Effects of H_2O on the Particle Size in the Vapor-Phase Synthesis of TiO_2

Hee Dong Jang
Div. of Minerals Utilization and Materials, Korea Institute of Geology, Mining and Materials, Taejon, 305-350, Korea

Vapor-phase synthesis of ultrafine TiO_2 particles was investigated experimentally in the simultaneous hydrolysis and oxidation of $TiCl_4$. Experiments were made for the control of particle size, size distribution and phase composition of ultrafine TiO_2 particles with the preheating of reactants. The molar ratio of $H_2O/TiCl_4$ was adopted as a variable for the control of particle size and size distribution in various reaction systems such as $TiCl_4-H_2O$, $TiCl_4-H_2O-O_2$, and $TiCl_4-H_2O-air$. As the molar ratio of $H_2O/TiCl_4$ increased from 2 to 12, the average particle size decreased from 45 nm to 19 nm, and the rutile content of TiO_2 powders increased from 21% to 54% in the $TiCl_4-H_2O$ system. Changes in the average particle size were the same in the $TiCl_4-H_2O-O_2$ system as in the $TiCl_4-H_2O$ system, but particle-size distributions were narrower in the $TiCl_4-H_2O-O_2$ system. The same tendencies of average particle size, size distribution and rutile content were also found in the $TiCl_4-H_2O-air$ system. A high production rate of ultrafine TiO_2 particles was obtained at the condition of high mole fraction of $TiCl_4$ and low gas-flow rate in the presence of water vapor and preheating of reactants.

Introduction

Metal oxide particles of less than 100 nanometer in particle size are considered as ultrafine or nanosized particles and expected to become precursors for the synthesis of new materials (Rice, 1990). Ultrafine TiO_2 powders are extensively used in cosmetics for high absorption of ultraviolet light, pigment, toner, and coating material. New applications of ultrafine TiO_2 particles are developed by many researchers: recently, the use of TiO_2 has been demonstrated as a photocatalyst in the removal of organics from wastewater streams (Ollis et al., 1991). In the above applications, the particle morphology, average size, size distribution, and phase composition are the key characteristics of powders which must be controlled.

Ultrafine TiO_2 particles can be produced by gas-phase and liquid-phase reaction. Preparation of ultrafine TiO_2 particles by gas-phase reaction of precursor vapors is considered as more important technology than liquid-phase reaction, because this method allows easy control of the condition, particle size, particle crystal structure and purity.

Synthesis of TiO_2 particles for the control of particle size and phase composition using vapor-phase reaction of $TiCl_4$ has been reported by many researchers. Suyama and Kato (1976), Akhtar et al. (1991), Kobata et al. (1991), and Jang and Jeong (1995) have studied the vapor-phase synthesis of TiO_2 particles by the oxidation of $TiCl_4$. The hydrolysis of $TiCl_4$ in the gas phase was investigated by Suyama et al. (1976) and Yeom et al. (1992, 1995). In the above studies, all results were focused on the extreme circumstances such as oxidation and hydrolysis. Akhtar et al. (1994) studied experimentally the simultaneous oxidation and hydrolysis reaction of $TiCl_4$ in the $TiCl_4$-H_2O-O_2 system using a hot wall aerosol flow reactor. The results of Akhtar et al. (1994)s focused on the morphology and the phase composition of titania with the variation of the mixing position and ratio of $TiCl_4$ and the water vapor.

In the commercial process, TiO_2 particles are prepared by a hydrocarbon assisted flame synthesis (Clark, 1975). In that process, water vapor is present from the combustion of hydrocarbon gas and plays a role in controlling the crystallinity and the particle size of the produced powders. Simultaneous oxidation and hydrolysis of $TiCl_4$ occur in the hydrocarbon assisted flame synthesis of TiO_2. Though these flame processes are mature technologies, the role of such chemical routes in determining particle characteristics is still not well understood fundamentally because the flame is a complex environment.

In the presence of water and oxygen there are two routes for $TiCl_4$ conversion to TiO_2: hydrolysis and oxidation. Hydrolysis of $TiCl_4$ takes place according to the overall reaction as follows:

$$TiCl_4 + 4H_2O \rightarrow Ti(OH)_4 + 4HCl \qquad (1)$$

$Ti(OH)_4$ can be made at the room temperature but it is converted to TiO_2 at the high temperature employed in the present study:

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \qquad (2)$$

Oxidation of $TiCl_4$ takes place according to the overall reaction as follows:

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2 \qquad (3)$$

Titania from the oxidation can be prepared at the sufficiently high process temperature above 700°C. Then, the process temperature determines the dominance of the hydrolysis or the oxidation of $TiCl_4$. When the process temperature is high enough to produce TiO_2 particles, the amount of water vapor may play an important role in determining the dominance of hydrolysis or oxidation of $TiCl_4$.

