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# Low temperature vapor-phase preparation of $TiO_2$ nanopowders

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The preparation of $TiO_2$ nanopowders by vapor-phase hydrolysis of $TiCl_4$ below 600 °C is studied in this paper. Influences of preparation variables, such as preparative temperature, residence time, reactant concentration, and $H_2O/TiCl_4$ mole ratio, on $TiO_2$ particle size, morphology and chlorine contamination are investigated, followed by discussion. It shows that the hydrolysis temperature exerts greatest influences, while the residence time hardly have impact on product particles below 400 °C, among the hydrolysis variables investigated. The chlorine contamination on nanopowders occurs during the preparation which can be greatly reduced by proper control on preparation variables. Unlike the high temperature gas-phase processes such as oxidation route and flame synthesis, low-temperature route shows the ready control on product powders, and thus obtains titania powders with small size, narrow size distribution and very weak agglomeration. In addition, the decreased energy consumption, retarded corrosion on the reactor and the reduced operation problems would be expected for the low temperature processes.

## Nomenclature

| | |
|---|---|
| $c$ | sticking coefficient |
| $C_0$ | total concentration of condensable species (molecules $cm^{-3}$) |
| CVD | chemical vapor deposition |
| $d$ | primary particle diameter (nm, $\mu$m) |
| $g$ | gas/vapor phase |
| $K_p$ | equilibrium constant of chemical reaction (in terms of partial pressures) |
| nm | nanometer |
| PVD | physical vapor deposition |
| $r$ | $H_2O/TiCl_4$ more ratio |
| s | solid state |
| $t$ | residence time (s) |
| WC | wet chemistry process |
| $\rho$ | true density of particle ($cm^3$ $g^{-1}$) |

## 1. Introduction

$TiO_2$ powders play important roles in the technology fields such as pigments, catalysts and supports, cosmetics, ceramics and so forth [1, 2]. Oxidation of $TiCl_4$ vapor, also known as the "chloride" process in titania industry [3–5], is a gas-phase preparative method or a chemical vapor deposition method (CVD) in which all reactants undergo gas/vapor phase chemical reactions to form powders. It now becomes one of the two routes for commercial production of titania powders, along with the classic sulfate route that is a kind of wet chemical (WC) method [1, 6, 7]. Compared with wet-chemical method, it does not involve batch operation, a large quantity of liquid/solid byproducts' treatment, and the strong tendency of hard aggregates formation [3], and is a preferred route from the point of view of environment protection. The oxidation route, however, tends to produce submicron pigmentary titania powders (0.1–0.4 $\mu$m). Now, increasing demands are emphasized on nanoscale $TiO_2$ particles ($<0.1$ $\mu$m) in advanced technology fields like fine ceramics, ultraviolet light absorber and photocatalysts [8, 9]. Table I shows diverse preparation methods.

$TiCl_4$ is a kind of inorganic and low cost precursor, it can be oxidized or hydrolyzed to prepare $TiO_2$ powders according to:

$$TiCl_4(g) + O_2(g) \rightarrow TiO_2(s) + 2Cl_2(g)$$

$$TiCl_4(g) + 2H_2O(g) \rightarrow TiO_2(s) + 4HCl(g)$$

The oxidation method is an important route and a typical gas-phase/CVD method. As we know in gas-phase processes, greater equilibrium constants ($K_p$) favor the obtaining of smaller particles and the $K_p$ value that exceeds $10^{2-3}$ is necessary for preparating nanoscale particles [18]. Fig. 1 shows the equilibrium constants of oxidation and hydrolysis reactions of $TiCl_4$. In Fig. 1, the hydrolysis $K_p$ is always kept above $10^5$ till 1500 °C, which favors the complete conversion of $TiCl_4$. In the case of oxidation reaction, $K_p$ decreases rapidly with the oxidation temperature; it is about $10^{1.6}$ at 1500 °C.

