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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<sub>2</sub> and SiO<sub>2</sub> agglomerates at least, which are dominated by the surface diffusion mechanism and the viscous flow transport mechanism, individually.

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#### 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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Nomen	clature	n <sub>a</sub>	$(m^{-3}m^{-3})$
а	surface area of particle (m <sup>2</sup> )	Na	number concentration of agglomerate $(m^{-3})$
$a_{\mathrm{a},k}$	surface area of agglomerate particle at the <i>k</i> th	$n_{\rm pp}$	primary particle size distribution function of
	bin (m <sup>2</sup> )		an agglomerate $(m^{-3}m^{-3})$
<i>a</i> <sub>final</sub>	surface area of completely fused spherical	$N_{\rm pp}$	primary particle number concentration of an
	particle (m <sup>2</sup> )		agglomerate (m <sup>-3</sup> )
$a_{\rm pp}$	surface area of primary particle (m <sup>2</sup> )	$N_{\rm s,pp}$	volume bin number of primary particle
A	pre-exponential factor	R	gas constant, 8.314 J mol <sup><math>-1</math></sup> K <sup><math>-1</math></sup>
$d_{\rm ag}$	geometric mean mobility equivalent diameter	t	time (s)
	of agglomerate (m)	Т	temperature (°C)
$d_{\rm am}$	mobility equivalent diameter of agglomerate (m)	$T_0$	ambient temperature, temperature at furnace
$d_{m,exp}$	mobility equivalent diameter of agglomerate	_	entrance (°C)
	from experimental measurement (m)	$T_{\rm f}$	furnace temperature (°C)
d <sub>m,sim</sub>	mobility equivalent diameter of agglomerate	$v_{a,k}$	volume of agglomerate particle at the <i>k</i> th bin
	from simulation (m)		(m <sup>3</sup> )
$d_{\rm p}$	particle diameter (m)	$v_{\rm pp}$	volume of primary particle (m <sup>3</sup> )
$d_{\rm pp}$	primary particle diameter (m)	у	objection function defined in Eq. $(9)$ (m <sup>2</sup> )
$d_{ m ppg}$	geometric mean diameter of primary particle (m)		
$d_{ppg,exp}$	geometric mean diameter of primary particle	Greek s	symbols
	from experimental measurement (m)		
d <sub>ppg,sim</sub>	geometric mean diameter of primary particle	$\sigma_{ m ag}$	geometric standard deviation of agglomerate
-	from simulation (m)	$\sigma_{ m ppg}$	geometric standard deviation of primary
E	activation energy (J mol <sup>-1</sup> )	-	particle
k	index of volume bin	δ	symbol for relative error
l	index of surface area bin	$ au_{ m s}$	characteristic sintering time (s)
L	distance from the inlet of furnace (m)		

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<sub>2</sub> and SiO<sub>2</sub>) 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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

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variable parameter combinations of A and E can be used for simulating for particle sintering. From the mathematic form of characteristic sintering time equation (an Arrhenius form), the relation is extremely possible. Panigrahi, Godkhindi, Das, Mukunda, and Ramakrishnan (2005) found that different apparent activation energies exist due to the phase transformation of micrometric titanium power in the sintering process, which provides evidence for variable apparent activation energy in sintering process. Even though a large variation of apparent activation energy has been reported, the relationship between the apparent activation energy and pre-exponential factor has not been studied yet. Meanwhile it is not difficult to find that the characteristic sintering time equation has an Arrhenius form. This relation between pre-exponential factor and activation energy has widely been discussed in other fields, e.g., for the Arrhenius form, kinetic compensation effect describing the linear relationship between A and E is said to occur for a family of related chemical process, notably heterogeneous catalysis. Whether this compensation effect exists in the characteristic sintering time equation needs to be determined to have a better understanding of the sintering model. This paper focused on proving there is similar kinetic compensation effect in the sintering processes of TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles, and population balance modeling is coupled to simulate the size evolution of particle population. Based on the sintering model, population balance modeling can be employed to simulate the evolution of particles due to sintering process under high temperature. The advantage of population balance modeling lies in their simplicity (Xu, Zhao, & Zheng, 2015; Zhao, Kruis, & Zheng, 2010; Zhao & Zheng, 2009). Furthermore, the discrete nature of the particles used to represent the system is very useful for multivariate population balances, i.e., containing other particle properties than particle size alone (Hao, Zhao, Xu, & Zheng, 2013; Xu, Zhao, & Zheng, 2014).