The purpose of the present study is to investigate the effect of H_2O on the primary particle size, size distribution, and phase composition of ultrafine TiO_2 particles by vapor phase reactions in the simultaneous oxidation and hydrolysis reaction of $TiCl_4$. For the comparison of results, various reaction systems such as $TiCl_4$-H_2O, $TiCl_4$-H_2O-O_2, $TiCl_4$-H_2O-air were adopted.

Experimental Studies

Apparatus

The experimental apparatus is shown in Figure 1. The apparatus consists of gas purification, reaction, powder collection and off-gas treatment parts, and data acquisition and control. Argon gas (99.999%) is injected as a carrier gas into the reactor through a heated column packed with copper powder (20/30 mesh) at 400°C, and a gas purifier (Hammond Drierite Co.) composed of $CaSO_4$ powder and molecular sieve.

A multistage aerosol reactor was made of quartz and consisted of zones for evaporation of $TiCl_4$, preheating of reactants, and reaction part. The reactor was 155 cm long, the length of the evaporation and the preheating zone was 40 cm each, and the length of the reaction part was 75 cm. The inside diameter of the evaporation zone was 5.0 cm. Liquid-phase $TiCl_4$ was fed through a long nozzle to this zone by using syringe pump. The preheating part consisted of a double pipe, the diameter of the inner tube was 3.0 cm, and the diameter of the outer tube was 5.0 cm. Argon gas and $TiCl_4$ vapor flow through the inner tube, and O_2 gas and water vapor flow through the outer tube. The nozzle for the mixing of reactants was installed before the reaction part. The diameter of the reaction part was 3.0 cm and the length for reaction zone was 30 cm. The temperature of each zone in the reactor was measured by a K-type thermocouple, and controlled separately by a computer. Ultrafine powder was collected by using a teflon membrane filter which has an average pore diameter of 20 μm.

Procedure

Argon gas was introduced to ensure an inert atmosphere in the reactor. The furnaces were heated to a predetermined temperature of each zone while Ar and O_2 gas were introduced at a flow rate of 2 L/min each. Liquid $TiCl_4$ was injected to the evaporation zone of the reactor at a constant

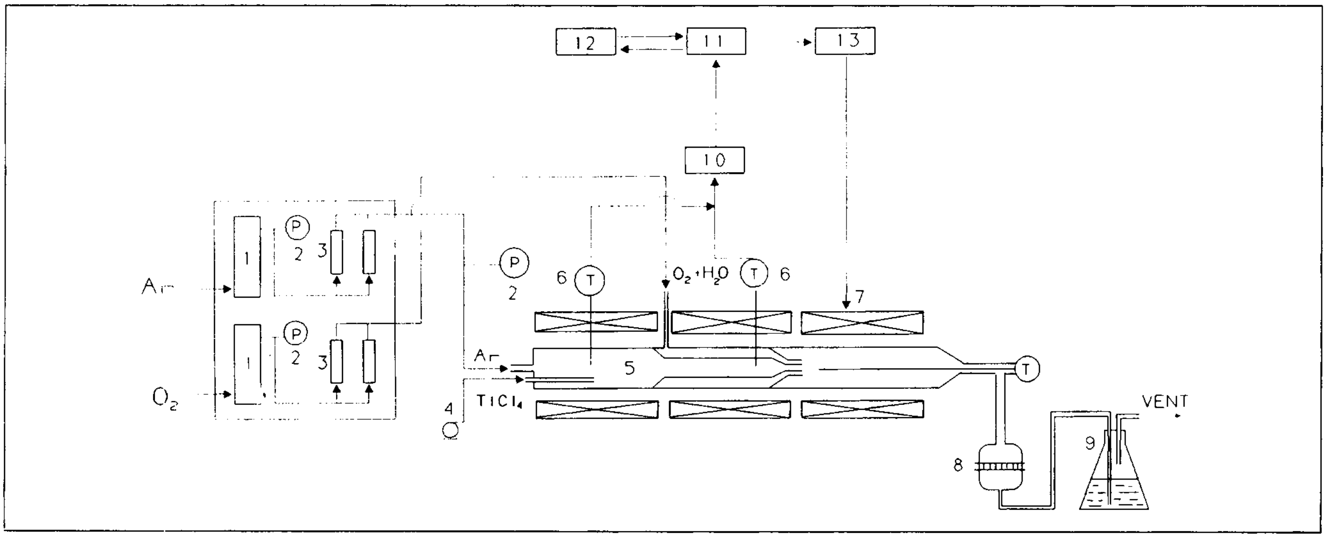

Figure 1. Experimental apparatus.

