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Heterogeneous oxidation of SO_2 by O_3-aged black carbon and its dithiothreitol oxidative potential

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ABSTRACT

Ozone (O_3) is an important atmospheric oxidant. Black carbon (BC) particles released into the atmosphere undergo an aging process *via* O_3 oxidation. O_3-aged BC particles may change their uptake ability toward trace reducing gases such as SO_2 in the atmosphere, leading to different environmental and health effects. In this paper, the heterogeneous reaction process between O_3-aged BC and SO_2 was explored *via in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Combined with ion chromatography (IC), DRIFTS was used to qualitatively and quantitatively analyze the sulfate product. The results showed that O_3-aged BC had stronger SO_2 oxidation ability than fresh BC, and the reactive species/sites generated on the surface had an important role in the oxidation of SO_2. Relative humidity or 254 nm UV (ultraviolet) light illumination enhanced the oxidation uptake of SO_2 on O_3-aged BC. The oxidation potentials of the BC particles were detected *via* dithiothreitol (DTT) assay. The DTT activity over BC was decreased in the process of SO_2 reduction, with the consumption of oxidative active sites.

Introduction

Black carbon (BC) generated from fuel and biomass burning is an important component of atmospheric aerosols. BC constitutes approximately 0.3 to 11.4 $\mu g/m^3$ of particle matter in the atmosphere (Zha et al., 2014). China is responsible for half of the BC emissions in Asia and on average, the emission accounts for 18.97% of the global value (Qin and Xie, 2012). BC absorbs solar radiation and shows both direct and indirect effects on radiative forcing (Jacobson, 2001). The absorbance effects of BC toward visible light reduce atmospheric visibility (Ma et al., 2010). Moreover, BC may induce adverse health effects, such as respiratory and cardiovascular diseases and allergies (Smith et al., 2009).

Fresh BC undergoes an aging process when it reacts with light or pollutants during long-distance transport. The aging process changes atmospheric components, the source and sink of gases, and the physicochemical properties and toxicity of BC itself, thereby affecting the climate and health. The large surface area of BC can provide reactive sites and interfaces for many heterogeneous reactions. The heterogeneous reactions of BC with SO_2, O_3, NO_2, and organic acids have been widely studied (Han et al., 2013a; Song et al., 2012; Orrling et al., 2011; Smith and Chughtai, 1995). Novakov et al. (1974) found that BC could catalytically oxidize SO_2 to sulfate in the presence of O_2 and water; thus, it might be an important source of atmospheric sulfate. Field observations and model calculations confirmed that the heterogeneous oxidation of SO_2 on particles was a major

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sink of SO_2 (Shi et al., 2008; Li et al., 2011). The presence of water accelerated the reaction of SO_2 to form sulfite, and O_3 promoted the formation of sulfate on the surface of sodium chloride (Li et al., 2007). Fresh BC showed hydrophobic properties. The hydroscopicity of BC was enhanced after it was mixed with sulfate, along with changes in morphology and particle size, which further affected its optical properties and radiation effects (Ma et al., 2010). Zhang et al. (2008) found that sulfate-aged BC, especially internally mixed BC, could be more efficient cloud condensation nuclei (CCNs). BC could also catalytically reduce NO_2 to NO and HONO (Monge et al., 2010). BC with higher oxygen content exhibited a weaker ability to reduce NO_2 to NO and HONO (Han et al., 2013b).

The surface structure of O_3-aged BC was modified *via* the formation of oxygen-containing species, including ketones, lactones, and anhydrides (Han et al., 2012; Liu et al., 2010). Li et al. (2013) proved that the contents of oxygen-containing functional groups, hydrophilicity, and oxidative potential of BC increased after ozone treatment. O_3-aged BC might induce more reactive oxygen species (ROS) formation and cytotoxicity (Holder et al., 2012). Shiraiwa et al. (2011) noted that long-lived reactive oxygen intermediates (ROIs) are formed in the reaction of O_3 with aerosol particles. These ROIs could have a key function in the chemical aging of PM. The physicochemical properties and environmental effects of O_3-aged BC need further research. The changes in oxidative ability might lead to changes in gas uptake ability, which affects secondary aerosol formation and associated environmental impacts.

The oxidative ability of O_3-aged BC was investigated in this study *via* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and ion chromatography (IC). The products were measured quantitatively, and the influencing factors are discussed. The dithiothreitol (DTT) assay was used to evaluate the oxidative potential changes of the BC particles.