As shown in Table I, the oxidation of $TiCl_4$ vapor is carried out at as high as 1400 °C [4], and thus is a high temperature gas-phase process in which the preparative temperature exceeds 900 °C. It has encountered several problems such as inconvenient control on products, the corrosion on reactor and some operation

TABLE I The preparation methods for $TiO_2$ powders[a]

| Preparation methods | Oxidation process (CVD) [4, 5] | Classic sulfate process (WC) [6, 7] | Flame synthesis (CVD) [10, 11] | Pyrolysis/Hydrolysis of organotitanium compound (CVD) [12, 13] | Inert gas condensation, IGC, (PVD) [14, 15] | Sol-Gel method (WC) [16, 17] |
|---|---|---|---|---|---|---|
| Reactant materials | $TiCl_4 + O_2$ | $TiOSO_4 + H_2O$ | $TiCl_4 + O_2 + H_2O$ | $Ti(OC_4H_9)_4$, for example | Ti, postoxidation to obtain $TiO_{2-x}$ | $Ti(OC_4H_9)_4$ for example |
| Procedure | Continuous | Batch | Continuous | Continuous | Batch | Batch |
| Preparative temperature (°C) | 1400–1500 | Hydrolysis below 100, calcination above 700 | above 1000 | 900, for example | See Refs. [12, 13] | Hydrolysis below 100, calcination at high temperature |
| Particle size (μm) | 0.1–0.4 | 0.1–0.4 | 0.03–0.06 | <0.1 | 0.005–0.015 | −0.015 |
| Agglomeration | Weak | Strong | Weak or strong | Weak | Weak | Strong |
| Yield | Commercialized | Commercialized | Commercialized | Lab scale | Lab scale | Lab scale |
| Byproducts | $Cl_2$, can be recycled | Large quantity, $H_2SO_4$, acid water, $SO_2$, $SO_3$ | $Cl_2 + HCl$ | $C_4H_8$ or $C_4H_9OH$ | — | $C_4H_9OH$ & organic solvent |
| Main challenges | Severe $TiCl_4$ corrosion at high temperature | High energy consumption; waste processing & recycling | Relatively wide size distribution | Expensive precursor; possible residual carbon in particles | Very small yield | Expensive precursor and organic solvents |

[a] *Note*: CVD, Chemical Vapor Deposition; PVD, Physical Vapor Deposition; WC, Wet Chemistry process.

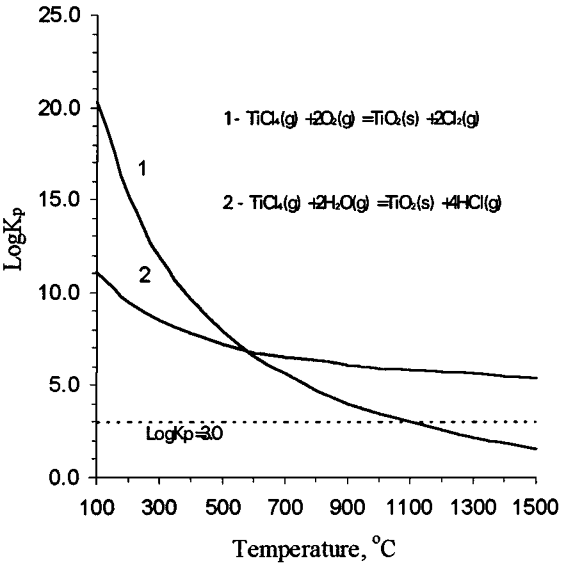

*Figure 1* The equilibrium constants ($K_p$) of oxidation and hydrolysis reactions (obtained by thermochemical calculation; the thermodynamic data come from Knache *et al.* [19]).

problems, which mainly arise from the high preparative temperature. In some researches, it shows that the use of metalorganic compounds, such as $Ti(OC_4H_9)_4$ and $Ti(OC_3H_7)_4$, can decrease the preparative temperature, however, some other problems like expensive cost, incomplete conversion of the reactants, residue carbon in product powders may occur [12, 13].

Though the hydrolysis of inorganic $TiCl_4$ vapor can prepare finer $TiO_2$ particles at much lower temperature, it is usually employed in flame synthesis in which the maximum temperature exceeds 1000 °C [10, 11]; in such case, the oxidation reaction is still the main reaction. The product control is not readily obtained because of the great temperature difference within a flame as well as the very high temperature. Though the hydrolysis of $TiCl_4$ is sometimes attached to the oxidation route, it mainly acts as a nucleation agent [20, 21]. As an independent preparation route, however, it hasn't been paid much attention and hence detailed information is still limited.