(1) Gas purifier; (2) pressure indicator; (3) flowmeter; (4) $TiCl_4$ feed pump; (5) aerosol reactor; (6) thermocouple; (7) tube furnace; (8) powder collector; (9) chlorine absorber; (10) amplifier; (11) A/D and D/A converter; (12) computer; (13) SCR.

rate of 1.05×10^{-3} mol/min during all the experiments by using a syringe pump (Keun-A Co. Model KASP 005). For the simultaneous oxidation and hydrolysis, liquid H_2O was injected to the heating mantle by using a syringe pump, and the water vapor was carried by O_2 gas. Then, the water vapor and O_2 gas were introduced to the preheating zone of the reactor. In the case of the hydrolysis of $TiCl_4$, the water vapor was carried by Ar gas. The reactants were heated to a predetermined temperature through a double pipe in the preheating zone. Then, reactants were allowed to be contacted with each other on leaving a concentric nozzle in the reaction zone.

Analysis

To measure the TiO_2 particle's shape, size and distribution, TEM (transmission electron microscope, Philips Model CM12) was used. The particle size and distribution were determined by counting more than 500 particles from TEM micrographs. The geometric standard deviation of particle size was obtained from a log-probability plot. A X-ray diffractometer (Rigaku Model RTP 300 RC) was used to determine the phase composition of the TiO_2 particles. The weight fractions of anatase and rutile phases in the prepared TiO_2 powders were calculated from the relative intensities of the strongest peaks corresponding to anatase and rutile as described by Spurr and Myers (1957).

Results and Discussion

TiO_2 particles from $TiCl_4 - H_2O$ system

Vapor-phase synthesis of uniform TiO_2 particles from the $TiCl_4$-H_2O system was difficult because the rate of hydrolysis is too fast to control the growth rate. However, if the nucleation conditions are well controlled, uniform particles will be obtained in the vapor-phase hydrolysis of $TiCl_4$. In previous studies (Suyama et al., 1976; Yeom et al., 1992, 1995), $TiCl_4$ and water vapor were mixed at the entrance of the reactor and introduced to the reaction zone to produce particles with varying experimental conditions. Then, the reactants would react at a lower temperature than the desired reaction temperature. Since the nucleation of TiO_2 is very fast, the nucleation, which is very dependent on temperature, would have progressed to a considerable extent before the reactants are heated to the temperature of the reaction zone in the tube furnace. Therefore, TiO_2 particles exhibiting a wide distribution including large sintered aggregates of primary particles were obtained from previous results because the condition of homogeneous nucleation could not be met due to the absence of preheating of reactants in the reaction zone.

Jang and Jeong (1995) found that the preheating of reactants before the reaction was an effective factor to get small and uniform particles in the $TiCl_4$-O_2 system, because homogeneous nucleation at the temperature of the reaction zone could be obtained. Therefore, TiO_2 particles formed by hydrolysis with the preheating of reactants were prepared at the fixed conditions of reaction temperature, gas flow rate, preheating temperature, and $TiCl_4$ mole fraction with the variation of molar ratio of H_2O to $TiCl_4$. Figure 2 shows the effect of water vapor on the particle size of TiO_2 particles.

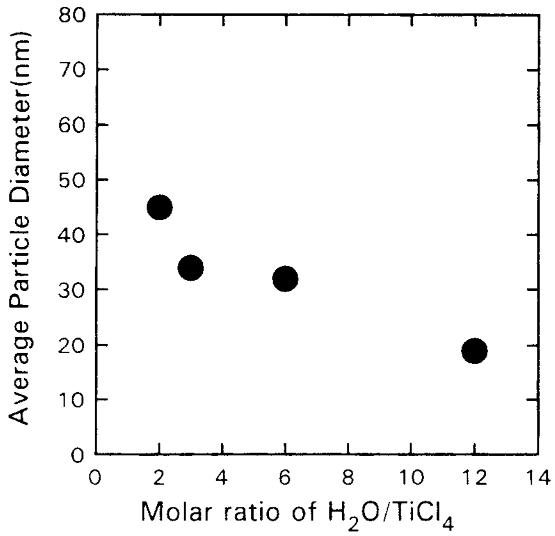

Figure 2. Effect of molar ratio of $H_2O/TiCl_4$ on the particle size in the $TiCl_4$-H_2O system.

