Synergistic effect in the humidifying process of atmospheric relevant calcium nitrate, calcite and oxalic acid mixtures

Qingxin Ma, Hong He*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing 100085, China

ABSTRACT

Hygroscopicity is a critical property for evaluating aerosol's environmental and climate impacts. Traditional view always considered hygroscopic behavior of aerosol as a water adsorption/absorption–desorption cycle in which the size, water content and morphology etc. are well characterized. However, the chemical reactions between coexisting components in mixed particles during humidifying-dehumidifying process are almost neglected. In this study, we found that there exists synergistic effect among $Ca(NO_3)_2$, $CaCO_3$ and $H_2C_2O_4$ mixtures during humidifying process. Substitution of strong acid (HNO_3) by medium acid ($H_2C_2O_4$) take place during vapor absorption on $Ca(NO_3)_2/H_2C_2O_4$ mixture. Moreover, the presence of nitrate exhibits a promotive effect to the reaction between $H_2C_2O_4$ and $CaCO_3$ under ambient condition. These results provoke us to rethink the hygroscopic behavior of mixed aerosol in which chemical reaction can greatly change the chemical composition, mixing state and consequently environmental and climate impacts.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Dicarboxylic acids (DCAs, or diacids) are ubiquitous in the atmosphere and represent a significant portion of the organic fraction of aerosols (Chebbi and Carlier, 1996). Due to their strong hydrophilic and hygroscopic properties, dicarboxylic acids are able to reduce surface tension of cloud condensation nuclei (CCN), which consequently affect the cloud formation and the global radiation balance (Facchini et al., 1999; Yu, 2000). Oxalic acid ($H_2C_2O_4$, or HOx) is the most abundant contributor to the total dicarboxylic acid mass in ambient organic aerosol particles, which has been detected in aqueous phase (fog, cloud, and precipitation) and particulate phases (Chebbi and Carlier, 1996; Kawamura et al., 2010; Yao et al., 2002; Yu, 2000). The primary sources of HOx include fossil fuel combustion, biomass burning and vehicle exhaust while the secondary formation pathways include photo-oxidation of volatile organic compounds (VOC) in gas-phase, aqueous phase, and heterogeneous processes (Carlton et al., 2007; Chebbi and Carlier, 1996; Warneck, 2003; Yu, 2000). There also observed a high correlation between sulfate and oxalate in aerosol collected at various locations, which was likely a result of the potential importance of the in-cloud formation pathway for both sulfate and oxalate (Yu et al., 2005).

Recently, field measurement results of analyzing Asian dust by single particle mass spectrometry (ATOFMS) showed that HOx was predominantly mixed with mineral dust during transportation in the atmosphere (Sullivan and Prather, 2007; Yang et al., 2009). In these studies, oxalic acid were typically detected as the conjugate anion, $[HC_2O_4]^-$ (m/z −89), in the ATOFMS. Sullivan and Prather (2007) proposed a mechanism to explain these observations. The diacids and their precursors which were produced from the photochemical oxidation of volatile organic compounds were partitioned to the alkaline Asian dust, subsequently the precursors underwent heterogeneous and aqueous oxidation. It indicates that there exists affinity interaction between HOx and dust particles, especially alkaline constituents. In contrast, by using X-ray absorption fine structure spectroscopy (XAFS), Furukawa and Takahashi found that most of the oxalic acid is present as metal oxalate complexes in the aerosols, especially present as Ca and Zn oxalate complexes (Furukawa and Takahashi, 2011). It seems that there exists a discrepancy between field measurement results and the conversion mechanism of oxalic acid to oxalate complexes has not been well recognized.

