

The Effect of CVD Reaction Variables on SnO₂ Powder Characteristics

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Ultrafine SnO₂ powder was prepared by the diffusion mixing gas-phase reaction of SnCl₄(g) and water vapor. The effects of reaction variables, such as the chloride partial pressure, the reaction temperature, and the residence time in the reactor, on the powder size were examined systematically. Calculated concentration and distribution of chemical species, using the Burke-Schumann diffusion mixing model, were compared with the experimental results. The effects of the reaction variables on the powder size were also discussed qualitatively.

Key words : Reaction variables, CVD reaction, Powder characteristics, Diffusion mixing, Chemical species

I. Introduction

Chemical vapor deposition (CVD) process is a promising method for the production of various ultrafine powders. For that reason, many studies have been carried out so far. However, most of the literature are concerned with the reaction conditions for the synthesis of ultrafine powders and the characteristics of the powders produced. There is a lack of any systematic analysis of the reaction processes that occur during the CVD process for the powder synthesis, that could predict the prepared powder characteristics, such as particle size, shape, and size distribution, depending on the reaction variables and conditions.

Previously, Friedlander¹⁾ has shown, on the basis of coagulation theory for the formation and growth of particles by the homogeneous nucleation in the gaseous phase, that the average size of particles was proportional to the volume density, the reaction temperature, and the coagulation time. It should be mentioned that even though Elliott et al.²⁾ performed their calculation earlier for the formation of metal-oxide aerosols from the gaseous phase system, assuming that there would be a concentration of chemical species in the reaction, so far there has been no attempt to check the applicability of this kind of calculation experimentally.

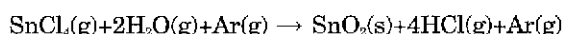
In this study, ultrafine SnO₂ powder was prepared through the diffusion mixing reaction of SnCl₄(g) and water vapor. The effects of the reaction variables, such as partial pressure of reactant gases, reaction temperature and residence time in the reactor, on powder size were investigated. Also, since the reaction would occur in a gaseous-phase reaction system with multi-component steady state flow, the concentration and the distribution of the early stage chemical species by means of the Burke-Schumann³⁾ model were calculated and compared with

the experimental results.

As a consequence, some useful information as to the effects of those variables on the size of powder could provide. And it would be expected that the present study can be useful for the precise control of reaction and in designing the reactor.

II. Experiments

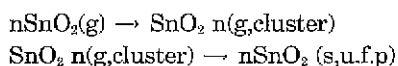
The governing reaction for the formation of ultrafine SnO₂ powder from the starting materials of SnCl₄(g) and 2H₂O(g) can be described as follows :



An axis-symmetrical cylindrical reactor was used for the preparation of fine SnO₂ powders by the diffusion mixing CVD reaction, with the following range of conditions; chloride partial pressure 0.4~11.2 kPa, water vapor partial pressure 0.3~2.2 kPa, reaction temperature 973~1223 K and the residence time in the reactor 0.18~1.11 sec, respectively. The diffusion mixing reaction occurs in the system between the supplying SnCl₄(g) which is diluted by Ar in inner side nozzle and H₂O(g) which is also diluted by Ar in the surrounding reactor.

III. Modeling of Burke-Schumann and Calculation

Fig. 1 illustrates the schematic of the diffusion mixing CVD reactor and the mechanism of particle formation. The coagulation of particles in the system can be described as follows :



The governing parameter for growth of particles would

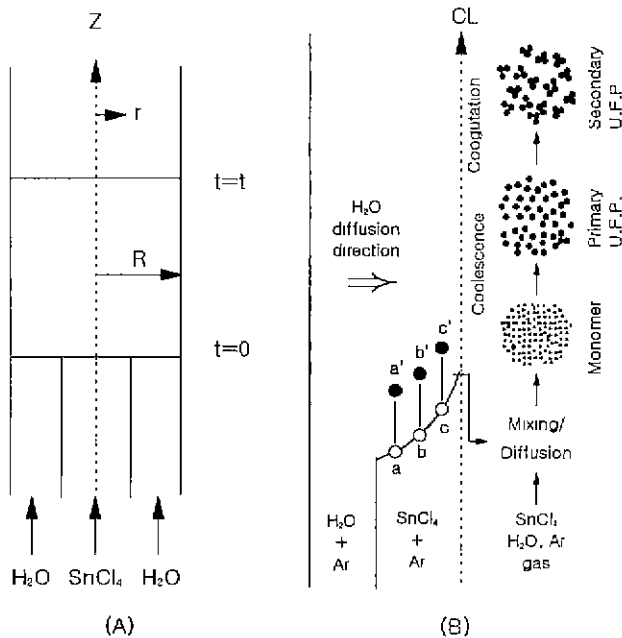


Fig. 1. (a) Schematic of CVD reactor used for the preparation of ultrafine powders (U.F.P) and (b) illustration of the reaction process that occurs inside the reaction chamber.

be regarded as a simple coagulation of particles in the reaction system.