Reaction temperature: 1,000°C; preheating temperature: 900°C; $TiCl_4$ feed rate: 1.05×10^{-3} mol/min; gas flow rate: 4 L/min.

As the molar ratio of $H_2O/TiCl_4$ was increased from 2 to 12 at constant reaction conditions, the average particle size of the powder decreased from 45 to 19 nm. Figure 3 also shows the TEM micrographs of TiO_2 particles produced at the condition of Figure 2. Particles having dense polyhedral mor-

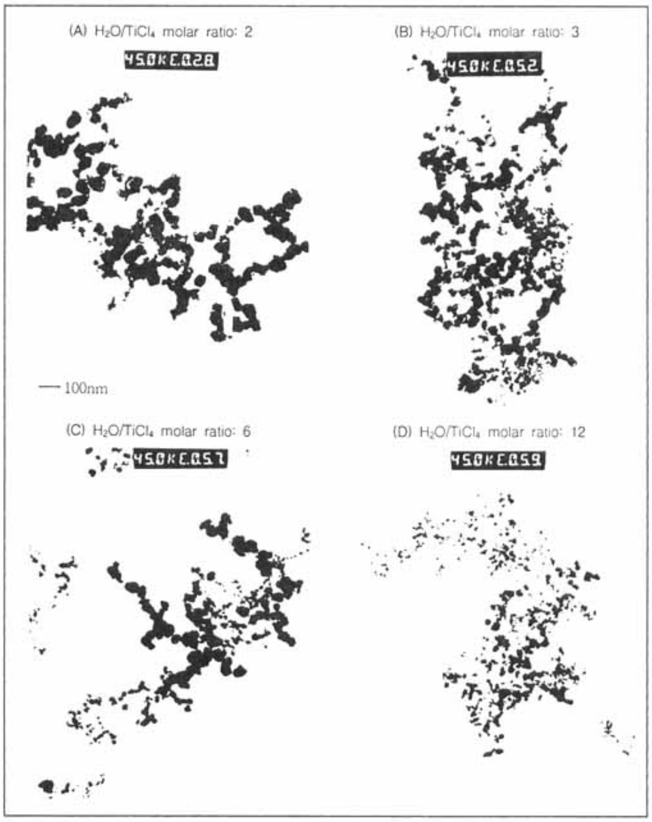

Figure 3. Transmission electron microscopic images of TiO_2 particles.

phology were found at all conditions, and the average particle size of TiO_2 powders became smaller as the molar ratio of $H_2O/TiCl_4$ was increased with all other conditions fixed (Figure 2). The particle-size distribution became broader as $H_2O/TiCl_4$ was increased from 2 to 6, but it became uniform at $H_2O/TiCl_4$ of 12. Particles prepared from even the small amount of the water vapor in this study is more uniform than previous results. Such differences in particle-size distribution between the present results and those by Suyama et al. (1976) and Yeom et al. (1995) are explained as the effect of the preheating of reactants to obtain a homogeneous nucleation in the reaction zone.

The change of primary particle size and size distribution in the present result is considered due to the role of the water vapor in the presence of preheating reactants. There are lots of small primary particles due to rapid nucleation rate in the initial stage of hydrolysis of $TiCl_4$, and those particles will grow into large particles by the coagulation. As the molar ratio of $H_2O/TiCl_4$ increases, a lot of water molecules will exist in the reaction zone. Excess water molecules may surround very small primary particles which are generated by the nucleation through the preheating of the reactants, then retard the coagulating chance for the growth of primary particles. Thus, TiO_2 particles having smaller size and uniform distribution could be obtained at the high molar ratio of $H_2O/TiCl_4$ in the present study.

Figure 4 shows the X-ray diffraction patterns of powders produced in the $TiCl_4$–H_2O system. The rutile content in TiO_2 particles was increased from 21 to 54% at a constant temperature (1,000°C) of reaction zone by increasing the molar ratio of H_2O to $TiCl_4$. This transformation was caused by the formation of rutile nuclei on the surface of anatase particles followed by the growth of rutile toward the interior. The formation of rutile nuclei can be accelerated as the particle size becomes very small (less than 100 nm in diameter). The rutile contents of TiO_2 particles in this experiment were more than 20% higher than previous results (Suyama et al., 1976; Yeom et al., 1995). The low rutile contents of previous works was considered due to the larger size of primary particles. High rutile contents in the present study could be explained by the formation of small particles at high ratios of H_2O to $TiCl_4$.

