



Competition between gas phase and surface oxidation of TiCl_4 during synthesis of TiO_2 particles

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Abstract—The effect of TiCl_4 surface reaction on the size of product TiO_2 particles is quantitatively investigated over a wide range of process conditions (temperature and reactant concentration) that are typically employed in industrial and research facilities. A model for titania aerosol dynamics is developed accounting for the simultaneous gas phase and particle phase (surface) oxidation rate of TiCl_4 . Using this model, the implications of these two chemical pathways on the size of product titania particles are elucidated. It is shown, for the first time, that TiCl_4 oxidation on the surface of freshly formed titania particles is most important at high TiCl_4 concentrations. A design diagram is presented mapping the significance of surface and gas-phase oxidation of TiCl_4 in terms of process temperature and initial TiCl_4 mole fraction. The model predictions are compared with experimental results and conflicting interpretations of the mechanism of titania formation by TiCl_4 oxidation in the literature are reconciled. This model can be used to investigate the significance of surface growth in gas-phase synthesis of fumed silica as well as other ceramic and metallic particles. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Vapor phase material synthesis; chemical kinetics and particle growth; chemical vapor deposition; particle production; coagulation and surface growth.

INTRODUCTION

Titania powders are made by TiCl_4 oxidation in industrial flame aerosol reactors at high temperatures and moderate, near atmospheric, pressures by the so-called 'chloride process' at a rate of 100 ton/day (Mezey, 1966; Stamatakis *et al.*, 1991). This is a major process making more than half of the annual worldwide consumption of over 3 million tons of TiO_2 aimed mostly for pigments and to a lesser extent as a paper filler, plastics, cosmetics, catalysts and even ceramic membranes (Thayer, 1998).

The fundamentals of this process are not yet well understood as chemical reaction and particle growth rapidly take place. As a result, it is hard to collect representative samples for particle sizing and eventual model development (Pratsinis, 1997). Even in the open literature, there are conflicting interpretations of TiO_2 formation and growth by TiCl_4 oxidation as a brief review will show shortly. This lack of understanding largely limits process development for manufacture of

titania. This is a pity given the fact that this flame process has high potential for manufacture of a wide spectrum of ceramic powders (Pratsinis, 1997).

George *et al.* (1973) systematically studied titania formation by TiCl_4 oxidation in a premixed CO/O_2 flame. They found that coagulation was dominant as the TiO_2 size distributions were largely self-preserving while surface reactions were inadequate to quantitatively explain the particle growth rate. Nevertheless, Suyama *et al.* (1975) and Suyama and Kato (1976) qualitatively proposed that nucleation and surface growth determined the primary particle size of titania made in hot-wall reactors. Morooka *et al.* (1989) showed that assuming rapid TiCl_4 oxidation and coagulation overpredicted the particle size and proposed that particle growth took place largely by oxidation of TiCl_4 on the particle surface. Akhtar *et al.* (1991), however, quantitatively showed that in their hot-wall reactor aggregate particles were formed by coagulation as they had a self-preserving size distribution. Hung and Katz (1992) studied titania formation in a counterflow diffusion flame reactor and postulated that particle formation took place by coagulation followed by surface growth and fusion as the particles encountered progressively higher temperatures during their flow out of the burner. More

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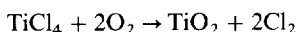
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recently, Jang and Jeong (1995) found that preheating the reactants prior to their oxidation reaction decreases the particle size and slightly narrows the particle size distribution. They proposed that nucleation and surface oxidation dominated titania particle growth in their hot-wall reactor.

Clearly there is a split in the current understanding of the fundamentals of titania particle formation and growth. This is attributed to a lack of a quantitative evaluation of the *simultaneous* gas phase and surface oxidation rates of TiCl_4 on the characteristics of product TiO_2 . This paper presents such an evaluation using established reaction rates of the global overall oxidation rate of TiCl_4 and its surface reaction. The growth of titania particles is simulated by a simple model of aerosol dynamics. The basics of TiO_2 formation are elucidated and a diagram is presented in which process conditions for titania synthesis by surface or gas-phase oxidation and coagulation are identified and compared to experimental data in the literature. This model can be used also in evaluating the significance of surface growth in a variety of processes involving aerosol synthesis of particles (e.g. fumed silica, alumina and metal particles from decomposition of precursor vapors).