1. Materials and methods

1.1. Reaction systems for DRIFTS studies

A Nicolet Nexus FTIR Spectrometer equipped with a mercury cadmium telluride (MCT) detector and DRIFTS optics (Model DRA-2CO, Harrick Scientific Corp., Chengdu, China) was used to record *in situ* infrared spectra ranging from 4000 to 600 cm^{-1}, with a resolution of 4 cm^{-1}.

Printex U black carbon (referred to as UBC hereafter, Degussa Company, Germany) was used as the model BC powder in the experiments.

The extinction coefficient of UBC particles is large, and DRIFTS cannot directly monitor it. Therefore, the UBC was mixed with the infrared-transparent material NaCl (≥99.999%, Beijing J&K Scientific Ltd. Beijing, China) at a mass ratio of 1:399. The particle samples (32 ± 1 mg) were placed in a cylindrical sample cell made of stainless steel (with a diameter of 8.1 mm and a depth of 0.5 mm). The sample surface was smoothed using a glass slide, and the sample cell was placed in the DRIFTS reaction vessel for the reaction.

The standard SO_2 cylinder gas (5714 mg/m^3, with the dilution gas of highly pure N_2) was supplied by the China Institute of Metrology. O_3 gas was produced from the vacuum UV-irradiation of high-purity O_2. Highly pure N_2 and O_2 cylinder gases (≥99.999%) were provided by the Department of Mechanics, Peking University. The relative humidity was controlled using a saturated steam generator *via* the blister test. The dilution gas in the reaction was highly pure N_2, and the total flow was kept at 200 mL/min. In every experiment, highly pure N_2 was used to purge the samples for 1 hr. The reaction gas at a specific concentration and relative humidity was not introduced until the adsorbed water IR peak stopped decreasing. The reaction was conducted at normal temperature and pressure. Three experiment systems were designed as follows: (1) reaction between fresh BC particles and gaseous SO_2 (86 mg/m^3, synthetic air dilution), relative humidity (RH) = 40%, expressed as UBC + SO_2; (2) reaction between O_3-aged (64 mg/m^3, 2 hr) BC particles (expressed as UBC (O_3)) and gaseous SO_2 (86 mg/m^3, synthetic air dilution), RH = 40%, expressed as UBC (O_3) + SO_2; (3) reaction between BC particles and simultaneous gaseous SO_2 (86 mg/m^3, synthetic air dilution) and O_3 (64 mg/m^3), RH = 40%, expressed as UBC + SO_2 + O_3.

Known masses of anhydrous Na_2SO_4 and BC (1:400 in NaCl) particles were mixed by grinding to obtain standard samples. The peak position and standard curves of SO_4^{2-} were obtained. In this experiment, the characteristic absorption peak of SO_4^{2-} occurred at 1140 cm^{-1}. The product concentration was then quantified with the standard curves:

$$C = 0.094A–0.025 \quad \left(R^2 > 0.99\right),$$

where, C (mg/g) is the concentration of sulfate and A is the integral area of infrared absorption peak of sulfate.

Light sources with two different bands were used in studying the effects of irradiation. UV illumination with the main wavelengths at 365 and 254 nm was applied with light intensities of 160 and 300 $\mu W/cm^2$, respectively. The light intensity was measured using a dual-channel UV radiation meter (UV-B, Photoelectric Device Ltd. of Beijing Normal University, Beijing, China).

1.2. IC analyses

For IC measurement, 13 ± 1 mg of the BC particles was spread in a quartz tube. The BC particles were treated with flowing O_3 or SO_2 to start the three reaction systems as described in Section 1.1. The reaction time was 3 hr. Then, 1 mg/mL of UBC deionized water solution was prepared and ultrasonicated for 20 min. Dionex ICS-2000 ion chromatography (ICS-2000, Dionex, Sunnyvale, California, USA) was used to measure the sulfate content in the extracting solution. An Ionpac AS-11 analytical column (AS-11, Dionex, Sunnyvale, California, USA), which is an electrochemical suppressor, was used. The eluents were gradient NaOH solutions with a flow rate of 1.2 mL/min, and the sample volume was 99 μL. The standard samples were 0 to 10 mg/L Na_2SO_4 solutions with a retention time of 24.7 min. The IC working curve is:

$$C = 1.953A + 0.053 \quad \left(R^2 = 0.999\right)$$

where, C (mg/L) is the sulfate concentration and A is the integral area of the sulfate chromatographic peak.