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The critical conditions for secondary nucleation of silica colloids in a batch Stöber growth process

Kan-Sen Chou *, Chen-Chih Chen

Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

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Abstract

In this work, we determined experimentally the critical total surface area of silica seeds in the solution to avoid the formation of new particles (i.e. secondary nucleation) in a batch Stöber growth process. This critical surface area corresponded to the balance between the generation rate of reaction intermediate from the hydrolysis of TEOS and its consumption rate via the growth of existing seeds. Further calculation showed that the secondary nucleation was probably related to the average distance between seed particles. When the distance between seeds exceeded a critical value for each growth condition, i.e. for each generation rate, one would then observe secondary nucleation. Otherwise, simple growth was observed. Higher generation rate corresponded to shorter distance.

Keywords: Silica colloid; Secondary nucleation; Critical specific surface area

1. Introduction

Since the investigation by Stöber et al. on the preparation of monodispersed silica colloids by means of hydrolysis of alkyl silicates was first published in 1968 [1], there have been a lot of research groups studying on the mechanism of nucleation and growth of these silica colloids [2–6]. Matosoukas and Gulari proposed a monomer addition growth model that the nucleation was the result of the reaction between two hydrolyzed monomers and the particles grew by monomer addition [2,3]. Bogush and Zukoski proposed an aggregative growth model in which the nucleation was resulted from the aggregation of subparticles to achieve sufficient stability provided by the surface potential; and after this, the particle grew by the aggregation of subparticles onto larger particles [4,5]. Blaaderen et al. [6] and Giesche [7] thought that the particle formation (i.e. nucleation) proceeded through an aggregation process of siloxane substructures that was influenced strongly by the surface potential of the silica particles and the ionic strength of the reaction medium and hence the particle grew through the surface reaction-limited process of hydrolyzed monomers or small oligomers. Boukari et al. by using small angle X-ray scattering found that the first particle to form in the solution was mass fractals with polymeric, open structure and could be considered as the primary particles [8,9]. These particles were followed by intraparticle densification process and smoothing of the interface into the usual compact, nonfractal, stable structures.

Last decade, due to the important applications of silica as catalysts, pigments, ceramics, photonic crystal, chromatographic material, etc., there were a lot of efforts on the preparation of desired particle size with very narrow size distribution. Bogush et al. used seeded growth technique to prepare large quantities of silica particles at mass fractions up to 17 wt% and found that during seeded growth, the particle size could be related to the total volume of added TEOS [10]. Giesche employed a continuous reactor system to prepare large silica particles of up to 3.6 μm and mass fraction of up to 10 vol% [11]. Kim et al. utilized a mixed semi-batch and batch procedure to prepare monodispersed silica colloids and found that by using a batch process followed by semi-batch process one could obtain better silica colloids and while other procedures were prone to produce secondary nucleation [12,13]. Nagao et al. demonstrated that the addition of electrolytes (KCl) could suppress the formation of new particles in seeded growth [14]. Generally, in these growth

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* Corresponding author. Tel.: +886 35 713691; fax: +886 35 715408.
E-mail address: kschou@che.nthu.edu.tw (K.-S. Chou).

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procedures, reactants are added to a system containing existing seeds. In the ideal situation, only growth of silica seeds proceeds through the surface reaction of hydrolyzed monomers whose reaction rate is first-order with respect to TEOS concentration [2,6,7]. Nevertheless, the crucial issue with these procedures is how to avoid the formation of any new particles during growth that will destroy the monodispersity of silica colloids. Chen et al. observed that under a given set of reaction conditions and total external surface of seeds, the smaller the seed particles, the fewer the newly formed particles during seed growth. While during growth with the same diameter particles as seeds, the larger the total surface area of the seeds, the fewer the newly formed particles [15]. Giesche, on the other hand, also remarked that the diffusion distance of the hydrolyzed TEOS to the seed particle surface might be too large for highly diluted seed dispersions or large seed sizes. Thus, at a constant SiO_2 concentration of seeds the available particle surface area decreased and the diffusion distance toward this surface increased with seed size [11].