THEORY

The overall oxidation reaction for TiCl_4 is



and can be carried out in the gas phase or on a solid surface. Hence, two distinct chemical pathways for oxidation of TiCl_4 vapor can be identified: First, vapor of TiCl_4 may react with oxygen in the gas phase forming titania or precursor (oxychloride) particles at rate R_g . Second, TiCl_4 vapor may react with oxygen on the surface of titania particles coating them with titania or precursor (oxychloride) films at rate R_s . As a result, the overall oxidation rate of TiCl_4 , R , can be written as (Pratsinis, 1997):

$$dC/dt = -R = -(R_g + R_s) \quad (1)$$

where C is the concentration of TiCl_4 vapor (mole/cm³). Pratsinis *et al.* (1990) have measured R in the effective temperature range of 813–1173 K and TiCl_4 mole fraction, $\phi = 5.6 \times 10^{-4}$, or concentration of 2.5×10^{-8} mole/cm³:

$$R = kC \quad (2)$$

where $k = 8.26 \times 10^4 \exp(-10681/T) \text{ s}^{-1}$ and T is the temperature, K for $\text{TiCl}_4/\text{O}_2 < 1/20$. More recently, Kobata *et al.* (1991) have compiled a number of reaction rate data over a range of temperatures and reactant concentration $k = 25 \times 10^4 \exp(-12268/T) \text{ s}^{-1}$. Ghoshtagore (1970) measured the growth rate of TiO_2 films by surface reaction of TiCl_4 between 673 and 1120 K and TiCl_4 mole fraction $\phi = 3.8 \times 10^{-5} - 1.2 \times 10^{-3}$:

$$R_s = k_s AC \quad (3)$$

where $k_s = 4.9 \times 10^3 \exp(-8993/T) \text{ cm/s}$, and A is the total aerosol surface area concentration (cm²/cm³) over which the TiCl_4 oxidation takes place. This area may be constant during film growth while it is rapidly changing during powder manufacture since it is the area of the newly formed titania particles.

To elucidate the role of these reaction rates, the concurrent dynamics of the titania aerosol need to be described and coupled to the kinetics through A . Though there are several models for particle growth at the above conditions, here the simplest possible one is chosen to explore the competition between TiCl_4 gas and surface oxidation during synthesis of TiO_2 aerosol neglecting the spread of its size distribution. Monodisperse models are quite attractive for description of aerosol dynamics involving concurrent gas-phase chemistry and transport. For example, Warren and Seinfeld (1985) developed such a model and it has been used in simulation of photochemical air pollution; Kim and Pratsinis (1989) developed another one that is used in simulation of manufacture of optical fiber preforms at AT&T while Panda and Pratsinis (1995) developed another one simulating synthesis of Al and Pd nanoparticles in a jet aerosol flow condenser (Haas *et al.*, 1997). Of course, lognormal (Megaridis and Dobbins, 1990) and sectional (Gelbard *et al.*, 1980) aerosol models provide more information on the dynamic behavior of the complete particle size distribution but they involve other assumptions, additional complexity and computational resources. Nevertheless, monodisperse models can describe reasonably well integral properties of the particle size distribution such as the aerosol area, average size and number concentration (Landgrebe and Pratsinis, 1990; Kruis *et al.*, 1993).

Thus, neglecting the spread of the aerosol size distribution and assuming perfect coalescence upon particle collision, the rate of change of the total particle concentration N , (#/cm³), is given by (Panda and Pratsinis, 1995):

$$dN/dt = I - 0.5\beta N^2 \quad (4)$$

where β is the collision frequency function of equally sized particles from free molecule to continuum particle size regime (Fuchs, 1964; Seinfeld, 1986: Chap. 10):

$$\beta = 8\pi D d_p \left[\frac{d_p}{d_p + \sqrt{2}g} + \frac{4\sqrt{2}D}{c d_p} \right]^{-1} \quad (5)$$

with the particle diameter, velocity and diffusivity d_p , c and D , respectively, while the parameter