The difference of diffusion mixing rate of source materials, according to reaction variables and conditions, would change the concentration and concentration distribution of chemical species in the reactor.

This is the basis of the model used by the Burke-Schumann diffusion mixing model⁹⁾ and also often used in the analysis of the diffusion mixing reaction¹⁻⁶⁾:

$$\partial C / \partial t - 1/r \cdot \partial / \partial r (rD \partial C / \partial r) = S$$

$$\text{B.C.: } \partial C / \partial r = 0 \text{ and } C = 0 \text{ at } r = 0.$$

$$\text{At } t = 0, C = C_0 \text{ for } r \leq R \text{ and } C = 0 \text{ for } r > R,$$

where C is the concentration and D is the diffusion coefficient⁷⁻⁹⁾ of source materials in the multi-component system, r is the radius of cylindrical reactor and S is the reaction rate of the reaction system, respectively.

The diffusion in the multi-component system could be calculated from

$$J_i = -C^2 / \rho \cdot M_i M_j D_{ij} \nabla X_j$$

where J and ρ are the flux and the density of chemical species and M is molecular weight of source materials.

Hirschfelder-Curtiss-Bird⁷⁾ suggested that the calculation of diffusion coefficient in the multi-component system is easy to repeat the calculation of diffusion of two-component. The diffusion coefficient (D_{ij}) of two-component system could be calculated from Lennard-Jones potential model.¹⁰⁾

The calculation, on the basis of the particles formation and growth model as above to predict which chemical

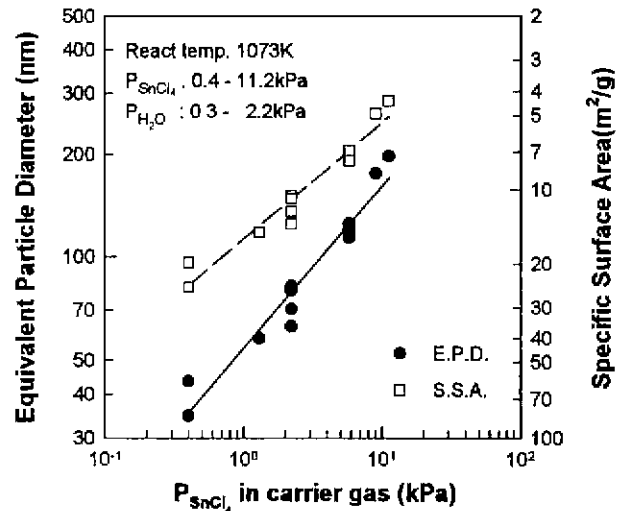


Fig. 2. Effect of P_{SnCl_4} on equivalent particle diameter and specific surface area.

species are being produced at the early stage and then how they grow by the physical coagulation, was performed. The concentration and concentration profile of the formed chemical species is described by the convection-diffusion equation.

IV. Results and Discussion

Fig.2 showed the particle size of powders prepared at 1073 K, with the water vapor partial pressure in the range of 0.3~2.2 kPa and the SnCl_4 partial pressure in the range of 0.4~11.2 kPa. The particle diameter, formed under the condition of the reaction temperature 1073 K, water vapor 2.2 kPa with changing the partial pressure of $\text{SnCl}_4(\text{g})$ 0.4, 2.2, 5.8 kPa was 34.70 nm (24.9 m^2/g), 62.83 nm (13.7 m^2/g), 113.59 nm (7.6 m^2/g), respectively. The equivalent particle diameter was calculated from the results of specific surface area measurements.

It is to be noted that the particle size was increased with the increase of $\text{SnCl}_4(\text{g})$ in carrier gas.

Particle size growth showed similarity when compare with 0.4 order by the coagulation from Friedlander¹¹⁾ calculated.

