Experimental verification of direct surface reaction model in an aerosol reactor

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Abstract

Nanometer-sized titania particles were prepared by thermal decomposition of titanium tetraisopropoxide (TTIP) in a furnace type aerosol reactor. Direct surface reaction (DSR) model was introduced because simple reaction coagulation (SRC) model, which is valid at high conversion, was found to be improper at high concentration and low conversion. The size of titania particles increased from 10 to 60 nm with increasing input concentration of TTIP from $7 \times 10^{-10}$ to $2 \times 10^{-8}$ mol/mL. Experimentally, the particle size was proportional to the $0.46^{th}$ power of the precursor concentration and this result was closer to the prediction of DSR model than that of the SCR model. The SCR model predicted that the exponent was 0.171. The diameter of product particles was decreased from 55 to 30 nm as the reaction temperature was increased from 250 to 550°C. The DSR model predicted the decreasing trend of the particle size with increasing temperature, whereas the SRC model simulation predicted that the size was an increasing function of the temperature.

Key words: Nanosize particles, Aerosol reactor, Direct surface reaction

1. INTRODUCTION

Preparation of nanosize particles in an aerosol reactor had been extensively investigated and designed, and analysis of the aerosol reactor became more predictable than ever. It is generally accepted that the size increases as the residence time, reactor temperature or input reactant concentration was increased. This tendency, however, has not been rigorously examined. Especially, the effect of temperature on the size has been controversial. Some experimental results show that the size is an increasing function of the temperature. Others report the reverse tendency.

A simple reaction and coagulation (SRC) model proposed by Wu et al. (1988) predicts that the size should be an increasing function of the temperature and input concentration. This model also shows that the reduced residence time due to the temperature rise does not account for the decrease of particle size. Therefore, we propose a new model that predicts the sharp dependency of size on the input concentration and the decreasing dependency of size on the temperature. Experimental results that confirm the validity of the current model are also reported.
2. MODELING OF THE PARTICLE GROWTH

The simple reaction and coagulation (SRC) model was proposed for overcoming calculational complexity of general dynamic equation (GDE). The SRC model gives valuable information regarding the operation of aerosol reactors without much calculation required in GDE. This model can also be used to find out quickly whether a given set of reactor conditions would result in growth or nucleation dominant operation. The SRC model predicts the average particle size, not the size distribution. Wu et al. (1988) showed that the result from the SRC model agreed closely with those of the more rigorous model for a wide range of reactor operating conditions.

In the SRC model, surface reactions with precursor gas were ignored for the purpose of calculational simplicity. The assumptions of SRC model was described in Table 1. However, when the decomposition of precursor occurs not only in gas phase but also on the surface of titania particles, the size and number concentration of particles are affected by the ratio of gas phase reaction to surface reaction. This model is named as a direct surface reaction (DSR) model. The difference between SCR model and DSR model was described in Table 2.

The governing equation of the number concentration and the mass concentration of particles are following.

Number balance:  
\[
\frac{dN_p}{d\tau} = k_r N_A m_1 - K_p N_p^2 \tag{1}
\]

where \( N_p \) = particle number concentration [#/cm³]
\( \tau \) = residence time [s]
\( k_r \) = reaction rate constant [s⁻¹]
\( N_A \) = number concentration of precursor [#/cm³]
\( K_p \) = collision kernel [cm³/s]

The relation between the conversion of the precursor and the number concentration of the precursor is

\[
N_A = N_{A0}(1-x_A) \tag{2}
\]

where \( N_{A0} \) = input number concentration of precursor at \( \tau = 0 \)
\( x_A \) = conversion of precursor

Combining Eq. (1) and Eq. (2) and dividing by \( k_r N_{A0} \), we have

\[
\frac{d(N_p/N_{A0})}{d(k_r \tau)} = (1-x_A) - K_p \left( \frac{N_{A0}}{k_r} \right) \left( \frac{N_p}{N_{A0}} \right)^2 \tag{3}
\]

and the mass concentration of particles is following.