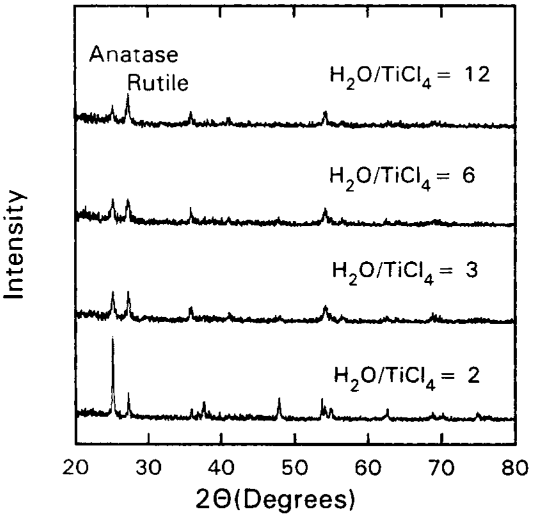

Figure 4. X-ray diffraction patterns for TiO_2 powders at different molar ratio of $H_2O/TiCl_4$ in $TiCl_4$–H_2O system.

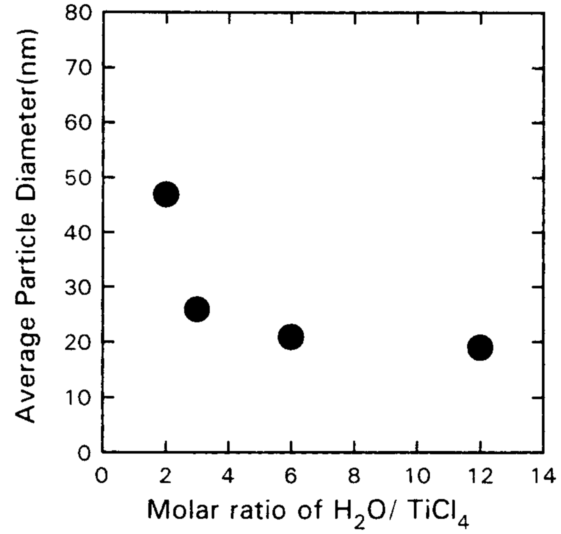

Figure 5. Effect of molar ratio of $H_2O/TiCl_4$ on the particle size in the $TiCl_4$-H_2O-O_2 system.

Reaction temperature: 1,000°C; preheating temperature: 900°C; $TiCl_4$ feed rate: 1.05×10^{-3} mol/min; gas flow rate: 4 L/min.

TiO_2 particles from $TiCl_4$–H_2O–O_2 system

TiO_2 particles from the simultaneous oxidation and hydrolysis reaction of $TiCl_4$ in the $TiCl_4$–H_2O–O_2 system were prepared to compare with the particles from the hydrolysis of $TiCl_4$. The experimental conditions were the same as the $TiCl_4$–H_2O system. As the molar ratio of H_2O to $TiCl_4$ was also increased from 2 to 12 at conditions of the other fixed variables, the average particle size of powder changed from 46 to 19 nm (Figure 5), but the geometric standard deviation, which represents the size distribution, showed nearly constant value of 1.40 (Figure 6). Figure 7 shows the TEM pictures of TiO_2 particles produced at the condition of Figure 5, and particles having dense polyhedral structure in particle morphology. The average particle size of TiO_2 powders became smaller as the molar ratio of $H_2O/TiCl_4$ was increased at all the fixed experimental conditions. In the particle-size distribution, particles from the $TiCl_4$–H_2O–O_2 system shows more uniform distribution than those from the $TiCl_4$–H_2O system.

According to the calculation of Akhtar et al. (1994) on the thermodynamic equilibrium conversion of $TiCl_4$ by oxidation and hydrolysis as a function of the water vapor loading, the $TiCl_4$ selectivity by oxidation/hydrolysis becomes equally important as the molar ratio of $H_2O/TiCl_4$ increases from 0 to 1. In the result of Akhtar et al. (1994), particles having a range from 20 to 200 nm in primary particle size were prepared, and a small decrease in the particle size was also found as the molar ratio of $H_2O/TiCl_4$ changed from 0.06 to 2.57 at the temperature of 1,000°C. However, there was no explanation on the change of primary particle size.

