The Production of Some Ultrafine Particles
by Gas Phase Reactions in Aerosol Reactors†

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Abstract

This paper summarizes the authors’ recent studies on properties of TiO₂ and nickel powders produced by gas phase reactions in aerosol reactors. The weight-average diameter and polymorphism of TiO₂ particles at temperatures lower than 1200°C were virtually unchanged 5-cm downstream from the nozzle mouth, and the effects of the residence time of gas and the reaction temperature were not dominant. However, the mean diameter of nickel powders produced by the hydrogenation of NiCl₂ at 1380°C was close to the theory assuming instantaneous fusion of coagulated particles. The fraction of rutile was maximum at ca. 1000°C. These results imply the importance of the fusion rate of particles and the heterogeneous deposition rate from the gas phase.

1. Introduction

Gas phase reactions have been used to produce ultrafine particles with novel functions. Although overall stoichiometric reactions are normally simple, complicated kinetic steps such as nucleation, deposition and fusion are involved. The synthesis of ultrafine particles have been investigated by many authors⁴⁻⁶, ¹⁰⁻¹², ¹⁵⁻¹⁷, ²⁰⁻²⁴, but there are many aspects which require further research.

Titania usually exists in two polymorphic forms; anatase and rutile. The anatase phase is preferentially obtained at lower temperatures, while the rutile phase is the most stable at any temperature and pressure. Matsumoto et al.¹⁰), George et al.⁵) and Suyama et al.²⁰⁻²²) studied the influence of experimental conditions and additives in the gas phase on the properties of TiO₂ particles.

The present paper summarizes studies¹¹,¹²) on the production of TiO₂ and nickel particles by gas phase reactions. In particular, the effects of various operating conditions on the particle size and the polymorphic composition of TiO₂ produced by the oxidation of TiCl₄ without additives have been investigated¹¹). The growth mechanism of nickel particles produced by the hydrogenation of NiCl₂¹²) is also cited in relationship to TiO₂ particles.

2. Experiment apparatus and procedure

2.1 TiO₂ production

The first series of the experiment¹¹) was carried out by using a reactor consisting of two mullite tubes with an inside diameter of 30 mm and length of 600 mm connected in series. The temperature inside the tubes was measured with 0.1 mm diameter platinum/platinum rhodium thermocouples. The reactor was heated by means of a resistance heater. The heated length of each furnace was 390 mm. Nitrogen and oxygen were dried over silica gel and in an ethanol-dry ice trap. TiCl₄ was of reagent grade quality. The TiCl₄ vapor was fed into the center of the reactor through an alumina nozzle of inside diameter 4 mm and outside diameter 6 mm, and it reacted with the oxygen.
which entered through the annular inlet to the reactor. The reaction was carried out at temperatures above 850°C where the TiCl₄ conversion was 100%. The particles produced were trapped on a filter paper in a dust collector. The concentration of TiCl₄ was determined by absorbing Cl₂ formed in the reaction in an aqueous potassium iodide solution.

The following investigation was performed: (1) the effects of the reaction temperature and the TiCl₄ and O₂ concentrations on the TiO₂ particle size and the weight fraction of rutile; (2) the transformation from anatase to rutile when the powder produced in the first furnace was aged in the second furnace (mode A); (3) the growth and transformation of the crystalites when not only the particles produced in the first furnace but also TiCl₄ was fed into the second furnace (mode B).

The experiments of mode A and B are illustrated in Fig. 1. The flow rates of N₂ and O₂ in the two modes were constant at 3.3 cm³/s and 10 cm³/s, respectively, based on 25°C. The particle size was measured by X-ray diffraction (Cu-Kα) and transmission electron-microscopy. The weight fraction of the anatase and rutile particles was calculated from the ratio of the X-ray diffraction intensities by Spurr and Myers' method.

The second series experiment was done by using a reactor with mullite tubes having an inside diameter of 52 mm arranged vertically or horizontally. The TiCl₄ vapor diluted with nitrogen was fed into the center of the reactor via an alumina nozzle of inside diameter 6 mm and outside diameter 10 mm. In some runs, particles were sampled by evacuation through a 1 mm i.d. platinum tube from different parts of the reactor, and they directly impinged on the electron microscope grid mounted in a small holder. Figure 2 shows the direct sampling system. The lateral distribution of the reaction zone was visualized by inserting alumina rods of 1 mm in diameter across the flame.

