Heterogeneous oxidation of SO₂ by O₃-aged black carbon and its dithiothreitol oxidative potential

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ABSTRACT

Ozone (O₃) is an important atmospheric oxidant. Black carbon (BC) particles released into the atmosphere undergo an aging process via O₃ oxidation. O₃-aged BC particles may change their uptake ability toward trace reducing gases such as SO₂ in the atmosphere, leading to different environmental and health effects. In this paper, the heterogeneous reaction process between O₃-aged BC and SO₂ 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 O₃-aged BC had stronger SO₂ oxidation ability than fresh BC, and the reactive species/sites generated on the surface had an important role in the oxidation of SO₂. Relative humidity or 254 nm UV (ultraviolet) light illumination enhanced the oxidation uptake of SO₂ on O₃-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 SO₂ reduction, with the consumption of oxidative active sites.

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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 μg/m³ 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 SO₂, O₃, NO₂, and organic acids have been widely studied (Han et al., 2013a; Song et al., 2012; Orling et al., 2011; Smith and Chughtai, 1995). Novakov et al. (1974) found that BC could catalytically oxidize SO₂ to sulfate in the presence of O₂ and water; thus, it might be an important source of atmospheric sulfate. Field observations and model calculations confirmed that the heterogeneous oxidation of SO₂ on particles was a major
sink of SO2 (Shi et al., 2008; Li et al., 2011). The presence of water accelerated the reaction of SO2 to form sulfite, and O3 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 efficiencies (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 NO2 to NO and HONO (Monge et al., 2010). BC with higher oxygen content exhibited a weaker ability to reduce NO2 to NO and HONO (Han et al., 2013b).

The surface structure of O3-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. O3-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 O3 with aerosol particles. These ROIs could have a key function in the chemical aging of PM. The physicochemical properties and environmental effects of O3-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 O3-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 SO2 cylinder gas (5714 mg/m3, with the dilution gas of highly pure N2) was supplied by the China Institute of Metrology. O3 gas was produced from the vacuum UV-irradiation of high-purity O2. Highly pure N2 and O2 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 N2, and the total flow was kept at 200 mL/min. In every experiment, highly pure N2 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 SO2 (86 mg/m3, synthetic air dilution), relative humidity (RH) = 40%, expressed as UBC + SO2; (2) reaction between O3-aged (64 mg/m3, 2 hr) BC particles (expressed as UBC (O3)) and gaseous SO2 (86 mg/m3, synthetic air dilution), RH = 40%, expressed as UBC (O3) + SO2; (3) reaction between BC particles and simultaneous gaseous SO2 (86 mg/m3, synthetic air dilution) and O3 (64 mg/m3), RH = 40%, expressed as UBC + SO2 + O3.

Known masses of anhydrous Na2SO4 and BC (1:400 in NaCl) particles were mixed by grinding to obtain standard samples. The peak position and standard curves of SO42− were obtained. In this experiment, the characteristic absorption peak of SO42− occurred at 1140 cm−1. The product concentration was then quantified with the standard curves:

\[
C = 0.094A - 0.025 \quad (R^2 > 0.99)
\]

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 W/cm2, respectively. The light intensity was measured using a dual-channel UV radiation meter (UV-B, Photovoltaic 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 O3 or SO2 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 Na2SO4 solutions with a retention time of 24.7 min. The IC working curve is:

\[
C = 1.953A + 0.053 \quad (R^2 = 0.999)
\]

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

The DTT assay is a rapid method to evaluate the oxidative potential of particles. It is based on the catalytic electron transfer from DTT to O₂. The DTT consumption rate reflects the redox activity or oxidative capacity of the substance. DTT reacts with dinitrothiocyanobenzene (DTNB) to produce 2-nitro-5-thiobenzoic acid, which is measured using an ultraviolet–visible (UV–vis) spectrophotometer (T6, PERSEE, Beijing, China) at a wavelength of 412 nm. The DTT activity is determined using the DTT consumption rate according to the slope of the linear regression of the data points and is normalized to particle mass. The calculation function is as follows:

\[
\text{DTT activity} = \frac{C \times (\text{abs}_0 - \text{abs}')}{\text{abs}_0 \times t \times M}
\]

where, \(\text{abs}_0\) is the absorbance when DTT does not react, \(\text{abs}'\) is the absorbance at redox reaction time \(t\), \(C\) (nmol) is the initial DTT concentration, \(t\) (min) is the reaction time, and \(M\) (μg) is the mass of the substance.

