Evaluation and Control of Particle Properties in Aerosol Reactors

The production of powders by aerosol routes spans a wide range of operating temperatures depending on the type of aerosol reactors used. The dominant mechanism of particle growth and evolution depends highly on the rate at which the reactions producing the condensible species are carried out. Numerical solutions of the discrete-sectional aerosol general dynamic equation that accounts for the interactions of the discrete clusters were obtained for conditions representative of the different types of aerosol reactors used for powder production today. Simplified reaction and coagulation equations that give fast and useful prediction of the evolution of aerosols associated with chemical reactions were derived, and a simple reaction-coagulation model was developed. The effects of reaction rate, initial vapor concentration, residence time, seed particles, and temperature profile on the properties of fine particles produced by gas-phase chemical reactions were evaluated using both models. Results show good agreement between the two.

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Introduction

Fine powders have become increasingly important in a number of high technology industries, particularly in ceramics. As the applications of the powders become more severe, so do the demands placed on the powder properties. Bowen (1980) suggested that an ideal powder used in fine ceramics should consist of roughly spherical, nonagglomerated, uniformly-sized particles preferably in the submicron-size range and with controlled chemical composition. Powder production from gaseous precursors has long been technologically important for such commodities as carbon black, fume silica, titanium dioxide, oxide ceramics, and magnetic powders. The technologies for the synthesis of particles, however, have been primarily empirical developments aiming at controlling various powder properties such as particle size and size distribution, internal porosity, extent of agglomeration, and material phase.

Aerosol reactors used for powder synthesis usually operate at elevated temperatures. Since the reaction rates depend exponentially on temperature, it is useful to classify the chemical processes in terms of the heat source. Flame or combustion systems, which have been used to synthesize carbon black and other powders, operate at temperatures in the range from 1,500 to 3,000 K. The reaction rates at these temperatures are very high and the reactions are completed on the order of milliseconds. An early technological application of plasmas is in powder synthesis (Fauchais et al., 1983). Plasmas can achieve the high temperatures needed for the synthesis of refractory materials, but require some optimal cooling schedule to control nucleation and reduce agglomeration upon collection. Powders that have been produced by plasmas include oxides, carbides, nitrides, borides, and pure elemental species. Laser-induced chemical reaction also has been used to synthesize fine powders (Cannon et al., 1982a,b). The heating rate in laser systems can be as high as 10^6 $K \cdot s^{-1}$. Peak temperatures measured optically range from 1,400 to 1,600 K. The particles form rapidly in a "flame" produced by the laser heating with the number concentration peaking and decaying by coagulation within a few tenths of a millisecond. The total time in the laser beam is about 2 ms. Finally, thermal processes for powder synthesis induce reaction by an external heat source. The powders produced by this route can be much coarser than those generated in flame processes. One of the oldest applications of this technique is in the production of carbon blacks (Walker, 1963). Other examples include the decomposition of metal alkoxides or silane gas to produce fine powders at relatively low temperatures (Okuyama et al., 1986; Wu et al., 1986, 1987a).

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The elementary processes involved in the formation and growth of particles from gaseous precursors include: 1) gas-phase chemical reactions; 2) surface reactions; 3) homogeneous nucleation; 4) heterogeneous condensation; 5) coagulation; and 6) coalescence or fusion. The differences in the properties of particles produced in the various reactors can be traced back to the differences in the relative importance of these processes. The reactions in high-temperature processes, i.e., plasma, laser, and flame reactors, are carried out at such a rate that high supersaturation levels are achieved, resulting in rapid nucleation of high number concentrations of very small particles. These particles then grow by coagulation. The end result, for temperatures below the melting point, is a powder consisting of low-density flocs. The rapid cooling of the particles in plasma and laser reactors to temperatures well below the sintering temperature should, in principle, minimize the formation of low-density agglomerates. On the other hand, slow chemical reaction rates that allow vapor and cluster deposition on the surfaces of existing particles to play a more important role in particle growth than coagulation should also lead to the production of uniformly-sized particles with minimal agglomeration.

The advances in aerosol physics and chemistry now have made feasible theoretical descriptions of the dynamical processes involved in particle formation and growth in chemical synthesis reactors. Although most of the research has been concentrated in the studies of aerosols in the environment, applications to powder synthesis in aerosol reactors have begun to gain increasing emphasis. A major problem confronted is that the chemical reaction mechanisms as well as many physical and chemical properties needed to describe the evolution of particles in aerosol systems are not known. The key features regarding the behavior of different reactor systems, however, can be extracted, without detailed knowledge of the reaction chemistry or shapes of the generated agglomerates, by using available aerosol models appropriate for these high source rate reactors. By focussing on the nucleation, vapor and cluster deposition, and coagulation, we can gain understanding on the behaviors and relationships between the various aforementioned reactor systems used for powder synthesis today. This study examines the effect of reaction rate, initial vapor concentration, residence time, and seed particles on the distributions of fine particles using two models. The results show that growth of refractory particles in a high source rate operation is dominated by coagulation that results in a broad particle-size distribution. Control of the reaction rate is the most effective way to suppress nucleation of new particles and to grow uniformly-sized particles.