On the other hand, calcite ($CaCO_3$) is an important ubiquitous mineral in the atmosphere as well as a reactive component of mineral dust aerosols. Due to its alkalescence, calcite has a significant neutralization effect on atmospheric acidic constituents, such as H_2SO_4, SO_2, HNO_3, NO_2, and carboxylic acids (Dentener et al., 1996; Prince et al., 2008; Usher et al., 2003). These reactions not only change atmospheric trace gas distributions but also modify the composition and mixing state of particles, and consequently affect the thermodynamic and optical properties of particles. For example, $Ca(NO_3)_2/CaCO_3$ mixture formed from heterogeneous reaction between nitric acid and calcite has been observed in both field

* Corresponding author. Tel.: +86 10 62849123; fax: +86 10 62923563.
E-mail address: honghe@rcees.ac.cn (H. He).

measurement and laboratory studies (Al-Abadleh et al., 2003; Laskin et al., 2005; Sullivan et al., 2007). Soluble calcium nitrate formed on calcite surface enormously enhanced the hygroscopicity of the mixtures and reactivity to other soluble gases (Al-Abadleh et al., 2003; Liu et al., 2008; Prince et al., 2008). However, little is known about the interaction between calcite and HOx in mixed mineral dust particles.

The hygroscopic behavior of individual components, such as $CaCO_3$, $Ca(NO_3)_2$, or $H_2C_2O_4$, were widely studied (Braban et al., 2003; Gibson et al., 2006; Gustafsson et al., 2005; Peng et al., 2001; Tang and Fung, 1997), while the hygroscopic behavior of these particle mixtures has been paid little attention except the $Ca(NO_3)_2/CaCO_3$ mixture (Al-Abadleh et al., 2003; Liu et al., 2008). It seems that oxalate may be probably formed from the calcite/oxalic acid mixture under humid condition although it is not clear yet. Here, we present the first laboratory study about the hygroscopic behavior of mixed calcite and HOx particles. A little amount of $Ca(NO_3)_2$ was added to this mixture to mimic atmospheric aged calcite particles. The aim of this work is to reveal the potential formation mechanism of oxalate complexes in mixed aerosol particles during the atmospheric aging process. It showed that the affinity between oxalic acid and alkaline dust might not be that simple and synergistic effect between different components plays an important role in the humidifying process.

2. Materials and methods

2.1. In situ Raman spectroscopy

Raman spectroscopy has been proven as a powerful tool and widely used to investigate the heterogeneous reactions and hygroscopic behavior of aerosol (Liu et al., 2008, 2010; Tang and Fung, 1997). In situ Raman spectra were recorded on a UV resonance Raman spectrometer (UVR DLPC-DL-03), which has been described in a previous article (Liu et al., 2010). Briefly, a continuous diode pumped solid state (DPSS) laser beam (532 nm) was used as the exciting radiation with the source power of 40 mW. The diameter of the laser spot on the sample surface was focused at 25 μm. The spectra resolution was 2.0 cm^{-1}. The instrument was calibrated against the Stokes Raman signal of Teflon at 1378 cm^{-1}. All experiments were conducted at 293 K. Particles were placed in an *in situ* cell as flow reactor. The relative humidity was controlled by adjusting the ratio of dry and humid nitrogen in the gas flow and it was recorded by a moisture meter (CENTER 314, China) with an accuracy $\pm 2\%$ RH and ± 0.1 K. The equilibrium time for each RH point was more than 30 min. A humidifying-dehumidifying (H–D) cycle represents that the relative humidity increased from 0 to 99% and then decreased to 0 step by step.

2.2. Vapor sorption analyzer

Water adsorption isotherms were measured with a modified vapor sorption analyzer at 278 K. The method has been described in a previous article (Ma et al., 2010). The mixed particles were first ground together and then evacuated at room temperature for 3 h with the pressure of 10^{-3} Torr. The evacuated particles were exposed to vapor with different RH to determine its adsorption isotherm by calculating the pressure change during the equilibrium process.

2.3. Chemicals

Externally mixed particles were prepared by grinding different components together and then were placed in a flow reactor. The molar ratio of HOx and calcite was unity according to the stoichiometry. $CaCO_3$ (AR, Beijing Yili Fine Chemical Co. Ltd.), $H_2C_2O_4 \cdot 2H_2O$

(AR, Beijing Yili Fine Chemical Co. Ltd.) and $Ca(NO_3)_2 \cdot 4H_2O$ (AR, Tianjin Jinke Chemical Co. Ltd.) were used as purchased. Distilled H_2O was degassed by heating prior to use.