The presentation of our work is divided into two parts. In this paper the influences of preparation variables, such as preparative temperature, residence time, $TiCl_4$ concentration and $H_2O/TiCl_4$ mole ratio, on $TiO_2$ particle size, purity and agglomeration are investigated followed by discussion. In a later paper, the influences of reactant mixing on particle size and morphology will be investigated; it shows that the mixing process of the two reactant streams also exerts noticeable effects on $TiO_2$ particles.

## 2. Experimental

Fig. 2 is the schematic diagram of experimental apparatus. The reactor is made of two concentric glass tubes that is externally heated in a vertical furnace. The length of heating zone is about 42 cm. The inner diameters are 20 and 30 mm, respectively, for two sections connected by a cone tube.

$TiCl_4$ (reagent class) is evaporated at different temperatures to obtain different vapor pressures and its vapor is carried into the reactor by $N_2$ gas (99.9%). Water vapor is introduced into reactor by dry air. The $TiCl_4$ vapor and the water vapor are mixed rapidly around the nozzle and form $TiO_2$ aerosol at atmospheric pressure. At the exit of the reactor, the product is collected by thermophoresis and glass-fiber filter as dry powders for characterization. The exhaust gas is cooled by a water jacket tube, followed by washing.

The particle morphologies are observed by Transmission Electron Microscopy (TEM) on a JEM-200cx

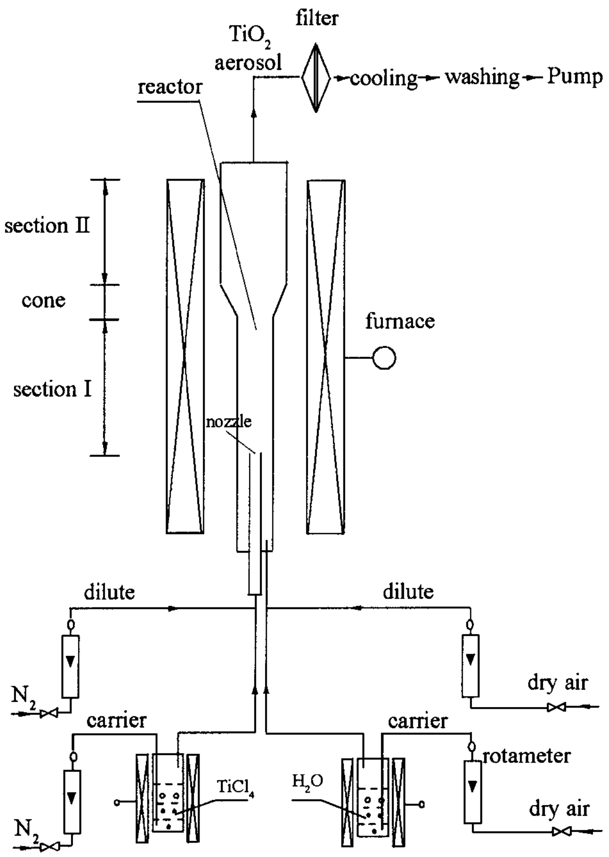

*Figure 2* The schematic diagram of experimental apparatus.

microscope operated at 200 kV. Elemental analysis of $TiO_2$ powder is carried out using Energy Dispersive X-ray Spectroscope (EDS) unit attached to a Scanning Electron Microscope (Amray 1910FE, USA); the dwell time is 100 s for all samples. The TG-DTA spectra are obtained in air atmosphere on a thermoanalyser (LCT-1, Beijing optic instrument Co., Beijing, China) from room temperature (25 °C) to 1000 °C at a speed of 10 °C/min. The specific surface areas of powders are measured by nitrogen adsorption at 77 K (ST-03, Beijing Analysis Instrument Factory, Beijing) using the BET equation. XRD patterns are gained on an X-ray diffractometer (BD86, Peking Univ. Instrument Inc.) operating at 40 kV, 20 mA using Cu$K_\alpha$ radiation.

## 3. Results and discussion

In this part, the influences of preparation variables such as preparative temperature, residence time, reactant concentration and composition on product particles are investigated, followed by discussion.

### 3.1. Preparative temperature

Table II gives the product particle diameters prepared at different temperatures when any other variables are kept constantly. The particle diameters are obtained from TEM images. Some of them are shown in Fig. 3.

