Journal of Aerosol Science 126 (2018) 143–151

Contents lists available at ScienceDirect

Journal of Aerosol Science

journal homepage: www.elsevier.com/locate/jaerosci

In situ analysis of aerosols by Raman spectroscopy – Crystalline particle polymorphism and gas-phase temperature

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ARTICLE INFO

Keywords:
Crystalline nanoparticles
Raman
TiO_2
Temperature
Polymorphism

ABSTRACT

We developed an *in situ* measurement system – based on linear Raman spectroscopy – to retrieve quantitative information on polymorphic modifications present in an aerosol. Besides, the Raman spectrum is utilized to determine the gas-phase temperature, which is a key parameter governing crystallinity. The particle polymorphism is obtained from the phonon modes of the particles, while pure rotational Raman spectroscopy is used for gas-phase thermometry. The approach is demonstrated for TiO_2 aerosols in air and CO_2 with different fractions of its two main polymorphs anatase and rutile. It forms the basis for future investigations in various gas-to-particle processes.

1. Introduction

Nanoparticles or nanostructured materials represent a broad area of scientific research and industrial development while being already widely commercially used because of their special properties and thus overwhelming application opportunities (Rao, Müller, & Cheetham, 2006). Next to characteristics like chemical composition, particle size, particle size distribution and morphology, crystal polymorphism is one key parameter that may have substantial influence on optical, chemical or mechanical functionality (Akurati, 2008).

For many applications, powders must fulfill certain requirements regarding the crystal polymorphism of the single particles. Sometimes even a certain ratio of particles with different polymorphic modifications determines the applicability and efficiency of the powder (Luttrell et al., 2014). This demand requires particle production processes that yield powders with either high polymorphic purity or precisely controllable mixtures of various polymorphs.

Due to the high number of operational parameters involved in the gas-phase synthesis of powders, the evaluation of their influence on the final product is essential. Here, *in situ* and online measurement techniques, capable of determining the above-mentioned particle properties including crystal polymorphism, can be extremely helpful (Pratsinis & Vemury, 1996).

Standard measurement techniques for the analysis of crystallinity are Transmission Electron Microscopy (TEM) (Wang, 2000), X-Ray Diffraction analysis (XRD) (Djenadic, Akgül, Attenkofer, & Winterer, 2010; Ingham, 2015), Differential Scanning Calorimetry (DSC) (Chiu & Prenner, 2011; Lu, 1996) or Nuclear Magnetic Resonance spectroscopy (NMR) (Marbella & Millstone, 2015).

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https://doi.org/10.1016/j.jaerosci.2018.09.008
Received 24 April 2018; Received in revised form 31 July 2018; Accepted 21 September 2018
Available online 22 September 2018
0021-8502/

In situ application of these techniques in synthesis processes is usually hardly possible, resulting in the need for physical sampling from the process for later *ex situ* measurements (Billinge & Levin, 2007). *In situ* approaches, such as Wide-Angle X-ray Scattering (WAXS) (Guo et al., 2015) or Powder X-ray Diffraction (PXRD) (Andersen, Bøjesen, Birgisson, Christensen, & Iversen, 2018) require extensive experimental effort and typically equipment like synchrotrons. Another frequently, yet mostly *ex situ* employed possibility for the analysis of the crystal polymorphism is Raman spectroscopy (Hsu & She, 1985; Li Bassi et al., 2005; Ma, Lu, & Zhang, 1998; Zhang, He, Zhang, Yin, & Chen, 2000). Liu et al. presented a qualitative approach to analyze crystallinity *in situ* during a flame synthesis process of TiO_2 and AlO_2 using Raman spectroscopy (Liu, Smith, & Tse, 2010). To the best of the authors' knowledge, this is so far the only system capable of *in situ* crystallinity characterization of aerosols using Raman spectroscopy. In gas-phase synthesis processes of crystalline nanoparticles, temperature is a fundamental parameter, which can be measured by numerous methods including Raman spectroscopy (Childs, Greenwood, & Long, 2000; Seeger, 2006).