The objective of this work is to investigate the critical condition corresponding to the formation of new particles in a seeded growth process. By carrying out a series of growth experiments, we will determine the critical condition where new (secondary) nucleation occurs and hence to establish a quantitative guideline for this batch Stöber growth process. Furthermore, this guideline has also practical application on the preparation of core–shell structural particles with silica as the shell. Using this guideline, we have successfully fabricated the silver core and silica shell composite particles [16].

2. Experimental

Reagent grade chemicals of TEOS (98%, Acros, USA), ammonia (28 wt%, Showa, Japan), anhydrous ethanol (99.5%, NASA, USA) and deionized water were used without further purification. All experiments carried out in this work were at ambient temperature (25 ± 2 °C).

2.1. Seed preparation

Batch process was used to prepare seeds for our growth experiments. First, a solution containing appropriate amounts of anhydrous ethanol, ammonia and deionized water was agitated for 5 min using magnetic stirrer to ensure homogeneity. Then a proper amount of TEOS was added to the solution and the reaction proceeded at ambient temperature for 24 h leading to the formation of silica colloids. We then recovered these silica colloids by a high-speed centrifuge (Himac CR 22G, Hitachi, Japan) and washed it by deionized water for three times before re-dispersing in deionized water for the growth runs. The experimental details of this work can be found in a previous paper [17] and are summarized in Table 1. To determine the volume fraction of silica in a re-dispersed solution, we took 5 ml of the solution, placed it in crucible, dried at 120 °C, and then measured the weight change. The density of silica colloids is assumed to be 2.0 g/cm^3 here. The particle size and its distribution were measured by scanning electron microscope (Hitachi-S4700, Japan). Roughly 50 particles were counted for each sample. Total surface areas of the seeds were then calculated based on the average particle sizes.

Table 1
Experimental conditions to obtain the seeds for growth studies

Average size (nm)	Relative standard deviation (%)	Experimental conditions (M)			
		TEOS	H_2O	NH_3	C_2H_5OH
596	3.4	0.28	14	2.0	11.3
423	5.2	0.28	14	1.0	11.7
281	6.4	0.28	14	0.37	12.0

2.2. Growth experiments

First, the seeds were dispersed in a solution containing specific quantities of water, ammonia and ethanol. The suspension was sonicated and stirred to ensure uniformity before the addition of a specific quantity of TEOS (added at once) to start the growth process. Three series of seeded growth experiments were performed here and whose conditions were listed in Table 2. After the growth experiment, we would check from the SEM picture whether there was any new small particles. The critical condition was defined as the one when less than five small particles are found from one such picture (usually around 1 in 50 seed particles). If no small particle was found, then we had a simple growth condition. On the other hand, if more than five additional small particles were found, we then had new nucleation under these conditions. Sequential growth was carried out by adding the total quantity of TEOS in several batches (instead of once). For example, to keep final concentration of TEOS at 0.536 M, if we added in two batches, then the equivalent TEOS to the system was the same as #1 of Table 2. If on the other hand it was added in six batches, the condition was equivalent to #3 of Table 2.

Table 2
Conditions of growth experiments for the determination of the critical specific seed surface area together with the calculated generation rate from Eqs. (1) and (2)

	Growth conditions				$r_{\text{generation}}$ (mol/(min dm^3))	
	TEOS (M)	NH_3 (M)	H_2O (M)	C_2H_5OH (M)	Giesche (Eq. (1))	Chen et al. (Eq. (2))
#1	0.268	0.37	10	13	3.9×10^{-3}	5.4×10^{-3}
#2	0.1787	0.37	10	13	2.6×10^{-3}	3.6×10^{-3}
#3	0.0893	0.37	10	13	1.3×10^{-3}	1.8×10^{-3}
Ref. [15]	0.215	2	6	–	8.9×10^{-3}	10×10^{-3}