The uniform size distributions and the change of the particle sizes in the $TiCl_4$–H_2O–O_2 system are considered the

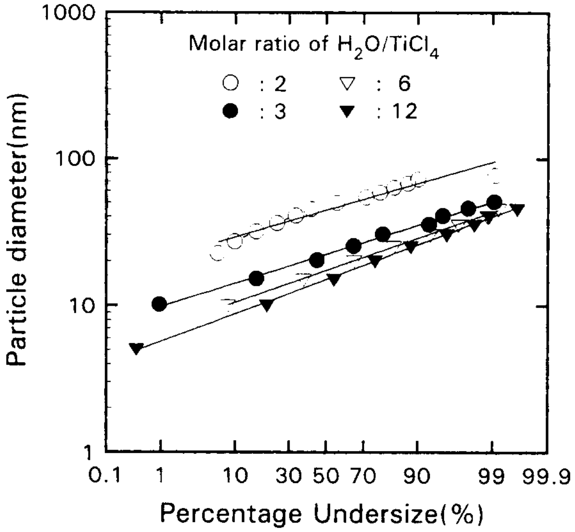

Figure 6. Log probabilities of powders with different molar ratio of $H_2O/TiCl_4$ in the $TiCl_4$-H_2O-O_2 system.

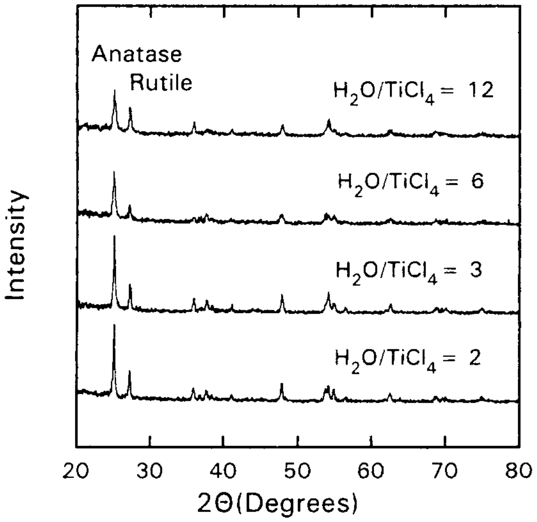

Figure 8. X-ray diffraction patterns for TiO_2 powders at different molar ratio of $H_2O/TiCl_4$ in $TiCl_4$-air-H_2O system.

same as those in the $TiCl_4$–H_2O system due to the role of the excess water molecules that may have retarding effects on the coagulation of small particles. However, the change of the primary particles size in the $TiCl_4$–H_2O–O_2 system was more dependent on the amount of water vapor than those of $TiCl_4$–H_2O system because the particle size decreased considerably with a small increase of the water vapor. The slow oxidation rate of $TiCl_4$ having a same $TiCl_4$ selectivity by oxidation/hydrolysis at high molar rates of $H_2O/TiCl_4$ may also play a role in keeping the small and uniform particle-size distribution.

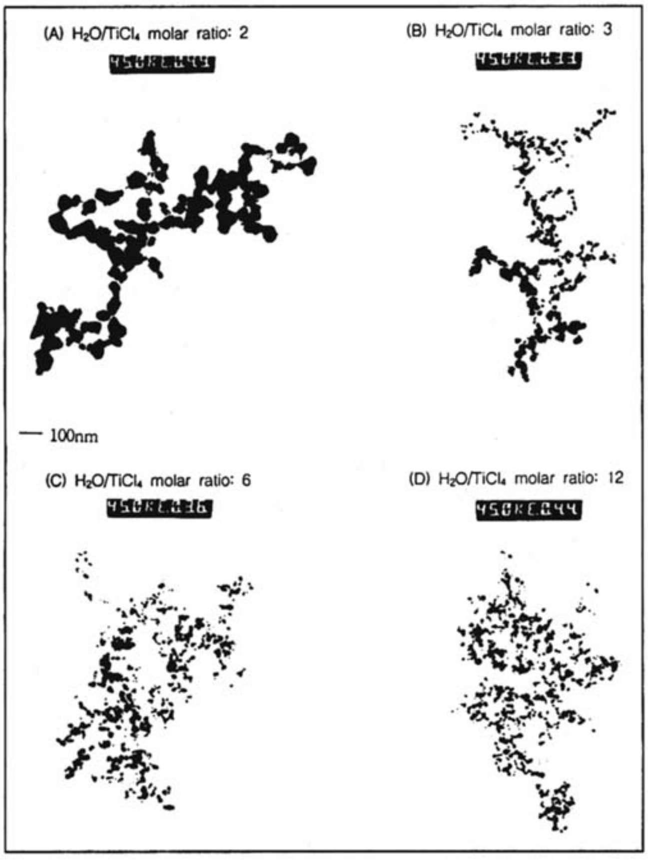

Figure 7. Transmission electron microscopic images of TiO_2 particles.

