Original Article

New approaches in lowering the gas-phase synthesis temperature of TiO₂ nanoparticles by H₂O-assisted atmospheric pressure CVS process

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ABSTRACT

H₂O-assisted atmospheric pressure chemical vapor synthesis is a modern economical process for the gas-phase synthesis of TiO₂ nanoparticles. In the present work, the influence of synthesis temperatures (100–800 °C) on the phase structure, nanoparticle size, morphology, and agglomeration is investigated by transmission electron microscopy, selected area electron diffraction, X-ray diffraction, thermogravimetry, and differential thermal analysis. Down to 400 °C, crystalline TiO₂ nanoparticles are synthesized and at 200 °C amorphous nanoparticles are formed. Therefore, a decrease in minimum synthesis temperature by more than 500 °C is achieved. In addition, the paper investigates the hypothesis that the high heat capacity of the H₂O particles is responsible for the achieved decrease in synthesis temperature and for the dramatic decrease in size, coalescence, coagulation, and agglomeration of the nanoparticles. It is shown that the nanoparticles size is considerably higher for nanoparticles produced with gas-phase H₂O particles in comparison to those produced with liquid-phase H₂O particles, (average size 41 and 13 nm, respectively), because of the lower heat capacity of gas-phase H₂O particles, thus confirming the hypothesis.

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1. Introduction

Nanomaterials with different morphologies and structures can be made by gas phase and liquid phase technologies [1]. The research on process engineering and scale-up is important for the commercial production and application of nanomaterials, because the properties and the structure of nanomaterials are not only determined by the nucleation and growth process, but also strongly affected by processing parameters, such as the method of mixing, the heat transfer or the temperature distribution [1,2].

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Metals, metal oxides, metal carbides, metal nitrides, and their composite nanoparticles can be manufactured by chemical vapor synthesis (CVS) [3–5], microwave plasma [6] and radio frequency plasma enhanced chemical vapor deposition [7]. In conventional CVS processes, faster pyrolysis at higher temperatures results in smaller particle size, but it enhances subsequent sintering and particle size growth [8]. On the other hand, slower decomposition rates at lower temperatures result in larger primary particles caused by surface reaction mechanisms [8,9]. Therefore, conventional CVS processes still face many problems. By using the H2O-assisted atmospheric pressure CVS (APCVS) process, TiO2 nanoparticles can be produced at lower temperatures without dramatic coalescence or coagulation, thus saving the present primary and secondary H2O particles [10].

Lowering the cost of the CVS process by lowering the synthesis temperature without compromising the quality of the synthesized materials will widen the scope of the applications of the CVS process [11]. Unlike high-temperature gas-phase processes such as oxidation and combustion synthesis routes [12,13], the low-temperature H2O-assisted APCVS process allows to control the product powders, yielding TiO2 powders with small size, narrow size distribution, and weak agglomeration. In addition, a decrease in energy consumption, retarded corrosion of the reactor and a reduction in operation problems can be expected for the low-temperature H2O-assisted APCVS process.

In addition to lowering the cost of CVs, the decrease in synthesis temperature by the H2O-assisted APCVS process has considerable influence on the TiO2 nanoparticle characteristics. Kuo et al. [14] showed that the visible-light activity of TiO2 photocatalysts increased as the synthesis temperature decreased. In other words, the minimum synthesis temperature for TiO2 nanoparticles is the best CVS reaction temperature for producing nano-TiO2 with high visible-light-responsive photocatalytic activity. In addition, Kuo et al. [14] suggested that the synthesis temperature should not increase because of the appearance of the rutile phase at higher temperatures.

In conventional CVS processes, the heat loss caused by the collisions with gas molecules only depends on the heat capacity of gas molecules (c_p) [15]. In the presence of H2O particles, TiO2 nanoparticles have collisions either with H2O or gas particles. Since the specific heat capacity of H2O is high, the heat loss caused by the collisions increases. The nanoparticles’ temperature significantly decreases leading to a lower coalescence and particle size growth. Therefore, much smaller nanoparticles are obtained.

In the present work, the minimum synthesis temperature for TiO2 nanoparticles is examined experimentally and theoretically. Our hypothesis that the high heat capacity of the H2O particles leads to a decrease in synthesis temperature is experimentally investigated.