Models of Particle Production Processes

Figure 1 illustrates the physical processes involved in particle formation from the gas phase. Gaseous precursors react to produce vapor molecules. If the vapor reaches sufficient level of supersaturation, ultrafine primary clusters are formed by homogeneous nucleation. Larger secondary particles are formed by the coagulation of clusters and by the simultaneous heterogeneous condensation of vapor molecules onto the clusters. If seed particles are introduced into the system, they may scavenge a considerable amount of condensible vapor and clusters, thereby reducing the potential for new particle formation.

Friedlander (1983) presented a theoretical model for aerosol formation by chemical reactions in the absence of coagulation in batch and flow aerosol reactors. Assuming that the classical theory of homogeneous nucleation is valid, four coupled nonlinear ordinary differential equations were derived to describe the time evolution of the total number concentration and total surface area of the aerosol, the first moment of the aerosol-size distribution (mean particle diameter), and the saturation ratio in the system.

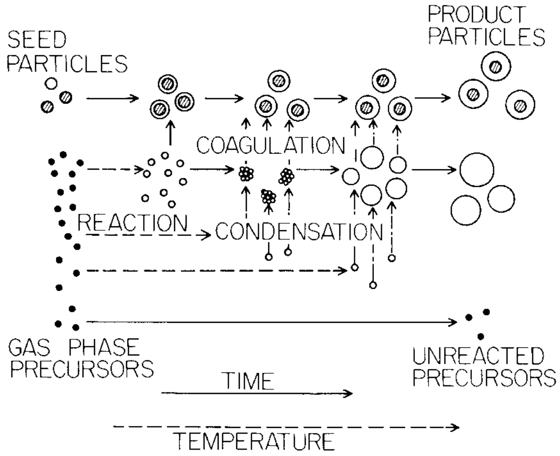


Figure 1. Processes contributing to particle formation from gas-phase chemical reactions.

The classical theory of homogeneous nucleation assumes that particles are formed by the successive addition of monomers to the clusters. The time scale for this process is assumed to be such that a steady-state cluster distribution is established. Using thermodynamic principles, one can determine a critical cluster size, below which the Gibbs free energy of the clusters increases with size and the clusters are thermodynamically unstable. Beyond this size, the free energy decreases with size so continued growth of the clusters is thermodynamically favorable. The critical cluster size, which is a function of the surface tension and the saturation ratio (the ratio of the actual partial pressure to the saturation vapor pressure), is often computed to be of atomic dimensions for aerosol reactor systems. The monomer production rates in these systems are extremely high, with dimensionless source rates (the ratio of the rate of monomer production to the rate of monomer-monomer collision at saturation vapor concentration) on the order of 10^{10}. Warren and Seinfeld (1984) have shown that in order for the steady-state cluster population approximation to be valid, the dimensionless source rate must be smaller than unity. It is clear that the steady-state assumption of the classical theory of homogeneous nucleation breaks down under conditions of powder synthesis systems, and a dynamical model accounting for the interactions of the clusters is needed.

As shown in Figure 1, particles range in size from the clusters containing small number of monomers to large particles. These particles evolve as a result of cluster-cluster, cluster-particle, and particle-particle collisions, as well as individual cluster and particle growth due to the accretion of vapor molecules.

Discrete-sectional (D-S) model

The dynamic behavior of the monomers, clusters, and aerosol particles in the formation processes is described by the aerosol General Dynamic Equation (GDE) (Gelbard and Seinfeld, 1979). The GDE can be expressed in the discrete form, separately representing monomers, dimers, trimers, etc., or in terms of a continuous particle-size distribution function. The former approach is well suited to the description of small clusters, but is cumbersome for modelling the growth of large particles. The latter approach is useful for describing the evolution of large particles, but inaccurately represents the small clusters. A discrete–sectional GDE was developed to overcome the numerical problems in modeling aerosol formation and growth under high source rate conditions (Wu and Flagan, 1987c). In the discrete–sectional GDE the aerosol size spectrum is separated into two parts. The smaller clusters, varying rapidly with time, are described by the number concentrations of discrete particle sizes, n-mers. The large clusters and aerosol particles are followed in terms of the mass concentrations of ranges in cluster size called sections. Monomer formation is described as a chemical source term. The aerosol size distribution changes with time due to the combined effects of coagulation and evaporation over the entire clusters and aerosol size spectrum. Since the dynamics of the small clusters are followed explicitly, it is not necessary to use the classical nucleation theory to describe new particle formation.

In this study, the following assumptions were made:

- Evaporation of monomers from clusters or particles can be ignored because of the very low saturation vapor pressure of the particulate materials.
- Particle deposition onto surrounding walls is negligible.
- Surface reactions can be neglected.
- When two particles collide, a single new spherical particle is formed. Its mass is equal to the combined mass of the two smaller particles.
- Particles are spherical and electrically neutral.
- Particles and vapor are uniformly distributed throughout the system.