In this paper the uncertain kinetic parameters in the classical characteristic sintering time equation of  $TiO_2$  and  $SiO_2$  nanoparticles were identified to examine if the compensation effect exists or not. By minimizing the difference between experimental measurements and simulation results using various parameter sets based on inverse problem methodology, we can determine appropriate parameter sets for simulating the sintering process. In details, the experiments for  $TiO_2$  and  $SiO_2$  from Seto et al. (1997) were adopted, and population balance modeling (PBM) was employed to simulate the sintering process. The population balance equations (PBE) for the mass and number of primary particles (PPs) were constructed to obtain the evolution of size distribution of primary particles within agglomerates. The polydispersity of primary particles in agglomerates (Heien & Pratsinis, 2007) was considered. Inverse problem methods were coupled to identify the effective parameters in the characteristic sintering time equation (the pre-exponential factor *A* and the apparent activation energy *E*) by fitting simulation results to experimental measurements. Detailed contour map describing the location of appropriate parameter sets was obtained.

### 2. Population balance modeling for sintering

#### 2.1. The experiments and sintering model

In the nanoparticle synthesis via gas-to-particle, sintering and agglomeration are two key mechanisms that affect the size and morphology of particles. Seto et al. (1997) studied the sintering dynamics of polydispersed nanometer-sized agglomerates in a preparation system consisting of two furnaces. The first furnace is for agglomerates generation, and the second is for sintering where agglomerates concentration is low enough to make agglomeration negligible. The second furnace is 1.5 m long with a set-point temperature maintained between 0.45 m and 0.75 m, the inner diameter is 13 mm. The flow rate is 2 l/min. Equation (1) was used as the temperature history of agglomerates where  $L_1$ =0.2 m,  $L_2$ =0.45 m,  $L_3$ =0.75 m, and  $L_4$ =1.5 m. The nanoparticles were considered to be fully entrained by the gas stream.

$$\begin{cases} T(L) = T_0, L \le L_1, \\ T(L) = \frac{T_f - T_0}{L_2 - L_1} (L - L_1) + T_0, & L_1 \le L \le L_2, \\ T(L) = T_f, L_2 \le L \le L_3, \\ T(L) = T_f \exp\left[-\ln\left(\frac{T_0}{T_f}\right)\frac{L - L_3}{L_3 - L_4}\right], & L_3 \le L \le L_4, \end{cases}$$
(1)

where  $T_0$  is the ambient temperature (298.15 K),  $T_f$  is the set temperature of the reactor, T(L) is the temperature at distance L from the inlet.

Sintering is characterized by the reduction rate of surface area, da/dt (*a* is surface area of agglomerate and *t* is sintering time), approximately described by the following equation (Koch & Friedlander, 1990):

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -\frac{a - a_{\mathrm{final}}}{\tau_{\mathrm{s}}}.$$

For TiO<sub>2</sub>, the characteristic sintering time  $\tau_s$  based on the surface diffusion model has the general formula as (Kobata et al., 1991; Xiong et al., 1993; Yang & Biswas, 1997):

$$\tau_{\rm s,TiO_2} = Ad_{\rm p}^4 T \exp\left(\frac{E}{RT}\right). \tag{3}$$

For SiO<sub>2</sub>, the classic sintering time model for SiO<sub>2</sub> based on the viscous flow model was shown below (Xiong et al., 1993; Ehrman et al., 1998):

$$\tau_{s,\mathrm{SiO}_2} = Ad_{\mathrm{p}} \exp\left(\frac{E}{RT}\right). \tag{4}$$