$$g = \frac{1}{3d_p l_a} \left[(d_p + l_a)^3 - (d_p^2 + l_a^2)^{3/2} \right] - d_p \quad (6)$$

with the mean free path for the particles

$$l_a = 8D/\pi c \quad (7)$$

The nucleation rate I (#/cm³/s) is equal to the rate of new particle (here, molecule) formation by gas-phase

chemical reaction over a wide range of conditions (Ulrich, 1971; George *et al.*, 1973; Xiong and Pratsinis, 1991):

$$I = R_p N_A \quad (8)$$

and N_A is the Avogadro number. It should be emphasized that this is a simplified representation of the actual process for lack of reliable information on the early stages of TiO₂ formation (Pratsinis *et al.*, 1990). Clearly, the first right-hand side (RHS) term of eq. (4) represents the addition of new particles by nucleation while the second RHS term stands for the loss of particles by coagulation.

Similarly, the rate of change of the total titania aerosol volume V (cm³/cm³) is given by

$$dV/dt = Iv_1 + R_s N_A v_1 \quad (9)$$

where v_1 is the volume of a TiO₂ molecule in solid state ($\rho_p = 4$ g/cm³). The first RHS term of eq. (9) accounts for the formation of titania aerosol volume by nucleation while the second RHS term accounts for the formation of titania aerosol by surface reaction. The average particle diameter,

$$d_p = (6V/\pi N)^{1/3} \quad (10)$$

while the total aerosol surface area concentration (cm²/cm³) is given by

$$A = N\pi d_p^2 \quad (11)$$

The above set of equations describes the overall TiCl₄ kinetics and TiO₂ aerosol dynamics at isothermal conditions. These conditions are used to clearly demonstrate the competition of the two reaction pathways at various temperature levels. The above set of equations was solved using the DGEAR routine (IMSL, 1980; Spicer, 1997).

RESULTS AND DISCUSSION

Selection of simulation conditions

Titania is made by the 'chloride' process by supplying TiCl₄ and oxygen at almost stoichiometric conditions (corresponding to TiCl₄ mole fraction, ϕ , near 0.5) in flame reactors operating at near atmospheric pressure and $T = 1000$ – 1500°C at very short residence times (e.g. Nelson *et al.*, 1963). On the other hand, typical conditions in research laboratories involve similar temperatures and pressures but longer residence times and lower TiCl₄ concentrations

(Table 1). As a result, here, the significance of gas phase or surface oxidation of TiCl₄ on the diameter of product TiO₂ is investigated at atmospheric pressure, $T = 1000$ – 1800 K and $\phi = 0.0001$ – 0.5 in oxygen carrier gas as in most laboratory studies. The overall oxidation rate of TiCl₄ was described using the rate of Pratsinis *et al.* (1990). The expression of Kobata *et al.* (1991) overpredicted the TiCl₄ conversion by 10% and the TiO₂ diameter by less than 1% at 1000 K while the predictions of the model by Kobata *et al.* (1991) were indistinguishable from those of the model of Pratsinis *et al.* (1990) at 1400 K. The use of oxygen instead of chlorine as carrier gas, as it would be appropriate for simulation of titania growth at highly concentrated synthesis conditions, did not alter the model results more than 1%. Finally, this model can be easily adopted to describe titania formation by TiCl₄ oxidation in the absence of surface reaction by merely setting $k_s = 0$ reducing it to that of Landgrebe and Pratsinis (1990).

TiO₂ formation and growth by surface and gas-phase oxidation of TiCl₄

Figure 1 shows the evolution of (a) the average particle diameter, d_p , and (b) the total particle number concentration, N , and aerosol surface area, A , accounting for surface reaction (solid lines) and neglecting it (broken lines, $k_s = 0$) at 1000 K and TiCl₄ mole fraction $\phi = 0.01$ at 1 atm from $t = 10^{-4}$ to 100 s. Figure 1(a) also shows the corresponding overall conversion, C/C_0 , of TiCl₄ (dotted line) at 1000 K.

