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Synergistic effect among Cl_2, SO_2 and NO_2 in their heterogeneous reactions on gamma-alumina

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HIGHLIGHTS

- Cl_2, NO_2 and SO_2 have synergistic effects when they react with the surface of γ-Al_2O_3.
- The presence of γ-Al_2O_3 seed aerosols greatly promotes the formation of secondary inorganic aerosols.
- Cl_2 can promote the formation of secondary sulfate and nitrate aerosols on γ-Al_2O_3 surface.
- The possible heterogeneous reaction mechanism of Cl_2, NO_2 and SO_2 on γ-Al_2O_3 surface are proposed.

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ABSTRACT

Severe haze in China has been a global concern in recent years. Most studies about the mechanism of haze formation mare only focused on the heterogeneous reactions of SO_2 and NO_2 on mineral aerosols. However, little is known about the role of molecular chlorine (Cl_2) in those reactions. Here, we investigated the heterogeneous uptake of Cl_2, SO_2 and NO_2 on γ-Al_2O_3 particles under different conditions using a quartz-based flow reactor. We found that the existence of γ-Al_2O_3 seed aerosols significantly promotes the formation of secondary chloride, sulfate and nitrate aerosols, and Cl_2, NO_2 and SO_2 have synergistic effects when they react on γ-Al_2O_3 surface under humid condition. The results also shows that Cl_2 can promote the formation of secondary sulfate and nitrate aerosols on γ-Al_2O_3 surface. Moreover, Cl_2 is much easier to react with the surface of γ-Al_2O_3 and form secondary Cl^- aerosol when comparing with NO_2 and SO_2, suggesting that Cl_2 is of great importance in atmospheric chemistry, it has the potential to alter the surface properties (e.g., chemical composition and fraction) of mineral aerosol, enhance the production of secondary inorganic aerosols in the troposphere, and thus cause adverse effects on the climate and human health.

1. Introduction

Haze is a phenomenon of air pollution, which executes adverse impacts on atmospheric visibility, global climate and human health (Nel, 2005; Penner et al., 1994). In recent years, persistent haze shrouded the North China Plain and has increased in the frequency of occurrence, the duration of a single haze event and the extent of the haze area (He et al., 2014; Zhang et al., 2012b). It is found that the severe haze pollution event in China was driven to a large extent by stagnant meteorological conditions, large emissions of primary air pollutants (e.g., SO_2, NO_x, NH_3, dust and smoke) and fast production of secondary inorganic aerosol, especially sulfate and nitrate (Cheng et al., 2016; Guo et al., 2014; Huang et al., 2014).

Mineral dust, which makes up a large fraction (30–60%) of global aerosols, is one of the most important types of particles in

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the atmosphere (Xu et al., 2011). Field studies estimated that about 1000–3000 Tg of such particles is emitted into the atmosphere annually (Dentener et al., 1996). Mineral dust can provide reactive surface for the heterogeneous reactions of pollution gases, which, in turn, would impact the composition and surface properties of mineral dust and further influence the climate and human health (Inyang, 2006; Tegen et al., 1996; Wu et al., 2013b; Zhao et al., 2015). Hence, the heterogeneous reactions of trace gases on mineral dust has been received much attention in recent years (Fu et al., 2007; Kolb et al., 2010). Alumina, mainly including α-Al_2O_3 and γ-Al_2O_3, is a typical component of mineral dust and is emitted into the atmosphere from wind-blown soil and solid-propellant rocket motor exhaust. In this study, γ-Al_2O_3 is chosen as a model oxide for its high surface area and superior chemical and thermal stability to obtain useful information about the mechanism of atmospheric heterogeneous reactions (Sun et al., 2015; Wu et al., 2013a).

Sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are of great importance in the atmosphere for their chemical reactivity (Song and Carmichael, 1999). SO_2 is the major precursor of secondary sulfate and sulfuric aerosols (Zhang et al., 2012a). Nearly half of SO_2 emitted into the atmosphere are converted to sulfate, and this sulfate often have association with mineral aerosol. Sulfate and sulfite aerosols are known to cause detrimental effects on biological health and affect the global climate directly by scattering solar radiation or act as cloud condensation nuclei and thereby affecting climate indirectly (Dentener et al., 1996; Langner et al., 1992; Ramanathan et al., 2001). NO_2 is another major component of air pollution with similar anthropogenic sources as SO_2. Field and model studies have shown that about 40% of nitrate formation in the atmosphere is associated with the heterogeneous reaction of NO_2 on mineral aerosol and could contribute to the occurrence of haze events. Moreover, NO_2 is closely related both the formation of acid rain and stratospheric ozone depletion.