To determine the DTT activity of the particles, 1 mg/mL of the particles was suspended in deionized water. The suspension was stirred and sonicated for 1 min. A series of test tubes were set, each containing 50 μL of 0.5 mmol/L DTT and 1.0 mL of 0.1 mmol/l potassium phosphate (pH = 7.3, containing 1 mmol/L ethylenediaminetetraacetic acid). A total of 25 μL of the prepared particle suspension was then added to each test tube and mixed thoroughly. The mixtures were incubated for 0, 5, 10, 15, and 20 min in a water bath at 37 °C. At the designated time, the reaction solution was filtered with 0.22 μm polytetrafluoroethylene membrane filters. About 100 μL of 1.0 mmol/L DTNB was then added to the solution. The absorbance was measured, and DTT activity was calculated using the function given above.

1.4. Uptake coefficient calculation

Uptake coefficient is an important quantitative indicator of the uptake or reaction ability of particles. It is defined as the ratio of production rate of particle surface products to the collision velocity between gas molecules and the particle surface (Li et al., 2007). If an irreversible chemical reaction of a gas molecule is observed on the particle surface, the uptake or reaction ability of particles is defined as the uptake coefficient which is expressed as \(\gamma_{\text{rxn}}\) (reactive uptake coefficient). In general, \(\gamma_{\text{rxn}}\) can be obtained according to:

\[
\gamma_{\text{rxn}} = \frac{\text{d}[P]_s}{\text{d}t} \frac{Z}{\nu}
\]

where, \(Z = \frac{1}{2} \nu A_s|G|\), \(\nu = \sqrt{\frac{kT}{M}}\), \(t\) is the reaction time, \(T\) is the ambient temperature, and \(R\) is the molar gas constant, \([P]_s\) is the concentration of product \(P\) during the surface reaction of gas molecule \(G\) on the particles, \(|G|\) is the concentration of \(G\) in the gas phase, \(Z\) is the collision frequency between \(G\) and particles, \(\nu\) is the mean molecular velocity of \(G\), \(M_G\) is the molecular weight of \(G\), and \(A_s\) is the effective surface area of the particles. In the experiment, the BET specific surface area was taken as the effective reaction area of the particles. The uptake coefficient of UBC toward SO₂ was calculated via the DRIFTS and IC methods, respectively.

2. Results and discussion

2.1. Heterogeneous reaction in the three reaction systems

2.1.1. Infrared spectra of O₃ or SO₂ with UBC or UBC (O₃) particles

Fig. 1a shows the time-dependent infrared spectra of UBC particles during reaction with 64 mg/m³ O₃. In the range from 1650 to 1840 cm⁻¹, a constantly increasing wide peak was observed, which was attributed to the carbonyl group C=O in ketones, acid anhydrides, and lactones (Liu et al., 2010). Han et al. (2012) observed similar BC structural changes via Raman and infrared spectroscopy. The infrared spectra of UBC and UBC (O₃) particles during their reactions with 86 mg/m³ SO₂ at a relative humidity (RH) of 40% are shown in Fig. 1b and c, respectively. The UBC + SO₂ system did not produce an observable sulfate absorption peak in the range from 1070 to 1216 cm⁻¹. This result could be attributed to the limited production of sulfate, which was not detectable by infrared spectroscopy. On the other hand, the UBC (O₃) + SO₂ system presented the characteristic peak of sulfate at 1070–1216 cm⁻¹, and the content of the sulfate kept increasing during 3 hr of reaction.

2.1.2. Effects of O₃

Fig. 2 shows the importance of O₃ pre-treatment of UBC particles in the reaction with SO₂. Fig. 2a presents the changes of sulfate production with time in the three reaction systems at RH of 40%: (1) UBC + SO₂ (86 mg/m³), (2) UBC (O₃) + SO₂ (86 mg/m³), and (3) UBC + SO₂ (86 mg/m³) + O₃ (64 mg/m³). Very little sulfate production is observed for system (1). The O₃-treated UBC particles (system (2)) show higher sulfate production compared to untreated UBC particles. For the simultaneous presence of O₃ and SO₂ (system (3)), the sulfate production on the BC surface is the highest. This result indicates that some active species can be formed on the surface of ozonized UBC to participate in the oxidation of SO₂. When O₃ is present during the reaction (system (3)), the active species are continuously produced on the surface of UBC and contribute to a higher oxidative capacity for SO₂.