Particle growth starts from about 4 nm corresponding to the molecular size of titania [Fig. 1(a)]. When the surface reaction is neglected, the particle number concentration increases at $t < 10^{-3}$ s [Fig. 1(b), broken lines] as new particles (molecules) are formed by chemical reaction. As the number of particles increases, coagulation becomes important and the chemical reaction cannot make up the loss of particles by coagulation so N starts to slowly decrease up to $t = 1$ s. At that time about 90% of TiCl₄ has been consumed [Fig. 1(a)] and the addition of new particles by pure gas-phase reaction slows down so coagulation completely takes over, decreasing N steeply at $t > 1$ s. The aerosol area increases rapidly at first ($t < 10^{-3}$ s) as addition of new particles by reaction is dominant [Fig. 1(b)]. Later on, as coagulation becomes important, A continues to increase but at a slower rate until it reaches a maximum at $t = 1$ s

Table 1. Summary of conditions from, experimental studies on the mechanism of TiO₂ particle production by TiCl₄ oxidation

	d_p (nm)	ϕ	T (C)	Proposed mechanism for TiO ₂ growth
George <i>et al.</i> (1973)	40–60	0.00005–0.0033	Up to 1400	Gas phase reaction and coagulation
Suyama <i>et al.</i> (1975, 1976)	60–700	0.006–0.11	850–1100	Surface growth
Morooka <i>et al.</i> (1989)	45–85	0.003–0.014	900–1200	Surface growth
Akhtar <i>et al.</i> (1991, 1992)	45–68	0.0002–0.001	900–1450	Gas phase reaction and coagulation
Jang and Jeong (1995)	30–70	0.0005–0.01	900–1100	Surface growth

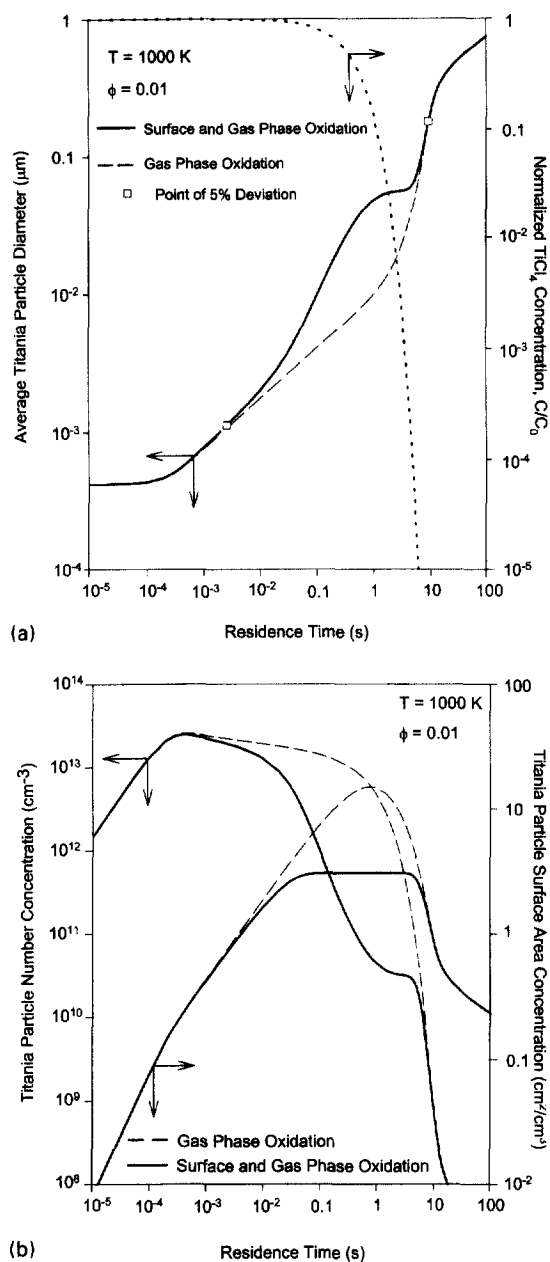


Fig. 1. The evolution of (a) average titania particle diameter and dimensionless TiCl_4 concentration (dotted line) and (b) total particle number and area concentrations accounting for surface oxidation of TiCl_4 (solid lines) or neglecting it ($k_s = 0$, broken lines) at initial TiCl_4 mole fraction $\phi = 0.01$ and $T = 1000$ K. The squares correspond to a difference of 5% in diameter between the model predictions accounting for surface reaction or neglecting it.

when the contribution of chemical reaction is no longer significant. At $t > 1$ s the aerosol area decreases by coagulation.