But, as seen in Fig. 2, even though the water vapor changed with the range of 0.3-2.2 kPa, the variation of particle size compared with $\text{SnCl}_4(\text{g})$ changed was not remarkable. This means that the diffusion rate of $\text{SnCl}_4(\text{g})$ which diffused slowly into reaction zone, mostly affected the formation and concentration distribution of chemical species than that of water vapor which diffuses fast.

Fig. 3 showed the calculated concentration and distribution of the chemical species using the model of the one-dimensional multi-component diffusion reaction.¹⁰⁾ The gas-phase reaction was assumed to occur diffusively by mixing of $\text{SnCl}_4(\text{g})$ with $\text{H}_2\text{O}(\text{g})$ at 1273 k; the conditions of $P_{\text{H}_2\text{O}}=2.2$ kPa and $P_{\text{SnCl}_4}=0.4$ kPa (curve A), 2.2

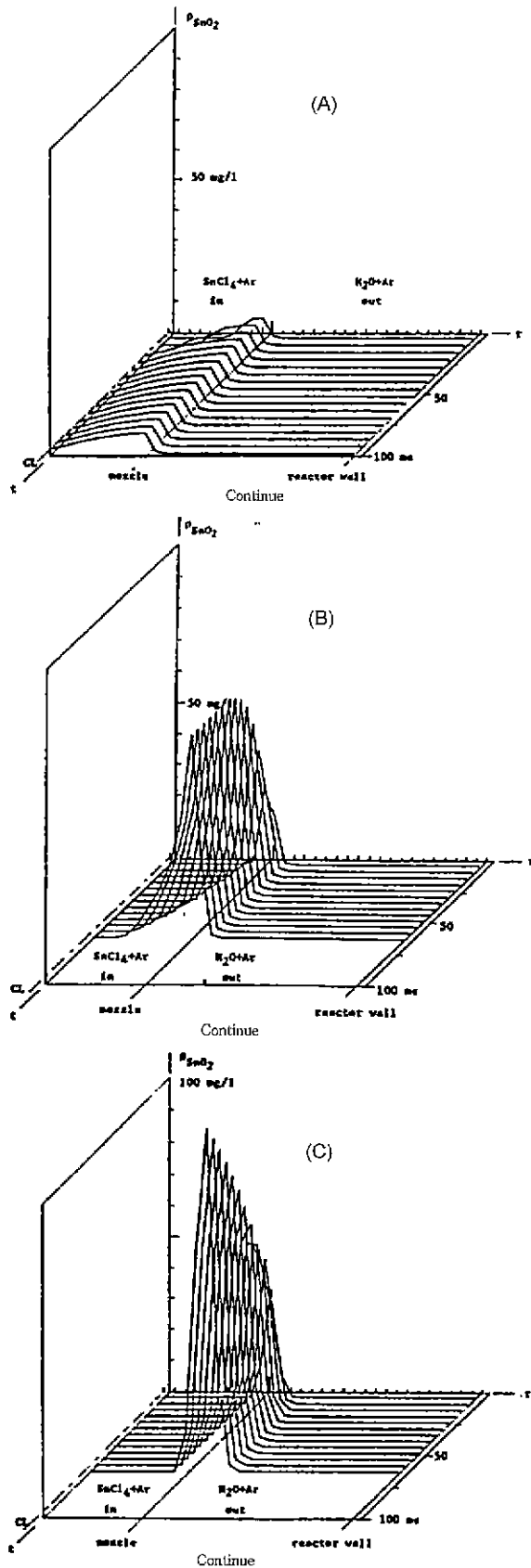


Fig. 3. Concentration profile of the chemical species at the reaction temperature 1273K and P_{H₂O} 2.2 kPa, P_{SnCl₄} (A) 0.4 kPa, (B) 2.2 kPa, (C) 5.8kPa

kPa (curve B) and 5.8 kPa (curve C) was set and the coagulation time was varied up to 100 ms.

For P_{SnCl₄}=0.4 kPa (curve A), the chemical species were mostly formed in the inner wall of the nozzle supplying the chloride and the concentration was distributed fairly homogeneously throughout the nozzle. The formation of chemical species was mostly ended within about 10 ms. At higher SnCl₄(g) (curve C), the concentration of the formed chemical species was higher and the reaction occurred sequentially. In addition, the high concentration zone of chemical species in the reactor moved towards the nozzle wall supplying chloride, as the SnCl₄(g) became higher and the reaction area became narrower.