TABLE II The particle diameters obtained at different hydrolysis temperatures

| $TiCl_4$ concentration vol. % | $H_2O/TiCl_4$ mole ratio | Residence time second | Hydrolysis temperature (°C) | Particle diameter (nm) |
|---|---|---|---|---|
| 0.55% | 20 : 1 | About 1.5 | 260 | 120 |
| | | | 330 | 50 |
| | | | 410 | 36 |
| | | | 525 | 18 |

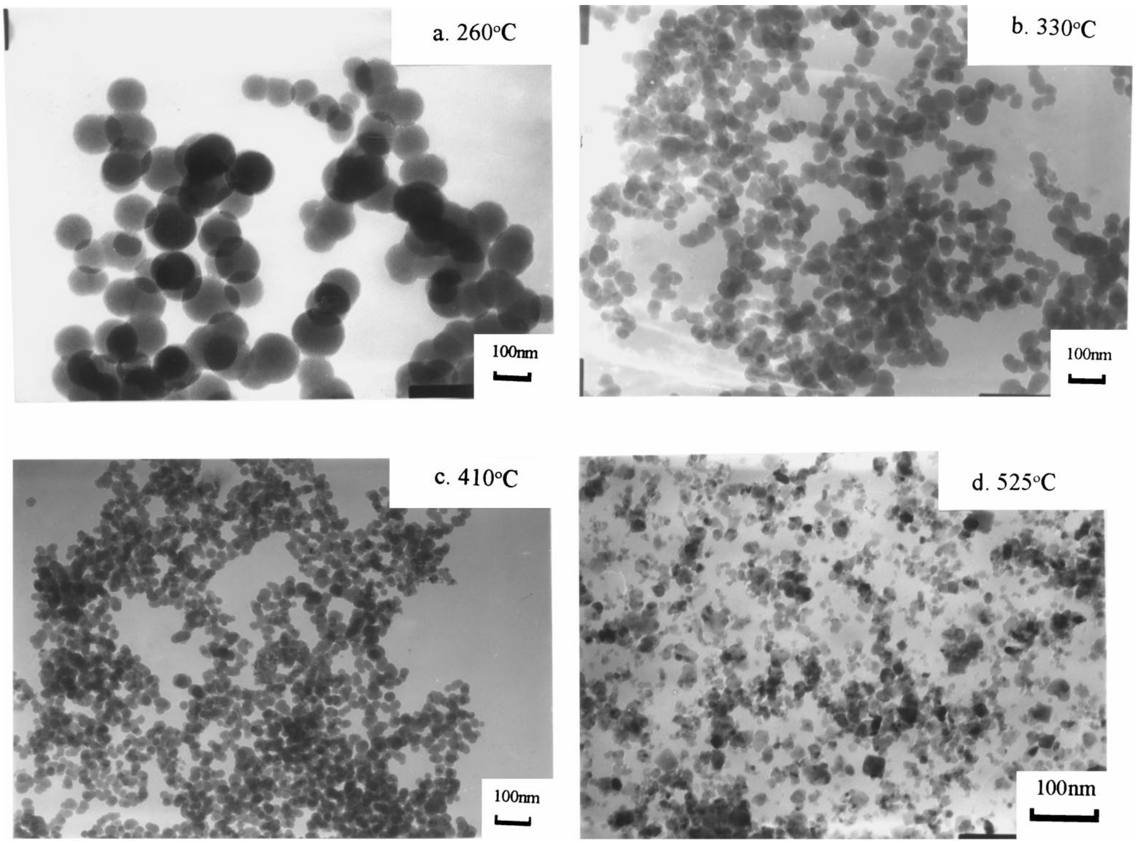

*Figure 3* TEM images of the product particles obtained at various temperatures. (a) 260 °C, (b) 330 °C, (c) 410 °C, and (d) 525 °C.

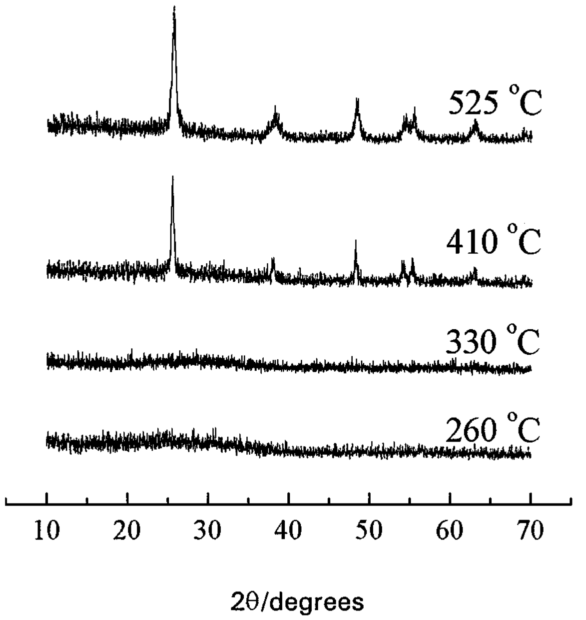

*Figure 4* XRD patterns of the titania powders obtained at different temperatures.