When surface reaction is taken into account (Fig. 1, solid lines), newly formed particles have considerable surface area at $t > 0.001$ s. Then, TiCl_4 oxidation on the particle surface competes effectively with gas-phase oxidation of TiCl_4 reducing the nucleation (or

formation) rate of new particles. As a result, particle losses by coagulation cannot be made up by nucleation (or gas-phase reaction) and the total particle concentration decreases faster than when surface reaction was neglected. This continues until $t \sim 1$ s when the reduction in N seems to nearly level off at $t \sim 5$ s. During this period, N has been decreasing so much that the contribution by pure gas-phase oxidation can almost balance the reduction by coagulation. Of course, as the TiCl_4 concentration decreases [Fig. 1(a)], the contribution by gas-phase oxidation becomes insignificant so N decreases again steeply, converging to the evolution of N in the absence of surface reaction ($t > 5$ s). Figure 1(a) shows that particle size increases much faster by surface than by gas-phase oxidation and coagulation ($t = 0.01$ –1 s) while the aerosol area remains nearly constant by the balance of surface growth and coagulation in the free molecule size regime up to $t \sim 5$ s [Fig. 1(b)].

It is worth pointing out that the area of atmospheric aerosols growing by surface reactions and coagulation in the free molecule regime remains constant as was measured by Husar and Whitby (1973) and annotated by Friedlander (1977, p. 274). In production aerosols, reactions last as long as reactants are available and here this is the case at about 5 s (while atmospheric reactions last much longer). Then, the area is no longer constant and decreases by coagulation as discussed above. It is worth highlighting the difference surface reaction makes on particle size: At $t = 1$ s the diameter of particles grown by surface and gas-phase reaction is 60 nm while in the absence of surface reaction d_p is only 10 nm. At longer residence times ($t > 5$ s), when there is no more TiCl_4 , coagulation dominates particle growth and the two models converge.

Effect of TiCl_4 mole fraction, ϕ , and T on TiO_2 particle diameter

Figure 2 shows the evolution of the particle diameter from $t = 10^{-4}$ s to $t = 100$ s for initial TiCl_4 mole fraction $\phi = 0.001$ and 0.1 at 1000 K accounting for the surface reaction (solid lines) and neglecting it (broken lines). At low TiCl_4 concentrations ($\phi < 0.001$), accounting for the surface reaction little affects the evolution of particle size. Clearly, gas-phase reaction and coagulation dominate particle formation and growth at this and lower TiCl_4 mole fractions at all residence times. For larger ϕ , higher TiCl_4 concentrations ($\phi = 0.1$) increase the significance of surface reaction. The abundance of available surface area of freshly formed TiO_2 participates and catalyzes the oxidation of TiCl_4 . Thus, at 1 s residence time, the average titania particle diameter accounting for surface reaction is 300 nm while neglecting it, gives d_p of only 15 nm. Of course, at very long residence times the predictions of the two models converge since again coagulation dominates and TiCl_4 has been fully converted. However, this may be a rather misleading assurance because this model neglects the finite coalescence (sintering) rate of titania. As a matter of fact,

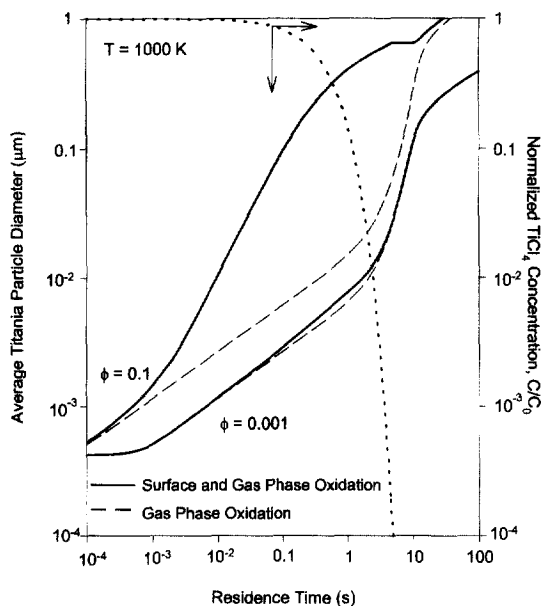


Fig. 2. The evolution of the average titania particle diameter accounting for surface oxidation of TiCl₄ (solid lines) or neglecting it ($k_s = 0$, broken lines) at initial TiCl₄ mole fraction $\phi = 0.001$ and 0.1 and $T = 1000$ K.