In the experiment, the IC method was also used to measure the concentration of sulfate produced on the surface of UBC particles. The results are shown in Fig. 2b. UBC itself may contain a small amount of elemental sulfur and sulfides, among other sulfur compounds, which may be slowly oxidized to sulfate. Therefore, a few sulfate substances were detected for the BC blank. The generation tendency of sulfate was consistent with our infrared results. The concentration of SO₄²⁻ on UBC + SO₂ particles was 0.5 mg/g. When the blank value of UBC particles was deducted, the SO₄²⁻ concentration for the UBC + SO₂ reaction reached 0.2 mg/g. The SO₄²⁻ production for the reaction of UBC (O₃) + SO₂ was 0.8 mg/g (after the blank value was deducted), which was improved by a factor of four compared to that for UBC + SO₂. The data indicated that the uptake ability of O₃-aged
UBC for SO2 was enhanced. With the coexistence of O3 and SO2, the uptake ability of UBC for SO2 was the highest (5.3 mg/g, after the blank value was deducted), being nearly 27 times higher than that of UBC + SO2.

The IC and DRIFTS results verified that heterogeneous SO2 oxidization on the surface of O3-aged UBC was enhanced, and more SO4$^{2-}$ was produced. However, the IC results were one order of magnitude higher than those of DRIFTS because DRIFTS measured the SO4$^{2-}$ concentration on the surface of diluted UBC particles (mass ratio of UBC to NaCl = 1:399), whereas IC measured the average SO4$^{2-}$ concentration of non-diluted UBC particles both in the bulk and on the surface.

The mechanism of the oxidation of SO2 on the surface of BC particles can be related to their oxidative capacity. Li et al. (2007) conducted a step-by-step oxidation of SO2 on the surface of NaCl via infrared spectroscopy. The O3-treated NaCl surface exhibits higher oxidative capacity for SO2, with sulfate as the final product. In our experiment of UBC (O3)+SO2, the enhanced uptake ability toward SO2 may be attributed to the H-abstraction reaction of hydrocarbon compounds on the surface of BC by O3 oxidation. As a result, the number of reductive active sites on the BC surface decreased, and the number of oxidative active sites increased. For the UBC (O3)+SO2 reaction system, the oxidative active sites produced were gradually consumed, and the production of sulfate reached its saturated value after 6 hr (see Fig. 4 in Section 2.2.2). For the UBC + SO2 + O3 reaction system, oxidative active sites were continuously produced in the presence of O3. Thus, the reaction activity can be maintained (data not shown).

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**Fig. 1** – DRIFT spectra with reaction time for different systems. (a) UBC + O3; (b) UBC + SO2; (c) UBC (O3)+SO2. UBC: Printex U black carbon. UBC + O3, UBC + SO2 and UBC (O3)+SO2 refer to Section 1.1.
2.1.3. Uptake coefficient
The uptake coefficients of UBC for SO2 were measured via DRIFTS and IC methods by using the BET specific surface area as the effective reaction area of UBC particles. The DRIFTS method was used to measure the diluted UBC particles, with a BET value of 1.32 m²/g. The IC method was used to measure the undiluted UBC particles, with a BET value of 97.63 m²/g. Table 1 shows the uptake coefficients in the three reaction systems obtained using the two methods. The difference between uptake coefficients obtained via the two methods was significant, but the change tendency was similar. The uptake ability of O3-aged BC for SO2 was significantly improved compared with that of fresh BC, and the uptake coefficient was improved by 1 to 2 orders of magnitude. With the coexistence of O3 and SO2, the uptake coefficient of UBC for SO2 was the highest, being 1 to 3 orders of magnitudes higher compared with that of fresh UBC.

2.2. Influencing factors for the heterogeneous reaction between SO2 and UBC (O3) particles
Freshly emitted BC particles may come in contact with O3 during the daytime in the atmosphere to form O3-aged BC particles, which would have higher oxidative capacity toward reducing gases, such as SO2. Relative humidity is an important influencing factor for heterogeneous reactions, and solar radiation plays an important role in photochemical transformation and aging of particles in the troposphere. To further explore the reaction mechanism and atmospheric impact of the reaction, environmental influencing factors, such as relative humidity and UV radiation, were investigated.

2.2.1. Effects of relative humidity
In the experiment, sulfate contents formed in the UBC (O3) + SO2 system with different relative humidity were detected via the DRIFTS method, as shown in Fig. 3. At a relatively dry condition, the sulfate formed on the surface may block the active sites to hinder further oxidation of SO2. With the increase of relative humidity (>40%), the production of sulfate increases. This may be because water molecules facilitate the adsorption of SO2 on the active sites so as to make its further oxidation easy. In addition, the initially isolated sulfate became mobile sulfate ions, which is conducive to the diffusion and continuous production of sulfate. When the relative humidity is higher than 40%, water molecules may compete with SO2 for the active sites so as to weaken the production of sulfate. Therefore, there is no noticeable increase of sulfate thereafter. This result indicates that O3-aged BC particles are more effective for the uptake of

![Fig. 3](image-url) - Influence of relative humidity on sulfate production of ozonized UBC particles in the reaction with SO2. UBC: Printex U black carbon.