3. Results

3.1. Raman spectra of oxalic acid dihydrate and anhydrous particles

At first, the Raman spectra of oxalic acid dihydrate and anhydrous particles were measured and the results are shown in Fig. 1. For dihydrate particles, several peaks at 111, 158, 185, 483, 577, 642, 858, 1383, 1494, 1636, 1692, and 1738 cm^{-1} are observed in the range of 50–2000 cm^{-1}, while two bands at 3445 and 3485 cm^{-1} are observed in the range of 2400–3800 cm^{-1}. The oxalic acid dihydrate molecular has the C_{2h} point group symmetry and eighteen normal modes which were summarized detailedly by Mohaček-Grošev et al. (2009).

According to the assignments in literatures (Ebisuzaki and Angel, 1981; Mohaček-Grošev et al., 2009; Nieminen et al., 1992), we made assignments of these peaks as follows. The peaks at 1636, 3445, and 3485 cm^{-1} are attributed to the bending mode (δ), symmetric (ν_s) and asymmetric (ν_{as}) stretching modes of hydrated water, respectively. These three peaks disappeared when the dihydrate particles were purged with dry N_2 for 2 h, as seen in the spectrum of anhydrous particles. The peaks at 1738, 1383, 858, and 483 cm^{-1} are assigned to the stretching mode of C=O, C–OH, C–C, and the out of plane bending mode of C=O, respectively. These peaks shifted to 1712, 1320, 850, and 486 cm^{-1} in the spectrum of anhydrous particles. The peak at 1692 cm^{-1} is due to the coupled C=O and C–O stretching modes. The peak at 1494 cm^{-1} is due to the COH deformation coupled to C–O and C–C stretching, which shifted to 1486 cm^{-1} for anhydrous particles. The peaks at 642 and 577 cm^{-1} are attributed to the out of plane bending and in plane deformation of COOH while in the anhydrous particles only the in plane deformation mode at 541 cm^{-1} is observed. The peaks at 180 and 158 cm^{-1} have been attributed to the translational lattice vibration of the water molecule (Ebisuzaki and Angel, 1981). However, these peaks can also be seen in the spectrum of anhydrous particles without position shift. Therefore, these peaks may be due to the inter-molecular hydrogen-bonding. Another peak at 111 cm^{-1} is the characteristic feature of the α-phase of oxalic acid dihydrate (Ebisuzaki and Angel, 1981), which shifts to 120 cm^{-1} for
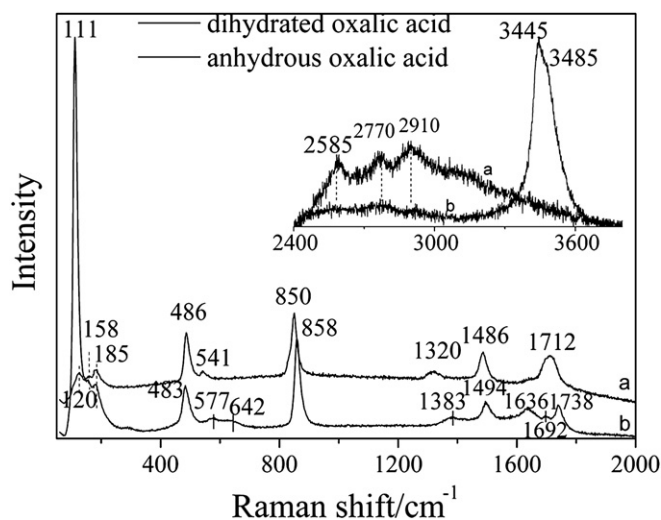

Fig. 1. Raman spectra of oxalic acid anhydrous (a) and dihydrate (b) particles. Inset shows the spectra in the range of 2400–3800 cm^{-1}.