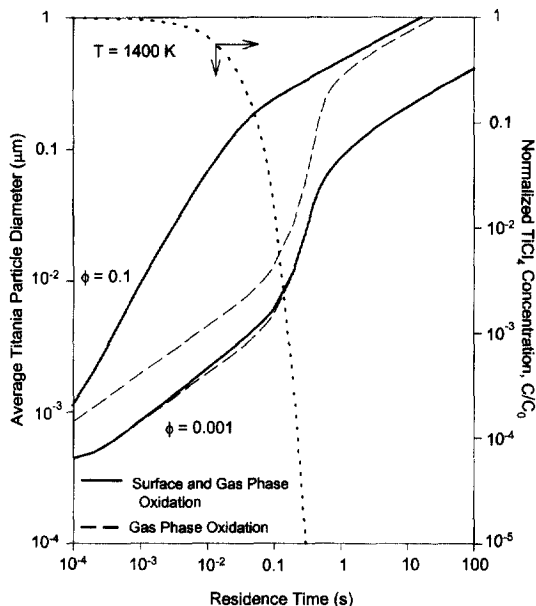


Fig. 3. The evolution of the average titania particle diameter and dimensionless TiCl₄ concentration (dotted line) accounting for surface oxidation of TiCl₄ (solid lines) or neglecting it ($k_s = 0$, broken lines) at initial TiCl₄ mole fraction $\phi = 0.001$ and 0.1 and $T = 1400$ K.

at these low temperatures the sintering rate of titania is rather slow, so colliding particles will not grow to single coalesced ones but will form aggregates of fine primary particles.

Figure 3 shows the evolution of titania particle diameter at $T = 1400$ K at $\phi = 0.1$ and 0.001 up to 100 s residence time. It should be noted that this temperature is outside the regime over which the overall and surface reaction rates have been measured so these results should be viewed with caution. Nevertheless, these reaction rates are routinely used at higher temperatures as is the case for SiCl₄ oxidation in manufacture of optical fibers (Powers *et al.*, 1978). Again, at intermediate residence times, accounting for surface reaction results in much larger particles than when it is neglected. A difference between 1000 and 1400 K is that the dominance of surface reaction occurs earlier on following faster conversion of TiCl₄.

These results point out that accounting for oxidation of TiCl₄ on the surface of newly formed titania particles substantially accelerates their growth. For example, at $\phi = 0.1$ it is clear that particles experience rapid growth up to 0.1 s by surface reaction while after that they grow rather sluggishly by coagulation. This is hardly surprising because $d_p \sim t$ during surface growth while during coagulation $d_p \sim t^{2/5}$ in the free molecule regime or $d_p \sim t^{1/3}$ in the continuum regime (Friedlander, 1977). This also shows that accounting for surface oxidation of TiCl₄, results in particle growth up to $d_p = 0.2 \mu\text{m}$ within 0.1 s when more than 98% of TiCl₄ has been consumed at 1400 K and $\phi = 0.1$. Prolonging the residence time increases the size by coagulation (which widens the size distribu-

tion) and, possibly, the extent of aggregation because sintering and coalescence may determine the structure of coagulating particles at this temperature and residence time.

Before concluding this section the significance of the assumption of rapid coalescence must be discussed. Neglecting coalescence, underpredicts the aerosol area since agglomerates have larger area than equivalent spheres. This assumption will be most important at short residence times, large d_p and low T especially when coagulation dominates particle growth. These two assumptions may partially compensate for each other. A detailed evaluation of these assumptions can be done with models accounting for the detailed size and structure distribution of agglomerate particles (Xiong and Pratsinis, 1993).