Number concentration balance:

\[
\frac{dY}{dX} = e^{-x_A Y^2} \tag{4}
\]

Mass concentration balance:

\[
\frac{dZ}{dX} = (1-x_A) \left[ 1 + RZ \right] \tag{5}
\]

Where \( X = \text{dimensionless time, } k_r \tau \)
\( Y = \text{dimensionless number concentration (DNC), } N_p/N_{A0} \)
\( A = \text{dimensionless collision kernel, } K_p/(N_{A0}/k_r) \)
\( Z = \text{dimensionless mass concentration (DMC), } M_p/N_{A0} m_1 \)
\( R = \text{ratio the surface reaction constant to the gas phase reaction constant, } k_s \pi d_p^2 N_{A0}/k_r \)

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\]
Simplifying Eq. (3) with dimensionless variables, then
\[ \frac{dY}{dX} = (1 - x_A) - AY^2 \]  
(4)

where \( X \) = dimensionless time, \( k_r \tau \) \( Y \) = dimensionless number concentration (DNC), \( N_p/N_{A0} \) \( A \) = dimensionless collision kernel, \( K_p(N_{A0}/k_r) \)

Mass balance:
\[ \frac{dM_p}{d\tau} = k_r N_{A0} m_1 + k_s (\pi d_p^2) N_p N_A \]  
(5)

where \( M_p \) = particle mass concentration \([\text{g/cm}^3]\) \( m_1 \) = mass of monomer \([\text{g/#}]\)

Substituting Eq. (2) into Eq. (5) gives
\[ \frac{dM_p}{d\tau} = k_r N_{A0}(1 - x_A)m_1 + k_s (\pi d_p^2) N_p N_{A0}(1 - x_A)m_1 \]  
(6)

\[ d_p = \left( \frac{6}{\pi \rho_p} \frac{M_p}{N_p} \right)^{\frac{1}{3}} = d_1 \left( \frac{Z}{Y} \right) \]  
(7)

where \( Z \) is a dimensionless mass concentration (DMC), \( M_p/N_{A0}m_1 \)

Dividing Eq. (6) by \( k_r N_{A0}m_1 \) and substituting Eq. (7) into Eq. (6) we have
\[ \frac{d(M_p/N_{A0}m_1)}{d(k_r \tau)} = (1 - x_A) \left[ 1 + \frac{k_s (\pi d_p^2)}{k_r N_{A0}} \left( \frac{M_p}{N_p N_{A0}} \right)^{\frac{1}{3}} \left( \frac{N_p}{N_{A0}} \right) \right] \]  
(8)

Simplifying Eq. (8) with dimensionless term, then
\[ \frac{dZ}{dX} = (1 - x_A) \left[ 1 + RZ^\frac{2}{3} Y^\frac{1}{3} \right] \]  
(9)

where \( R \) is a ratio of the surface reaction constant to the gas phase reaction constant, \( k_s (\pi d_p^2) N_{A0}/k_r \), and \( d_1 \) is a monomer diameter.

Chemical reaction:
\[ \frac{dN_A}{d\tau} = k_r N_{A0} \]  
(10)

Substituting Eq. (2) into Eq. (10) gives
\[ \frac{dx_A}{d(k_r \tau)} = k_r N_{A0}(1 - x_A) + k_s (\pi d_p^2) N_p N_{A0}(1 - x_A) \]  
(11)

Substituting Eq. (7) into Eq. (11) and dividing by \( k_r N_{A0} \) we have
\[ \frac{dx_A}{d(k_r \tau)} = (1 - x_A) \left[ 1 + \frac{k_s (\pi d_p^2)}{k_r N_{A0}} \left( \frac{M_p}{N_p N_{A0}} \right)^{\frac{1}{3}} \left( \frac{N_p}{N_{A0}} \right) \right] \]  
(12)

Simplifying Eq. (12) with dimensionless term, then
\[ \frac{dx_A}{dX} = (1 - x_A) \left[ 1 + RZ^\frac{2}{3} Y^\frac{1}{3} \right] \]  
(13)

It should be noted that, in the DSR model, the conversion \( x_A \) is a function of \( Z \) and \( Y \).

### 3. MATERIAL AND METHODS

Titania particles of controlled size were obtained by decomposing the titanium tetraisopropoxide (TTIP) in a tubular type aerosol reactor, of which detail is reported elsewhere (Kim et al., 1994). Particles were prepared by varying the reactor temperature between 280 and 540°C. Precursor concentration were varied between \( 7 \times 10^{-10} \) and \( 2 \times 10^{-8} \) mol/mL by adjusting the speed of syringe pump. The experimental conditions were summarized in Table 3. The residence time in the reactor was 3 ~ 4 sec. The conversion of the TTIP into titania was measured by analyzing the propylene at the exit of

<table>
<thead>
<tr>
<th>Table 3. The conditions of experiment.</th>
</tr>
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<tbody>
<tr>
<td><strong>The type of carrier gas and auxiliary gas</strong></td>
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<td><strong>The rate of carrier gas</strong></td>
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<td><strong>The Temp. of feed line</strong></td>
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<td><strong>The Temp. of reactor</strong></td>
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<td><strong>The concentration of TTIP</strong></td>
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<td><strong>The residence time</strong></td>
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the reactor by gas chromatograph with flame ionization detector. For measurement of particle size, the titania particles were collected at a fixed interval. The size of titania particles was measured by using TEM.