The discrete–sectional GDE to describe the aerosol evolution with a chemical reaction source for monomers is a coupled set of ordinary differential equations,

$$\rho \frac{d}{dt}\left(\frac{N_1}{\rho}\right) = S_0 - \sum_{i=1}^{k} \beta_{1i} N_1 N_i - \left[\sum_{r=1}^{M} {}^{1}\overline{\overline{\beta}}_{1r} Q_r\right] N_1 \tag{1}$$

$$\begin{aligned} \rho \frac{d}{dt}\left(\frac{N_i}{\rho}\right) = {} & \frac{1}{2} \sum_{j=1}^{i-1} \beta_{i-jj} N_{i-j} N_j - \sum_{j=1}^{k} \beta_{ij} N_i N_j \\ & - \left[\sum_{r=1}^{M} {}^{1}\overline{\overline{\beta}}_{ir} Q_r\right] N_i, \quad 2 \le i \le k \end{aligned} \tag{2}$$

$$\begin{aligned} \rho \frac{d}{dt}\left(\frac{Q_l}{\rho}\right) = {} & \frac{1}{2} \sum_{i=1}^{l-1} \sum_{j=1}^{l-1} {}^{1}\overline{\beta}_{ijl} Q_i Q_j - \left[\sum_{i=1}^{l-1} {}^{2}\overline{\beta}_{il} Q_i\right] Q_l \\ & - \frac{1}{2} {}^{3}\overline{\beta}_{ll} Q_l^2 - \left[\sum_{i=l+1}^{M} {}^{4}\overline{\beta}_{il} Q_i\right] Q_l \\ & - \left[\sum_{i=1}^{k} {}^{2}\overline{\overline{\beta}}_{il} N_i\right] Q_l + \sum_{i=1}^{k} \sum_{r=1}^{l-1} {}^{3}\overline{\overline{\beta}}_{irl} N_i Q_r \\ & + \frac{1}{2} \sum_{i=1}^{k} \sum_{j=1}^{k} {}^{4}\overline{\overline{\beta}}_{ijl} N_i N_j, \quad 1 \le l \le M \end{aligned} \tag{3}$$

where

N_i = number concentration of clusters with i-mers

Q_l = mass concentration of aerosol particles in section l

ρ = density of the gas

k = dividing size between the discrete and sectional regimes

M = total number of sections

S_0 = generation rate of monomers by a chemical reaction

β_{ij} = Brownian coagulation coefficient of spherical particles with i- and j-mers

Fuchs' interpolation formula that expresses the coagulation rate function for the whole range of Knudsen numbers from the free molecule to the continuum regime was used. The enhancement of the coagulation rate due to van der Waals forces highly depends on the Hamaker constant used (Alam, 1987); since we could not accurately estimate the Hamaker constant, the effect of van der Waals forces was not included in the simulation. ${}^{1}\overline{\overline{\beta}}_{ir}$, ${}^{2}\overline{\overline{\beta}}_{il}$, ${}^{3}\overline{\overline{\beta}}_{irl}$, and ${}^{4}\overline{\overline{\beta}}_{ijl}$ are the discrete–sectional coagulation coefficients accounting for the interactions of particles between the discrete and sectional regimes. ${}^{1}\overline{\beta}_{ijl}$, ${}^{2}\overline{\beta}_{il}$, ${}^{3}\overline{\beta}_{ll}$, ${}^{4}\overline{\beta}_{il}$ are the inter- and intrasectional coagulation coefficients (Gelbard and Seinfeld, 1980) to count the interactions of particles inside the sectional regime.

Simplified reaction–coagulation (SRC) model

The discrete-sectional model can relatively accurately describe the evolution of the entire particle-size distribution. The sectional representation makes it relatively efficient computationally, at least by comparison with solving the integro-differential equation that results from using the continuous particle-size distribution. Nonetheless, the computational demands of this method can be severe in the face of the many calculations required for reactor design and optimization studies. A simpler model can be derived, which gives valuable information regarding the domain of operation of aerosol reactors. This simplied model (SRC model) can be used to indicate whether a given set of reactor conditions would result in growth or nucleation dominant operation. In this model, the aerosol-size distribution is represented by two modes. The first, called the nuclei mode, follows the evolution of the fine particles and clusters. The second, called the seed mode, describes the evolution of the seed particles. Mass is added to the nuclei mode from the reaction source, and is removed by the seed particles. Both the nuclei and the seed modes are monitored by the number and mass concentrations N_H and M_H, and N_S and M_S, respectively. Four differential equations are sufficient to describe the aerosol system,

$$\rho \frac{d}{dt}\left(\frac{N_H}{\rho}\right) = S_0 - K_H N_H^2 - K_{HS} N_H N_S \tag{4}$$

$$\rho \frac{d}{dt}\left(\frac{M_H}{\rho}\right) = S_0 - \overline{m}_H K_{HS} N_H N_S \tag{5}$$

$$\rho \frac{d}{dt}\left(\frac{N_S}{\rho}\right) = -K_S N_S^2 \tag{6}$$

$$\rho \frac{d}{dt}\left(\frac{M_S}{\rho}\right) = \overline{m}_H K_{HS} N_H N_S \tag{7}$$

with initial conditions

$$N_H = M_H = 0 \tag{8}$$

$$N_S = N_{S_0} \tag{9}$$

$$M_S = M_{S_0} \tag{10}$$

K_H, K_{HS} and K_S represent the global coagulation coefficients of the two modes, i.e.,

$$K_H = \frac{1}{2}\beta(\bar{d}_H, \bar{d}_H), \quad \bar{d}_H = \sqrt[3]{\frac{6M_H}{\pi\rho_p N_H}}$$

$$K_S = \frac{1}{2}\beta(\bar{d}_S, \bar{d}_S), \quad \bar{d}_S = \sqrt[3]{\frac{6M_S}{\pi\rho_p N_S}}$$

$$K_{HS} = \beta(\bar{d}_H, \bar{d}_S), \quad \bar{m}_H = \frac{\pi}{6}\bar{d}_H^3\rho_p$$

Note that the SRC model can only predict the average particle size of each of the two modes, not the size distribution.