For the above reasons, the heterogeneous reactions of SO_2 and NO_2 on mineral dust are of great concern, and have been extensively investigated by laboratory studies (He et al., 2014; Liu et al., 2012; Ma et al., 2008). The results show that there is a synergistic effect between SO_2 and NO_2 in their heterogeneous reaction on mineral dust. As a crucial oxidant, the coexisting of NO_2 in the atmosphere could promote the formation of sulfate from adsorbed SO_2 on mineral dust. However, this interaction mechanism between SO_2 and NO_2 on mineral dust are still ambiguous. In addition, many model results reveal a systematic tendency to overestimate SO_2 and NO_2 concentrations and underestimate SO_4^{2-} and NO_3^- concentrations, which means that there are some unknown sources of secondary sulfate and nitrate aerosol (Barrie et al., 2001; Kasibhatla et al., 1997).

Reactive halogen species (RHS) are a group of important atmospheric pollutants. They can be emitted directly from a variety of industrial sources and can be produced by photochemical oxidation of sea salt aerosol. RHS play a variety of roles in atmospheric chemistry. They involve in the partitioning of OH/HO_2 and NO/NO_2, the oxidation of sulfur (IV), the production of nitric acid, and hence influence the formation of secondary inorganic aerosols. Molecular chlorine (Cl_2), as one of the most abundant reactive halogen species, can compromise air quality as it undergoes fast photolysis to form chlorine radicals, which are strong atmospheric oxidants and can expedite the degradation of tropospheric ozone and a variety of VOCs.

Substantial efforts have been put into detecting Cl_2 in the atmosphere because of its significant effect on the atmospheric chemistry. For example, Spicer et al. (1998) observed mixing ratios of Cl_2 approaching 150 pptv at a North American coastal site. Cl_2 in the Atlantic marine boundary layer (up to 35 pptv at night) and in the Los Angeles region (reaching 200 pptv at night) have also been observed (Lawler et al., 2011; Riedel et al., 2012). Recently, Liao et al. (2014) reported an unexpected high level of Cl_2 reaching up to 400 pptv in the Arctic marine boundary layer in Barrow, Alaska. Despite the appearance of high concentration of Cl_2 in the atmosphere, the atmospheric reactions of Cl_2 haven't attracted significant scientific attention. To the best of our knowledge, the heterogeneous oxidation reactions of Cl_2 towards aerosol particles have not yet been reported, preventing a direct comparison of their relative importance.

In this work, the heterogeneous reactions of Cl_2, SO_2 and NO_2 on the surface of γ-Al_2O_3 have been studied under various conditions, for instance, co-existing gases, relative humidity, UV light, reaction time, and the concentrations of gases. The role of γ-Al_2O_3 seed aerosols and Cl_2 on the atmospheric reactions has also been evaluated. Moreover, the possible heterogeneous reactions mechanism of Cl_2, NO_2 and SO_2 on γ-Al_2O_3 surface were discussed. The results of this study are helpful to understand the formation of secondary inorganic aerosols in the troposphere involving Cl_2, SO_2 and NO_2. It also provides significant information of the role of Cl_2 on the atmospheric chemistry.

2. Material and methods

2.1. Materials

The γ-Al_2O_3 particles (20 nm, 99.99% purity) used in this study was purchased from Alfa Aesar, USA. Before the experiment, γ-Al_2O_3 was washed repeatedly with distilled water and then centrifuged until the concentration of Cl^- in the supernatant solution was below the detection limit. Dried in the oven until a constant weight was reached, then ground to a particle size of <250 μm and stored at −20 °C for further use.

The specifications of the gases used in this experiment are as follows: synthesized air (80% N_2 + 20% O_2, 99.999% purity), SO_2 (1% in N_2), NO_2 (1% in N_2) and Cl_2 (1% in N_2). All gases were purchased from Beijing Haipu Gas Industry Co. Ltd.

2.2. Generation of reactants

Fig. 1 shows the schematic diagram of this setup. The concentrations of SO_2, NO_2 and Cl_2 used in this study were adjusted by mixing SO_2, NO_2 and Cl_2 standard gases with synthetic air (80% N_2 + 20% O_2) using four mass flow controllers (MFC). Before entering the reactor, all those gases were mixed sufficiently in the mixing ball. Humidity in the reactor was generated by passing a flow of synthetic air through ultrapure water.

2.3. Uptake experiments

In the present study, a quartz-based flow reactor was used to investigate the formation of sulfate, nitrate and chlorine ions on γ-

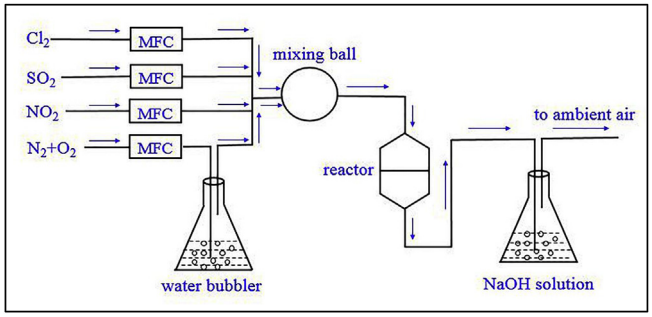

Fig. 1. Schematic diagram of experimental setup. MFC: Mass flow controller.