Discovering paths to optimized nanoparticle characteristics

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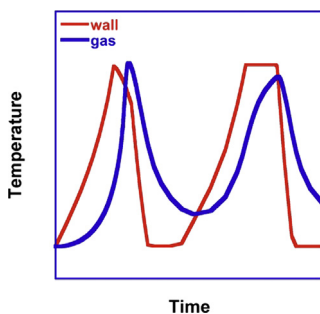
HIGHLIGHTS

- A method is described that solves part of the inverse problem of process design.
- Optimized process parameters are predicted for nanoparticle characteristics.
- The degree of crystallinity is estimated quantitatively.

GRAPHICAL ABSTRACT

A novel tool is described to solve part of the inverse problem of process and materials design discovering synthesis process parameters for optimized nanoparticle characteristics based on a Monte Carlo type algorithm. Examples for time-temperature profiles are presented for titania nanoparticles optimizing simultaneously size and agglomeration as well as specific surface area and crystallinity.

ARTICLE INFO

ABSTRACT

In contrast to materials properties, particle characteristics such as size, specific surface area, degree of agglomeration or crystallinity can be directly controlled by the synthesis process and also be determined experimentally without or with minimal further processing. Although particle characteristics only indirectly influence the (extrinsic) materials properties such as processability or charge carrier mobility and lifetime, they are key parameters to improve materials or device performance in applications. Process parameters – especially the time-temperature-profile in gas phase synthesis – control these nanoparticle characteristics. In this contribution a novel method is presented to discover paths to optimized nanoparticle characteristics in chemical vapor synthesis. As examples, physically realistic time-temperature profiles are predicted for a minimized degree of agglomeration at a desired primary particle size and a maximized degree of crystallinity at a desired specific surface area for the case of titania. The method relies on the integration of a simple model describing particle formation and growth into a Monte Carlo optimization algorithm. The results are surprising but can be rationalized using our understanding of particle formation and growth.

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1. Introduction

Nanoparticle characteristics determine the properties of materials and the performance of devices in which they are incorporated such as heterogeneous catalysts or printed electronics (Buesser and Pratsinis, 2012). Chemical vapor synthesis (CVS) is a gas phase process enabling the scalable production of nanoparticles (Gutsch et al., 2002). The nanoparticles obtained are typically of small size and narrow size distribution. They have a low degree of agglomeration and high crystallinity respectively low defect

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density. CVS process parameters, especially the time–temperature-profile – $T(t)$-profile – control these nanoparticle characteristics. Here we present a novel method to discover $T(t)$-profiles optimizing nanoparticle characteristics. Experimentally, corresponding position-temperature-profiles – $T(x)$-profiles – can be imposed using a multiple-zone high-temperature induction furnace (Djenadic and Winterer, 2017).

In CVS, precursor molecules are supplied in a gas flow and react upon introduction of energy thereby generating small particles by homogeneous nucleation – often by chemical nucleation through an irreversible decomposition reaction (Winterer, 2002). These nuclei grow by coagulation and coalescence into more or less agglomerated particles. Simultaneous solution of differential equations describing these processes can be used to model the CVS process (Winterer, 2002). Corresponding characteristic times determine the particle characteristics (Schilling and Winterer, 2014). The main characteristic of nanoparticles is of course their size but also how they are assembled. Depending on the characteristic times of coagulation and coalescence, hard or soft agglomerates are formed (Grass et al., 2006). It is possible to determine the degree of agglomeration in the model by following the evolution of surface area and volume and comparison of agglomerate with primary particle size (Kruis et al., 1993).

So far, process parameter maps and simulations scanning parameter fields including statistical experimental design have been used most often to find routes to optimized particle characteristics, i.e. tailoring or designing nanoparticles (Grass et al., 2006; Landgrebe et al., 1990; Soravia, 1996; Gutsch et al., 2005). Only recently, Gröschel et al. describe an algorithm to find reaction conditions for the production of nearly monodisperse silicon nanoparticles in a hot wall reactor with optimized width of the size distribution. (Gröschel et al., 2012) Here, we report a novel method to discover time-temperature-profiles of a hot wall reactor for optimized particle characteristics such as size, surface area, degree of agglomeration and crystallinity. The method can be extended to other process parameters, particle characteristics and synthesis processes.

