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ScienceDirect
Atmospheric Environment 41 (2007) 4611–4621
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Single particle Raman spectroscopy for investigating atmospheric heterogeneous reactions of organic aerosols

Alex K.Y. Lee, Chak K. Chan*

Department of Chemical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received 12 October 2006; received in revised form 19 March 2007; accepted 22 March 2007

Abstract

Heterogeneous reactions of organic aerosols with atmospheric oxidants are important processes that affect the hygroscopicity and cloud condensation nuclei (CCN) activities of atmospheric aerosols. An electrodynamic balance (EDB) coupled with Raman spectroscopy is a particularly attractive platform for studying atmospheric reactions since it allows long-duration (days) particle levitation and reactions at atmospherically relevant low-oxidant concentrations can be investigated. In this study, we demonstrated the use of an EDB/Raman system to investigate the heterogeneous reactions of oleic acid particles with ozone (240–280 ppb) under ambient temperatures (22–24 °C) and dry conditions (relative humidity $<5\%$) over a period of 20 h. The Raman signatures of the ozone-processed oleic acid particles indicate the formation of oxidation products predominately consisting of peroxidic compounds (O–O groups of peroxides and/or ozonides), carbonyl (C=O) and hydroxyl (O–H) functional characteristics, which are consistent with the predictions of the Criegee mechanism as well as the results reported in the literature. We also confirmed that the Raman signatures of the reacted particles at atmospheric and much higher (>10 ppm) ozone concentrations are practically the same, which provides assurance to the use of elevated ozone concentrations in reaction studies of the oleic acid–ozone system in the literature. The ratio of the percentage of mass loss (due to evaporation of volatile organic products) to the percentage of oleic acid conversion was estimated to be 0.05. Furthermore, the oxidation products that remained in the particle phase were more hygroscopic than were their hydrophobic parent molecules.

Keywords: Organic aerosols; Oleic acid; Heterogeneous reactions; Hygroscopic properties; Electrodynamic balance (EDB); Raman spectroscopy

1. Introduction

Atmospheric aerosols undergo various physical and chemical aging processes throughout their lifetimes. In particular, organic species in atmospheric particles are susceptible to reactions with gas-phase atmospheric oxidants, such as ozone, OH and NO_3 radicals (Rudich, 2003; Donaldson and Vaida, 2006; Seinfeld and Pandis, 2006). The reaction products formed via these chemical aging processes, which are often referred to as heterogeneous oxidation or heterogeneous reactions, are expected to be more oxygenated and hygroscopic than are their organic precursors (Decesari et al.,

*Corresponding author. Tel.: +852 2358 7124; fax: +852 2358 0054.
E-mail address: keckchan@ust.hk (C.K. Chan).

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doi:10.1016/j.atmosenv.2007.03.040

2002; Asad et al., 2004). Such reactions consequently affect the cloud condensation nuclei (CCN) activities and the light-scattering properties of atmospheric organic aerosols and consequently global climate change (Kanakidou et al., 2005). Furthermore, these reactions potentially alter the gas-phase chemistry because heterogeneous processes not only consume gas-phase oxidants, but they also release volatile organic products from aerosols (Molina et al., 2004; Thornberry and Abbatt, 2004). Nevertheless, our understanding of the heterogeneous oxidation of organic aerosols is only preliminary.

Numerous experimental techniques have been developed for studying the heterogeneous reactions of organic aerosols. Common approaches include using a coated-wall flow tube, an aerosol flow tube and an aerosol chamber coupled with different types of online mass spectrometric techniques (e.g., Bertram et al., 2001; Smith et al., 2002; Zahardis et al., 2005; Ziemann, 2005). Real-time mass spectrometric measurements allow molecular identification of the reaction products with high time resolutions for mechanistic and kinetic characterization of reactions. In addition, some studies monitored the compositional changes of organic particles or organic films using FTIR and the reaction products were further characterized using offline GCMS and/or LCMS analyses (Eliason et al., 2003; Hung et al., 2005). In some cases, the hygroscopic properties and the CCN activity of the reacted particles have also been studied using a hygroscopicity tandem differential mobility analyzer (Broekhuizen et al., 2004; Vesna et al., 2006). Overall, these approaches are valuable for obtaining information on the speciation and properties of the products of heterogeneous reactions but they involve rather complicated sampling and analytical systems.

The electrodynamic balance (EDB) has been widely accepted as a unique tool for measuring the hygroscopic growth of aerosols, including those containing organic compounds (e.g., Ha et al., 2000; Choi and Chan, 2002; Chan et al., 2005). The stationary levitation of a particle under controlled conditions has also facilitated laser spectroscopic analyses. For example, Davis and co-workers pioneered the use of single-particle Raman spectroscopy using an EDB to study the morphological resonance structures in the inelastic scattering of droplets (Aardahl et al., 1996) and chemical reactions such as those involving SO_2 and hydroxide particles (Aardahl and Davis, 1996). Other researchers also demonstrated the use of Raman spectroscopy for studying mass transfer processes (e.g., Moritz et al., 1996; Trunk et al., 1998) and other particle phase reactions (e.g., Esen et al., 1996; Musick and Popp, 1999). Since the concentration of levitated droplets can be easily determined in an EDB, spectroscopic characterization of supersaturated droplets as a function of droplet concentration is also possible. For example, Fung and Tang (1988) measured the Raman spectra of ammonium bisulfate droplets at low to supersaturation concentrations. Our group has recently used Raman spectroscopy to study contact ion pairs formation in supersaturated droplets (Zhang and Chan, 2000) and fluorescence spectroscopy to study the distribution of solvated and free water in levitated droplets (Choi et al., 2004; Choi and Chan, 2005).

With the ability to levitate a stationary particle for an extended period of time (days), an EDB/Raman system offers three distinct advantages in studying heterogeneous reactions of organic aerosols. First, it can in situ monitor the chemical changes in the levitated particle. Raman spectroscopy is complementary to FTIR and allows the detection of many functional groups. A particularly interesting functional group in organic oxidation reactions is the peroxidic group, which has an appreciable Raman peak but a very weak FTIR signal (Lin-Vien et al., 1991; Socrates, 2001). Raman spectroscopy, thus, is advantageous in revealing information about the peroxidic group formation. Second, long exposure of gas-phase reactants at concentrations relevant to atmospheric applications is possible in an EDB. This can be important as most previous studies used gas-reactant concentrations that are much higher than atmospheric concentrations to compensate for the short duration of exposure. Third, any changes in the hygroscopic properties of the reacted particle and in the particle mass due to the evaporation of volatile organic compounds and the addition of atmospheric oxidants can be easily determined by balancing voltage measurements in our system. Although detailed chemical speciation, including molecular identification, of the levitated reacted particle is not readily available (Haddrell and Agnes, 2004) and the size of particles studied are larger than typical atmospheric particles, an EDB/Raman system offers a convenient and relatively inexpensive alternative to studying heterogeneous reactions. To the best of our knowledge, this system