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On-line monitoring of primary and agglomerate particle dynamics

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ABSTRACT

The detailed evolution of primary and agglomerate particle growth during flame spray synthesis of 30 g/h of zirconia nanoparticles is monitored online by a differential mobility analyzer (DMA), an aerosol particle mass (APM) analyzer and a condensation particle counter (CPC) as well as thermophoretic sampling/microscopy. The differences between measured projected-area equivalent diameter, diameter of gyration and mobility diameter are elucidated. Particles were sampled from distinct positions in the flame at up to 1700 K and 10^{18} particles/m^3 using a probe allowing continuous aerosol extraction and rapid dilution with quench air that effectively suppressed coagulation. Primary particle growth was complete at ~10 cm above the burner at about 1500 K as the primary particle size did not change radially and axially downstream. As expected, the average agglomerate size increased with axial distance from the burner. Larger agglomerates, however, were observed at the edges of the aerosol plume attributed to prolonged residence time due to lower gas velocities there. Results were compared to off-line particle size characterization by nitrogen adsorption and thermophoretic sampling/transmission electron microscopy.

1. Introduction

The properties of nanoparticles including their effects on health and environment depend largely on the composition, structure and size of agglomerates and constituent primary particles. Therefore, the control of these features as well as the understanding of their growth in the gas-phase is of major importance both for nanomaterial production in aerosol reactors as well as for environmental aerosols. Online and real-time monitoring is an invaluable tool to study formation and growth of such particles and ultimately to control them. The corresponding diagnostics, however, remain challenging, especially during nanoparticle production as high concentrations and temperatures prevail. As a result, particle properties typically are determined after synthesis by time-consuming off-line analyses – too late for influencing the production process and steering it toward desired particle characteristics.

Non-intrusive online diagnostics are preferred to study and monitor nanoparticle production (Pratsinis & Mastrangelo, 1989) since they offer high spatial resolution and do not interfere with particle growth and the reactor flow field (Baron & Willeke, 2001). In flame aerosol reactors, that are investigated here as an exemplary high temperature synthesis process, light scattering has been applied for instance to obtain primary particle size and fractal dimension of soot (Sorensen et al., 1992).

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However, the spectral inversion for agglomerates is challenging, requiring additional information e.g. from intrusive thermophoretic sampling (Hung & Katz, 1992; Xing et al., 1999; Kim & Choi, 2003). Beaucage et al. (2004) applied small-angle X-ray scattering (SAXS) for non-intrusive determination of primary particle size and volume fraction during diffusion flame synthesis of silica. Camenzind et al. (2008) monitored the formation of compact and agglomerate nanoparticles in laminar and turbulent flames, respectively, by SAXS and thermophoretic sampling. The use of SAXS, however, is limited by the required synchrotron radiation source while relating recorded spectra to particle characteristics is challenging as it involves again sophisticated data inversion.

Thermophoretic sampling may be among the intrusive methods interfering the least with an aerosol process due to small probe size, flow orientation and short residence time (Dobbins & Megaridis, 1987). It relies on the size-independent deposition of nanoparticles on a transmission electron microscopy (TEM) grid by thermophoresis. It has been applied widely to study the growth of mixed oxide (Hung & Katz, 1992), soot (Köylü et al., 1997), Al_2O_3 (Xing et al., 1999) and TiO_2 (Arabi-Katbi et al., 2001; Tsantilis et al., 2002) nanoparticles, but requires subsequent off-line TEM analysis of the primary and/or agglomerate particle size. Mueller et al. (2004) applied this method to track zirconia primary particle growth during flame spray pyrolysis (FSP), as here. The geometric standard deviation, $\sigma_{g,p}$, of their primary particles decreased with height above burner (HAB), in agreement with theory (Heine & Pratsinis, 2007). Gröhn et al. (2012) studied the primary particle size evolution of zirconia by thermophoretic sampling along the centerline of a laboratory-scale FSP reactor and found good agreement with a detailed fluid-particle dynamics model with respect to the evolution of temperature, velocity, precursor droplet evaporation and final primary particle diameter. A detailed monitoring and understanding of agglomerate size and structure dynamics has been, however, quite elusive!