The chemical reaction kinetics in aerosol reactors are rarely known. For present purposes we have assumed that the rate of production of condensible vapors is first order in reactant concentration,

$$r_p = \rho\frac{dC_p/\rho}{dt} = -\rho\frac{dC_A/\rho}{dt} = k_A C_A \tag{11}$$

where

C_p = concentration of condensible vapors

C_A = concentration of the reactant gas

k_A = reaction rate constant

The generation rate of monomer in an isothermal reactor is then

$$S_0(v_1, t) = r_p N_{AV} = (k_A C_{A0} e^{-k_A t}) N_{AV} \tag{12}$$

where C_{A0} is the initial concentration of the reactant gas, and N_{AV} is Avogadro's number. The time required for complete reaction is estimated as $5/k_A$. This is the time when 99.3% of the reactant is converted to products. Obviously, if the reaction mechanisms and kinetics are known for the system of interest, S_0 should be replaced accordingly.

Particle Formation and Growth in Isothermal Reactors

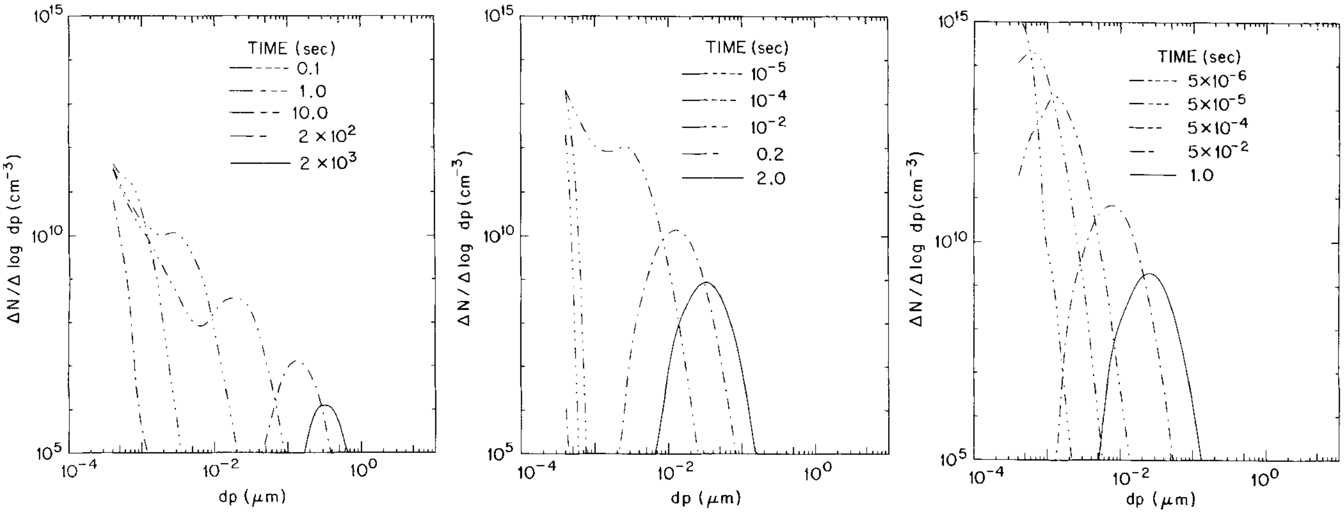
The case of constant source rate reactors has been examined by Friedlander (1983). Operation at a constant source rate requires continuous adjustment of the reactor temperature to increase the rate constant as the reactants are consumed. This increase must be such that it precisely balances the loss of the reactants and is in general difficult. As we will see later, the optimal operating conditions for powder production may be such that neither the rate constant nor the reaction rate remains invariant. We begin our examination of powder synthesis with the simpler case of an isothermal reactor. In this case, the reaction rate constant stays fixed. The reaction rate, however, decreases with time due to the depletion of the reactants. For the examples considered in this section, the physical properties will be those corresponding to the production of TiO_2 by the thermal decomposition of titanium tetraisopropoxide (Okuyama et al., 1986),

$$Ti(OC_3H_7)_4 \rightarrow TiO_2 + 4C_3H_6 + 2H_2O$$

The reaction is assumed to be first order in $Ti(OC_3H_7)_4$.

Homogeneously-generated particles

Figures 2a–b show the evolution of the particle-size distributions for values of the reaction rate constant, k_A, of 0.01, and 100 s^{-1}, respectively. Figure 2c presents the results for the case of instantaneous decomposition of the precursor, $k_A \gg 100\ s^{-1}$, which leads to particle growth purely by coagulation. The initial reactant concentration in each case is $5.25 \times 10^{-10}\ mol \cdot cm^{-3}$. The reaction temperature is 600°C. Prior to depletion of the reactant vapors by thermal decomposition, there exist large differences in the evolution of the particle-size distributions. After



a. $k_A = 0.01\ s^{-1}$ b. $k_A = 100\ s^{-1}$ c. $k_A \gg 100\ s^{-1}$, pure coagulation case

Figure 2. Evolution of the TiO_2 particle-size distributions with an initial TTIP concentration of $5.25 \times 10^{-10}\ mol \cdot cm^{-3}$.