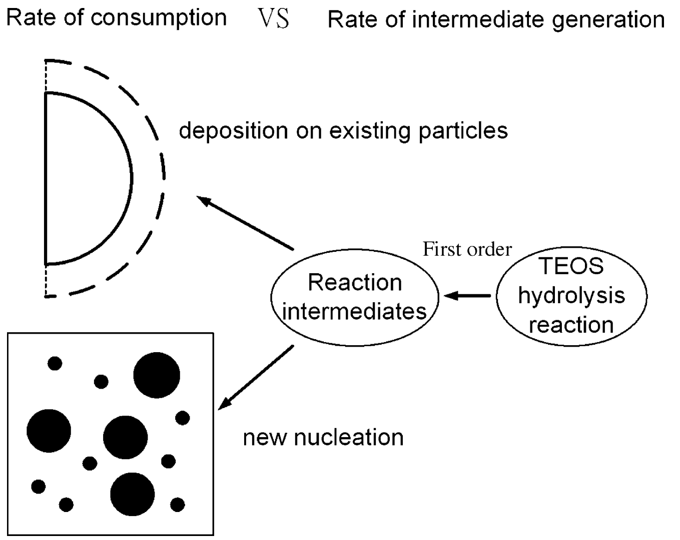

Fig. 1. Schematic graph of the generation and consumption of intermediate for particle growth.

3. Results and discussion

First shown in Fig. 1 is a schematic diagram of the generation and consumption of reaction intermediate [$Si(OC_2H_5)_{4-X}(OH)_X$] for particle growth. The basic concept here is that when the generation rate is smaller than the consumption rate by seeded growth, we will then have simple growth. The final size can be easily predicted by the total quantity of TEOS added to the system [10,11]. Yet, when the generation rate is greater than the consumption rate of seeded growth, some of the reaction intermediate will have chance to aggregate to form new particles that will destroy the monodispersity of the product.

Next shown in Fig. 2 are the results from our series of growth experiments. Here, two seeds of particle size 596 and 281 nm are tested, respectively, and in order to maintain a nearly constant solution environment, the generation rate is adjusted mainly by varying TEOS concentrations as indicated in Table 2. In the literature, there are two similar equations proposed by Giesche (Eq. (1)) [7] and Chen et al. (Eq. (2)) [18], respectively, to describe the hydrolysis rate. In this work, both equations are applied to estimate the generation rate and the calculated values are of the same magnitude.

$$r_{\text{generation}} = 2.36\,\text{s}^{-1}\exp\left\{\frac{-3256\,\text{K}}{T}\right\}[H_2O]^{1.18}[NH_3]^{0.97}[\text{TEOS}] \tag{1}$$

$$r_{\text{generation}} = 74.36\,\text{min}^{-1}\exp\left\{\frac{-3067\,\text{K}}{T}\right\} \times [H_2O]^{1.267}[NH_3]^{0.971}[\text{TEOS}] \tag{2}$$

Clearly for any specific generation rate (i.e. a specific growth condition), we observe simple growth if we have large number of seeds (or large total surface area of seeds) in the reactor, and new nucleation when we have only small number of seeds. And in between, a critical point exists. Our results also indicated that when the seed size is large, we would need more specific seed surface area (i.e. higher seed concentration) to avoid the formation of new particles, which is consistent with the results from Chen et al. [15]. Exhibited next in Fig. 3 are SEM pictures corresponding to the different situations for the case of 596 nm seed experiments.