2. 2 Production of nickel particles

Nickel powders were produced in a vertical reactor of inside diameter of 35 mm. The nozzle was a mullite tube with an inside diameter of 9 mm connected to a mullite tube of 24 mm i.d. The nickel vapor was generated by heating pelletized anhydrous nickel chloride in the evaporating chamber of the nozzle side. The nickel chloride vapor was blown into the reactor through the nozzle using argon as a carrier gas, and it reacted with the hydrogen

Fig. 1 Reactor modes for aging and 2nd reaction.

\[ d_f = 30 \text{ mm}, \quad d_N = 4 \text{ mm}; \quad Q_{d}(\text{O}_2) = 10 \text{ cm}^3\text{s}^{-1}, \quad Q_{d}(\text{N}_2) = 3.3 \text{ cm}^3\text{s}^{-1}, \quad Q_{d}(\text{TiCl}_4) = 0.073 - 0.169 \text{ cm}^3\text{s}^{-1} \]

Fig. 2 Examples of reaction zones. \[ d_f = 52 \text{ mm}, \quad d_N = 6 \text{ mm}, \quad Q_{d}(\text{O}_2) = 25 \text{ cm}^3\text{s}^{-1}, \quad Q_{d}(\text{N}_2) = 6.7 \text{ cm}^3\text{s}^{-1}, \quad Q_{d}(\text{TiCl}_4) = 0.24 \text{ cm}^3\text{s}^{-1}; \quad t = 0.12 \text{ s} \]
introduced through the annular space enclosing the nozzle. The rate of vaporization of the nickel chloride was determined by measuring the amount of HCl which was absorbed in aqueous NaOH at the outlet of the reactor.

3. Results and discussion

3.1 Reaction zone

Figure 2 illustrates a map of the reaction zone in the 52 mm i.d. reactor. Since the concentration of TiCl₄ was low, the reaction was controlled by the diffusion of oxygen toward the core of the jet. The length of the unreacted core decreased with increasing reaction temperature. The lateral expansion of the jet was not remarkable because the diffusion of particles was very slow compared to that of gas.

3.2 Particle size

TiO₂ particles

Figure 3 shows a transmission electron micrograph of the TiO₂ particles collected at the outlet of the furnace. Most particles were round or cubic. The mean diameter of crystallites, calculated from the X-ray diffraction with Si as an internal standard agreed closely with the value obtained by electron-microscopy. This indicates that the particles were single crystals with few defects.

Figure 4 reveals the effect of the reaction temperature on the size of the TiO₂ particles. The concentration of TiCl₄ is the value in the gas leaving the nozzle. The size of the particles produced in the first furnace (○) decreased somewhat with increasing temperature. The results obtained with the 52 mm i.d. reactor show the same tendency. The mean size of TiO₂ particles sampled 5 cm downstream from the nozzle mouth was nearly equal to that at the reactor outlet. The symbols ● in Fig. 4 represent the particle size in mode A, in which particles were aged at 1000°C in the second furnace, while the symbols ● denote the particle size in mode B, in which the feed gas was also introduced into the second furnace. There was no change in the particle size when the particles issuing from the first furnace were simply aged at 1000°C in the second furnace.

Figure 5 indicates that the particle size increases with increasing initial TiCl₄ concentration. The oxygen concentration is the value in the gas entering the annular space. The contact time was calculated from the gas velocity through the nozzle, and was roughly 0.4 s.

Assuming that all of the TiCl₄ reacts at the nozzle mouth (t = 0), and that fresh crystals are produced by instantaneous fusion as a result of interparticle collisions due to the Brownian motion, the mean particle size is given by

$$d_p = 1.88 \left( \frac{6kT}{\rho_s} \right)^{1/2} \psi^{1/2} r^{1/2}$$  \hspace{1cm} (1)

where the effective residence time in the furnace, t, is calculated at the reaction temperature. The experimental data of dₚ is 5 times smaller than Eq. (1) at 1000°C and 3 ~ 4 times smaller at 1100°C, respectively. The above results show that the growth of TiO₂ particles
ended within 5 cm downstream from the nozzle mouth. The growth by intra-aggregate fusion of coagulated particles\cite{23,24} at 1000°C hardly occurred after the particles grew beyond 50 ~ 60 nm under the condition tested. Similar results were reported by Suyama and Kato\cite{21} at 1100°C.

The fusion of TiO₂ particles is controlled by the surface diffusion of oxygen ions\cite{1,2,13,14}. Nichols and Mullins\cite{13} simulated the coalescence of a sphere onto a wall. The surface diffusion coefficient of TiO₂ was given by Anderson\cite{1} as follows:

\[
bD_B/(m^3.s^{-1}) = 3.5 \times 10^{-6} (T/K) \times \exp(322kJ/mol^{-1}/RT) \tag{2}
\]

The calculation indicates that the fusion of TiO₂ crystals larger than several nm in diameter is not significant in the range of \(T < 1200°C\) under the present experimental conditions.

When a second reaction was carried out at 1000°C, however, the particle diameter increased by about 1.5 times (equivalent to a 3.3-fold increase in the volume) as shown in Fig. 4\cite{11}. Therefore, the growth of larger particles is considered to proceed via the heterogeneous deposition of TiCl₄ as well as the coalescence of very small particles. The coincidence of the data of George et al.\cite{5} with Eq. (1) is due to the high temperature of their reaction. Particle growth by simple aging was also observed when the second furnace was kept at 1200°C.

