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Spatially resolved flame zone classification of a flame spray nanoparticle synthesis process by combining different optical techniques

D. Kilian [a], S. Engel [b,c,d], B. Borsdorf [b,d], Y. Gao [b,d], A.F. Kögler [b], S. Kobler [b], T. Seeger [b,d,e], S. Will [b,c,d], A. Leipertz [b,c,d], W. Peukert [a,c,d,*]

[a] *Institute of Particle Technology, Friedrich-Alexander University of Erlangen-Nuremberg, Cauerstrasse 4, 91058 Erlangen, Germany*
[b] *Institute of Engineering Thermodynamics, Friedrich-Alexander University of Erlangen-Nuremberg, Am Weichselgarten 8, 91058 Erlangen, Germany*
[c] *Cluster of Excellence – Engineering of Advanced Materials (EAM), University of Nuremberg, Naegelsbachstrasse 49b, 91052 Erlangen, Germany*
[d] *Erlangen Graduate School in Advanced Optical Technologies, University of Erlangen-Nuremberg, Paul – Gordan-Str. 6, 91052 Erlangen, Germany*
[e] *Institute of Engineering Thermodynamics, University of Siegen, Paul-Bonatz-Str. 9-11, 57076 Siegen, Germany*

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ABSTRACT

Flame spray synthesis of silica nanoparticles is characterized by a set of complementary optical techniques. By means of laser-sheet based Mie scattering imaging, 2D-chemiluminescence imaging and coherent anti-Stokes Raman spectroscopy (CARS) local information on spatial droplet distribution, combustion zone, nucleation zone and temperature in the flame could be obtained. In addition, the outcomes from optical metrology are validated by thermophoretic sampling at different flame heights and the synthesized powders were analyzed by N_2 gas sorption. By comparing these results the flame can be quantitatively classified into three distinct zones: (i) the droplet zone where precursor atomization and evaporation take place, (ii) the nucleation zone indicated by SiO^*/Si^* radicals as a preliminary species before SiO_2 particle formation and (iii) the sintering zone characterized by the highest temperatures in flame. In addition the spatial spreading of the nucleation zone as a function of precursor concentration is investigated. Theoretical calculations and experimental results show an extended nucleation regime for the lowest precursor concentration compared to higher concentrations. Although this study is performed with hexamethyldisiloxane (HMDS) precursor to synthesize silica nanoparticles as a model system, dimensionless analysis shows that the results, concerning the spray formation, can be transferred to the synthesis of other materials as well.

1. Introduction

Flame spray pyrolysis (FSP) is, amongst other gas phase techniques, one of the most versatile, cost-effective, scalable and easy-to-handle processes (Camenzind et al., 2005; Strobel & Pratsinis, 2007). For this reason it is widely used both in research and in industry for the synthesis of oxide nanomaterials including TiO_2, Al_2O_3, ZnO and SiO_2 (Teoh et al., 2010). The particle formation in FSP can be described by several subsequent process steps namely precursor atomization, droplet

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[*] Corresponding author at: Institute of Particle Technology, Friedrich-Alexander University of Erlangen-Nuremberg, Cauerstrasse 4, 91058 Erlangen, Germany. Tel.: +49 913 185 29400; fax: +49 913 185 29402.
E-mail address: wolfgang.peukert@fau.de (W. Peukert).
URL: http://www.lfg.uni-erlangen.de (W. Peukert).

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evaporation, precursor combustion, particle nucleation, particle growth, agglomeration and sintering. Nevertheless, there is a lack of knowledge on the spatially resolved localization of these formation processes in the flame. Classifying the flame into distinct regions allows for a deeper understanding of the particular underlying processes. Furthermore, experimental data are needed for modeling and simulation of particle formation mechanisms and kinetics in flames.

These data can be obtained by optical diagnostic tools, which are widely used in combustion research to investigate transient phenomena without disturbing the sensitive combustion process by positioning mechanical probes into the flame (Eckbreth, 1988; Kohse-Höinghaus & Jeffries, 2002; Leipertz et al., 2010).