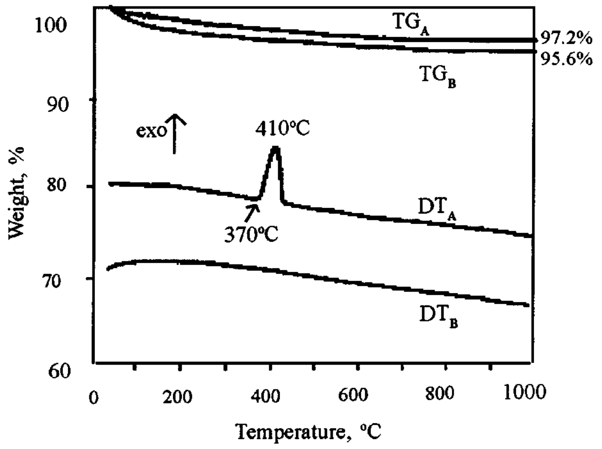

*Figure 5* TG-DTA analysis results.

TABLE III The particle diameters obtained from BET equation and TEM images

| Temperature (°C) | 260 | 330 | 410 | 525 |
|---|---|---|---|---|
| Specific area ($m^2$/g) | 13.5 | 32.5 | 44.6 | 85.9 |
| $d_{\mathrm{BET}}$ (nm) | 115.7 | 48.1 | 35.0 | 18.2 |
| $d_{\mathrm{TEM}}$ (nm) | 120 | 50 | 36 | 18 |

It is clear that the particle diameters decrease with the increasing reaction temperatures. In Fig. 3, when the reaction temperature is 410 °C or below, the particles have round or near round shape, while at 525 °C the particles are polyhedral, showing the high crystallinity. The XRD patterns in Fig. 4 show that the crystalline structures are the anatase for the samples obtained at 410 and 525 °C, and the amorphous structures for those obtained at 330 and 260 °C.

Fig. 5 is the results of TG-DTA analysis for the samples obtained at 330 and 525 °C. The curve $\mathrm{DTA}_{330}$ has an exothermic peak starting from 370 °C, indicating the phase transformation from the amorphous to the anatase. No more phase transformation occurs below 1000 °C. The curve $\mathrm{DTA}_{525}$ shows no peak from room temperature to 1000 °C. In these two cases, the weight losses are both very small, about 4.4 and 2.8%, respectively. Furthermore, there is no endothermic peaks that are attributed to the dehydration of titanium hydrates.

Table III gives the specific surface areas (S) that are obtained from the nitrogen absorption (BET) and the equivalent diameters ($d_{\mathrm{BET}}$) of the samples according to:

$$d_{\mathrm{BET}} = 6/(\rho \cdot S)$$

(considering $\rho = 3.84\,\mathrm{g/cm^3}$ for the anatase structure)

Obviously, the diameters obtained from the specific surface areas and the TEM images agree with each other very well. This implies that the particles are in solid other than in porous state in which the $d_{\mathrm{BET}}$ will be far smaller than the $d_{\mathrm{TEM}}$ [13, 22]. From 260 to 525 °C, the particle diameters decrease from 120 to 18 nm. Therefore, the particle size is highly sensitive to preparative temperature, and thus it is adjustable.

In high temperature processes, there are some similar cases [5] in which the particle diameters decrease with the increasing preparative temperatures. However, the reverse cases are often encountered when particle sintering/coalescence becomes a controlling factor [23]. For instance, for the high temperature oxidation of $TiCl_4$ and the low temperature processes of pyrolysis of $Ti(OC_4H_9)_4$, the relationships between the particle size and the preparative temperature are reverse to the low temperature hydrolysis of $TiCl_4$ in this paper [4, 13, 22, 24]. As is known, the particle size is determined by the relative rate of particle growth to particle nucleation [5]. In above cases, the particle sizes increase as the preparative temperatures increase, since elevated preparative temperatures not only accelerate the nucleation rate but also the particle sintering rate. This is a challenge for high temperature gas-phase processes and causes some troubles to the product control.