4. RESULTS AND DISCUSSIONS

Conversion of TTIP at the various initial concentration of TTIP was shown in Figure 1. The reactor temperature was set at 430°C and the temperature of the feed line was kept at 170°C. The rate of feed flow was maintained at 1 L/min, and the auxiliary flow was fixed at 1 L/min. The initial concentration of TTIP was controlled by adjusting pumping rate of syringe pump. The reactor wall was precoated with titania. As shown in Figure 1, the conversion of TTIP decreases from 100 to 77% with an increasing initial concentration from $7 \times 10^{-10}$ and $2 \times 10^{-8}$ mol/mL.

The order of reaction and rate constant at temperature, 430°C, were calculated from the experimental data. The order of reaction ($n$) was assumed to be less than 1, because the thermal decomposition of TTIP occurs more on titania surface than in a gas phase in which the order reaction is 1. The calculation was carried out by the following equation which is the general performance equation of plug flow reactor for the $n^{th}$-
order reaction.

\[
\frac{k}{C_{A0}^{1-n}} = \frac{1-(1-x_A)^{(1-n)}}{\tau (1-n)}
\]  

where \(k\) is a rate constant, \(C_{A0}\) is an initial concentration of TTIP, \(n\) is the order of reaction, \(\tau\) is the residence time of reactant in the reactor and \(x_A\) is a conversion of TTIP. In Figure 2, \(1/C_{A0}^{(1-n)}\) vs \([1-(1-x_A)^{(1-n)}]/[\tau (1-n)]\) was plotted. The experimental data shows a good linearity when \(n\) is 0.7 and the rate constant, the slope, is 0.0022 (mol\(^{0.3}/\)mL\(^{0.3}\) sec).

The size of as-prepared particles was measured from TEM photographs. The mean diameter of particles with changing the initial concentration of TTIP was shown in Figure 3. The mean size of particles was increased from 10 to 60 nm with increasing the initial concentration of TTIP. The TEM photographs of titania particles made in this experimental condition was shown in Figure 4. As shown in Figure 3, the change of particle size in DSR model was more sensitive than that in SCR model, since \(R\), the ratio of surface reaction to gas phase reaction, was increased as the input concentration of TTIP was increased. The particle size predicted by the SRC model was proportional to the 0.17\(^{th}\) power of TTIP concentration, which underestimates the experimental value, 0.46. The value was 0.76, when it was
estimated by DSR model.

The particle size at various input TTIP concentration lies between the prediction of SCR and of DSR model.

When the concentration of input TTIP is increased, the initial concentration of condensable TiO₂ monomers which are produced from thermal decomposition of TTIP is increased. The increased monomer concentration of TiO₂ in gas phase results in a high supersaturated state. The droplet current increased as increasing the saturation ratio of monomer. According to the growth law, the size of particle which is produced at higher supersaturated state is also larger. Therefore, it is reasonable that the particle size is increased as initial concentration of TTIP is increased.

Our experimental results were compared with the results of Okuyama group (Okuyama et al., 1986, 1989; Wu et al., 1988). The experimental conditions of this group along with the current report were summarized in Figure 5. The number above the symbol is the size of particles. In Okuyama’s experiment, the particle diameter was 36 nm at 2 × 10⁻⁹ mol/mL of TTIP and 400°C. This particle size is larger than 23 nm produced at 3 × 10⁻⁹ mol/mL of TTIP and 430°C in our experiment. Two experiments were carried out until TTIP was completely exhausted. In spite of the input concentration of TTIP is higher in our experiment than that in Okuyama’s experiment, we had a smaller parti-

Figure 5. Summary of experimental conditions in Okuyama group and this work.

Figure 6. Change in conversion of TTIP with reaction temperature (The initial mole flow rate of TTIP: 3 × 10⁻⁵ mol/min, The total flow rate of carrier gas: 2 L/min).

Figure 7. Change in particle size of TiO₂ with reaction temperature (The initial mole flow rate of TTIP 3 × 10⁻⁵ mol/min, The total flow rate of carrier gas: 2 L/min).
This phenomenon is thought to be caused by the difference of residence time. The residence time is 14 sec and 3.5 sec for Okuyama’s experiment and our experiment respectively. Therefore, the Okuyama’s particles which grew longer were larger in diameter than ours and, the size of particles strongly depended on collision rather than surface chemical reaction.