Xia et al. [16] stated that although the hydrolysis of TiCl4 can be linked to oxidation, it mainly acts as a nucleation agent; however, not much attention was paid on the hydrolysis as an independent preparation route and therefore detailed information is still limited. Hence, in the present work, the effect of hydrolysis on lowering the gas-phase synthesis temperature of TiO2 nanoparticles at atmospheric pressure is studied.

2. Experimental

The raw materials used in this study were TiCl4 (purity > 99.99%, Merck), oxygen (99.999%) and H2O (99.9%). The carrier gas was highly pure argon (99.999%). Fig. 1 shows a schematic illustration of the experimental apparatus. A hot-wall, atmospheric pressure, horizontal quartz reactor with an inner diameter of 80 mm and a length of 800 mm was used. The liquid precursor (TiCl4) was vaporized in a vertical bubbler in an oil bath. The precursor was introduced into a horizontal quartz tube reactor by bubbling argon through a precursor container. In addition, H2O was introduced into the reactor by bubbling argon through an H2O container.

The vapor concentration of the precursor was calculated, assuming that the carrier gas through the bubbler was completely saturated. A mass flow meter was used for the measurement of the TiCl4 flow rate. The precursor was introduced into the reactor at a flow rate of 50 g/h. Since the bubblers were scaled, the reductions of precursors during
each test were measured with respect to the total gas flow rate (2.1 L/min) and sampling time. Pure argon was introduced directly into the reactor at a flow rate of 0.5 L/min under atmospheric temperature and pressure. For TiCl₄ oxidation, oxygen gas was introduced at a flow rate of 0.5 L/min under atmospheric temperature and pressure. In the final step, the H₂O was introduced directly to the reactor at a flow rate of 0.5 L/min. The total gas flow rate was maintained at 2.1 L/min, resulting in equal residence time in the reactor for all runs. The furnace consisted of a fully recrystallized quartz reactor with an isothermal hot zone (Effective Reaction (ER) zone) and an adjustable accurate temperature controller. While passing through the reactor, the generated monomers underwent coalescence, coagulation, agglomeration, and sintering, finally ending up as TiO₂ nanoparticles. The produced nanoparticles were collected in the cold trap which consisted of a chamber, with inlet and outlet lines. The chamber was maintained in an ice-water bath.

All experiments were carried out 3 times and no large differences (1–5 nm) in particles diameter were observed. Before all runs, the internal surface of the quartz reactor was cleaned by laboratory alcohol (Ethanol, 96%). After cleaning the internal surface, the reactor was purged with pure argon at a flow rate of 0.5 L/min for 10 min. After that, sampling was carried out for 30 min at the constant above-mentioned flow rates.

To examine the effects of the ER zone temperature and find the minimum temperature for generating anatase TiO₂ nanoparticles by the H₂O-assisted APCVS process, experiments were carried out at different ER zone temperatures of 800, 700, 600, 400, 200 and 100 °C, respectively.

To study the effects of the heat capacity of the H₂O particles on the minimum synthesis temperature, two experiments were carried out. Firstly, liquid-phase H₂O particles with a high heat capacity of about 4.18 [(J/kg K)] were introduced directly into the reactor. Secondly, H₂O particles were introduced into the gas phase. The heat capacity of H₂O particles in the gas phase is about 2.08 [(J/kg K)] and therefore is significantly lower than the liquid phase.

Transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray diffraction methods (XRD), thermogravimetry (TGA) and differential thermal analysis (DTA), were used to characterize the produced TiO₂ nanoparticles. The transmission electron microscopy (TEM) images and SAED patterns for the TiO₂ nanoparticles were obtained on a Philips-EM-208S instrument with a tungsten filament at an accelerating voltage of 100 kV and a vacuum system which operates in the 10⁻⁹ Torr range. The crystal structure of the TiO₂ nanoparticles was characterized by X-ray diffraction (XRD). Patterns were recorded on a Philips-PW1800 diffractometer using Cu Kα radiation (λ = 1.54 Å) and a scanning angle between 10° and 90°. The average crystallite size was determined from the XRD measurements using the Scherrer equation [17]:

\[
    D = \frac{0.9 \lambda}{\beta \cos \theta}
\]

where D is the crystallite size (nm), λ the wavelength of X-ray used (1.542 Å for Cu Kα₁), θ half of the diffraction peak angle, and β the full width at half maximum (FWHM) of the peaks (radians).