A differential mobility analyzer (DMA) and an aerosol particle mass (APM) analyzer, were employed by Scheckman et al. (2009) to determine the effect of process variables on the size and structure of silica nanoparticles made in a vapor-fed flame through their mass-mobility relation. As particles from all streamlines were sampled at a fixed position above the flame with an inverted funnel, the evolution of morphology and particle growth was not monitored. Also Eggersdorfer et al. (2012) used DMA–APM to study the effect of FSP reactor operating conditions on zirconia primary particle size and extent of aggregation but without describing the evolution of particle morphology. Samples were extracted at a fixed position above the flame and good agreement was attained for the primary particle size between mass-mobility data and off-line diagnostics (transmission electron microscopy and nitrogen adsorption). Eggersdorfer et al. (2012) further observed that agglomerates were formed at low precursor concentration and flame temperature while aggregates were formed at high concentration and temperatures.

Extraction of particle samples along the axis of silica-producing flat-flames was realized by Ulrich et al. (1976) with an approximately 5 mm thin nitrogen-purged sonic probe. The aerosol quench time in the probe was as low as 0.2 ms and considered sufficient to suppress growth processes. The primary particle diameter evolution was determined by off-line nitrogen adsorption while agglomerate sizes could not be measured. Goertz et al. (2011) employed a similar probe but placed it at a fixed position normal to the flow of a reactor for gas dynamically-induced silica synthesis. They demonstrated that sampling from the probe recirculation zone can be avoided by using a probe tip which is beveled at an angle of 30° with respect to the flow direction. The size distribution of spherical particles was determined by TEM micrograph analysis. Kasper et al. (1997) sampled metal and soot nanoparticles from a laminar diffusion flame through a hole drilled into a horizontal steel tube. The aerosol sample was rapidly diluted and cooled by nitrogen flowing in the tube. Homogenous nucleation inside the probe was found not to affect the measured soot particle size distribution significantly.

Here, a sampling method for continuous and stable sample extraction as well as rapid dilution is combined with the well-established mass-mobility particle sizing to determine the evolution of primary and agglomerate particle characteristics online during production of zirconia nanoparticles by flame spray pyrolysis (FSP). By axial and radial mapping of the flame and its downstream nanoparticle plume, a detailed description of the evolution of agglomerate and primary particle size distributions is achieved. Results are compared to off-line diagnostics by nitrogen adsorption and thermophoretic sampling/microscopy focusing on the distinct differences of agglomerate size by varied measurements. This system is selected as an example process to test the method as nanostructured ZrO_2 is a basic ceramic material for a number of applications (Mueller et al., 2004). FSP reactors are used to synthesize nanoparticles for a multitude of other advanced materials (Strobel & Pratsinis, 2007) from various precursors (Teoh et al., 2010) and even active devices (Pratsinis, 2010).

2. Experimental

2.1. Nanoparticle synthesis

A laboratory-scale flame spray pyrolysis (FSP) reactor described in detail by Gröhn et al. (2012) and shown schematically in Fig. 1 was employed for synthesis of zirconia nanoparticles. The precursor solution of zirconium 2-ethylhexanoate (Umicore, Valirex, 18 wt% Zr) and xylenes (Thommen–Furler, 253-VL51TE) with 1 mol/l Zr concentration was fed at 4 ml/min to the center capillary of the spray nozzle and atomized with 5 l/min of O_2 (99.95%, PanGas) at 3.5 bar pressure drop. The resulting spray was ignited with a surrounding premixed flame of 1.25 l/min CH_4 and 2.5 l/min O_2. All gas flows were kept constant by mass flow controllers (Bronkhorst, EL-flow) and are reported at 273.15 K and 1.013×10^5 Pa. The FSP reactor was mounted on a two-dimensional traversing system (Föhrenbach, Unipos 110) allowing to take samples at different axial and radial positions in and above the flame. Product powders were collected ~1 m above the flame on glass-fiber filters (Whatman, GF/A, Ø 150 mm) with the help of a vacuum pump (Busch, Seco SV 1040C).