## 3.2. Residence time

Different residence times are set by varying the length of heating zone. When the reaction temperature, $TiCl_4$ concentration and $H_2O/TiCl_4$ mole ratio are fixed at 360 °C, 0.4%, and 20, respectively, the particle sizes at different residence times are shown in Table IV. It shows that the particle sizes do not vary with the residence times to a wide extent (0.3–3600 s). This may be attributed to the condensation-controlled other than coagulation-controlled process [23]. This fact favors the particle size control during low temperature hydrolysis of $TiCl_4$. In high temperature gas-phase preparation of metal oxide particles [22, 24–26], the particle sizes are sensitive to the residence time. Ulrich [24] gave a relationship between the particle size and the residence

TABLE IV The particle sizes at different residence times

| Residence time (s) | 0.3 | 0.8 | 1.4 | 2.0 | 4.0 | 3600[a] |
|---|---|---|---|---|---|---|
| Particle diameter (nm) | 34 | 37 | 36 | 35 | 36 | 36 |

[a] *Note*: It is the size of the particles that continuously deposited on the inner wall of the reactor for 1h during preparation.

time, taking fumed silica as the example; it could be expressed as:

$$d = \frac{6}{\rho \cdot S}, \quad \text{where } S = 1.8\times 10^{8}(T^{1/2}\cdot c\cdot C_0\cdot t)^{-2/5}$$

Such sensitivity, due to frequent Brown collision and coalescence at high temperature, is encountered in the oxidation process and in the pyrolysis or hydrolysis of organotitanium compounds.

To avoid excessive particle growth in high temperature processes, some measures such as quenching the product aerosol [25] and adding some kinds of electrolytes for reducing particle collisions [4, 20, 27] have been taken. However, new problem such as possible incomplete conversion of reactants might arise in some cases [22, 25, 28], since there is not enough time for converting the reactants into products before flowing out of the reactor.

### 3.3. Reactant concentration and composition ($TiCl_4$ concentration and $H_2O/TiCl_4$ mole ratio)

The $TiCl_4$ concentration (volume concentration, v/v) is adjusted by changing the evaporation temperature of $TiCl_4$ liquid. The preparative temperature, $H_2O/TiCl_4$ mole ratio and residence time are fixed at 345 °C, 10 and 1.5 s, respectively. The particle sizes at different $TiCl_4$ concentrations are shown in Fig. 6.

In Fig. 6, it shows that the particle diameters increase with the increasing $TiCl_4$ concentrations, though the tendency is nonlinear. The similar results are obtained in other gas-phase preparations [5, 13, 22].

For the hydrolysis reaction:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

The $H_2O/TiCl_4$ mole ratio ($r$), or the reactant composition, is often far greater than the stoichiometric ratio (2 : 1) for the complete conversion of $TiCl_4$ and for accelerating the hydrolysis reaction according to the law of mass action. Various mole ratios are obtained by changing the evaporation temperature of water evaporator and fixing that of the $TiCl_4$. Fig. 7 shows the particle diameters at different mole ratios when the reaction temperature (330 °C) and the $TiCl_4$ concentration (1%, v/v) are fixed. In Fig.7, the particle sizes decrease as the mole ratios increase, and such tendency becomes slower at larger mole ratios.

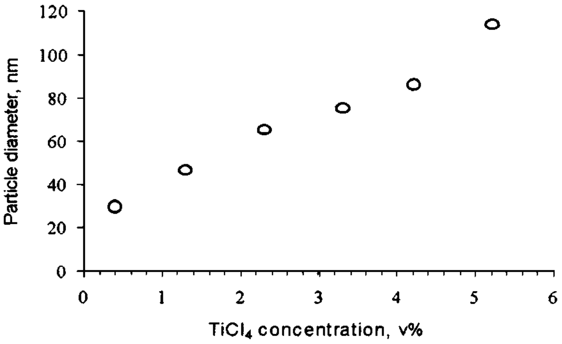

*Figure 6* The particle sizes at different $TiCl_4$ concentrations.

