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Fluid-particle dynamics during combustion spray aerosol synthesis of ZrO_2

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ABSTRACT

Owing to its versatility and low cost, flame spray pyrolysis (FSP) is becoming an increasingly promising method for industrial production of a broad spectrum of nanoparticles. To assist understanding and scale-up of the current laboratory process, a computational model has been constructed for the example of zirconia nanoparticle synthesis. Therefore, a computational fluid dynamics (CFD) description of the spray flame originating from a twin-fluid atomizer and coaxial diffusion burner was combined with droplet and nanoparticle dynamics. The model predicted well average primary ZrO_2 particle diameters even though global chemical reactions, immediate nanoparticle formation upon precursor oxidation and monodisperse particle dynamics were employed. This model is self-containing and does not rely on experimental input data such as temperature or velocity fields. The model was validated at different process conditions with phase-Doppler anemometry (PDA) for spray characteristics, Fourier-transform infrared spectroscopy (FTIR) flame temperature measurements as well as nanoparticle sampling in and above the flame.

1. Introduction

Flame spray pyrolysis (FSP) is a promising method [1,2] for industrial-scale production of single- or multi-component nanoparticles [3] of almost all periodic table elements [4]. For example, biomaterials [5], catalysts [6], food fortification [7], battery materials [8], and advanced pigments [9] have been developed using laboratory FSP reactors with typical production rates of about 10–20 g/h. In order to facilitate scale-up of the FSP process to a cost-efficient industrial production line, robust and simple computational models accounting for the governing mechanisms in FSP synthesis of nanoparticles are required [10].

In FSP, organic solutions comprising a metal-containing precursor are typically atomized with oxygen or air and ignited to generate a spray flame [2]. Following droplet evaporation and precursor conversion, nanoparticles are formed and grow by coagulation, sintering and/or surface growth [11]. The resulting particle characteristics (e.g. primary particle size, crystallinity and extent of aggregation or hard-agglomeration) strongly depend on the properties of the spray flame and define the performance of the nanoparticle-based products [2]. So far, two reactor types have been systematically investigated to better understand and simulate nanoparticle synthesis by FSP: a laboratory-scale unit with up to 10–20 g/h [2] and a pilot-scale system with up to 1 kg/h production rate [12].

Madler et al. [2] determined line-of-sight average flame temperatures of spray flames producing silica from a hexamethyldisiloxane-ethanol feed by Fourier-transform infrared spectroscopy (FTIR) and fitting a blackbody Planck function with the measured radiance spectra of hot CO_2 [13,14]. Maximum line-of-sight flame temperatures of 2400–2600 K were reported for 9 g/h SiO_2 production rate [2]. Based on the FTIR flame temperature profile, 10 μm initial droplet diameter, turbulent jet dynamics without temperature correction [15], and a monodisperse single droplet combustion model [16,17], Madler et al. [2] predicted complete ethanol droplet evaporation at 2 mm above the burner for sonic dispersion gas exit velocity.

Characterization of the pilot-scale FSP reactor was carried out for production of 100 and 300 g/h ZrO_2 nanoparticles from zirconium *n*-propoxide/1-propanol/ethanol by Mueller et al. [11]. Measured FTIR temperature profiles and calculated temperature-corrected gas velocities of a turbulent jet [15] provided the basis for modeling ZrO_2 nanoparticle growth by monodisperse aerosol dynamics [18] accounting for coagulation and sintering. The model did not include droplet formation, dynamics and evaporation but assumed instantaneous nanoparticle nucleation at a certain flame height. Good agreement with measured primary particle diameters was obtained by applying the best-performing zirconia sintering rate from the literature [19].

Heine and Pratsinis [20] measured droplet concentrations, size distributions and gas velocities in the ZrO_2 producing pilot-scale FSP flames of Mueller et al. [11] by Phase-Doppler Anemometry (PDA). Along with the FTIR flame temperatures, this set the

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Nomenclature

B_M	Spalding mass transfer number
d	diameter (m)
D	diffusion coefficient (m^2/s)
ε	mass flux fraction
E	activation energy (J/mol)
F_M	film thickness correction factor
γ	surface tension (N/m)
h	latent heat (J/kg)
k	thermal conductivity ($W\,m^{-1}\,K^{-1}$)
μ	dynamic viscosity (Pa s)
m	mass (kg)
$\dot{m}$	mass flow (kg/s)
Nu_0	Nusselt number
Ω	ZrO_2 molar volume (m^3/mol)
Pr	Prandtl number
Q	heat (J)
ρ	density (kg/m^3)
R_g	universal gas constant ($J\,K^{-1}\,mol^{-1}$)
Re	Reynolds number
σ_g	number based geometric standard deviation
Sc	Schmidt number
Sh_0	Sherwood number
SSA	particle specific surface area (m^2/kg)
τ_s	characteristic sintering time (s)
t	time (s)
T	temperature (K)
T_{bp}	boiling point at 1 atm (K)
u	velocity (m/s)
w	grain boundary width (m)
We	Weber number
X	mole fraction
Y	mass fraction