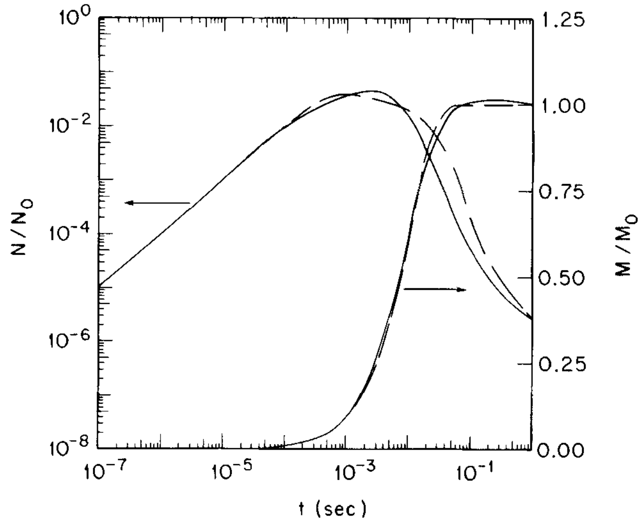


Figure 3. Comparison of the total normalized number and mass concentrations from the D-S (——) and SRC (- - -) models for an initial TTIP concentration of 5.25×10^{-10} mol · cm^{-3} and k_A = 100 s^{-1}.

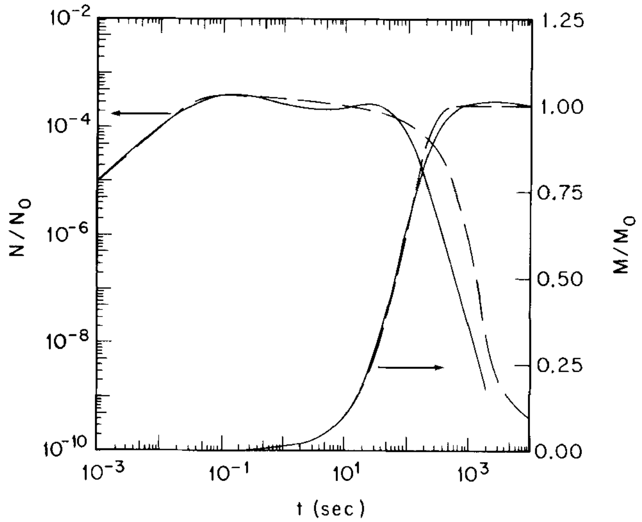
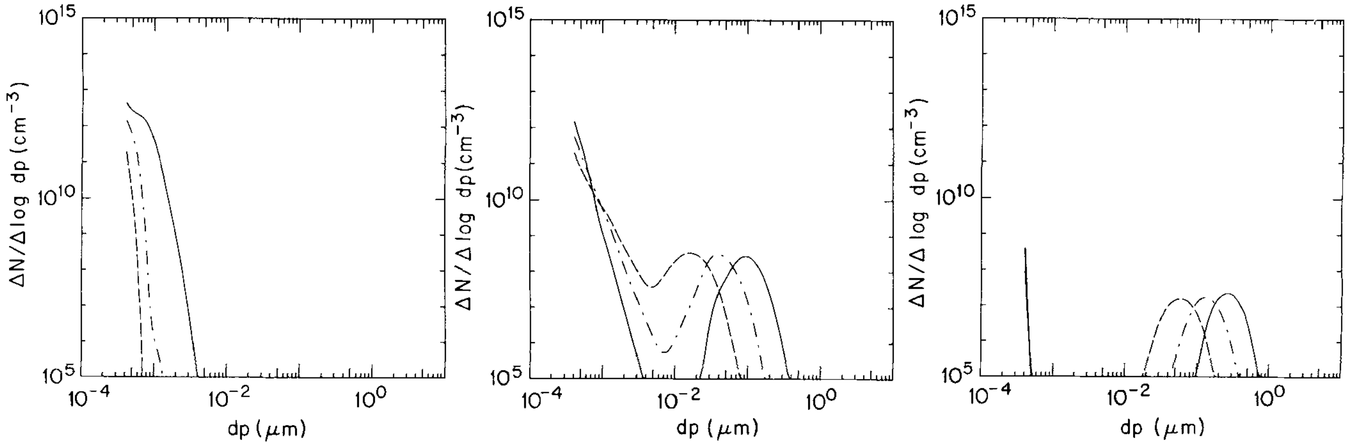


Figure 4. Comparison of the total normalized number and mass concentrations from the D-S (——) and SRC (- - -) models for an initial TTIP concentration of 5.25×10^{-10} mol · cm^{-3} and k_A = 0.01 s^{-1}.

sufficient time has elapsed, Brownian coagulation becomes dominant causing the size distributions to approach the self-preserving distribution function (Wang and Friedlander, 1967). Slower reactions take longer time to finish. The final size distributions show the effects of residence time on the average particle size and the spread of the size distribution.