Consequently, in this work, an optical Raman setup and method to analyze aerosols qualitatively and quantitatively regarding the polymorphic modification of the particles and the temperature of the gas-phase simultaneously is presented. Both solid phase crystallinity and gas-phase temperature are extracted from the same Raman spectrum, which represents a superposition of spectral shares of the gas as well as the solid phases. Titanium dioxide (TiO_2), a very prominent and commonly used particle system, where polymorphism plays an important role, serves as a reference particle system. It can be found in nature in form of the minerals rutile, anatase (both tetragonal crystal system) and brookite (orthorhombic system) (Akurati, 2008; Winkler, 2003). For industrial and commercial applications, generally the pure forms of anatase and rutile and especially mixtures of both are utilized. For this reason, they are subject of this investigation.

2. Materials and methods

In the context of this work, Raman measurements were conducted on three different sample types: (i) test aerosols created in a dispersion cell, described in Fig. 1, (ii) bulk powder of the pure polymorphs of TiO_2 and (iii) heated air at ambient pressure.

Rutile (Titanium(IV) oxide) with a mean particle size smaller than 100 nm and a purity of 99.5% (trace metals basis) and anatase (Titanium(IV) oxide) with a mean particle size smaller than 25 nm and a purity of 99.7% (trace metals basis) were purchased from Sigma Aldrich, Germany, and used as delivered.

The test aerosols were created by dispersion of defined mixtures of the two powders into a gas-phase with an ultrasonic homogenizer (Bandelin Sonopuls HD 2200), which was operated at a pulse repetition rate of 1 Hz with each pulse lasting 700 ms. The gas-phase was either ambient air or carbon dioxide (CO_2) at 293 K and ambient pressure. In order to prevent overexposure of the detector, the mass of powder inserted into the aerosol cell (see below) was chosen depending on the polymorphic fractions and was gradually reduced from 20 mg (for pure rutile) down to 5 mg (for pure anatase), due to the high Raman cross section of anatase. For each operational condition, 10 Raman spectra with an integration time of six seconds each were recorded subsequently. The laser power in the focus point was about 2.5 W.

For the acquisition of reference Raman spectra of the solid phase, measurements of the bulk pure powders were taken outside the cell with the identical Raman sensor, just with reduced laser power of 220 mW and an integration time of 200 ms.

Similarly, Raman spectra of a temperature conditioned air stream were also acquired outside the aerosol cell (with high laser power). The temperature of gas-phase was varied from 293 K to 823 K by the usage of a heating cartridge. To cover Raman shifts down to about 60 cm^{-1}, the temperature measurements were conducted without the use of the longpass filters inside the Raman sensor head. For the validation of the temperature evaluation procedure, gas temperatures in the optical focus point were determined additionally by thermocouple (type K) measurements.

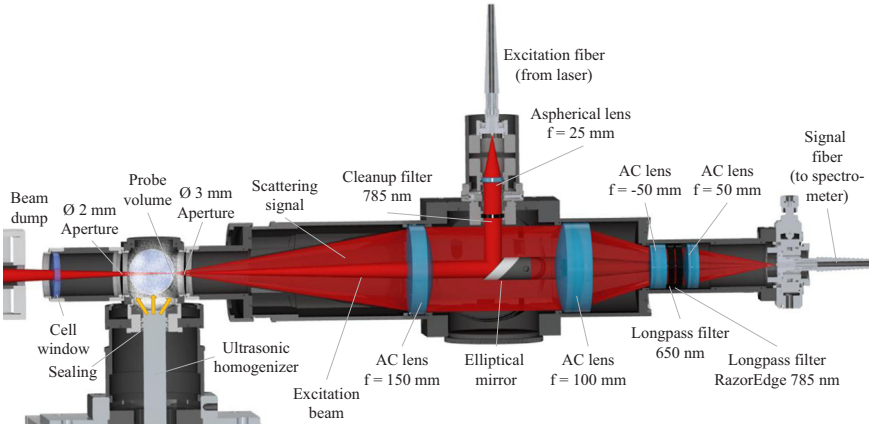

Fig. 1. The measurement setup, consisting of the particle dispersion cell (left) and the connected optical Raman sensor head (right).