2. Methodology

2.1. Particle formation and growth model

Titania is a model material for the CVS process as synthesis is possible over a wide range of process parameters and particle characteristics are readily available by experimental and theoretical methods. We use the metalorganic precursor titanium isopropoxide and oxygen as reactants (Djenadic and Winterer, 2012).

Differential equations describing particle generation and growth combined with differential equations describing heat transfer and heat production by the chemical reaction are used to model the CVS process and are solved using finite differences with an adaptive step size 5th order Runge-Kutta algorithm (Press et al., 1986). For the precursor decomposition (number density $N_{\text{precursor}}$) we use simple first order kinetics

$$\frac{dN_{\text{precursor}}}{dt} = -k \cdot N_{\text{precursor}} \tag{1}$$

with a reaction velocity constant

$$k = k_0 \cdot \exp\left\{-\frac{E_A}{k_B T}\right\} \tag{2}$$

with a pre-exponential factor $k_0 = 3.96 \cdot 10^5$ s^{-1} and an activation enthalpy of $E_A/k_B = 8479$ K (Okuyama et al., 1990). Particle coagulation is described with a coefficient assuming monodisperse particles

$$\frac{dN}{dt} = -\frac{1}{2}\beta \cdot N^2. \tag{3}$$

The Fuchs interpolation formula is used to compute the coagulation coefficient β (Pratsinis, 1988). The characteristic time for coagulation is then estimated by

$$\tau_{\text{coll}} = \frac{1}{\beta N}. \tag{4}$$

The evolution of the aerosol volume V is followed by

$$\frac{dV}{dt} = -\nu_1 \frac{dN_{\text{precursor}}}{dt} \tag{5}$$

with the monomer volume ν_1 (Kruis et al., 1993). The evolution of the aerosol surface area A is described by

$$\frac{dA}{dt} = N\frac{da}{dt} + a\frac{dN}{dt} \tag{6}$$

where a is the surface area of a single agglomerate particle and N is their number density (Kruis et al., 1993). The characteristic time for coalescence is estimated assuming grain boundary diffusion

$$\tau_{\text{sinter}} = \frac{k_B T \cdot d^4}{16\sigma w \Omega \gamma D_{\text{gb}}}, \quad D_{\text{gb}} = D_0 \exp\left\{-\frac{Q}{k_B T}\right\} \tag{7}$$

where σ is a numerical constant depending on the sintering mechanism (here, 32 is used assuming grain boundary diffusion as rate limiting), w is the grain boundary width (0.5 nm), Ω is the volume of the diffusing species ($1.56 \cdot 10^{-29}$ m^3 for O^{2-}), γ is the interfacial enthalpy (0.35 J/m^2 for grain boundary energy), and D_{gb} is the grain boundary diffusion coefficient (with $D_0 = 1.5 \cdot 10^{-7}$ m^2/s and $Q = 29{,}909$ J/K for oxygen diffusion in TiO$_2$ (Liao et al., 1997; Chiang et al., 1997). The development of the surface area of a particle by coalescence can be described by

$$\frac{da}{dt} = -\frac{1}{\tau_{\text{sinter}}}(a - a_s) \tag{8}$$

where a_s is the surface area of a completely coalesced particle (Kruis et al., 1993).

The energy balance includes terms for (convective) heat transfer and reaction enthalpy for the precursor decomposition

$$\frac{dT}{dt} = \frac{\alpha}{c_p \rho L}(T_w - T) - \frac{\Delta_R H \cdot c_0 \cdot k \cdot \exp\{-k \cdot t\}}{c_p \rho} \tag{9}$$

where α is the heat exchange coefficient, c_p the heat capacity, ρ the gas density, $\Delta_R H$ the enthalpy of reaction and c_0 the initial precursor concentration (Jakubith, 1991).

The residence time is calculated from the volume of the reactor and the volume flow through the reactor:

$$\tau_{\text{residence}} = \frac{V}{\bar{V}} \tag{10}$$

The primary particle size is computed from particle volume ν and surface area a according to

$$d_{\text{pri}} = \frac{6\nu}{a} \tag{11}$$

and the agglomerate particle size is obtained by

$$d_{\text{agg}} = \left(\frac{6\nu}{\pi}\right)^{\frac{1}{3}} \tag{12}$$

from which we estimate the degree of agglomeration by

$$N_{\text{agg}} = \left(\frac{d_{\text{agg}}}{d_{\text{pri}}}\right)^3 \tag{13}$$

Our simple 1D model cannot take into account distributions in residence time and temperature. Therefore, it will not be possible to