

The influences of heterogeneous reaction on particle optical properties: a laboratory case of SO₂ on hematite and hematite-NaCl mixture

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Abstract—The particle optical property variation for heterogeneous reaction of SO₂ on hematite and hematite-NaCl mixture was investigated in a static reaction chamber at 298 K using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The increases of absorption and backward scattering coefficients are commonly higher in mixture with 50-70% NaCl than pure hematite and other mixtures. For both pure hematite and mixture, under reactions of 1-10% O₂ concentrations, the absorption and backward scattering coefficients are in a higher increment than those of 20-30% O₂ concentrations. The absorption and backward scattering coefficients rise by commonly larger magnitudes at high SO₂ concentration than low SO₂ concentration, in a quicker approach to equilibrium.

Keywords—mineral aerosol; sea salt; heterogeneous reaction; optical property

I. INTRODUCTION

Mineral aerosol is a major contributor to the tropospheric aerosol budget which is estimated to be about one half of the total amounts, with annual amount of 1000-3000 Tg [1]. The annual amount of dust from Asia is up to 800 Tg [2], more than 50% of the total amount of global dust (~1500 Tg) [3]. Iron has been demonstrated to be one of the most important components in mineral aerosol, and hematite is the dominant source of iron oxides in dry particles [4].

SO₂ is a prevalent industrial emission whose oxidation leads to sulfate and even acid rain, and its transport and transformation become thus a subject of great environment interest. It is well documented that gaseous SO₂ could react directly with mineral aerosol to form particulate sulfate [5-7]. Nearly half of the global emissions of SO₂ are converted to particulate sulfate which is known to play a critical role in the global climate change. In addition, sea salt is also believed to mix with mineral dust to form sulfate. In recent years, many researchers have investigated the formation of sulfate by heterogeneous reactions of SO₂, COS with metal oxides, sea salt, dust and their mixtures [8-13]. Despite sulfate has a significant impact on the global climate change, up to now, the knowledge of SO₂ heterogeneous reaction impacts on optical

properties of mineral particles or its mixtures with sea salt is far from completeness.

In order to better understand the optical property of aging mineral particles from emission over source areas to transportation over downwind regions for example ocean etc., it is necessary to investigate the uptake and heterogeneous reaction of SO₂ on dust and their mixture with sea salt. The objective of this study is to analyze the evolution of dust particle optical properties by laboratory simulation of heterogeneous reactions of SO₂ on pure hematite and hematite-NaCl mixtures.

II. EXPERIMENTS AND METHODS

A. Materials

Hematite was synthesized according to a procedure of Schwertmann [14]. X-ray diffraction (Rigaku D/MAX-II-X-ray diffractometer with Cu K α) was used to verify the purity of the synthesized hematite, which has an average particle size of 20-30 nm as determined by transmission electron microscopy (TEM, JEOL, JEM-2010). NaCl was purchased from Alfa Aesar with a purity of 99.999%. A series of hematite-NaCl mixtures with 10-90% mass fractions of NaCl were prepared by wet impregnation of hematite with a saturated aqueous solution of NaCl. The mixtures were then dried at 373 K for 6 h and kept in a desiccator at 68% RH for 48 h before further use.

Gaseous oxygen (99.999% purity) and argon (99.999% purity) were introduced through an air dryer before use. SO₂ (97 ppm, SO₂/N₂, Shanghai Yunguang Specialty Gases Inc.) was used without further purification. Other chemicals were of analytical grade.

B. Experiments

In situ DRIFT spectra were recorded in the wavenumber of 1150 cm⁻¹ ($\lambda=8.6 \mu\text{m}$) using a Nicolet FTIR spectrometer equipped with a high-sensitivity MCT detector and a Spectra-Tech Diffuse Reflectance Accessory. The schematic diagram of the DRIFTS apparatus was shown in previous report [15].

IR spectra were recorded at a resolution of 4 cm^{-1} , and 100 scans were averaged for each spectrum resulting in a time resolution of 1 min. A 30 mg sample (the thickness was about 2.16 mm) was placed on a sample holder of the reaction chamber. The chamber was then flushed with argon (120 mL min^{-1}) to blow off water and other physisorbed impurities, and a background spectrum of the sample was recorded. Subsequently SO_2 in Ar at a certain concentration and O_2 were introduced into the chamber for 3 min, after which the inlet and outlet of the chamber were closed. IR spectra were collected as a function of time. A sample temperature controller was used to control the reaction temperature.

C. Methods

The extinction coefficient (σ_e) is defined with Beer-Lambert's law as follow

$$I = I_0 e^{-\sigma_e \chi} \quad (1)$$

Where I_0 is the intensity of the initial light, I is the remaining light intensity after passing through a medium with the thickness χ .

The Kubelka-Munk (KM) theory is followed

$$F(R'_\infty) = (1 - R'_\infty) / 2R'_\infty = K/S \quad (2)$$

Where R'_∞ is the reflectance of the sample relative to that of an appropriate reference material, with the sample and reference both satisfying the "infinite depth" criterion. K and S are the absorption and backward scattering coefficients of the sample, respectively.

III. RESULTS AND DISCUSSION

A. Reactions of hematite-NaCl mixtures at different mass ratios

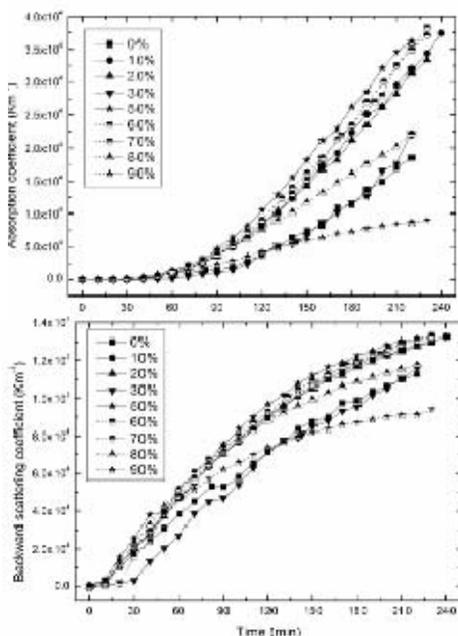


Figure 1. The absorption and backward scattering coefficients for

heterogeneous reaction of SO_2 on hematite and hematite-NaCl mixtures at the wavelength of $8.6\ \mu\text{m}$.