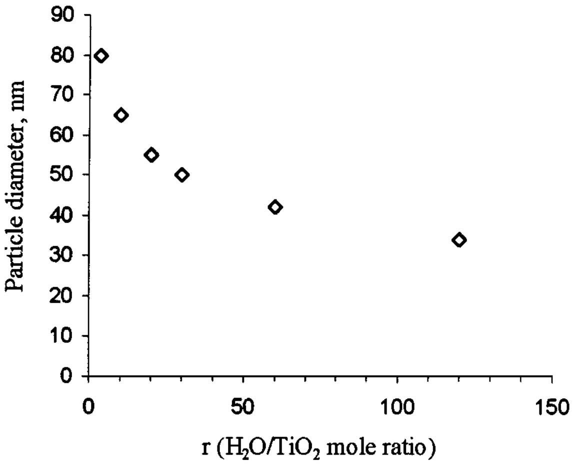

*Figure 7* The titania particles produced at different $H_2O/TiCl_4$ mole ratios.

### 3.4. Chlorine contamination

High purity is essential for excellent performance of nanopowders. In this work, gas-phase hydrolysis of $TiCl_4$ produces HCl gas that may be absorbed on $TiO_2$ nanopowders having large surface areas. This causes chlorine contamination problem in $TiCl_4$ hydrolysis method.

The investigation on chlorine contamination shows that the preparative temperature has remarkable influences on the chlorine content in product powders. HCl is a kind of volatile substances and thus might be removed by heat treatment. Two titania aerosols are prepared at 300 and 520 °C respectively by fixing any other preparative variables, followed by filtering at 150 °C for obtaining the dry powders. Both are then heat-treated at different temperatures for 1 h. Their chlorine contents (wt. %) are determined by the Energy Dispersive Spectroscopy (EDS) attached to a SEM, shown in Table V.

In Table V, the 300 °C sample contains around 1 wt. % chlorine even after heating at 1000 °C. The amorphous structure that is a disordered structure obtained at 300 °C may be responsible for the presence of $Cl^-$ anions (absorbed on $TiO_2$ clusters) in the product particles. In this case, the chlorine is difficult to be completely removed by heating. Another possible $Cl^-$ source is the incomplete conversion of the $TiCl_4$ because of the low reaction temperature and the short residence time (1.5 s). In contrast, the 520 °C sample shows very low chlorine contents. In this case, the particles have crystalline (anatase) structure as shown in

TABLE V The chlorine contents (wt %) in $TiO_2$ powders

| Heating temp. (°C) | Before heating | 400 | 600 | 800 | 1000 |
|---|---|---|---|---|---|
| 300 °C sample | 7.10 | 5.23 | 3.71 | 2.27 | 1.05 |
| 520 °C sample | 0.60 | 0.09 | 0.00 (500 °C) | — | — |

TABLE VI The chlorine contents in $TiO_2$ powders obtained at different filtering temperatures

| Filtering temperature (°C) | 20 | 100 | 200 | 300 | 400 |
|---|---|---|---|---|---|
| Chlorine content (wt %) | 6.37 | 1.66 | 1.08 | 0.48 | 0.06 |

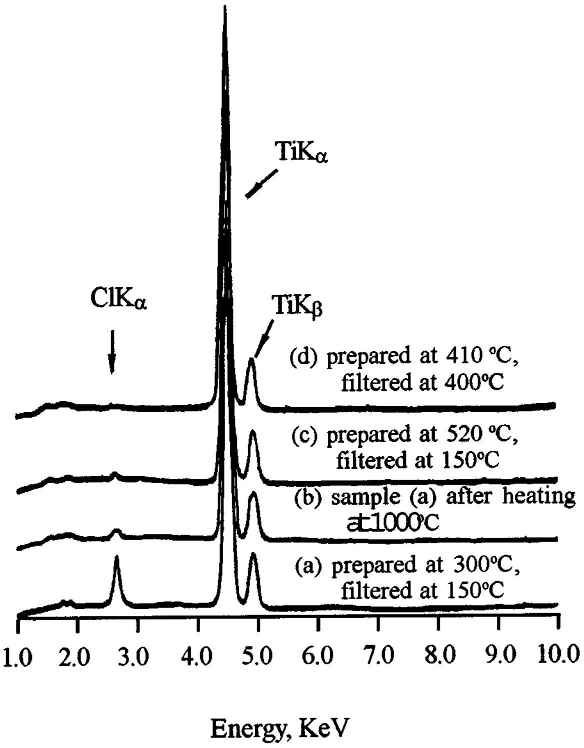

*Figure 8* EDS spectra of some $TiO_2$ samples obtained at various filtering temperatures.

