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Identification of the compensation effect in the characteristic sintering time model for population balances

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ABSTRACT

The sintering of agglomerates under high temperature determines the diameter and morphology of particles. Accurate sintering model is essential to the process simulation for the particle dynamics. A method of combining population balance modeling and inverse problem methodology was applied in sintering simulation process to investigate relationship between effective kinetic parameters in the characteristic sintering time model, i.e., two dynamic parameters (the pre-exponential factor A and the apparent activation energy E). The polydisperse primary particle (PP) model was introduced to consider the inhomogeneous structure in agglomerates. Two inverse problem methodologies, tabulation method and response surface method, were employed by fitting simulation results to experimental measurements. A contour map about the difference between simulation results and experimental measurements as a function of various parameter sets was obtained. Optimal values were obtained when the difference is small. A linear relationship between the two uncertain kinetic parameters was identified, which is similar to the kinetic compensation effect in the Arrhenius equation for reaction rate. The linear relationship holds true for the sintering of both TiO_2 and SiO_2 agglomerates at least, which are dominated by the surface diffusion mechanism and the viscous flow transport mechanism, individually.

1. Introduction

Nanoparticle synthesis via aerosol route has recently attracted growing interests from the scientific and industrial communities because it can produce high-purity nanoparticles with specially tailored chemical and physical property, e.g., hybrid component and high specific surface area (SSA), which can be used to produce ceramics, catalysts, electric and optical materials (Seto, Hirota, Fujimoto, Shimada, & Okuyama, 1997). With respect to the events involved in the synthesis process (e.g., nucleation, condensation, coagulation, sintering), coagulation and sintering strongly influence the size and morphology of nanoparticles. In the aerosol processes (Nakaso et al., 2001), highly concentrated nanosized nuclei grown from gas monomers by nucleation and surface reaction undergo rapid Brownian agglomeration. At a high temperature, the resultant nanoparticles may fully coalesce into dense spheres almost instantaneously, as the agglomeration rate is far smaller than the sintering rate. As the aerosol reactor cools down, the sintering rate may be far smaller than the

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Nomenclature

a	surface area of particle (m^2)
$a_{a,k}$	surface area of agglomerate particle at the kth bin (m^2)
a_{final}	surface area of completely fused spherical particle (m^2)
a_{pp}	surface area of primary particle (m^2)
A	pre-exponential factor
d_{ag}	geometric mean mobility equivalent diameter of agglomerate (m)
d_{am}	mobility equivalent diameter of agglomerate (m)
$d_{m,exp}$	mobility equivalent diameter of agglomerate from experimental measurement (m)
$d_{m,sim}$	mobility equivalent diameter of agglomerate from simulation (m)
d_p	particle diameter (m)
d_{pp}	primary particle diameter (m)
d_{ppg}	geometric mean diameter of primary particle (m)
$d_{ppg,exp}$	geometric mean diameter of primary particle from experimental measurement (m)
$d_{ppg,sim}$	geometric mean diameter of primary particle from simulation (m)
E	activation energy ($J\ mol^{-1}$)
k	index of volume bin
l	index of surface area bin
L	distance from the inlet of furnace (m)
n_a	agglomerate size distribution function ($m^{-3}\ m^{-3}$)
N_a	number concentration of agglomerate (m^{-3})
n_{pp}	primary particle size distribution function of an agglomerate ($m^{-3}\ m^{-3}$)
N_{pp}	primary particle number concentration of an agglomerate (m^{-3})
$N_{s,pp}$	volume bin number of primary particle
R	gas constant, 8.314 $J\ mol^{-1}\ K^{-1}$
t	time (s)
T	temperature (°C)
T_0	ambient temperature, temperature at furnace entrance (°C)
T_f	furnace temperature (°C)
$v_{a,k}$	volume of agglomerate particle at the kth bin (m^3)
v_{pp}	volume of primary particle (m^3)
y	objection function defined in Eq. (9) (m^2)

Greek symbols

σ_{ag}	geometric standard deviation of agglomerate
σ_{ppg}	geometric standard deviation of primary particle
δ	symbol for relative error
τ_s	characteristic sintering time (s)

agglomeration rate, leading to fractal-like agglomerates consisting of a large number of primary particles (PPs). The sintering events involved directly determine the morphology and size of particle product. However, the sintering kinetics is still under study (Kirchhof, Schmid, & Peukert, 2004).

The sintering process is usually described by the evolution of surface area which is found to approach its final value exponentially (Koch & Friedlander, 1990). Many researchers had studied the sintering dynamics by experiments or simulation. Seto, Shimada, and Okuyama (1995) used the two-dimensional sectional method of population balance modeling to simulate the sintering process of fractal agglomerates (TiO_2 and SiO_2) in an aerosol reactor where only sintering occurs. They found that primary particles coalesce at temperatures that are 50–100% of the bulk melting points of the corresponding particle materials. A similar reactor system built by Kirchhof, Forster, Schmid, and Peukert (2012) was employed to obtain detailed experimental measurements with sufficient heating and cooling times at the inlet and outlet. Yang and Biswas (1997) proposed a new parameter set, i.e. pre-exponential factor A and apparent activation energy E for TiO_2 nanoparticles, using the *in situ* light scattering data. Tsantilis, Briesen, and Pratsinis (2001) proposed a new characteristic sintering time model for silica particle by extending the particle size dependence of the melting point of metals to the sintering model. Simulations using the new characteristic time model were carried out for a variety of conditions with good agreement between the experiments and the simulation results except at larger temperatures. Based on their sintering equation form, Shekar et al. (2012) combined a kinetic model with the response surface method to identify effective model parameters for silica nanoparticles by fitting the model to the experimental measurements. Buesser, Grohn, and Pratsinis (2011) used molecular dynamics (MD) simulations to study the sintering rate and obtained a new characteristic sintering time model of TiO_2 nanoparticles, which was thought to be effective especially when the diameter of primary particles is small.

In fact, up to now researches mainly focused on identifying the effective sintering parameter sets (A, E) in certain experimental cases which even cannot be regarded as being universal (Park & Rogak, 2003). Several differing sintering parameter sets were proposed (Ehrman, Friedlander, & Zachariah, 1998; Kobata, Kusakabe, & Morooka, 1991; Xiong, Kamal Akhtar, & Pratsinis, 1993; Yang & Biswas, 1997). Johannessen, Pratsinis, and Livbjerg (2001) also proposed different apparent activation energy for TiO_2 in a diffusion flame reactor with temperature closer to 2000 K. They attributed the considerable difference to different reactors. They proposed that various apparent activation energy levels corresponding to different experimental conditions should exist because of the phase transformations from amorphous to anatase and rutile. Even though parameter sets from different researches vary greatly, but still can be successfully applied to simulate specific sintering processes of nanoparticles. This fact makes us wonder if there exists a relationship between A and E, which implies