Subscripts

b	grain boundary
c	capillary
d	droplet
g	gas
i	initial
j	species index
l	liquid
p	primary particle
s	droplet surface

framework for the description of FSP-synthesis of zirconia nanoparticles by a multi-component droplet evaporation and polydisperse particle dynamics model along the centerline. Therefore, the evaporation model of Abramzon and Sirignano [21] was extended to account for multi-component droplets. The overall droplet composition was assumed to remain constant during evaporation as (internal) boiling was omitted and diffusion too slow to mix the solution efficiently. Polydisperse particle dynamics were solved with a sectional model [22] in terms of aerosol number and area [23] assuming immediate nanoparticle formation upon precursor evaporation and accounting for coagulation and sintering. Good agreement with measured primary particle diameters and geometric standard deviations [11] was attained.

The models of Mueller et al. [11] and Heine and Pratsinis [20] include only one spatial dimension and rely on experimental temperature or velocity profiles as input data. Thus, their application for model-predicted parametric studies toward reactor design and scale-up is limited. Advances in computational resources have made flame aerosol process design with computational fluid dynamics (CFD) feasible, enabling more accurate predictions since the most important process mechanisms (e.g. coagulation rate and residence time at high temperature) can be resolved in all spatial dimensions. Furthermore, it is possible to simulate the complete flame aerosol process without having to rely a priori on experimental input data under certain conditions. Groehn et al. [24] applied such an approach to reactant mixing-limited synthesis of silica in a diffusion flame. Since the hexamethyldisiloxane precursor was provided in the vapor phase, this model did not include droplet dynamics and evaporation. Nanoparticle growth was described by monodisperse aerosol dynamics accounting for coagulation and sintering. The simulation results obtained without adjustable parameters were consistent with measured temperature and fuel conversion profiles [25] as well as primary particle diameters [26].

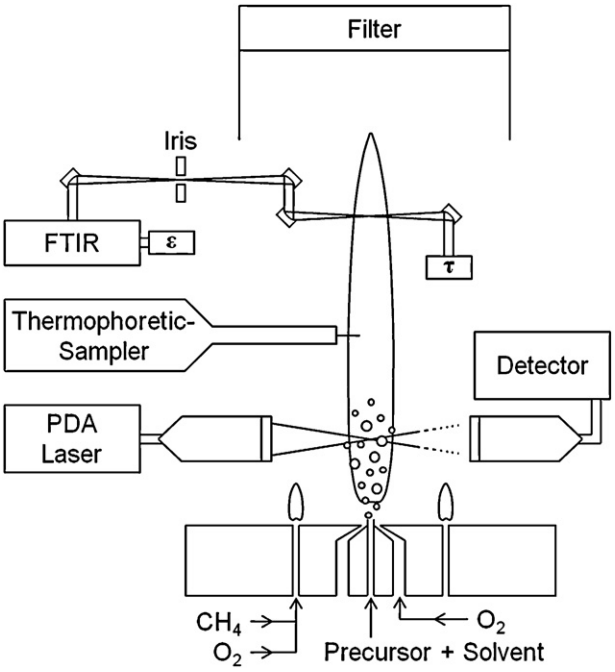

Fig. 1. Schematic of the experimental set-up with FSP reactor, non-intrusive PDA spray and FTIR flame temperature diagnostics, as well as thermophoretic sampler and product filter for nanoparticle collection.

Here, a robust and simple CFD-based model of the flame spray pyrolysis process is proposed interfacing spray, fluid, combustion and aerosol dynamics. These are solved without adjustable parameters or need of experimental data by using a commercial CFD software [27] to predict zirconia nanoparticle characteristics. Fourier-transform infrared spectroscopy, phase-Doppler anemometry and thermophoretic sampling are employed to validate the model-predicted temperature and velocity profiles as well as droplet and particle characteristics for a set of process conditions.

2. Experimental

2.1. Set-up

Fig. 1 shows a schematic of the laboratory-scale FSP reactor [28] and flame diagnostics. 4 ml/min of precursor solution consisting of zirconium *n*-propoxide (70 wt% in 1-propanol, Sigma–Aldrich) and ethanol (>99.8%, Sigma–Aldrich) was supplied with a syringe pump (Inotech, IER-232) through the center capillary (0.41 mm i.d.) of the reactor. The zirconium concentrations were 0.5 and 1 M corresponding to ZrO_2 production rates of 14.8 and 29.6 g/h,