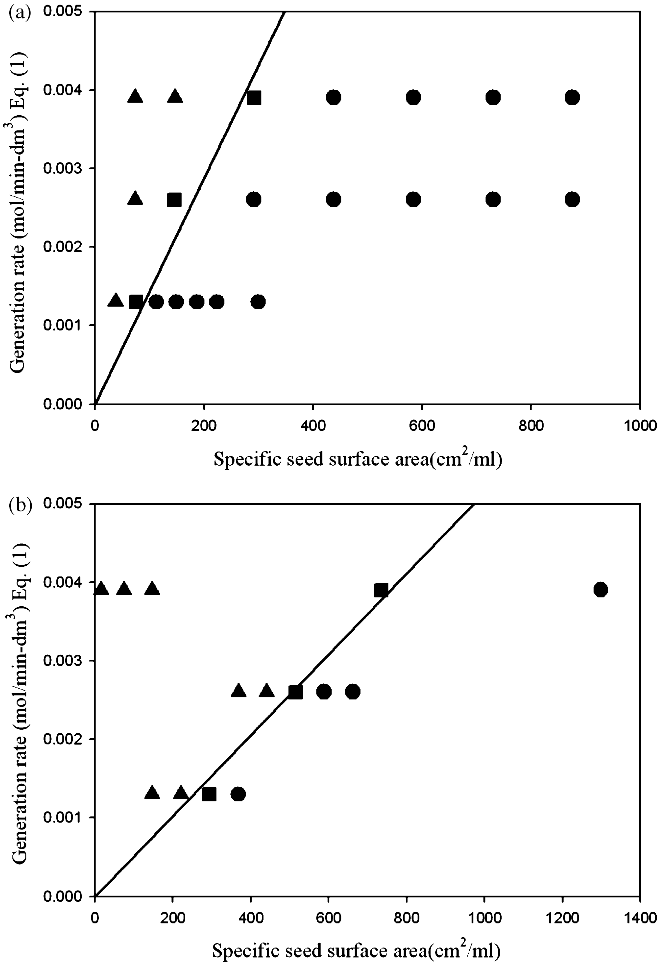

Fig. 2. Relationship between the generation rate and specific surface area of seeds (per unit volume of solution) during the growth process. The circle, square and triangle denote simple growth, critical condition and new nucleation, respectively. Seed size: (a) 281 nm and (b) 596 nm.

To further explore the meaning of this critical condition for secondary nucleation, the average distance (edge-to-edge) between seed particles is calculated by assuming a simple cubic uniform distribution of these seeds. The results are now exhibited in Fig. 4. For clear observation the boundary of critical condition, the experimental data are best fitted by quadratic polynomial ($R^2 = 0.977$) and expressed as dash curve. It suggests that for each generation rate, there exists a corresponding critical diffusing distance, which is irrelevant to the seed size. In other words, this result suggests that at a specific rate of generation, the reaction intermediates would have only a certain limited time of diffusion to find a seed surface for growth. Otherwise, these species will aggregate to form new nuclei. It is a competition between the diffusing time for growth against the time for secondary nucleation. At a higher generation rate, the time available for growth would be

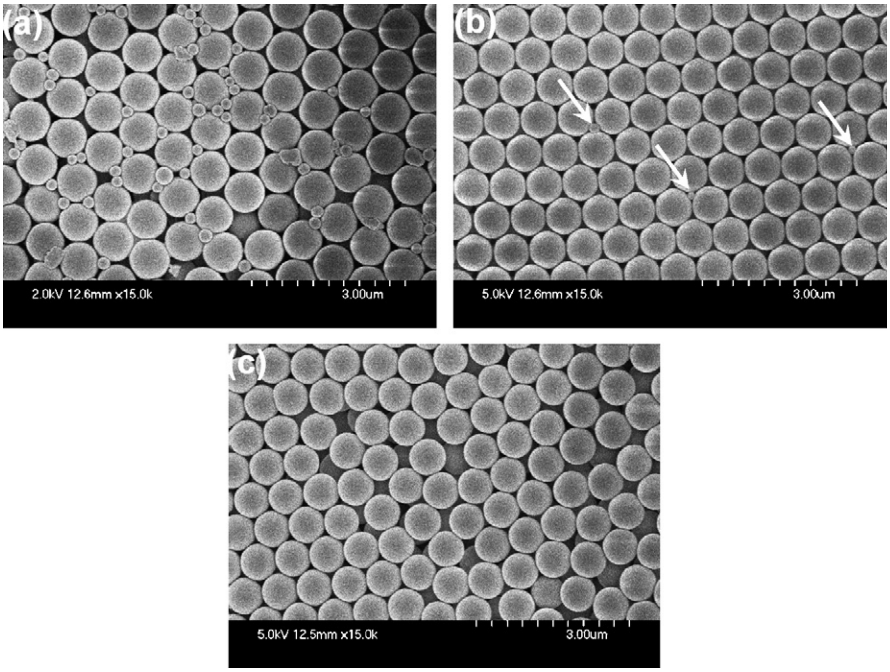

Fig. 3. The respective SEM pictures for various situations (seed size = 596 nm): (a) obvious new nucleation; (b) around the critical point; (c) simple growth.

shorter and consequently a shorter critical distance between seed particles.

