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Process control for the synthesis of ZrO_2 nanoparticles using FSP at high production rate

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ABSTRACT

A numerical method of combining CFD with the particle dynamics was developed to study the effect of processing parameters on the formation of nanoparticles by Flame Spray Pyrolysis for up scaling the synthesis of zirconia nanoparticles. This investigation employed a commercial CFD code to simulate the gas flow field and droplet dynamics while three numerical models were developed to predict dynamic viscosity and surface tension of precursor solutions, the sauter mean diameter (SMD) of droplets during atomization and the particle growth inside the flame by coagulation and sintering. The simulation results were compared with experimental data available in this study and literature. The validated models were used to predict the effect of processing parameters, in particular, the effect of pressure drop, sheath gas, oxidant/mixture volume feed ratio (VFR), production rate and precursor concentration on flame dynamics and particle growth. The results show that increasing pressure drop and VFR will be able to decrease the residence time and sintering of nanoparticles in the flame. The variation of inlet sheath gas feeding had a negligible effect on the fluid flow and final particle size. The results also showed that by keeping the VFR and pressure drop at a fixed predicted value, similar particle size can be achieved at higher production rates using fixed precursor concentration.

1. Introduction

Zirconia nanoparticles of characteristic length less than 20 nm have a large potential for industrial applications. Along with high strength and toughness, zirconia also possesses good hardness, wear resistance and thermal shock resistance [1]. These properties have led to the use of zirconia-based components in a number of engineering applications. In addition to their extensive use as gas sensors [2], they are also used in interferometric filters [3], solid oxide fuel cells [4], catalysts [5], thermal barrier coating [6], as well as in dental ceramics [7]. The properties of nanomaterials are extremely dependent on the synthesis method as well as on the processing route; therefore, it is quite important to select the most appropriate technique for preparation of nanomaterials with desired chemical purity, phase and morphology. This challenge is more increased by the necessity to produce them in large amounts while keeping the cost to the minimum. Various techniques, including liquid phase synthesis such as sol gel process [8], gas phase (aerosol) synthesis (chemical vapor synthesis (CVS) [9], and Flame Spray Pyrolysis [10–13]) have been the most commonly used routes for the synthesis of zirconia nanopowders. The aerosol synthesis is quite attractive compared to liquid phase synthesis since it is a one step process and doesn't require several sequential steps to form nanoparticles [14,15]. Flame Spray Pyrolysis (FSP) has become one of the best aerosol synthesis techniques, since both organic and inorganic precursors can be used to produce nanoparticles [16]. This method has many advantages over the other methods as it is low-cost, easy to control particle size, simple processing, high production yield, and easy to convert to mass manufacturing [17]. Fig. 1 shows the schematic of Flame Spray Pyrolysis. Liquid solution containing precursor and fuel is fed into a capillary tube and dispersed by the oxidant. The initial size of droplets depends on many parameters including nozzle geometry, oxidant and solution flow rates, solution properties and relative velocity of solution and oxidant. Heine and Pratsinis [12] calculated the droplet lifetime at different initial droplet sizes based on the temperature and velocity profiles reported by Mueller et al. [10] and Heine and Pratsinis [12]. Droplet life time and traveling distance increased significantly as the initial droplet size increased. Larger droplets can even escape from the flame which may cause hollow particles [18]; therefore, good care must be taken to achieve small droplets with uniform distribution. After atomization, the solution is ignited by using a small methane–oxygen pilot flame which is positioned around the nozzle tip. In FSP the energy of the flame is used to drive chemical reaction of the precursor to produce clusters which quickly grow into nanoparticles by coagulation and sintering. The primary particle size and degree of agglomeration are very important indexes for final product performance which will be determined by the properties of the flame [16]. The extent of aggregation of primary particles can be distinguished by the strength of the forces that hold them together. These aggregates can either be held together by strong chemical or sintering bonds (hard-agglomerates; formed

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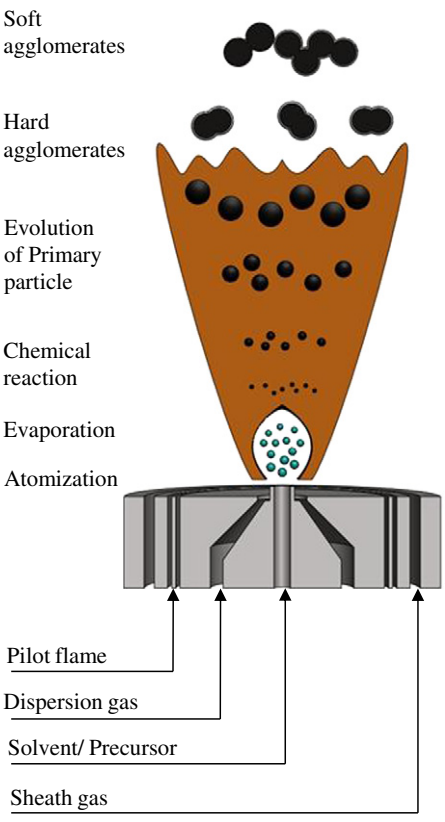