*A* is the pre-exponential factor (s m<sup>-4</sup> K<sup>-1</sup>), *R* is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and *E* is the apparent activation energy (kJ/mol),  $d_p$  is the diameter of particles. The parameter set (*A*, *E/R*) for TiO<sub>2</sub> has been reported from different sources, such as (7.44 × 10<sup>16</sup>, 31,032) from Kobata et al. (1991), (1.67 × 10<sup>16</sup>, 31,090) from Yang and Biswas (1997) and (8.3 × 10<sup>24</sup>, 30,190) from Xiong et al. (1993). Molecular modeling (Buesser et al., 2011) was employed to deduce effective form of the sintering equation for TiO<sub>2</sub> nanoparticles. For SiO<sub>2</sub>, (6.3 × 10<sup>-13</sup>, 82,993) was proposed by Xiong et al. (1993), (6.3 × 10<sup>-8</sup>, 61,000) was proposed by Ehrman et al. (1998). Tsantilis et al. (2001) introduced  $d_p$ , min into the similar equation for SiO<sub>2</sub> to modify apparent activation energy *E* especially in the region where  $d_p$  is small. Based on the new form, Shekar et al. (2012) used inverse methodology (response surface method) to estimate the appropriate sintering parameters.

#### 2.2. Population balance modeling for the sintering

Based on the experiment and sintering model describing the sintering process of particle, the particle-resolved PBM was employed here to simulate the sintering process of particle population. PBM is a powerful tool for general simulation, which has been applied by many groups (Hao et al., 2013; Kostoglou & Konstandopoulos, 2001; Kostoglou et al., 2006; Mukherjee, Sonwane, & Zachariah, 2003; Rosner & Yu, 2001; Tandon & Rosner, 1999) to agglomeration or sintering. The PBM is capable of directly describing the dynamic evolution of internal variables (e.g., size and surface area) of each simulation particle (it represents a certain number of real particles having similar state with the simulation particle) (Zhao & Zheng, 2006, 2008, 2013). For the sintering, polydispersed primary particle (PP) model (Heine & Pratsinis, 2007), considering internal inhomogeneous structure within agglomerates, was coupled here to describe the evolution of the inhomogeneous structure of primary particles in agglomerates.

According to the experimental measurements (Seto et al., 1997), the size distribution at the entrance of the furnace followed a lognormal distribution as

$$n_{\rm a}(d_{\rm am}) = \frac{N_{\rm a}}{\sqrt{2\pi} \ln \sigma_{\rm ag}} \exp\left[-\frac{\ln^2(d_{\rm am}/d_{\rm ag})}{2\ln^2 \sigma_{\rm ag}}\right] \frac{1}{d_{\rm am}},\tag{5}$$

where  $n_a(d_{am})dd_{am}$  means the number concentration in the diameter range  $d_{am}-d_{am}+dd_{am}$ ;  $d_{ag}$  and  $\sigma_{ag}$  are the geometric mean diameter and geometric standard deviation. At the inlet,  $d_{ag}=91$  nm,  $\sigma_{ag}=1.5$ , the number density  $N_a$  is  $10^{13}$  m<sup>-3</sup>. For SiO<sub>2</sub>,  $d_{ag}=66$  nm,  $\sigma_{ag}=1.53$ . Primary particles in agglomerates were assumed to follow another lognormal distribution as

$$n_{\rm pp}(d_{\rm pp}) = \frac{N_{\rm pp}}{\sqrt{2\pi} \ln \sigma_{\rm ppg}} \exp\left[-\frac{\ln^2(d_{\rm pp}/d_{\rm ppg})}{2\ln^2 \sigma_{\rm ppg}}\right] \frac{1}{d_{\rm pp}},\tag{6}$$

where  $n_{pp}(d_{pp})dd_{pp}$  means the number concentration of primary particles in the diameter range  $d_{pp}-d_{pp}+dd_{pp}$ ;  $d_{ppg}$  and  $\sigma_{ppg}$  are the geometric mean diameter and geometric standard deviation. At the inlet,  $d_{ppg}=3.8$  nm,  $\sigma_{ppg}=2.06$ . For SiO<sub>2</sub>,  $d_{ag}=7.5$  nm,  $\sigma_{ag}=1.47$ . It was noted that the experimental data from Seto et al. (1997) is size-classified and is regarded as absolutely right in this study.

