crust, metal oxides (e.g. SiO_2, Al_2O_3, Fe_2O_3) make great contributions to tropospheric mineral dust (Chen et al., 2012; Usher et al., 2003). Thereinto, transition metal ions, such as Fe(III) and Mn(II), promote various oxidation processes by the help of oxygen. Earlier studies have investigated the reactive sites responsible for weak or strong adsorption of trace gases on particle surfaces (Goodman et al., 2001; Usher et al., 2002). Influenced by steel smelting and coal combustion, enhanced iron concentrations were previously observed during haze episodes (G. Li et al., 2017a). Hence, the heterogeneous reaction on iron-rich particles could be viewed as a typical course in laboratory research.

As key contributors of atmospheric particulate matters during haze time, sulfur-containing aerosols have attracted worldwide concern (Cheng et al., 2016; Harris et al., 2013; Huang et al., 2014; Kumar and Francisco, 2017; Wang et al., 2016). Sulfate can limit the formation of environmental persistent free radicals (Feld-Cook et al., 2017) and sulfite can initiate the efficient conversion of NO_2 to HONO (Ma et al., 2017). With phases changing after particle hydration and dehydration in different humidity environments, sulfate trends to determine particle mixing structures (W. Li et al., 2017b). Furthermore, sulfate species account for aerosol toxicity (Fang et al., 2017), and may lead to frequent occurrence of lung cancer (Raaschou-Nielsen et al., 2016) and brain injury (Underwood, 2017). Mechanisms responsible for the sulfate formation on mineral dust particles, however, are still not well understood, hindering the forecast and mitigation of haze (Dowd et al., 2017).

The interaction of water with metal oxides is ubiquitous in the atmosphere, from mineral dust dissolution and adsorption/desorption reactions to the reaction of water with secondary aerosols (Brown et al., 1999; Hoffmann et al., 1995). It has been widely recognized that water adsorbed by particles plays a central role in determining the heterogeneous reactivity towards reactive trace gases in the atmosphere (Tang et al., 2016). Hence, relative humidity (RH) is considered as an important index when discussing the heterogeneous reaction of SO_2 on mineral dust (Huang et al., 2015; Tan et al., 2017; Yang et al., 2017; Zhang et al., 2018). The interactions of SO_2 with other trace gases in various RHs have been widely concerned and thoroughly explained (Huang et al., 2015, 2016; Park et al., 2017). The interaction of SO_2 with H_2O on dry particles contains the initial moisture absorption stage and the subsequent heterogeneous oxidation stage (Dowd et al., 2017), which were scarcely distinguished by previous studies. Moreover, authentic mineral particles are constantly transported from arid desert regions to humid urban areas, undergoing series of humid variations (Yang et al., 2017; Zhuang et al., 1992). It is unascertained whether the sulfate formed on dry particles would influence the later adsorption of SO_2 after H_2O addition. The heterogeneous reaction of SO_2 on mineral particles under changing humidity conditions is still not clear.

Therefore, the heterogeneous uptake of SO_2 on fresh (unreacted) and sulfated (after 120 min in-situ exposure to SO_2 under dry condition) particles under various humidity conditions were systematically investigated using in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and ion chromatography (IC) in this work. The uptake coefficients for the heterogeneous uptake of SO_2 in various stages were estimated and the reaction mechanism was further summarized. This work could help understand the SO_2 adsorption on Fe-rich particles in different scenarios depended on RH and provide extremely key parameters for atmospheric chemistry models.

2. Materials and methods

2.1. Materials

The hematite particles were prepared according to the method reported previously (Schwertmann and Cornell, 2000). Since the uptake capacity is influenced by particle size (Zhang et al., 2016), prepared particles were passed through a 200-mesh sieve before experiments to make the size uniform. Transmission electron microscopy (TEM) image shows the morphology of hematite with an average particle size of 57.42 ± 17.37 nm (Fig. 1). Based on the XRD (X-ray diffraction) analysis, the prepared particles are pure hematite (Figure S1). The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) of the hematite is measured to be 34.01 $m^2 \cdot g^{-1}$ (Micromeritics TriStarII3020, Micromeritics Instrument Co., USA).

The specifications of the gases included in the experiments are as follows: calibration SO_2 (98.4 ppm in N_2, Shanghai Qingkuan Co., LTD),

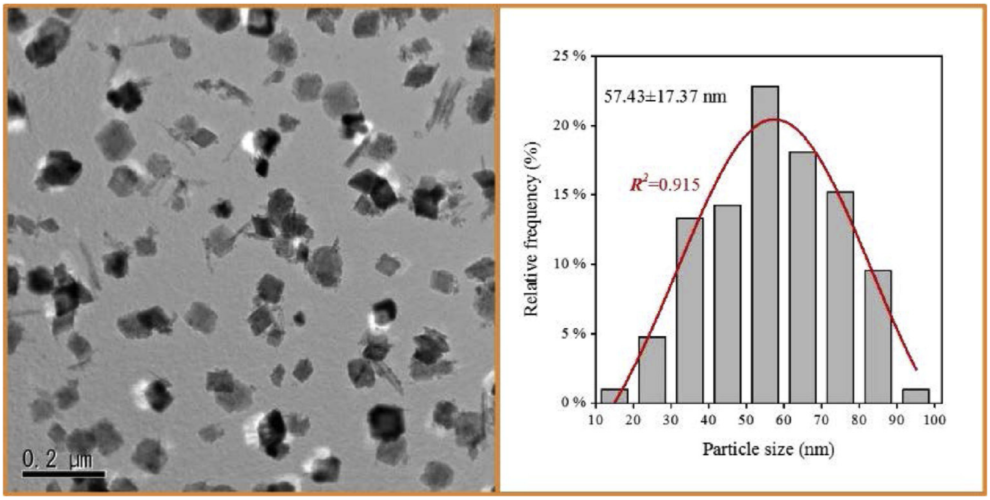

Fig. 1. (a) Transmission electron microscopy (TEM) image and (b) particle size distribution of hematite nanoparticles. 100 particles were counted to calculate the average particle size. The distribution is well fitted by a Gaussian function with R^2 of 0.915.