In the case of low SnCl₄(g), H₂O(g) diffused rapidly to the dilute SnCl₄(g) and the formation reaction proceeded in the homogeneously mixing state. On the other hand, in the case of high SnCl₄(g), H₂O(g) diffused slowly to dense SnCl₄(g) and the position of reaction boundary moved towards the nozzle wall. When the reaction occurred in the narrow area of the upper side of nozzle wall (curve C), it was expected that growth by surface reaction, as well as coagulation, would take place.

Fig. 4 showed when the reaction temperature was increased from 973 to 1223 K, under the conditions of P_{H₂O}=2.2 kPa and P_{SnCl₄}=0.4, 2.2, 5.8 kPa, the particle diameter of powders changed accordingly. For P_{SnCl₄}=2.2 kPa and P_{H₂O}=2.2 kPa, the respective average particle sizes became 89.93 nm (9.6 m²/g) at 973 K, 79.86 nm (10.8 m²/g) at 1073 K and 38.87 nm (22.2 m²/g) at 1223 K. This clearly showed that the particle size decreased as the reaction temperature was increased. The temperature dependence of the particle size as predicted by Friedlander's coagulation model¹⁾ was different from the observation made in this study in that it predicts an increase of particle size, being proportional to 0.2 order of the temperature.

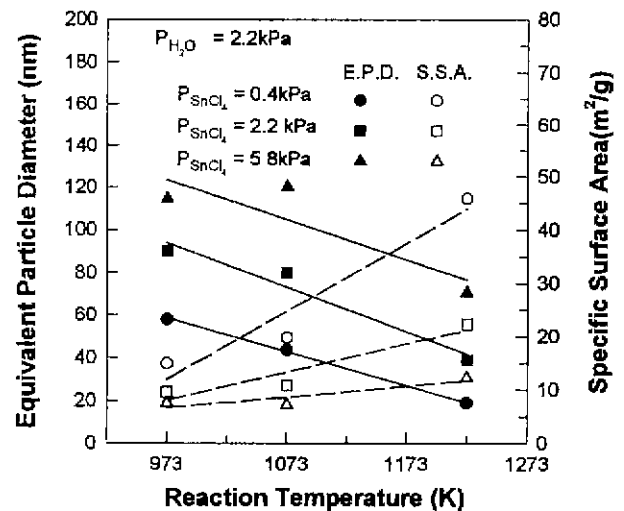


Fig. 4. Effect of reaction temperature on equivalent particle diameter and specific surface area.