The PBE for the mass and the number of primary particle were constructed to obtain the evolution of size distribution of primary particles within agglomerates. Polydispersity of agglomerate was considered in the work, which was thought to be closer to the actual agglomerates as shown in Fig. 1.

The polydispersed PP distribution within an agglomerate k with volume  $v_{a,k}$  and surface area  $a_{a,k}$  was discretized into  $N_{s,pp}$  bins, resulting in the following conservation relations:

$$\begin{cases} v_{a,k} = \sum_{l=1}^{N_{s,pp}} (N_{pp,k,l} v_{pp,k,l}), \\ a_{a,k} = \sum_{l=1}^{N_{s,pp}} (N_{pp,k,l} a_{pp,k,l}), \end{cases}$$
(7)

where the *l*th bin is with representative volume  $v_{pp,k,l}$ , area  $a_{pp,k,l}$  and primary particle number  $N_{pp,k,l}$ . It was a set rule that the sintering process would not change the scope of PP diameter within the agglomerate *k* ranging from  $d_{pp,k,\min}$  to  $d_{pp,k,\max}$ , but alter the number of PPs in each bin (i.e., changing the size distribution). For the agglomerate *k*,  $d_{pp,k,\min} = d_{pp,k,\max}^2$ ,  $d_{pp,k,\max} = (a_{final,k}/\pi)^{1/2} = (6v_{a,k}/\pi)^{1/3}$ . The population balance equation of  $N_{pp,k,l}$  in each bin was built as follows (Heine &

Actual aggregates, volume v, surface area a



Fig. 1. Description for sintering of agglomerates and polydispersed primary particles.

Pratsinis, 2007):

$$\begin{cases} \frac{dn_{pp,k,l}}{dt} = \left(\frac{dn_{pp,k,l}}{dt}\right)_{loss} + \left(\frac{dn_{pp,k,l}}{dt}\right)_{gain}, \\ \left(\frac{dn_{pp,k,l}}{dt}\right)_{gain} = -\frac{v_{pp,k,l-1}}{v_{pp,k,l}} \left(\frac{dn_{pp,k,l-1}}{dt}\right)_{loss}, \\ \left(\frac{dn_{pp,k,l}}{dt}\right)_{loss} = -\frac{n_{pp,k,l}}{\tau_{s,l}} \frac{a_{pp,k,l-(a_{lnal,k}/n_{pp,k,l}^{mono})}{\pi_{s,l}}, \end{cases}$$
(8)

where  $a_{\text{final},k}$  is the surface area of the sphere after complete coalescence of k,  $\tau_{s,l}$  is the characteristic sintering time dependent of the *l*th PP size,  $n_{\text{pp},k,l}^{\text{mono}} = v_{a,k}/v_{\text{pp},k,l}$ . Solving above equations can help us obtain the time evolution of agglomerates and its internal primary particles size distributions.

In our previous work (Hao et al., 2013), this polydispersed model was employed to simulate the synthesis process of  $TiO_2$  via gas-phase method. The simulation results for the synthesis process involving nucleation, agglomeration and sintering agree well with the experimental measurements. This polydispersed model was used here again to simulate the individual sintering process. In the experiment (Seto et al., 1997), a two-stage plug reactor was used, in which coagulation and nucleation was thought as the dominant events in the first reactor and sintering is the dominant events in the second reactor is less than  $10^{13}/m^3$  making coagulation negligible, which was demonstrated by Seto et al. (1997). Their experimental data suggested mobility diameter of agglomerates remains stable if the temperature of the second reactor is below 800 °C, which means sintering is the only mechanism dominating the size and surface area change of particles. Even if the coagulation was considered in the second reactor, the effect can be neglected.