Techniques for imaging chemiluminescent radicals, i.e. OH* and CH* chemiluminescent species are frequently used in combustion research to locate the combustion zone and to obtain information on the local heat release rate or the air to fuel ratio (Haber et al., 2000; Kojima et al., 2005; Higgins et al., 2001). However, very little is known on the location of the nucleation regime in the FSP process. For example, the silicon atom distribution has been measured by resonance-enhanced multiphoton ionization spectroscopy, showing that an increase in silane concentration directly increases the silicon atom density in the flame (Zachariah & Joklik, 1990). For OH* and SiO* measurements, laser-excited fluorescence spectroscopy was carried out (Zachariah & Burgess, 1994). Both series of measurements were done in a quasi one-dimensional stagnation point counterflow diffusion flame reactor. However, these results cannot directly be transferred and applied to turbulent premixed O_2/CH_4 FSP processes. Moreover, emission spectroscopy of OH* and SiO* chemiluminescence has been carried out to obtain insight on the decomposition mechanism of hexamethyldisiloxane (HMDS) and how it influences the OH* radical formation in CH_4–N_2/air counterflow diffusion flames (Chagger et al., 1996). Profiles of SiO* mole fraction have been obtained in low pressure premixed H_2/O_2/HMDS flames by laser-induced fluorescence and emission spectroscopy in a flat flame burner (Glumac, 2001). Recently, emission lines resulting from HMDS as precursor could be detected in a propane/air flame. The emission lines could be assigned to Si* (252 nm) and SiO* (220–265 nm) in the work of Burkert et al. (2013). Both of these investigations were performed in a spray-free environment and are therefore rather complex to transfer to the FSP process.

For the visualization of the droplet regime, laser-sheet based Mie scattering is often used. This technique is often applied in combustion engine research, where information on the group combustion number, spray cone angle, spray density and droplet evaporation rate are needed. The Mie scattering technique is also coupled to luminescence imaging or phase Doppler anemometry (droplet-size and velocity detection) with the aim to optimize the combustion chamber, fuel injection or the combustion process itself (Seung-Min et al., 2007; Adam et al., 2009). To the best of our knowledge there is no previous work on gathering the spatial droplet distribution by laser-sheet based Mie scattering in flame spray synthesis of silica nanoparticles or any other nanoparticulate material.

The flame temperature is a critical parameter with respect to droplet evaporation, nucleation, growth and coalescence of nanoparticles in flame synthesis (Ulrich & Subramanian, 1977) and has to be measured in a non-invasive manner in order to keep the FSP process undisturbed. Therefore, we measure the temperature in different flame locations directly during particle production. Previously, the flame temperature was measured by Fourier-transformed infrared spectroscopy (Kammler et al., 2003; Mädler et al., 2002; Mueller et al., 2004; Gröhn et al., 2012) or by multi-line NO laser-induced fluorescence thermometry (Kronemayer et al., 2007). Furthermore, ultra-violet (UV) emission spectroscopy has been utilized in particle-laden flames (Obertacke et al., 1996). One of the most advanced techniques for the pointwise measurement of gas phase temperatures is coherent anti-Stokes Raman scattering (CARS) as it provides detailed temporal and spatial temperature information superior to UV emission or FTIR (Seeger & Leipertz, 1996; Seeger et al., 2003). For more detailed information on the CARS measurement technique used for the temperature measurements presented in this paper we refer to the literature (Engel et al., 2012).

Our objective is to gain deeper insight into the complexity of the FSP process and in the interplay between the different particle formation steps by applying several complementary in situ optical techniques. Flame spray synthesis of silica nanoparticles is carried out by combustion of a precursor solution of ethanol and HMDS. A unique combination of in situ techniques allows the characterization of the spatial distribution of liquid phase droplets, gaseous species and intermediate reaction products in two dimensions between 0 mm and 32 mm height above the burner (HAB). The axial and radial temperature distribution has been measured point-wise by pure rotational CARS. Using this technique the hottest zones in the flame can be identified. For gathering the spatial droplet distribution in the spray flame a laser-sheet based Mie scattering imaging technique has been used. In order to get information in which area the combustion process and precursor decomposition takes place, the chemiluminescence of OH*, CH* and SiO*/Si* radicals in the flame is imaged. The chemiluminescence imaging of SiO*/Si* radicals plays a key role in our measurements as it is directly related to the precursor decomposition and thus the particle nucleation regime (Glumac, 2001). Therefore, we also investigated the influence of the precursor concentration on the spatial position of the nucleation regime. To the best of our knowledge, the imaging of SiO*/Si* radicals inside a two-dimensional plane has been applied in this investigation for the first time. In order to validate our conclusions from the combination of the optical in situ techniques, thermophoretic sampling is additionally carried out. By the aid of this technique nanoparticulate aerosol particles can be deposited without any size classification below 500 nm (Kammler, 2002). Furthermore, the product powder is analyzed by N_2 gas sorption.

2. Materials and methods

2.1. Flame spray pyrolysis

The synthesis of silica particles is carried out by spray combustion of a 0.5 mol/l HMDS (Fluka, 98.5%)/ethanol (VWR, 99.9%) precursor mixture. In Fig. 1 a schematic picture of the FSP process is shown. Depending on process parameters the