The growth mechanism of TiO₂ particles is summarized in Fig. 6\cite{11}. The residence time of the particles in the reactor was in the range of 0.05 ~ 0.3 s in the present experiment. This was not long enough for agglomerated particles
to fuse into larger particles at temperatures below 1100°C. However, when some unreacted titanium chloride was present, filling the space between the attached particles, fusion occurred at temperatures of 1100°C. This is also valid for particles larger than a few tens of nm. Any smaller particles would probably have coalesced at lower temperatures.

**Nickel particles**

Figure 7 shows the effect of temperature on the mean size of nickel particles. The mean particle size is virtually equal to the theoretical value of Eq. (1) at 1380°C which is close to the melting point of nickel (1450°C).

3.3 Fractional rutile content

Figure 8 shows the effect of reaction temperature on the weight fraction of rutile in the TiO₂ particles. Suyama et al. reported that the weight fraction of rutile increased with increasing reaction temperature. However, the present results as well as those of Matsumoto et al. indicate that the weight fraction of rutile was at a maximum when the temperature of the first reactor was 1000°C. The existence of this maximum in the rutile content was observed irrespective of reactor dimensions and whether or not an aging or a second reaction took place in the second furnace. The rutile fraction in the particles sampled at 5 cm downstream from the nozzle coincides with that at the exit of the reactor. It was reported that the rutile content in a flame reactor operated at 1450 ~ 1650°C was very low. Shannon and Park and others have indicated that the rutile phase is nucleated on the surface and then spreads in the anatase body. The anatase-rutile transformation rate is given by,

\[ (1 - \alpha)^{\frac{1}{2}} = c - 2k_t t / (\rho_d \omega_d) \]  

where \( \alpha \) is the fraction of transformation completed. Figure 9 shows the coefficient of the transformation on the basis of Eq. (3). Even at 1200°C, the transformation rate is very slow, and the spreading rate of the rutile phase is in the order of 0.1 nm·s⁻¹. Thus, within the residence time of the present experiment (0.05 ~ 0.3 s), only several layers of the anatase structure could be transformed into the rutile. The decrease in the rutile content at higher temperatures can be explained by the following mechanisms.

(I) Competitive reaction model

Figure 10 illustrates this model. The first
stage of the reaction is the preferential formation of clusters of anatase. The clusters of anatase either grow into anatase particles or else are transformed into clusters of rutile. As soon as the anatase clusters grow into anatase particles, the transformation virtually stops. With increasing reaction temperature, the rate of transformation of the anatase particles into rutile decreases because the rate of fusion increases.

(II) Heterogeneous deposition model

As shown in Fig. 8, the rate of formation of rutile particles in the second reaction is strongly affected by the polymorphic phase composition of the particles entering the second furnace. This implies the heterogeneous deposition of rutile from gaseous TiCl₄ on the particle surface which is already transformed to rutile is important. At higher temperatures, TiCl₄ reacts with oxygen more quickly to form TiO₂ particles. Thus, TiCl₄ disappears at an earlier stage of the reaction. After the consumption of TiCl₄, an increase in the rutile fraction may not be expected.

To specify the mechanism for the formation of rutile particles, it is important to evaluate the mass transfer rate of oxygen into the core of the jet and the reaction rate of TiCl₄ with oxygen². Future research must focus on this point.

4. Conclusion

Ultrafine TiO₂ particles were produced by gas phase oxidation of TiCl₄ without additives in aerosol reactors operated in the laminar regime. The weight-average diameter of TiO₂ particles increased with an increase in the TiCl₄ concentration. The reaction terminated within 5 cm downstream from the nozzle mouth, and the effects of the residence time of gas and the reaction temperature were not dominant. The mean diameter of nickel powders produced by the hydrogenation of NiCl₂ at 1380°C was close to Eq. (1). The intra-aggregate fusion was strongly related to the heterogeneous deposition and the temperature.

The fraction of rutile took a maximum at ca. 1000°C. Models were proposed for the explanation, but more research is needed to elucidate the exact mechanism.

Nomenclature

- b : thickness of diffusion
- C₀₂ : volume fraction of oxygen
- c : constant
- D_B : surface diffusion coefficient
- d_T : inside diameter of reactor
- d_N : inside diameter of nozzle
- d_D : weight-mean diameter of primary particles
- k : Boltzmann constant
- k_r : reaction rate coefficient defined by Eq. (3)
- L : length of reaction space
- Q_a(i) : flow rate of i-component in annular space.
  The volume of gas is measured at 25°C
- Q_n(i) : flow rate of i-component in nozzle space.
  The volume of gas is measured at 25°C
$Q_s(N_2) \ : $ flow rate of sheath gas measured at 25°C.
The velocity is equal to that of nozzle gas.
$R \ : $ gas constant
$T \ : $ reaction temperature
$t \ : $ residence time of nozzle gas calculated
at reaction temperature
$
\alpha \ : $ fraction of rutile
$\rho_s \ : $ density of particles
$\psi \ : $ volume fraction of solids at reaction
temperature

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