The PBM was verified by comparing the simulation result with that from the modeling of Shekar et al. (2012), and characteristic sintering time from Shekar et al. (2012) was also employed in our simulation process. Both experimental conditions were from Seto et al. (1997), including the temperature history of particle population, the residence time at different temperature time and component concentration at the inlet. It may be worth noting that the dynamic events (nucleation, coagulation, sintering) in two reactors were simulated by Shekar et al. (2012), and collision diameter of agglomerates was employed in the sintering process. But in our work, the size distribution at the outlet of the first reactor was considered as direct input, and mobility diameter of agglomerates (surface area equivalent diameter) was employed to characterize the evolution. We also compared our simulation results of the average diameter of primary particles with experimental data to validate our PBM model. It was found that PBM in this work is capable of describing the evolution of agglomerates in the sintering process, as shown in Fig. 2. The evolution of size distribution of agglomerates and primary particles in the second reactor with different set temperatures also agreed better with the experimental measurements, as shown in Fig. 3.

# 3. Inverse problem methodology

Response surface method (RSM) and tabulation method (TM) were employed here as the inverse problem methodologies (or optimization algorithm) to identify the effective dynamic parameter sets. Tabulation method was used by Mosbach, Aldawood, and Kraft (2008) to evaluate a detailed chemistry homogeneous charge compression ignition (HCCI) engine model. RSM was employed by Braumann, Kraft, and Mort (2010) to identify unknown parameters in granulation models. Shekar et al. (2012) combined RSM with a kinetic model to identify effective characteristic sintering model.

The basic idea of RSM is to fit a model, usually by a simple algebraic expression such as a second-order polynomial, to data. A surrogate but accurate enough local model is constructed to replace the actual response of the system to uncertain



**Fig. 2.** Comparison of average primary particle diameter from the model proposed by Shekar et al. (2012) and the population balance modelling in this work (using same sintering parameters proposed by Shekar et al., 2012) at different reactor temperature. The experiment was proposed by Seto et al. (1997).



Fig. 3. Evolution of size distribution of agglomerates and primary particles. Sintering model parameters were from Kobata et al. (1991). The experimental measurements and monodisperse model were given by Seto et al. (1997).

parameter sets. Usually experiment design is coupled to reduce the experiment times needed to construct the response surface. Under the condition of limited data we used, the surrogate model should be constructed in a finite narrow parameter space around hot spots to ensure high accuracy. This is accomplished either by an appropriate initial set based on empirical value or by some search methods, such as using the Halton sequence (Braumann, Man, & Kraft, 2011) to search hot spots randomly first. RSM is a more accurate tool compared with TM in most cases, but at the disadvantage that it might not have a unique solution. TM stores any obtained results to deduce the response at the point that we are interested within the region by fitting process, which means that any response in a relatively large region can be obtained. The accuracy of TM

In our case, PBM was built to simulate the process and to obtain the simulation response (e.g., the size of agglomerates and primary particles) within the parameter space. Optimal parameter sets were identified when the simulation response was closest to the known experimental measurements. Here, the parameter space is (A, E/R) and the simulation response is ( $d_m$ ,  $d_{ppg}$ ). The objection function y was constructed as following to characterize the difference between simulation results and experimental measurements:

$$y = \sum_{T_{\rm f} = 900,1000,1200 \cdot C} \left[ \left( d_{\rm m,sim}(A, E/R, T_{\rm f}) - d_{\rm m,exp} \right)^2 + \left( d_{\rm ppg,sim}(A, E/R, T_{\rm f}) - d_{\rm ppg,exp} \right)^2 \right]$$
(9)

Generally speaking, both the method is capable of identifying the optimal parameter sets (which are the parameters making *y* at minimum). The difference is that from RSM some certain parameter sets can be obtained, while from TM the relation between *y* and parameter sets can be drawn.

# 4. Results and discussions

In this work, random distributed data points were used in TM first to draw a contour map of the difference y at parameters sets (ln(A), E/R) for TiO<sub>2</sub> and SiO<sub>2</sub> as shown in Fig. 4. The accuracy of the TM method depends mainly on the amount of data used. The amount of data (i.e., 450 random distributed points for TiO<sub>2</sub> in RSM) used was regarded as enough.