The rutile content in TiO_2 particles was increased from 16 to 24% with the increase of the molar ratio of H_2O to $TiCl_4$ (Figure 8). This increase in the rutile content was smaller than the increase in the $TiCl_4$–H_2O system, and was considered due to low selectivity of rutile phase during the oxidation of $TiCl_4$. Results of Suyama et al. (1976) reported a higher rutile content in the hydrolysis of $TiCl_4$ than in the oxidation. However, more study is required to distinguish the difference of the rutile content at the equivalent particle size between the $TiCl_4$–H_2O and the $TiCl_4$–H_2O–O_2 system. In the results of Akhtar et al. (1994), there was little effect of the $H_2O/TiCl_4$ ratio, which had changed from 0 to 2.57 on the phase composition of titania. Their results showed only 3% rutile content in TiO_2 particles at the temperature of 1,000°C. In the reaction system of Akhtar et al. (1994), $TiCl_4$ vapor and O_2 gas were mixed at the reactor inlet, and then the mixed stream met the water vapor at the reaction temperature. Therefore, there was a high possibility of nucleation of TiO_2 in the mixed stream of $TiCl_4$ vapor and O_2 gas before the mixed stream met the water vapor at the high temperature, therefore, it was difficult to find the effect of water vapor on the particle size and rutile content of TiO_2. However, in the present study, the water vapor and O_2 gas were mixed and introduced to the outer tube of the preheating zone, and then transferred to the reaction zone to meet the preheated $TiCl_4$ vapor from the inner tube of the preheating zone. Therefore, water vapor, oxygen, and $TiCl_4$ vapor meet together in the reaction zone at the same temperature, so the precise effect of water vapor on the rutile content and particle size of TiO_2 particles can be examined in the present study.

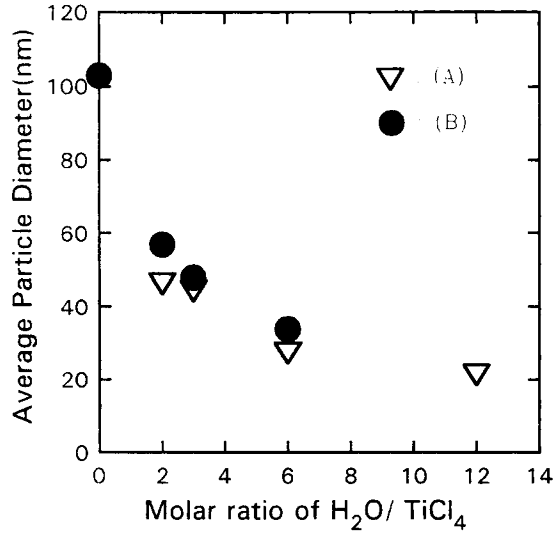

Figure 9. Effect of molar ratio of $H_2O/TiCl_4$ on the particle size in the $TiCl_4$-H_2O-air system.

(A) Reaction temperature: 1,000°C; preheating temperature: 900°C; gas-flow rate: 4 L/min; $TiCl_4$ feed rate: 1.05×10^{-3} mol/min. (B) Reaction temperature: 1,000°C; preheating temperature: 900°C; gas-flow rate: 2 L/min; $TiCl_4$ feed rate 2.05×10^{-3} mol/min.

TiO_2 particles from $TiCl_4-H_2O$-air system

TiO_2 particles from the $TiCl_4$-H_2O-air system were prepared to compare the results with those obtained in the other systems. As the molar ratio of $H_2O/TiCl_4$ was increased from 2 to 12 at otherwise constant reaction conditions, the average particle size of the powder decreased from 47 to 22 nm (Figure 9), but the particle-size distributions were not changed with the value of 1.42 for the geometric standard deviation. The rutile content in TiO_2 particles was increased from 20 to 33% with the increase of the molar ratio of H_2O to $TiCl_4$. These results of the change of particle size and rutile content were very similar to the results of the $TiCl_4$-H_2O-O_2 system.

In the results of the $TiCl_4$-H_2O-O_2 system and the $TiCl_4$-H_2O-air system, it was expected that the ultrafine TiO_2 particles could be synthesized at the higher mole fraction of $TiCl_4$. Therefore, experiments at the condition of a high feed rate of $TiCl_4$ (2.0×10^{-3} mol/min) and a low gas-flow rate (2 L/min) were performed to investigate the effect of water vapor on the particle size and rutile content of TiO_2 particles with the variation of mole ratio of $H_2O/TiCl_4$. The particle size was changed from 103 to 32 nm, as the water vapor content increased (Figure 9). As expected, the large average particle size of 103 nm was produced in the absence of water vapor because of the high mole fraction of $TiCl_4$ and low gas-flow rate. A average particle size of 32 nm was obtained at $H_2O/TiCl_4$ molar ratio of 6. As the water vapor content increased in the vapor phase, the rutile content of TiO_2 particles was also increased from 18 to 35%. Therefore, the higher production rate of ultrafine TiO_2 particles could be obtained in the presence of water vapor in the vapor-phase synthesis, and such an effect of the water vapor on the particle size could play an important role in designing the flame reaction system for ultrafine particles.