Temperature effects on the decomposition of TTIP were tested in an aerosol reactor. The change in conversion of TTIP with reactor temperature was summarized in Figure 6. The initial mole flow rate of TTIP was fixed at $3.4 \times 10^{-5}$ mol/min. The total flow rate of carrier gas, Helium, was maintained at 2 L/min. The conversion of TTIP was increased dramatically at temperatures between 250 and 300°C. The conversion of TTIP reached to unit at over 400°C. Figure 7 is a plot of the mean size of titania particles as a function of reaction temperature. The mean size of titania particles was decreased from 55 to 30 nm with increasing the reaction temperature from 280 to 540°C. TEM photographs of these particles were shown in Figure 8.

The slope predicted by the DSR model in Figure 7 was $-0.6 \times 10^{-3}$, which is the same negative slope of $-1.04 \times 10^{-3}$ in this report. Whereas, the slope predicted by the SCR model was positive. The DSR model was found to be a better model than the SCR model in
As shown in Figure 5, in Okuyama’s experiments, the size of particles was increased from 18.8 to 37.2 nm with increasing the reaction temperature. A higher concentration of TiO₂ vapor can be obtained from thermal decomposition at a higher temperature. Thus, the particle size distribution shifts to larger sizes as the reaction temperature is increased.

According to the nucleation theory, the size of critical nuclei is decreased with increasing temperature and, the number of nuclei is increased with increasing temperature. On the basis of our experimental results, TTIP was completely converted into the titania particles at the Okuyama’s experimental conditions. Therefore, it is suggested that the Okuyama’s experiments were carried out under the condition that the fast nucleation is dominant, in which the nucleation is terminated and collision of particles is a dominant growth mechanism. As a result, the growth of particles in Okuyama’s experiments is affected not by chemical reaction of TTIP but by the collision after chemical reaction.

However, the size of particles was decreased with increasing the reaction temperature in our experiments. Our experiments were carried out at a hundred times higher input concentration of TTIP and, shorter residence time than Okuyama’s experiments. The operating temperature is in the range from 250 to 550°C. The conversion of TTIP was less than unity, especially at below 350°C. Therefore, the degree of chemical reaction of TTIP affected the size of particles.

It is reasonable that the conversion is increased as the reactor temperature increases. But the particle size should have been also increased with the reaction temperature if the Okuyama et al.’s argument is correct. This discrepancy can be explained by the different operating conditions. At an early stage of the particle formation, large number of TiO₂ nuclei are formed as the reactor temperature is increased. And the heterogeneous condensations on to the particles are minimized. This becomes significant as the concentration of TTIP is increased and the conversion level is kept low. If the TTIP concentration is low and residence time is long, the Okuyama’s result would be obtained.

From Figure 2, the order of TTIP decomposition is found to be 0.7, when the initial TTIP concentration varies from $7.1 \times 10^{-10}$ to $2.1 \times 10^{-8}$. The activation energy and the frequency factor, determined from the Arrehenius plot (Figure 9), are 19150 J/mol and 0.0497 (mol⁰.³/mL⁰.³ sec), respectively.

5. CONCLUSIONS

From the study for the preparation of nanometer-sized titania particles in an aerosol reactor, the following conclusions were drawn.

The size of titania particles that were prepared by thermal decomposition of TTIP was increased from 10 to 60 nm with increasing the input concentration of TTIP from $7 \times 10^{-10}$ to $2 \times 10^{-8}$ mol/mL. The particle size was proportional to the 0.46th power of the precursor concentration. The exponent should be 0.171 if calculated by using the SRC model, which was not consistent with the experimental value. However, the proposed DSR model predicted the experimental result better than the SRC model.

The conversion of TTIP decreased with increasing
input concentration of TTIP. The rate of decomposition of TTIP increased with increasing input concentration of TTIP and, the rate of increase was proportional to $C_{A0}^{0.7}$, where $C_{A0}$ is an input concentration of TTIP.

The size of product particles decreased from 55 to 30 nm with increasing reaction temperature from 250 to 550°C. The DSR model predicted the decreasing trend of the particle size with increasing temperature, while the SCR model does not. The conversion and the rate of decomposition of TTIP increased with increasing reaction temperature. The constant of reaction rate was found to be

$$k=0.0492 \exp\left[\frac{-19150}{8.3141 \cdot T(K)}\right]$$

and the order of reaction was 0.7.

REFERENCES