A V-type valley was presented for both  $TiO_2$  and  $SiO_2$ . The corresponding parameter sets seemed to be on a line. Then we tried to use RSM method to identify corresponding parameter sets making *y* minimum. The first step of RSM was to use the Hilton sequence generating random points to find the hot spot (which means the possible effective parameter sets) and then a



**Fig. 4.** Obtained value *y* (the difference between simulation results and the experiments) at parameter sets  $(\ln(A), E/R)$  in the characteristic sintering time of (a) TiO<sub>2</sub> and (b) SiO<sub>2</sub>.



**Fig. 5.** Change in the average agglomerate mobility diameter and primary particle diameter for  $TiO_2$  with the reactor temperature: (a) experimental measurements and simulation results were given by Seto et al. (1997), (b) sintering parameters were from the tabulation method and (c) sintering parameters were from the response surface method.



**Fig. 6.** Change in the average agglomerate mobility diameter and primary particle diameter for  $SiO_2$  with the reactor temperature: (a) experimental measurements and simulation results were given by Seto et al. (1997) and (b) sintering parameters were from the response surface method.

Table 1							
The relative	errors	using	various	parameter	sets	for	TiO <sub>2</sub> .

Temperature (°C)	600	900	1000	1200	1500
$\delta \gamma < 0.10$					
$\delta d_{m,sim}$	< 0.012	< 0.019	< 0.037	< 0.058	< 0.066
$\delta d_{\rm ppg,sim}$	< 0.056	< 0.063	< 0.068	< 0.074	< 0.091
δd <sub>m</sub>	< 0.045	< 0.153	< 0.114	< 0.156	< 0.096
$\delta d_{\rm ppg}$	< 0.171	-	< 0.316	< 0.103	< 0.029
Seto et al., 1997					
$\delta d_{\mathrm{m}}$	0.072	0.249	0.237	0.094	0.157
$\delta d_{\rm ppg}$	0.348	-	0.725	0.134	0.024
Kobata et al., 1991					
$\delta d_{\rm m}$	0.042	0.159	0.115	0.098	0.097
δd <sub>ppg</sub>	0.139	_	0.981	0.262	0.050

# Table 2

The relative errors using various parameter sets for SiO<sub>2</sub>.

Temperature (°C)	900	1200	1350	1500	1650	1750
δ <i>y</i> < 0.10						
$\delta d_{m,sim}$	< 0.0034	< 0.0048	< 0.0062	< 0.0067	< 0.0130	< 0.0083
$\delta d_{\rm ppg,sim}$	< 0.0027	< 0.0024	< 0.0039	< 0.0054	< 0.0061	< 0.0072
$\delta d_{ m m}$	< 0.0158	< 0.0172	< 0.0139	< 0.0213	< 0.0544	< 0.0516
$\delta d_{ m ppg}$	< 0.2620	< 0.4093	< 0.4415	< 0.5088	< 0.1407	< 0.3119
Seto et al., 1997						
δd <sub>m</sub>	0.0089	0.0093	0.0204	0.0494	0.1891	0.1738
$\delta d_{\rm ppg}$	0.0048	0.2071	0.1315	0.1010	0.0822	0.0349
Shekar et al., 2012						
δd <sub>m</sub>	0.0449	0.0037	0.0801	0.1068	0.0767	0.1356
$\delta d_{ m ppg}$	0.0085	0.0676	0.3488	0.3689	0.2105	0.2323
Xiong et al., 1993						
$\delta d_{\rm m}$	0.0076	0.0057	0.0018	0.0037	0.2344	0.2155
$\delta d_{ m ppg}$	0.2230	0.3805	0.3457	0.3976	0.0870	0.2139
Ehrman et al., 1998						
δd <sub>m</sub>	0.0076	0.0056	0.0040	0.0699	0.2326	0.2151
$\delta d_{ m ppg}$	0.2226	0.3811	0.3370	0.2891	0.0948	0.2138