Fig. 1. Schematic of FSP apparatus.

at intermediate temperature) or bonded by weak physical van der Waals forces (soft-agglomerates; formed once sintering and growth of primary particle diameter stops). Tsantilis and Pratsinis [19] identified the regions of soft-, hard- and non-agglomerate silica particles in the high temperature flames on the basis of particle sintering and coalescence. The region of hard agglomerates is defined at the point where collision aggregate diameter/primary particle diameter, d_c/d_p is equal to 1.01 while the transition from hard to soft agglomerates is defined at the point where the primary particle diameter has reached 99% of its final d_p. Grohn et al. [20,21] defined the transition point at 95% of the final d_p to compensate the fluctuation of his numerical accuracy. The design of FSP systems is complex because the mixture of precursor and fuels needs to be atomized and efficient combustion is so difficult to achieve due to the variation of liquid properties which have a direct effect on the size and properties of nanoparticles. Advanced computational models have been developed to gain an insight to the FSP process. Most of the studies have been focused on particle modeling based on experimental data [10–13] and only one single numerical investigation reported on the lab scale production (14.8 and 29.6 g/h) without investigating the process parameters [21]. The properties of the nanoparticles in FSP depend on so many parameters, such as nozzle design, droplet size and lifetime, temperature, velocity and oxidant content. The design of the FSP nozzle and its parameters is therefore critical in order to up-scale the production. In this study, investigation is performed to examine the effect of process parameters on the growth of zirconia particles. A commercial CFD code, ANSYS FLUENT was used to solve the multicomponent droplet evaporation, combustion and gas flow field in FSP. The CFD code is coupled with an in-house Fortran code which is developed based on the Kruis et al. [22] model to simulate the particle growth during FSP. The employed mathematical models have been strongly tested against experimental data. The prediction of gas dynamics, initial droplet size and primary particle diameter in FSP process were validated against the documented experimental measurement [10–13]. The aim of the present study is to optimize the FSP process in order to have a controlled scaling up at higher production.

2. Liquid properties and composition

The solution used in this study was the mixture of zirconium n-propoxide (ZnP, Alfa Aesar, 70 wt.% in n-propanol) diluted in Ethanol (ethanol, ReAgents, >99.8%) resulting in precursor solutions of 0.5, 1, 1.5, 2 and 2.23 M ZnP. The viscosity of the solutions was determined with a Brookfield viscometer (LVDV-II-Pro) operated with an Ultra Low (UL) adapter to allow low viscosity measurement (down to 1 mPa s). The viscometer closed chamber tube was immersed in a Fisher Scientific water bath which could control the temperature from 0 to 100 °C. The viscometer was calibrated with the calibration fluid provided by Brookfield Engineering Laboratories at 25 °C. The viscosities were measured at different applied torques ranging between 10 and 100%. All the measurements were performed three times under steady state conditions. The reproducibility in measurement was within 2%. The surface tension of precursor solutions was measured by the Du Nouy ring method, using a Sigma 703 surface tensiometer at 25 °C. The tensiometer was calibrated with distilled water before each use. Surface tension was measured three times at each concentration, and the degree of reproducibility was within 0.1 mN/m.

3. Theoretical model

In this study, Eulerian approach was used to treat the continuous phase using Shear Stress Transport (SST) k–ω model [23] for turbulence description. The droplet flow field was modeled using DPM Lagrangian formulation by following discrete trajectories of droplets defined according to initial position, size and velocities. A monodisperse model was developed to predict the evolution of nanoparticles based on a detailed calculation of species concentration, density, velocity and temperature within the flame.

3.1. Gas dynamics

The continuous phase is assumed to be an ideal gas and as illustrated in Fig. 2, the FSP configuration has an axisymmetric geometry and a two dimensional model is employed to reduce the complexity and computational time. The governing equations for the 2-D model in the Cartesian tensor form are:

– Mass conservation equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j}\left(\rho u_j\right) = 0 \tag{1}$$

– Momentum conservation

$$\frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}\left(\rho u_i u_j\right) = -\frac{\partial p}{\partial x_i} + \frac{\partial \left(\tau_{ij}\right)_{eff}}{\partial x_j} + \frac{\partial}{\partial x_j}\left(-\rho \overline{u'_i u'_j}\right) \tag{2}$$

where $-\rho\overline{u'_i u'_j}$ is the Reynolds stress, which represents the effect of turbulent fluctuation on the fluid flow.

– Energy transport equation

$$\frac{\partial}{\partial t}(\rho E) + \frac{\partial}{\partial x_i}\left[u_i(\rho E + p)\right] = \frac{\partial}{\partial x_j}\left(k_{eff}\frac{\partial T}{\partial x_j} - \sum_j e_j J_j + u_i\left(\tau_{ij}\right)\right) + S_h. \tag{3}$$

Fluid in turbulent reacting flows is often considered as Newtonian and hence the shear stress can be related to velocity gradient.

$$\left(\tau_{ij}\right)_{eff} = \mu_{eff}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) - \frac{2}{3}\mu_{eff}\frac{\partial u_k}{\partial x_k}\delta_{ij} \tag{4}$$