<table>
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<tr>
<th>Table 1 – Uptake coefficients of UBC (Printex U black carbon) particles for SO2 by the two methods.</th>
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<td>DRIFTS</td>
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DRIFTS: diffuse reflectance infrared Fourier transform spectroscopy; IC: ion chromatography; UBC + SO2 and UBC + SO2 + O3 refer to Section 1.1. UBC (1:400) means that UBC was mixed in NaCl powder for DRIFTS experiment with the dilution ratio of 400.
gaseous compounds in the atmosphere during the night when the relative humidity is high.

### 2.2.2. Effects of UV radiation

Fig. 4 shows the sulfate production in the UBC (O3) + SO2 + 40% RH system with or without UV radiation. When no UV radiation was present, the production of sulfate reached its stable state after 3 hr. As the reaction proceeded, a slight decrease was observed. Smith and Chughtai (1995) observed the production of sulfate and a water-insoluble S\(^-\)Os substance during the heterogeneous reaction of SO2 and soot. The water-insoluble S\(^-\)O substance led to the poisoning and deactivation of BC particles (Nienow and Roberts, 2006). When illuminated under 365 nm radiation, the sulfate production did not present remarkable changes compared with the absence of UV. Triplet sulfur dioxide (3SO2) can be produced by 365 nm irradiation of SO2, which could form SO3 via homogeneous oxidation. However, in the presence of O2 as oxidant, the photooxidation rate of SO2 was relatively low; thus, sulfate production was not promoted by 365 nm irradiation.

Under 254 nm irradiation, sulfate production was more efficient than that without UV. The sulfate production was increased consistently over 6 hr. The promoting effects could be attributed to the activation of substances on the surface of O3-aged BC particles under 254 nm illumination. Monge et al. (2010) demonstrated that polycyclic aromatic hydrocarbons (PAHs) or benzene ring compounds that contain carbonyl or carboxyl groups on BC particles could form reactive substances when activated by UV illumination, which made the adsorption and oxidation of SO2 easier.

### 2.3. DTT assay of UBC (O3) particles during the reaction with SO2

During the reduction of SO2 on the surface of UBC (O3) particles, the oxidizing ability of BC particles is expected to decrease. To confirm this hypothesis, the oxidative potential of BC particles was measured via DTT assay. The DTT activity of fresh BC was 0.036 nmol/(µg·min). When exposed to 64 mg/m³ O3, the DTT activity gradually increased and reached 0.067 nmol/(µg·min) after 3 hr. Based on our previous analyses, the contents of oxygen-containing species and radicals on the surface of O3-aged BC particles increased, which promoted the reaction of DTT and led to a higher oxidative potential (Li et al., 2013). In addition, O3-aged BC particles presented stronger hydrophilicity. As such, these particles can be efficiently dispersed in water (Li et al., 2013). This property provided a larger surface area and more active sites. The DTT activity and sulfate production (IC results) at different reaction times in the UBC (O3) + SO2 + 40% RH system are shown in Fig. 5. More sulfates were formed, while the DTT activity gradually decreased with increasing reaction time. Sulfate formation was negatively correlated with DTT activity, with a correlation coefficient \( R^2 \) of 0.8384 (as shown in Fig. 5b). During the O3 oxidation of BC particles, the DTT activity of the particle increased, whereas SO2 reduction decreased the DTT activity by consuming the active sites on the surface of the particles. Ntziachristos et al. (2007) found that sulfate presented significantly negative correlation with DTT activity in real atmospheric film samples, which is in accordance with our results.

![Fig. 4](image4.png)

**Fig. 4** – Influence of UV illumination on sulfate production of ozonized UBC particles in the reaction with SO2. UBC: Printex U black carbon; UV: ultraviolet.

![Fig. 5](image5.png)

**Fig. 5** – Changes (a) and relationship (b) of dithiothreitol activity and sulfate production of ozonized UBC particles in the reaction with SO2. UBC: Printex U black carbon.
3. Conclusions

Ozone-aged BC particles presented stronger oxidative uptake ability for SO2 compared with fresh BC particles. The uptake coefficient calculated from the produced sulfate was improved by 1 to 2 orders of magnitude. High relative humidity and 254 nm UV radiation facilitated further uptake of SO2 on O3-aged BC particles. The oxidation of SO2 consumed active sites on the O3-aged BC particles, which resulted in reduced sulfate, which may lead to climate and health effects.

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