Criteria for TiO₂ synthesis by coagulation or surface growth

The above results indicate that at high initial TiCl₄ mole fractions (e.g. $\phi > 0.001$) surface growth may significantly affect the size of product TiO₂ particles. Thus, pure gas-phase reaction is responsible for the early formation of titania particles. These particles may have large enough surface area to catalyze TiCl₄ oxidation on their surface and prevent significant formation of new TiO₂ particles by pure gas-phase reaction. Since fewer particles are present, they are growing larger by surface reaction rather than by gas-phase reaction and coagulation. Of course at long residence times when virtually all TiCl₄ has been converted to TiO₂, coagulation again determines the particle growth rate. At very long residence times the

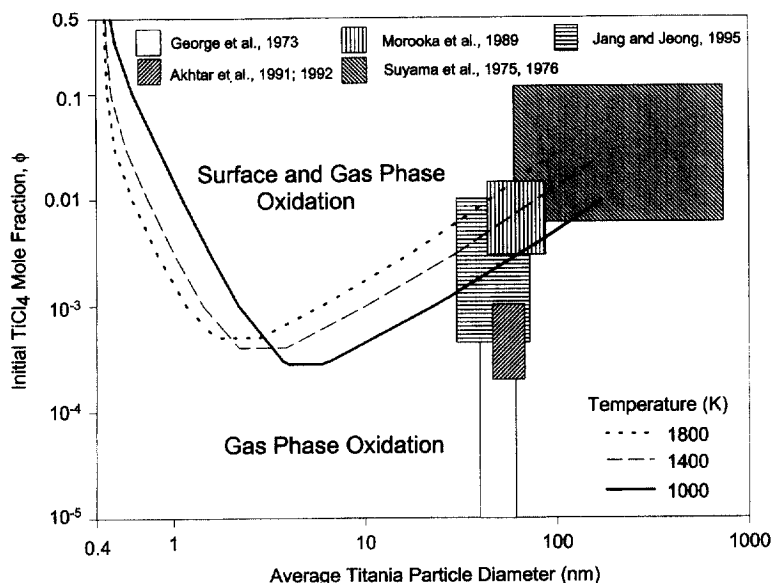


Fig. 4. Regions of TiCl_4 mole fraction and product TiO_2 primary particle diameter in which surface growth or gas-phase reaction and coagulation dominate at 1000, 1400, 1800 K. Process conditions of various experimental studies are shown also (Table 1).

mechanism of TiO_2 formation may have little effect on particle size. However, typical residence times are not that long, especially, taking into account that sintering affects the coalescence rate of colliding particles. Hence it may be significant to know process conditions that favor particle growth by surface oxidation rather than by pure gas-phase oxidation.

Typically, it is required to produce titania of a specific size, among other characteristics, depending on the final application. It would be of interest to select process conditions that favor surface growth during production of titania of that size. Figure 4 shows a diagram of the initial TiCl_4 mole fraction, ϕ , and product TiO_2 diameter, d_p , in which particle growth is dominated either by surface oxidation or gas-phase oxidation of TiCl_4 at various T . Each boundary is the isopleth of particle diameters in which the model that accounts for surface oxidation predicts a particle diameter 5% larger than that of the model that neglects surface reaction [squares in Fig. 1(a)]. For example, during an actual process at isothermal conditions, gas-phase reaction and coagulation (or nucleation) dominates at the early stages of the process and consequently at very small particle sizes (left region outside of the U shaped curves). Later on and for $\phi > 0.0005$, surface reaction dominates (middle region). For long residence times, coagulation again becomes important (right region). Figure 4 shows that surface reaction affects titania growth at high TiCl_4 mole fractions ($\phi > 0.001$) for synthesis of particles in the range of 50–1000 nm. Outside this region, coagulation dominates and the resulting particles may have broad size distributions as dictated by the self-preserving theory.