20 mg from each of the synthesized prepared TiO₂ nanopowders from all experiments underwent thermogravimetry and differential thermal analysis (TG-DTA) in an argon atmosphere using a Rheometric Scientific STA-1500 machine. Thermogravimetric analysis of the all samples was performed using an Al₂O₃ sample holder in a nitrogen atmosphere at a flow rate of 50 mL min⁻¹ with a heating rate of 10°C/min from 20 to 1000°C.

3. Results and discussion

3.1. Effect of the ER zone temperature

The synthesis conditions are summarized in Table 1. The synthesis temperature was varied from 800 to 100 °C. By H₂O-assisted APCVS process the TiO₂ nanoparticles were achieved at synthesis temperatures down to 200 °C, but at 100 °C, the production rate of TiO₂ nanoparticles was too low to yield a significant number of nanoparticles.

Fig. 2 shows X-ray diffraction patterns (XRDs) from the TiO₂ nanopowders synthesized by H₂O-assisted APCVS at different synthesis temperatures (samples 1–5 in Table 1). The particles synthesized at 400 °C and above show crystalline peaks that can be clearly identified as anatase TiO₂. On the other hand, the nanoparticles synthesized at 200 °C show no crystalline peaks but a broad hump indicating that only amorphous particles are produced.

In previous studies [18–21] comprehensive experimental, thermodynamics and kinetics studies of simultaneous oxidation/hydrolysis showed that nanoparticles synthesized above 700 °C were the result of either the oxidation or the hydrolysis reactions. Rahiminezhad-Soltani [22] showed that both oxidation and hydrolysis of TiCl₄ have negative free standard energies, ΔG⁰, in the temperature range between 298 and 1200 K, but the oxidation reaction has higher activation energy and thus the oxidation reaction does not occur up to 700 °C at atmospheric pressure. According to Refs. [23,24] hydrolysis of TiCl₄ dominates the synthesis process of TiO₂ nanoparticles but oxidation of TiCl₄ dominates at high temperatures.

As the synthesis temperature increases from 200 to 600 °C, the thermal velocity, the kinetic energy and the reaction rate increase due to higher mobility and collisions and thus more crystalline TiO₂ nanoparticles are synthesized, leading to an increase in the height of the peaks in the XRD profiles (cf. Fig. 2c–e). When the synthesis temperature is further increased to 700 °C (cf. Fig. 2b), the oxidation reaction starts to occur partly and less crystalline TiO₂ nanoparticles are obtained. Therefore, as shown in Fig. 2 by increasing the temperature from 600 °C up to 700 °C the peaks of (1 0 3), (1 1 2) and (2 1 3) disappear. At a synthesis temperature of 800 °C, the oxidation reaction dominates the hydrolysis reaction and the intensity of the crystalline peaks in the XRD profile increases again, indicating more crystalline TiO₂ nanoparticles are generated (cf. Fig. 2a).

It should be pointed out that an identical sample setup and an identical amount of powder was used for all XRD measurements. Therefore, a lower intensity of the crystalline peaks
Table 1 – Process parameters used for the synthesis of TiO₂ nanoparticles by the H₂O-assisted APCVS route.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Argon flow rate (sccm)</th>
<th>Oxygen flow rate (sccm)</th>
<th>Precursor concentration (g/h)</th>
<th>ER zone temperature (°C)</th>
<th>Crystal structure (XRD)</th>
<th>Titania size (nm) (XRD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>500</td>
<td>50</td>
<td>800</td>
<td>Anatase</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>500</td>
<td>50</td>
<td>700</td>
<td>Anatase</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>500</td>
<td>50</td>
<td>600</td>
<td>Anatase</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>500</td>
<td>500</td>
<td>50</td>
<td>400</td>
<td>Anatase</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>500</td>
<td>50</td>
<td>200</td>
<td>Amorphous</td>
<td>Not specified</td>
</tr>
<tr>
<td>6</td>
<td>500</td>
<td>500</td>
<td>50</td>
<td>100</td>
<td>Not specified</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 2 – XRD patterns of TiO₂ nanoparticles prepared at different synthesis temperatures: (a) 800 °C, (b) 700 °C, (c) 600 °C, (d) 400 °C, and (e) 200 °C.

is not only an indication that lower crystalline nanoparticles were synthesized but also an indication of a higher volume fraction of amorphous nanoparticles. Also, the synthesis time held constant and this would mean the height of the peaks indicates how much volume crystalline powder was generated.

