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Using X-ray computed tomography and micro-Raman spectrometry to measure individual particle surface area, volume, and morphology towards investigating atmospheric heterogeneous reactions

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ABSTRACT

Heterogeneous reactions on the aerosol particle surface in the atmosphere play important roles in air pollution, climate change, and global biogeochemical cycles. However, the reported uptake coefficients of heterogeneous reactions usually have large variations and may not be relevant to real atmospheric conditions. One of the major reasons for this is the use of bulk samples in laboratory experiments, while particles in the atmosphere are suspended individually. A number of technologies have been developed recently to study heterogeneous reactions on the surfaces of individual particles. Precise measurements on the reactive surface area, volume, and morphology of individual particles are necessary for calculating the uptake coefficient, quantifying reactants and products, and understanding the reaction mechanism better. In this study, for the first time we used synchrotron radiation X-ray computed tomography (XCT) and micro-Raman spectrometry to measure individual $CaCO_3$ particle morphology, with sizes ranging from 3.5–6.5 μm. Particle surface area and volume were calculated using a reconstruction method based on software three-dimensional (3-D) rendering. The X-ray computed tomography was first validated with high-resolution field-emission scanning electron microscopy (FE-SEM) to acquire accurate $CaCO_3$ particle surface area and volume estimates. Our results showed an average difference of only 6.1% in surface area and 3.2% in volume measured either by micro-Raman spectrometry or X-ray tomography. This indicates that micro-Raman spectrometry is suitable for measuring individual particle surface area and volume at the microscale. However, X-ray tomography and FE-SEM can provide more morphological details of individual $CaCO_3$ particles than micro-Raman spectrometry. Rhombohedrons with FE-SEM-measured edge lengths can also be used to estimate surface areas and volumes if 3-D particle information is not available. This study demonstrated that X-ray computed

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tomography and micro-Raman spectrometry can precisely measure the surface area, volume, and morphology of an individual particle. These measurements are critically important for investigating heterogeneous reactions in the atmosphere.

Introduction

In the atmosphere, aerosol particles can undergo heterogeneous reactions with trace gases during their residence and long-range transport (Grassian, 2001; Usher et al., 2003). These reactions alter the chemical composition of the gaseous and particulate phases species within the atmosphere, which affects atmospheric oxidizability and physicochemical properties of aerosol particles, thus eventually impacting air quality, climate change, and global biogeochemical cycles (Hatch and Grassian, 2008; Zhu et al., 2011; Chen and Zhu, 2014; Tang et al., 2016). The uptake coefficient, which is calculated during kinetic studies of atmospheric heterogeneous reactions, describes the transfer of the reactive gas onto the surface of atmospheric particles. This is a key parameter for evaluating the significance of heterogeneous reactions in the atmosphere, and thus for constructing air-quality models. The main uncertainty in calculating the uptake coefficient arises from uncertain measurements of the particle reactive surface area. Indeed, there are no published articles to our knowledge that accurately measure the surface areas of atmospheric particles in connection with kinetic studies of atmospheric heterogeneous reactions.

Both bulk and individual particles are used in lab-based studies of atmospheric heterogeneous reactions (Hatch and Grassian, 2008; Zhao et al., 2011). Studies that use bulk powder samples are limited by the diffusion of reactive gases to inner layers, which makes it difficult to accurately calculate the reactive surface area. Additionally, uptake coefficients can vary by several orders of magnitude, depending on whether the Brunauer–Emmett–Teller (BET) or geometric surface area of a sample cell is used for calculations (Hanisch and Crowley, 2001). Studies using individual particles are closer to real atmospheric conditions as compared to studies using bulk particles; it is also easier to determine the reactive surface area using individual particles and more convenient to investigate the role of water in heterogeneous reactions (Zhao et al., 2011). Reactive gas uptake occurs over the entire surface of each individual particle during heterogeneous reactions on individual particles. Accurate measurement of the particle reactive surface area is thus an important precondition to correctly calculate reactive uptake coefficients. It is also necessary to quantify reactants and products for uptake coefficient calculations, which can be derived from individual particle volume combined with the associated particle density. Morphology observations of individual particles can be used to map surface changes and phase transformations during heterogeneous reactions, which are important towards a better understanding of reaction mechanisms. Instruments with high spatial resolution are needed to measure these parameters of individual particles with diameters that can range from tens of nm to tens of μm.

Laser confocal micro-Raman spectrometry can be used to study individual microscale particles due to the high spatial resolution (up to 1 μm) of the method. Micro-Raman spectrometry has been used for in-situ studies of heterogeneous and multiphase reactions, as well as hygroscopicity of individual microscale particles combined with sample cells and gas flow systems (Liu et al., 2008; Zhao et al., 2011, accepted for publication). The physical surface area and volume can be regarded as the reactive surface area and volume for particles that do not have surface tunnel structures, such as crystal calcite ($CaCO_3$). Reconstructing a three-dimensional (3-D) copy of a particle to measure its surface area and volume is a practical technique, as it is difficult to directly measure individual particle surface area and volume. Laser confocal micro-Raman spectrometry can be used for continuous point-by-point mapping of an object to delineate its 3-D shape, when combined with a motorized XYZ-stage. Following this, appropriate 3-D software can be used to reconstruct a rendered sample, and compute its surface area and volume. Additionally, individual particle morphology at the microscale can be observed and recorded by optical microscopy, as is commonly involved during micro-Raman spectrometry. However, other types of measurements with higher spatial resolution must still be used to validate this new method, even though the 1-μm spatial resolution of Raman mapping is sufficient to theoretically image a microscale particle.

X-ray microscopy is widely used to nondestructively image the interior of thick, opaque specimens (Pfeiffer et al., 2006; Christiansen et al., 2017; Jang et al., 2017) as X-rays can penetrate deeply into samples. Computed tomography (CT) is commonly used to obtain 3-D data, which is reconstructed using filtered-back-projection algorithms (Kak and Slaney, 1988; Han et al., 2016; Cohen et al., 2017). A Fresnel zone plate-based transmission X-ray microscope can resolve two-dimensional (2-D) structures at better than 15-nm resolution (Chao et al., 2005) due to the development of FZPs (Lai et al., 1992; Yun et al., 1999; Di Fabrizio et al., 1999; Chao et al., 2005) and the availability of synchrotron radiation sources (Chao et al., 2000; Awaji et al., 2001; Aoki et al., 2006; Liu et al., 2007). By combining FZP-based X-ray microscopy with CT (Weiss et al., 2000; Schneider et al., 2002; Kalender, 2006), X-ray nanotomography can achieve tomographic reconstruction with a spatial resolution of ~60 nm (Weiss et al., 2000; Larabell and le Gros, 2004; Yin et al., 2006). This allows for the possibility of determining the 3-D structure of micron-sized and nano-sized materials, while also approximating their surface area and volume (Chen et al., 2008).

In this study, we carried out nano X-ray computed tomography using synchrotron radiation at the U7A beamline of the National Synchronton Radiation Laboratory (NSRL) of the University of Science and Technology of China (Tian et al., 2008). 3-D software was used to render individual $CaCO_3$ particles to accurately calculate particle volume and surface area to validate the precision of micro-Raman spectrometry mapping technique (Raman mapping) to measure the particle volume and surface. The 2-D morphology and dimensions of