response surface was constructed around this hot spot. In our case, for TiO<sub>2</sub> 350 random points were generated in the range: In (*A*):20–50, *E*/*R*:10,000–60,000 and 100 extra special points located in the bottom of the valley to ensure accuracy (these points were then stored in TM) were used to find the hot spot. Once the response surface was constructed, a simple algebraic expression was obtained. In this case, the minimum value of *y* for TiO<sub>2</sub> was 41.30, the corresponding optimal parameter set was (32.42, 42,343). Given the quadratic term of *y*, there was little difference between this optimal point from RSM and the points on the line which all made *y* range between 41 and 60. It was meant that the points on the line from TM can also be regarded as the optimal points. Three discretely distributed points on this line, ln(A)=28.48, 31.31 and 35.60, were applied in the simulation to verify this assumption, as shown in Fig. 5. Compared with the parameter set from Kobata et al. (1991), the optimal points both from TM or RSM leads to same results and were more effective in this case. Same phenomenon can be found for SiO<sub>2</sub>, optimal parameter set was (-33.26, 92,503.4), as shown in Fig. 6. The limit for the validity of the new parameter sets was that the particle size should be larger than approximately 2 nm. The model broke down if the particle size went down to a few nanometers due to the high internal pressure of smaller particles (Koparde & Cummings, 2005).

In addition, the relative errors using various parameter sets were evaluated according to

 $\begin{cases} \delta y = |y - y_{\text{opt}}|/y_{\text{opt}}, \\ \delta d_{m,\text{sim}} = \left| d_{m,\text{sim}} - d_{m,\text{sim}}^{\text{opt}} \right| / d_{m,\text{sim}}^{\text{opt}}, \\ \delta d_{\text{ppg,sim}} = \left| d_{\text{ppg,sim}} - d_{\text{ppg,sim}}^{\text{opt}} \right| / d_{\text{ppg,sim}}^{\text{opt}}, \\ \delta d_{m} = \left| d_{m,\text{sim}} - d_{m,\text{exp}} \right| / d_{m,\text{exp}}, \\ \delta d_{\text{ppg}} = \left| d_{\text{ppg,sim}} - d_{\text{ppg,exp}} \right| / d_{\text{ppg,exp}}. \end{cases}$ 



Fig. 7. The relationship between ln(A) and E/R of different expressions for TiO<sub>2</sub> and SiO<sub>2</sub>.



**Fig. 8.**  $\ln(k)$  against 1/T using different characteristic sintering time models for SiO<sub>2</sub> ( $d_p$ =10 nm).

(10)

where  $y_{opt}$  is the minimum objection function with the optimal parameters,  $d_{m,sim}^{opt}$ , and  $d_{ppg,sim}^{opt}$  are the simulation results using the optimal parameters. While we set  $\delta y$  below 0.10, the relative errors are calculated over several different temperature points. Obviously, the relative errors of our simulation results are basically lower than that of pre-existing simulation in a wide range of objection function y (Tables 1 and 2). The optimized simulation results show the best agreement with the experimental measurements as shown in Figs. 5 and 6.

Just as we noted at the beginning of this paper, strongly different characteristic sintering times can be found from different sources. Based on several optimal parameter sets identified in this work and parameter sets reported before, the hypothesis that the compensation effect in the characteristic sintering time equation may exist was verified for both  $TiO_2$  and  $SiO_2$  as shown in Fig. 7.

As known, sintering is driven by the deviation of the free energy of the irregular agglomerate from that of the compact particle. The accuracy of the widely used sintering model largely depends on how effective the characteristic sintering time equation is used. Even these parameter sets varies greatly, they can still describe the sintering process. The reason for this phenomenon has been revealed: there exists a linear relationship between two effective parameters, which can be seen in Fig. 7.