Fig. 4, which results in difficult incorporation of $Cl^-$ anions in $TiO_2$ grains. Besides, the higher temperature accelerates the hydrolysis reaction for more complete conversion of $TiCl_4$.

Further investigation shows that the chlorine content is controlled by not only preparative temperature but also the filtering temperature. Table VI shows the chlorine contents of the samples prepared at 410 °C but filtered at different temperatures. As it shows, the chlorine in the samples tend to disappear when filtered at 400 °C, while it is rich in the wet sample obtained from the condensation of water vapor on the inner wall of cooling jacket tube at 20 °C. Some EDS spectra are shown in Fig. 8.

### 3.5. Particle agglomeration/aggregation

Hard aggregates should be avoided in high-added-value powders, which is especially emphasized in the production of ceramic powders, since their presence leads to the formation of pores and flaws during ceramics fabrication [29, 30]. The apparent density of a titania powder is obtained from the weight and the bulk volume of the powder before any treatment. The results show that they are around $0.04\,g/cm^3$ and insensitive to preparation variables. The equivalent voidage is about 99%, if considering the true density of $3.84\,g/cm^3$ for the anatase. In other words, only about 1% of bulk volume of a powder is occupied by $TiO_2$ particles, implying the loose packing between titania nanoparticles.

The diameters of the sample prepared at 525 °C are 18.2 and 17.7 nm respectively, determined by nitrogen absorption (BET) and the XRD patterns (calculated using the Scherrer relationship: $d_{hkl} = 0.9\lambda/B_{hkl}\cos\theta$ [31], for the peak of $2\theta = 25.3°$). The value of $(d_{\text{BET}}/d_{\text{XRD(TEM)}})^3$, which is an indicator for particle agglomeration/aggregation, is only 1.09. There are some similar examples in Table III. All of these show the small difference between $d_{\text{BET}}$ and $d_{\text{TEM/XRD}}$.

The above facts show that there is very weak agglomeration in as-prepared $TiO_2$ nanopowders. On the one hand, low temperature gas-phase hydrolysis avoids the drying and calcination procedures of wet-chemical processes that may cause agglomeration problem due to the residual “glue” -OH groups. The product particles are absorbed and separated by surrounding gases. On the other hand, the hydrolysis preparation is carried out far below the high temperature processes (>900 °C) in which the hard aggregates might be formed due to the incomplete particle sintering. Therefore, the weakly agglomerated $TiO_2$ nanopowders are obtained.

Low temperature gas-phase processes, compared with high temperature ones, will consume less energy, and thus results in lower costs. Moreover, it leads to a decreased attack of the corrosive gases on the reactor. Besides, the growth rate of products around the reactant nozzle is expected to be lowered, and the coarsening/sintering of the particles that deposits on the inner surface of reactor is also expected to be greatly prevented.

## 4. Conclusion

1. Nanosized $TiO_2$ particles with regular shape and narrow size distribution can be obtained by vapor-phase hydrolysis of $TiCl_4$ below 600 °C by properly adjusting the preparation variables.

2. Among the preparation variables investigated, the preparative temperature exerts the greatest influences on particle size and morphology. The titania particle sizes decrease as the preparative temperatures increase. The TG-DTA study shows that the particles start to crystallize from about 370 °C.

3. The sizes of the particles obtained below 400 °C hardly change with the residence times to a wide extent (0.3–3600 s). This may be attributed to a condensation-controlled other than a coagulation-controlled process, which favors the particle size control during preparation.

4. The particle sizes increase as $TiCl_4$ vapor concentrations increase. The $H_2O/TiCl_4$ mole ratio also has influences on product particles; the increasing $H_2O/TiCl_4$ mole ratios are favorable for the conversion of $TiCl_4$ and obtaining of smaller particles.

5. The chlorine contamination on $TiO_2$ powders occurs during preparation. The preparative temperature has remarkable influences on chlorine contents in product powders. In addition, the filtering temperature is also an important factor. The preparation above the

crystallization temperature and the filtering at properly high temperature are beneficial for removing Cl element from powders.

6. The agglomeration of as-prepared $TiO_2$ particles is very weak, which is attributed to the low preparative temperature as well as the absorption and protection of gases between particles.

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