The most fascinating result of this study, however, is the identification of the surface growth region of the

diagram (inside the U shaped curves for each T). There, particles of narrow size distribution with limited extent of agglomeration can be made. Though the present model does not describe the dynamics of the particle size distribution, Pratsinis (1988) has shown that when coagulation and condensation simultaneously take place, the resulting particles have size distribution narrower than that dictated by the self-preserving theory (Friedlander, 1977). Since growth by surface reaction is equivalent to growth by condensation in the free molecule regime, we should expect relatively narrower size distributions for the particles made in the surface growth region rather than in the pure gas-phase reaction region. For synthesis of non-aggregate powders such as desired in pigments and cosmetics, one should operate in this region. However, if aggregate particles with high specific surface area are desired such as in photocatalysis and catalysis, in general, surface growth should be minimized and particles should be made outside this region.

Comparison with experimental results

Figure 4 shows also the conditions at which titania powders were made by various investigators. Table 1 lists the range of average size of titania powders made by these researchers and the corresponding range of ϕ and T . For example, George *et al.* (1973) who reported that surface growth was not important in their experiments, had operated at $\phi = 10^{-5}$ – 10^{-3} up to 1650 K. Their conditions confined them well outside the surface growth region of this process as Fig. 4 shows. Likewise, Akhtar *et al.* (1991) who produced titania at $\phi = 0.0002$ – 0.001 had operated just outside the surface growth region and coagulation determined particle growth at their conditions. Suyama

et al. (1975, and Suyama and Kato (1976) who claimed nucleation and surface growth as the mechanism for titania particle formation operated at high TiCl₄ volume fractions ($\phi = 0.006\text{--}0.11$) and Morooka *et al.* (1989) (for whom $\phi = 0.003\text{--}0.014$) are in excellent agreement with Fig. 4. Hung and Katz (1992) operated at $\phi = 0.0002$ and were outside the surface growth region for early stage particle formation. So Fig. 4 is in agreement even with their speculation. The majority of the data by Jang and Jeong (1995) belong to the surface growth region of Fig. 4 in agreement with their assessment that nucleation and surface growth dominated titania formation. As a matter of fact, all their primary particle size distributions have geometric standard deviations below the self-preserving limit ($\sigma_g = 1.45$) that slightly decrease as ϕ increases in agreement with the expectation of narrower size distributions with increased dominance of surface reaction (Pratsinis, 1988).

CONCLUSIONS

During synthesis of titania powders by TiCl₄ oxidation at high temperatures, the initial mole fraction of TiCl₄, ϕ , largely determines the significance of pure gas phase or surface oxidation. Simply put, high TiCl₄ concentrations result in high concentrations of TiO₂ nuclei that have enough surface area to consume TiCl₄ by surface reaction and effectively quench pure gas-phase oxidation of TiCl₄. At the other extreme, low TiCl₄ concentrations produce low concentrations of TiO₂ nuclei that never have enough area for surface reaction to compete with pure gas-phase reaction. As a result, nuclei are continuously formed at high enough concentrations and grow by coagulation.

A model was developed for this process elucidating these phenomena using literature expressions for the reaction rates and accounting for the titania aerosol dynamics neglecting the spread of the distribution and the coalescence rate of titania at isothermal conditions. This model quantitatively defined the regions of dominance of gas and surface oxidation of TiCl₄ at various process temperatures. Furthermore, it explained and reconciled apparent conflicts in the literature regarding the fundamentals of titania formation and growth by TiCl₄ oxidation.

It is particularly significant in relation to the discovery of specific process conditions where surface growth is dominant indicating the possibility of synthesis of particles with narrow size distributions. Even a small reduction (say 10%) in the polydispersity of the product may have significant impact in this industry given its huge product volumes, more than a million tons per year.

The results of this simple model should not be surprising as surface growth is dominant in flame synthesis of carbon blacks which is similar to flame synthesis of titania by TiCl₄ oxidation. Likewise there is a strong likelihood that surface growth can be important in aerosol synthesis of fumed silica, lightguide

preforms, and other ceramic and metallic powders and nanoparticles that are made by gas-phase reaction (oxidation or thermal decomposition) of precursor vapors. This model can be used for a quick evaluation of the significance of surface growth provided that the required chemical data are available. Furthermore, models that explicitly account for simultaneous chemical reactions including gas-phase and surface growth, coagulation and sintering of polydisperse aerosols will further contribute to revealing of conditions for synthesis of monodisperse titania and other, even nanosize powders.

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