This linear relationship, exists both in TiO<sub>2</sub> case and SiO<sub>2</sub> case, is not a unique phenomenon in this sintering of nanoparticles but similar to the so-called kinetic compensation effect, found in the Arrhenius equation for the thermal decomposition of some solid compounds which characterizes the linear relationship between apparent activation energy *E* and pro-exponential factor function  $\ln(A)$ , i.e.,  $\ln(A) = aE + b$ . This kinetic compensation effect was related to, but distinct from, the so-called isokinetic relationship concept (Barrie, 2012a, 2012b), which considered that different  $\ln(k) \sim 1/T$  lines caused by various experimental conditions will have the intersection point ( $T_{iso}$ ,  $k_{iso}$ ), where *k* represents the reaction rate. In our case, *k* is the characteristic sintering time. If the isokinetic relationship was exhibited, as shown in Fig. 8, which demonstrates that the compensation effect does exist. Factually, the sintering (or thermal restructuring) is an activated process, and it was also found that the rate coefficient for restructuring of silver agglomerates follows an Arrhenius form with a characteristic energy of restructuring (Weber & Friedlander, 1997).

We emphasized here the activation energy in the original manuscript should be "apparent activation energy". As known, for the elementary reactions the activation energy represents the difference between the average energy of the activated molecules and that of all the molecules. However, for the global reactions the so-called activation energy is empirical and apparent, which usually depends on the temperature. In this work, the conclusion that different apparent activation energy should be used for different experimental conditions was based on the fact that differing apparent activation energy has been reported from different experiments. Johannessen et al. (2001) pointed out that a plausible reason is the difference of reactors and procedures of obtaining the characteristic sintering time. The temperature and heat rate of the reactors in different experiments varied in a large range. For example, Kobata et al. (1991) measured the sintering rate with temperature between 1123 K and 1473 K, and Xiong et al. (1993) studied furnace temperature from 1300 K to 1700 K. As for other cases, the temperature can be as high as 2000 K. Johannessen et al. (2001) took the view that phase transformations during the process make it unlikely that the sintering can be described by an expression based on single apparent activation energy. It is known that TiO<sub>2</sub> nanoparticles produced via gas-phase method leads to amorphous, anatase and rutile  $TiO_2$ . The phase transformation is associated with the sintering process. In the preparation process, anatase  $TiO_2$ arises firstly at relatively low temperature and then transforms to rutile at higher temperature. The transformation rate of anatase to rutile (A-R transformation) depends strongly on the conditions, under which the particles were produced (Kobata et al., 1991; Ahonen et al., 2001). The transition was associated with Arrhenius-type kinetic reaction with varied apparent activation energy which was reported to depend on the size of particles and temperature (Wang, Mishra, Zhao, & Huang, 2013; Zhang & Banfield, 2000). Sintering is another process associated and competed with the A-R transformation (Ahonen et al., 2001; Wang et al., 2013). The increased mobility of the atoms during the A-R transformation enhances the sintering rate (Kumar et al., 1992). It was concluded that sintering rate is associated with the phase transformation which depends on the preparation conditions.

This linear relationship between two most important uncertain dynamic parameters involved in the characteristic sintering time model can help us on identification of effective and universal sintering model, but also implies that it is not so important to identify designated effective parameters sets (*A*, *E*) for the characteristic sintering time model. The variable apparent activation energy level implies that differing parameter sets may be available. By the relationship identified in this work, the pre-exponential factor can be easily obtained. The work left may be studying the characteristic of variability of apparent activation energy level in different phase transformation processes.

#### 5. Conclusions

The sintering of agglomerates under high temperature determines their surface area and internal inhomogeneous structure. The population balance equations for the mass and number of primary particles were constructed to obtain the evolution of size distribution of primary particles within agglomerates. The polydisperse primary particles (PP) model was employed here, which has advantage in numerical precision with respect to the monodisperse PP model. Aiming to the sintering experiment reported by Seto et al. (1997), we proved that there exists a linear relationship between the effective parameter sets for the sintering of nanoparticles using the tabulation-based inverse problem method to minimize the

difference between experimental measurements and PBM numerical results. The kinetic compensation effect in the characteristic sintering time which is in the Arrhenius form was found. It describes a linear relationship between ln(A) and *E*. This linear relationship is first proposed for sintering process of nanoparticles and correlated differing sintering model parameters reported before, but also implies that it was not essential to specify single apparent activation energy to characterize sintering process which was associated with the environment-depended phase transformation.

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