Conclusion

The effect of water vapor on the particle size, size distribution, and rutile content of ultrafine TiO_2 particles was investigated in the simultaneous hydrolysis and oxidation of $TiCl_4$ by the gas-phase reaction. Experiments have been made with the introduction of the preheating of reactants in the various reaction systems such as $TiCl_4$-H_2O, $TiCl_4$-H_2O-O_2, and $TiCl_4$-H_2O-air systems. As the molar ratio of $TiCl_4$ to H_2O increased from 2 to 12, the average particle size decreased from 45 nm to 19 nm and the rutile fraction of TiO_2 powders increased from 21% to 54% in $TiCl_4$-H_2O system. In the $TiCl_4$-H_2O-O_2 system, the changes of average particle size and rutile fraction were nearly the same as the $TiCl_4$-H_2O system, but narrower particle-size distributions than the $TiCl_4$-H_2O system were obtained at the same conditions. The same tendency as the $TiCl_4$-H_2O-O_2 system on the changes of average particle size, size distribution, and rutile content was also found in the $TiCl_4$-H_2O-air system. In the presence of the water vapor and the preheating of reactants in the vapor phase, high production rate of ultrafine TiO_2 particles could be obtained at the condition of higher mole fraction of $TiCl_4$ and lower gas flow rate.

Acknowledgment

This research was supported by the Korean Ministry of Trade and Industry. The author acknowledges stimulating discussions with Professor Sheldon K. Friedlander of the University of California at Los Angeles.

Literature Cited

Akhtar, M. K., Y. Xiong, and S. E. Pratsinis, "Vapor Synthesis of Titania Powder by Titanium Tetrachloride Oxidation," *AIChE J.*, **37**(10), 1561 (1991).

Akhtar, M. K., S. Vemury, and S. E. Pratsinis, "Competition between $TiCl_4$ Hydrolysis and Oxidation and Its Effect on Product TiO_2 Powder," *AIChE J.*, **40**, 1561 (1994).

Clark, H. B., *Titanium Dioxide Pigment, Pigments: 1*, Marcel Dekker, New York (1975).

Jang, H. D., and J. Jeong, "The Effect of Temperature on Particle Size in the Gas-Phase Production of TiO_2," *Aerosol Sci. Tech.*, **23**, 553 (1995).

Kobata, A., K. Kusakabe, and S. Morooka, "Growth and Transformation of TiO_2 Crystallites in Aerosol Reactor," *AIChE J.*, **37**, 347 (1991).

Ollis, D. F., E. Pelizzetti, and N. Serpone, "Photocatalytic Destruction of Water Contaminants," *Environ. Sci. Tech.*, **5**, 1523 (1991).

Rice, R. W., "Ceramic Processing: an Overview," *AIChE J.*, **36**, 481 (1990).

Spurr, R. A., and H. Myers, "Quantitative Analysis of Anatase-Rutile Mixtures with an X-ray Diffractometer," *Anal. Chem.*, **29**, 760 (1957).

Suyama, Y., K. Ohmura, and A. Kato, "Formation of Rutile-TiO_2 Powders by Vapor Phase Reaction," *J. Jpn. Chem. Soc.*, **59**, 146 (1976).

Suyama, Y., and A. Kato, "TiO_2 Produced by Vapor-Phase Oxigenolysis of $TiCl_4$," *J. Amer. Ceramic Soc.*, **59**, 146 (1976).

Yeom, S. M., K. H. Kim, D. W. Shim, and C. G. Park, "Preparation and Characterization of Fine TiO_2 Powders by Vapor-Phase Hydrolysis of $TiCl_4$," *J. Kor. Ceram. Soc.*, **29**, 525 (1992).

Yeom, S. M., S. H. Lee, and K. H. Kim, "Synthesis and Characterization of TiO_2 Ultrafine Powder by Chemical Vapor Deposition," *J. Kor. Ceram. Soc.*, **32**, 37 (1995).

Manuscript received Oct. 28, 1996, and revision received Mar. 27, 1997.