The SRC model does not predict the size distribution, but can be used to examine the number and mass concentrations, and mean particle size. Figures 3 and 4 show the comparison of the results from the D-S and SRC models. The number concentrations shown are normalized by N_0, the maximum monomer concentration, and the mass concentrations by M_0, the total mass concentration of the condensible species, TiO_2, based on the initial precursor concentration. We compare here the zeroeth and the third moments of the particle-size distribution as a function of time for fast (k_A = 100 s^{-1}) and slow (k_A = 0.01 s^{-1}) reactions. Both Figures 3 and 4 show that the two models give very similar results from $t = 0$ to $t = \tau_{rxn}$, where $\tau_{rxn} = 1/k_A$. Since chemical reaction dominates during this time interval, narrow cluster-size distributions result. The difference between the number concentrations predicted by the two models increases from $t = \tau_{rxn}$ to $t = 10\tau_{rxn}$ because of the competition between coagulation and chemical reaction that produces a bimodal distribution during this period, Figure 2a. Reaction approaches completion and slows down after $t = 5\tau_{rxn}$. Coagulation causes the large clusters to grow, forming aerosol particles in an accumulation mode. For $t > 10\tau_{rxn}$, reaction is insignificant, and coagulation completely dominates the aerosol evolution, bringing it back to a single-mode aerosol. As the aerosol returns to a single mode, the difference gradually reduces, but increases again for $t \gg 10\tau_{rxn}$. This is because the SRC model uses a monodisperse approximation for the two modes. Its predicted coagu-



a. t = 0.01 s

b. t = 10 s

c. t = 100 s

Figure 5. Evolution of the particle-size distributions.

k_A = 0.1 s^{-1} and initial concentrations of TTIP of 5.25×10^{-9} mol · cm^{-3} (——); 5.25×10^{-10} mol · cm^{-3} (- · - ·); and 5.25×10^{-11} mol · cm^{-3} (- - -).

lation rates are smaller than those from the more detailed D-S model, causing the difference between the two models to increase when integrated over time. Since the mass of the clusters is relatively small, the discrepancy between the mass concentrations is also small.

Figures 5a–c show the effects of the initial vapor concentration on the evolution of the aerosol-size distribution calculated using the D-S model for $k_A = 0.1\ s^{-1}$. The shapes of the size distributions are very similar to each other. The average particle size at a given time increases with increasing initial vapor concentration.

From the above calculations, we observe that coagulation plays an important role in the evolution of refractory aerosols produced in isothermal systems. The reason for the lack of dependence of the ultimate shape of the particle-size distribution on the reaction rate is that large numbers of particles are produced in the initial nucleation burst. Since the second-order coagulation process is very important at such high number concentrations, it dominates once the reaction is completed.

Growth of seed particles

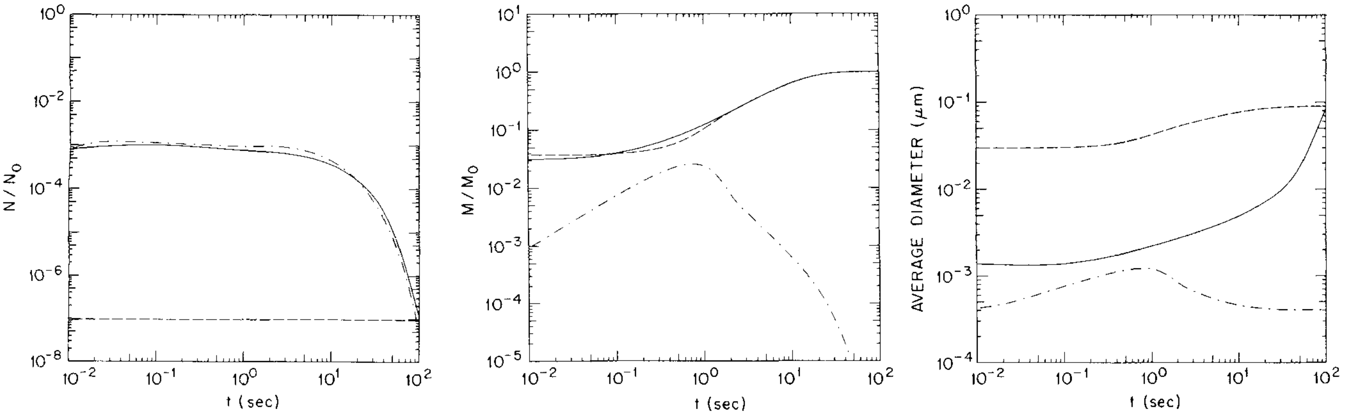
Supermicron-size particles can be grown in typical aerosol reactor residence times if seed particles are introduced along with the gaseous reactants, provided the reaction rate is limited to favor seed growth by vapor and/or cluster deposition instead of allowing nucleation of new stable particles (Alam and Flagan, 1986). Wu and Flagan (1987b) have shown that very small changes in reactor operation can make the difference between successful growth of the seed particles and runaway nucleation. Important features of the growth of seed particles can be seen using the aerosol models. We begin with seed particle growth at fixed rate constants.