B. Reactions of hematite-NaCl mixture under different O_2 concentrations

It is necessary to investigate whether O_2 concentration has directly influence on the transition ratio of SO_2 to sulfate. Fig. 2 reports the absorption and backward scattering coefficients for heterogeneous reactions of SO_2 on the mixture with a fraction of 60% NaCl under different O_2 concentrations.

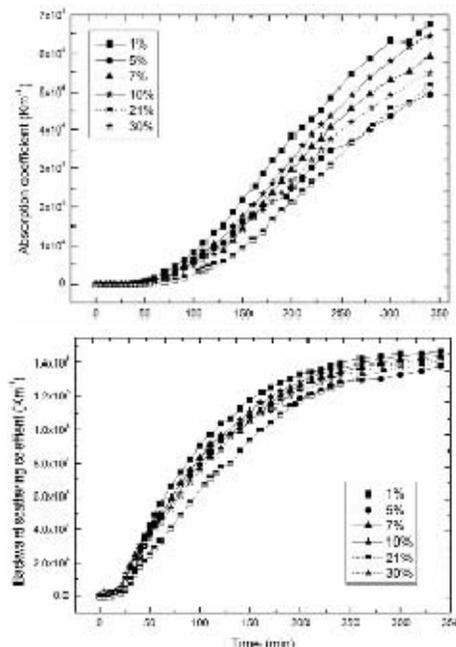


Figure 2. The absorption and backward scattering coefficients for heterogeneous reaction of SO_2 on 60% hematite-NaCl mixture at different O_2 concentrations.

All of absorption and backward scattering coefficients showed an increasing trend with reaction time at different conditions of O_2 concentrations. Before 60 min, the backward scattering coefficient behaved a drastic increase. Subsequently, it showed a slight increasing trend with reaction time and increased to equilibrium after 300 min. As shown in Fig. 2, the absorption and backward scattering coefficients were commonly higher at O_2 concentrations of 1-10% than that of 20-30%. This may be attributed to the formation rate of sulfate by $\text{SO}_3^{2-}/\text{HSO}_3^-$ which was dominant at 1-10% O_2 concentrations was faster than the oxidation of SO_2 .

C. Reactions of hematite-NaCl mixture under different SO_2 concentrations

The absorption and backward scattering coefficients for heterogeneous reactions of SO_2 at different concentrations on particles of 60% hematite-NaCl mixture are shown in Fig. 3. The absorption and backward scattering coefficients under different SO_2 concentrations also showed an increasing trend with reaction time. Similar to heterogeneous reactions of different O_2 concentrations, the backward scattering coefficient

also showed a sharp increasing trend before 60 min, and subsequently a slight increase with reaction time.

It was easily found that the absorption and backward scattering coefficients were commonly larger at high SO₂ concentrations than low SO₂ concentrations, and the scattering coefficients of higher SO₂ concentration got to equilibrium earlier. These results indicated that the aged mineral particles among sulfate cycle over remote oceanic regions have a more significant influence on solar radiation budget as well as the stronger cooling effect than pure particles.

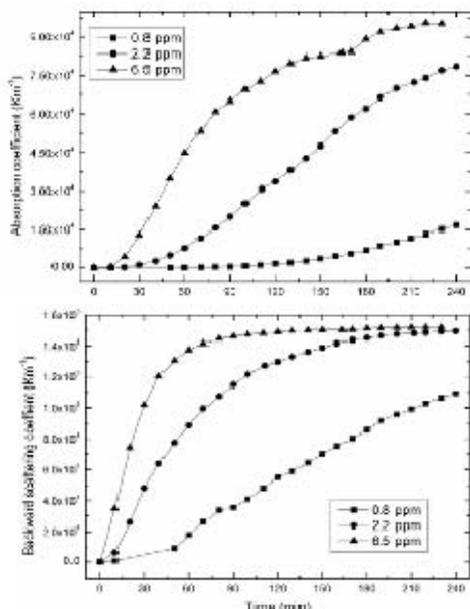


Figure 3. The absorption and backward scattering coefficients for heterogeneous reaction of different SO₂ concentrations on 60% hematite-NaCl mixture.

IV. CONCLUSIONS

The optical property for heterogeneous reactions of SO₂ on hematite and hematite-NaCl mixtures was investigated in a static reaction chamber at 298 K using in situ DRIFTS. The absorption and backward scattering coefficients were commonly higher for 50-70% NaCl mixtures than pure hematite and other percentage mixtures. O₂ concentration has an important influence on the transition ratio of SO₂ to sulfate, the absorption and backward scattering coefficients were higher for 1-10% O₂ concentrations than 20-30% O₂ concentrations. The absorption and backward scattering coefficients were commonly larger at high SO₂ concentration than low SO₂ concentration, and the backward scattering coefficients of higher SO₂ concentration got to equilibrium earlier.

ACKNOWLEDGMENT

This work is supported by the National Natural Science Foundation of China (No. 40533017, 20377008, 40605001), the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry of China (LAPC-KF-

2006-05) and the Shanghai Tongji Gao Tingyao Environmental Science & Technology Development Foundation.

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