Furthermore, to prepare large particles, a sequential seeded growth procedure is often carried out, i.e. the total quantity of TEOS is added in several batches to the seeds, otherwise new nucleation may occur to destroy the monodispersity. In this case, Fig. 4 can be a simple guideline. The two SEM pictures show the results from two different sequential growth experiments. The total quantity of TEOS added is the same, yet in one case it was added in two batches (symbol ▼) while six batches in the other case (symbol ▲). Clearly when the point was above the curve we observed new nucleation. On the other hand, when the point was below the curve, we observed only simple growth. Here the final size was 780 nm as predicted by the total amount of TEOS added to the system.

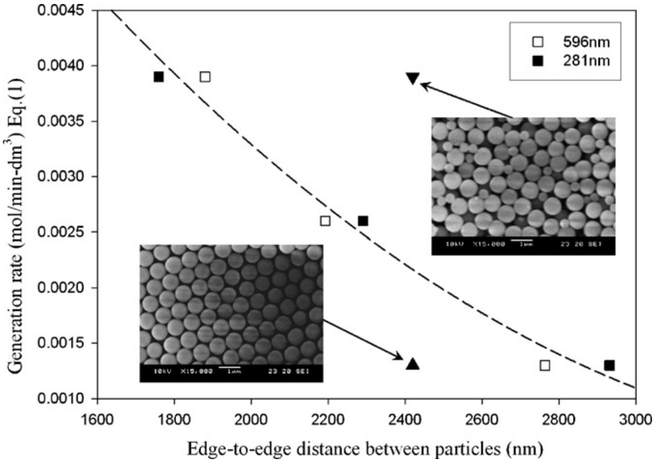

Fig. 4. Relationship between the generation rate and average edge-to-edge distance between seed particles for both seed sizes. The experimental data are best fitted by quadratic polynomial ($R^2 = 0.977$) and expressed as dash curve. The inserted SEM pictures are the results from two sequential seeded growth, where the seed size is 423 nm and total added TEOS is 0.536 M. (▼) 0.268 M, two batches, and (▲) 0.089 M, six batches.

Chen et al. [15] had also studied this problem. However, they used only one growth condition (also shown in Table 2) and summarized their results in terms of critical specific seed surface area versus seed size. Extrapolation technique was applied in their work to get the critical seed surface area (unlike direct observation in our work) and it went directly from $1 \times 10^{10}\ \mathrm{ml}^{-1}$ to zero. On the other hand, according to our Fig. 4, the estimated critical distance for their growth condition was about 1000 nm. However, when we used their specific seed surface area data, the calculated critical distance were around 4000–5600 nm, much larger than our prediction. This large critical distance seemed to suggest that it was very difficult to nucleate under their experimental conditions. The major difference between our growth conditions and Ref. [15] was the concentration of ammonia (0.37 M vs. 2.0 M). A higher concentration of ammonia would increase the ionic strength of the solution, which might suppress the nucleation [6]. Another possible effect of ammonia would be the change of surface charge density which also might have some influence on the aggregation efficiency of these intermediate species. Nevertheless, Giesche had also suggested that the use of ammonia concentrations between 0.1 and 1 M to be advantageous for seeded growth experiments [11]. More work is needed to further clarify this discrepancy.

4. Conclusions

We have shown in this work that there exists a critical specific surface area of seeds for a batch growth process below which the formation of new particles will occur. Below this critical point, the rate of generation of reaction intermediates exceeds that of consumption by growth, and hence new particles will be formed to destroy the monodispersity of the products. We also found that this critical condition can be expressed as a critical distance between seed particles for each generation rate, with shorter distance for higher generation rates. In other words, it is the time required for the species to diffuse to seed surface versus the time for secondary nucleation. Simple growth will result when the average distance becomes small by putting more seed particles in the reactor or by lowering the generation rates such as adding small amounts of TEOS in several batches to achieve the final desired size.

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