Figures 6a–c represent the normalized number and mass concentrations, and number-averaged diameter, respectively, calculated for an initial TTIP concentration of 5.25×10^{-10} mol · cm^{-3}, a 0.03 μm monodisperse seed aerosol concentration of 3×10^7 cm^{-3}, and $k_A = 0.1\ s^{-1}$. The solid lines represent the results calculated using the D-S model. The number and mass concentrations here are normalized total concentrations, since the D-S model does not allow tracking of the seed and nucleated particles separately. The dashed and dashed-dotted lines represent the seed and nucleated particles, respectively, calculated by the SRC model. The normalized number and mass concentrations calculated by these two models, Figures 6a–b, for seed growth dominant conditions, show excellent agreement.

Figures 6a–c show that it is possible to grow seed particles while suppressing nucleation, provided the reaction is sufficiently slow. The time to complete the reaction is long, on the order of 100 s or longer. An aerosol reactor with such residence time would be very large. Increasing the reaction rate would decrease the required residence time and reactor volume, but could easily result in runaway nucleation. Consider what would happen if seed particles were introduced into a high source rate reactor. This is illustrated in Figures 7a–c for $k_A = 100\ s^{-1}$. It is apparent that the seed particles do not begin to grow until reaction is nearly completed. Instead, the fast reaction leads to the production of a large number of small nuclei that grow by coagulation. Only at long times do they begin to coagulate with the seed particles to an appreciable extent. Thus, the seed particles have little effect if the reaction rate is too high. Obviously, there is a middle ground between these two cases. However, there are better approaches for the growth of seed particles.

Particle Growth in Nonisothermal Reactors

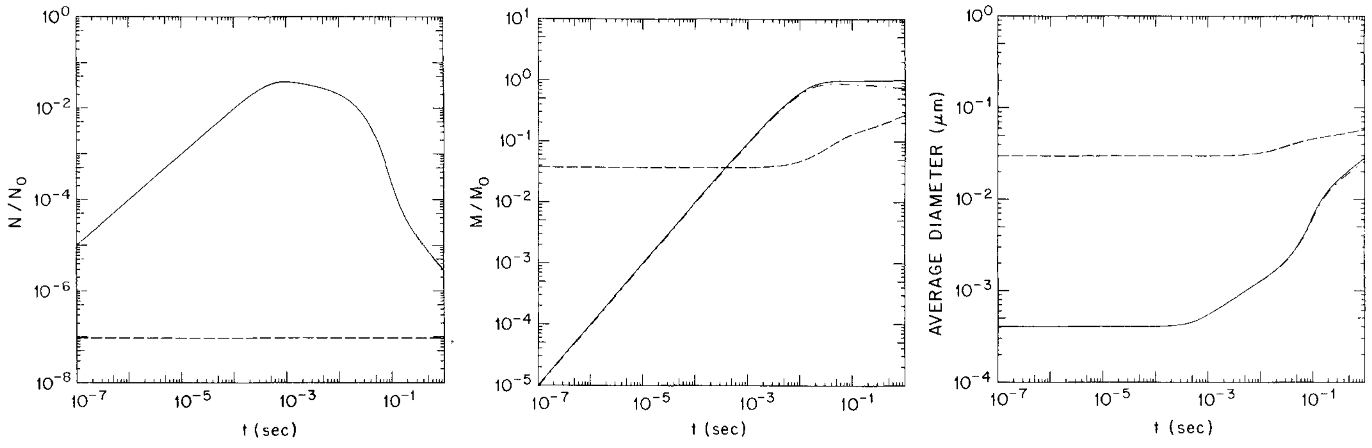
Alam and Flagan (1986) demonstrated that seed particles could be grown to supermicron sizes with limited residence times if the reaction rate is initially low and gradually accelerated as the particles grow and scavenge condensible reaction products at increasing rates. The ability of a growing seed aerosol to suppress nucleation in a reactor with a reaction rate that increases with time is illustrated by the number (dashed lines) and mass (solid lines) distributions shown in Figure 8. In all cases, the reaction rate profiles are designed to ensure complete reaction within a 50-s residence time. Like the constant rate case, the linear rate variation, Figures 8a–b, results in new particle formation and a broad, coagulation dominated aerosol. Figures 8c–d clearly demonstrate that nucleation can be eliminated



a. Total number concentration normalized by N_O. b. Total mass concentration normalized by M_O. c. Number averaged particle diameter.

Figure 6. Comparison of the results from the D-S and SRC models for an initial TTIP concentration of 5.25×10^{-10} mol · cm^{-3}, 0.03-μm seed particle concentration of 3×10^7 cm^{-3}, and $k_A = 0.1\ s^{-1}$.

— results from the D-S model.
– – – seed particles from the SRC model.
– · – · new particles from the SRC model.



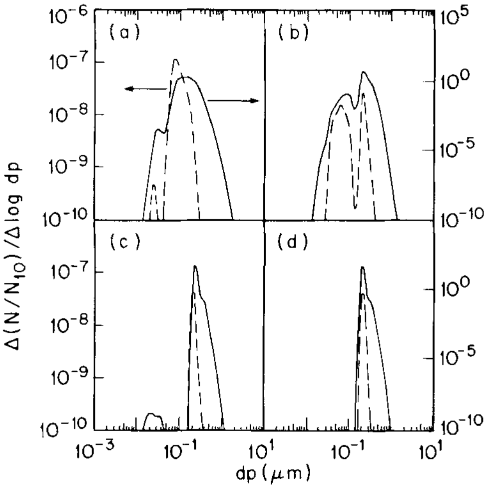
a. Total number concentration normalized by N_O. b. Total mass concentration normalized by M_O. c. Number averaged particle diameter.