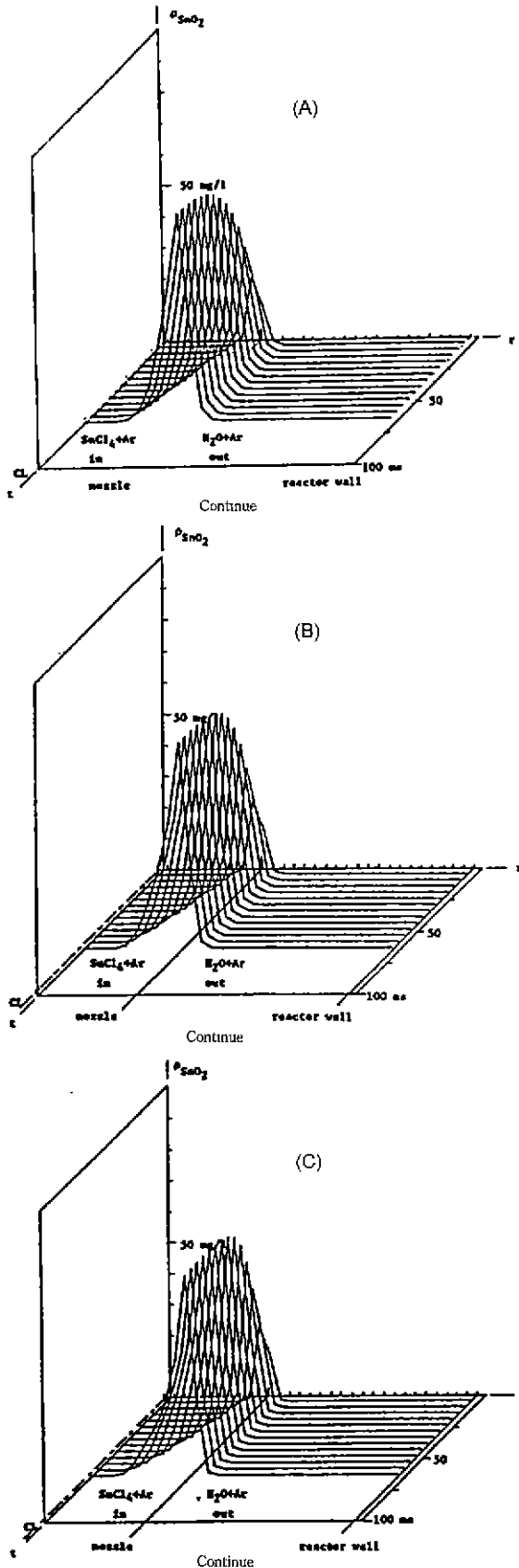


Fig. 5. Concentration Profile of the Chemical Species at the Reaction Temperature (A) 1073 K, (B) 1173 K and (C) 1273 K

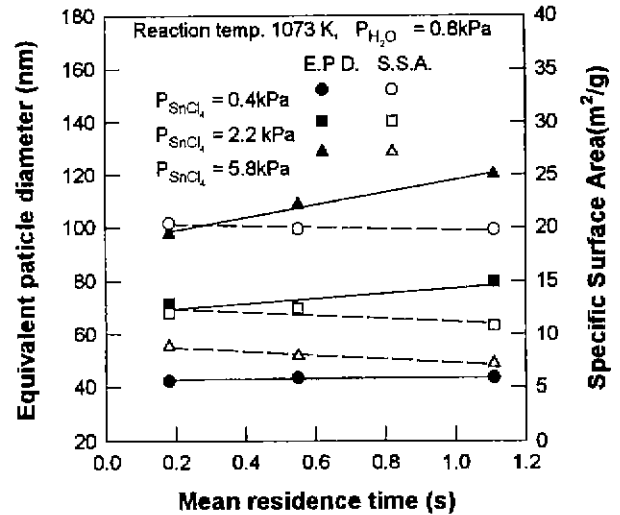


Fig. 6. Effect of residence time on equivalent particle diameter and specific surface Area.

It is considered that the temperature plays a dominant role for the formation of chemical species in this process.

Fig. 5 showed the calculated results of the effects of the reaction temperature on the concentration of formed chemical species as the reaction temperature changed from 1073 K (A), 1173 K (B), to 1273 K (C) under the conditions of P_{SnCl_4} 0.4~2.2 kPa and P_{H_2O} 2.2 kPa. At 1073 K (A), the early stage formation of SnO_2 the chemical species, occurred preferentially in the narrow area of the upper position on the inner wall change of nozzle supplying the chloride. Even though the reaction temperature changed from 1173 K to 1273 K, the concentration of SnO_2 , chemical species, in the temperature range of this calculation, was not remarkable. The reason for this seems to be caused by the fast diffusion and the formation of chemical species.

Fig. 6 showed the variation of the observed powder size with changing residence time in the reactor, 0.18~1.11 sec, under the condition of 1073 K, P_{H_2O} 0.8 kPa, P_{SnCl_4} 0.4~5.8 kPa. In case of high $SnCl_4(g)$ of, 5.8 kPa, the powder size increased with the increasing residence time in the reactor. In case of low $SnCl_4(g)$ of, 0.8 kPa, however, the residence time had little effect on the size of particles produced. This observation was also different from the prediction by Friedlander's coagulation theory¹⁾ which indicated that the particle size should increase, being proportional to 0.4 order of coagulation time.

From the calculated results of Figs. 3 and 5, it was to be noted that with low $SnCl_4(g)$, the coagulation was finished within 10 ms, while in high $SnCl_4(g)$ the reaction is continuously going on by coagulation and surface reaction. In this study, within the range of reaction conditions, the formation and coagulation was completed instantly at the early stage of reaction, so that it was reasonable to assume that the residence time in the reactor had little effect on the growth of the particle.

V. Conclusions

In the preparation of ultrafine powders of SnO₂ through the diffusion mixing CVD reaction, the effect of the reaction variables, such as SnCl₄(g) partial pressure, the reaction temperature, the residence time in the reactor, on the size of particle, the concentration and the distribution of chemical species was examined. As the result, it was acknowledged the correlation of the concentration and distribution of chemical species with the size of formed particles and was explained the result of the experiments by means of the diffusion mixing model. Finally, in the diffusion mixing CVD reaction, the calculation of concentration and distribution of chemical species for the formation and growth, might be useful to predict the particle characteristics and for the precise control of reaction.

Acknowledgment

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