Figure 7. Results from the SRC model for the case with 3 × 10^7 cm^{-3} of 0.03-μm seed particles, initial TTIP concentration of 5.25 × 10^{-10} mol · cm^{-3}, and k_A = 100 s^{-1}.

— without seed particles.
--- seed particles.
-·-· nucleated particles.

effectively if the initial rate is very low and the rate is accelerated as the particle grows.

Submicron particles of relatively uniform size can be grown in a single-stage reactor without the introduction of seeds by beginning the reaction at a very low rate, allowing a small fraction of the precursor to produce seed nuclei *in situ* by homogeneous nucleation. The reaction rate is slowly accelerated to promote growth by vapor and cluster deposition as the small particles grow and become increasingly effective vapor scavengers. This technique has been demonstrated experimentally and theoretically by Wu et al. (1986, 1987a) in the production of uniformly-sized silicon particles by silane pyrolysis. The gradual increase in the reaction rate was achieved by increasing the temperature along the length of a tubular reactor. Their calculations were carried out using the rate expression for the rate-limiting step reported by Purnell and Walsh (1966), $SiH_4 + M \rightarrow SiH_2 + H_2 + M$. The nucleating and condensing species were assumed to be elemental silicon. The evolution of the particle-size distribution (Wu et al., 1987a) is shown in Figure 9. We see that the concentrations of small clusters are high initially, but decrease rapidly by coagulation. The slow reaction allows the condensible products to be scavenged by the seed nuclei before the small clusters can grow to clusters too large to effectively diffuse to the existing seed particles. As a result, the particles grow appreciably at a relatively constant number concentration. Comparison of the particle-size distributions in Figure 9 and those in Figures 2a–c shows that the size distribution is substantially narrower when growth is by vapor and cluster deposition rather than coagulation.



a. $k_A = 0.1$ s^{-1}.
b. $k_A = 0.05 + 0.002t$ s^{-1}.
c. $k_A = 0.033 + 0.0013t + 0.00004t^2$ s^{-1}.
d. $k_A = 0.025 + 0.001t + 0.00006t^2$ s^{-1}.

Figure 8. Particle number and mass distributions, starting with an initial TTIP concentration of 5.25 × 10^{-10} mol · cm^{-3} and 0.205-μm seed particle concentration of 2.44 × 10^6 cm^{-3} at time t = 50 s.

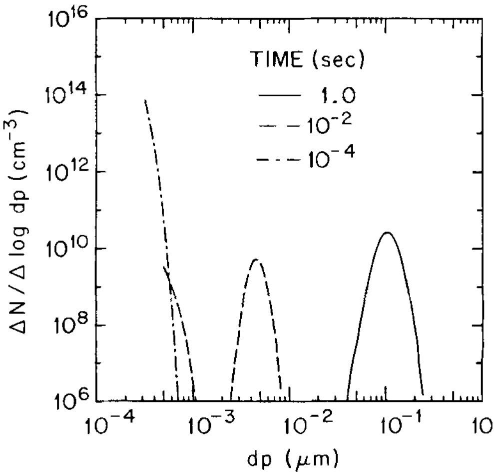


Figure 9. Aerosol size evolution starting with an initial vapor concentration of 5.25 × 10^{-7} mol · cm^{-3} and a gradually increasing reaction rate (After Wu et al., 1987a).

Conclusion

The reaction rates in aerosol systems used to synthesize fine particles commercially, namely thermal, flame, and plasma reactors, can vary over orders of magnitude. However, the physical processes that control the particle evolution in all these systems are the same, namely reaction and coagulation.

Two models for aerosol evolution in powder synthesis were described. Numerical solutions to the general dynamic equation for aerosols that takes into account the discrete nature of the small cluster sizes, while remaining practical for the description of the growth of large particles, were obtained using the discrete–sectional model. An approximate method that follows the growth of both seed and homogeneously-nucleated particles was developed. The results from the simplified reaction-coagulation model were shown to agree closely with those of the more exact model for a wide range of reactor operating conditions. Hence, it is a useful tool for the preliminary characterization of reactor operation under a particular set of operating conditions.

Using these models, several features of aerosol reactor operation have been demonstrated. Growth of refractory particles in either a high source rate or a constant source rate operation is dominated generally by coagulation that results in broad particle-size distributions that do not differ appreciably from one system to another regardless of the initial reactant concentration. Seed particles can be grown in isothermal reactors, but the rate must be very low, leading to unrealistically long residence times. On the other hand, if the rate is initially kept low and accelerated as the seed nuclei grow and become more effective at scavenging condensible reaction products and small clusters, the formation of new stable particles by homogeneous nucleation can be effectively suppressed. The particles can thus be grown significantly. Uniformly-sized submicron particles also can be synthesized in a single-stage reactor without the use of externally produced seed particles. This can be accomplished by initially reacting a small amount of reactants at a very small rate to produce seed nuclei *in situ*. The reaction rate can then be increased gradually to insure growth by deposition and complete consumption of the reactants in available residence time.

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