Fig. 3(a and b) shows TEM images and selected area electron diffraction (SAED) patterns comparing the TiO₂ nanoparticles obtained at synthesis temperatures of 800 and 700 °C, respectively. To determine the crystal structure for the nanoparticles synthesized at 800 °C from the SAED patterns, the PASAD-tools software was used [25]. A profile was deduced from the SAED pattern by azimuthal integration and the positions of the crystalline peaks were determined by peak fitting. The peaks indexed in Table 2 confirm the TiO₂ anatase crystal structure (JCPDS number 21-1272). A comparison of the SAED pattern in Fig. 3a and b, reveals more intense and continuous rings for the specimen synthesized at 800 °C, indicating that more crystalline TiO₂ nanoparticles are produced and that their size is smaller. This is also confirmed in the TEM bright-field images in Fig. 3. Both, amorphous and crystalline nanoparticles can be observed at a synthesis temperature of 700 °C. The amorphous particles are marked by “A” in the TEM bright-field image in Fig. 3b.

Nakaso et al. [9] showed that in solitary oxidation synthesis processes the surface reactions dominate the gas phase reactions at lower temperatures. Due to surface reactions, the condensed clusters of TiOCl₂ serve as seed nuclei at the exit of the ER zone, where the rest of the unreacted precursor condenses out forming partially oxidized Ti oxychlorides. As the temperature drops, they transform into TiO₂ upon thermal decomposition [9]. This results in large amorphous particles. Therefore, it can be concluded that the TiO₂ nanoparticles synthesized at a temperature of 700 °C are the result of incomplete oxidation reactions. Both, crystalline nanoparticles produced by hydrolysis reactions and large amorphous nanoparticles produced by oxidation reactions are obtained at the synthesis temperature of 700 °C. This explains the observed decrease in crystalline nanoparticles at 700 °C. At the synthesis temperature of 800 °C, because of a decrease in surface reactions and thus the number of oxidized Ti oxychlorides, the produced crystalline TiO₂ nanoparticles increases again.

To quantify the effect of the synthesis temperature on the average nanoparticle size, the Scherrer equation was used [17]. At a synthesis temperature of 200 °C, only amorphous nanoparticles are produced. At synthesis temperatures of 400, 600, 700 and 800 °C, the particles show a crystalline structure
Fig. 3 – TEM images and SAED patterns of TiO$_2$ nanoparticles synthesized at: (a) 800 °C and (b) 700 °C.

Table 2 – Analysis of the SAED pattern.

<table>
<thead>
<tr>
<th>Number</th>
<th>Reflection</th>
<th>Position [nm$^{-1}$]</th>
<th>d [Å]</th>
<th>Simulated intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>101</td>
<td>0.284</td>
<td>3.520</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>004</td>
<td>0.420</td>
<td>2.378</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>0.528</td>
<td>1.892</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>105</td>
<td>0.588</td>
<td>1.699</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>211</td>
<td>0.600</td>
<td>1.666</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>204</td>
<td>0.675</td>
<td>1.480</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>116</td>
<td>0.733</td>
<td>1.364</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>220</td>
<td>0.747</td>
<td>1.337</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>215</td>
<td>0.790</td>
<td>1.264</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>224</td>
<td>0.857</td>
<td>1.166</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>321</td>
<td>0.956</td>
<td>1.043</td>
<td>4</td>
</tr>
<tr>
<td>12</td>
<td>219</td>
<td>1.105</td>
<td>0.866</td>
<td>4</td>
</tr>
</tbody>
</table>
with average nanoparticle sizes of 10, 35, 40 and 13 nm, respectively.

There are two main reasons why the average TiO$_2$ particle size decreases again at a synthesis temperature of 800 °C: (1) as the hydrolysis of TiCl$_4$ is sometimes linked to the oxidation route, it acts as a nucleation agent and therefore this phenomenon causes nanoparticles size reduction [16]; (2) in the gas-phase processes, a greater equilibrium constant (K$_p$) favors the formation of smaller particles [16]. Therefore, at a synthesis temperature of 800 °C, where complete oxidation reactions dominate the synthesis process, the size of the TiO$_2$ nanoparticles decreases because the equilibrium constant (K$_p$) is larger [16]. At 700 °C, on the other hand, due to dominating surface reactions and incomplete oxidation reactions [9], larger nanoparticles are reached.

Fig. 4 shows the equilibrium constants of oxidation and hydrolysis reactions for TiCl$_4$. At a temperature of 800 °C mainly complete oxidation reactions occur, and the oxidation reactions dominate over the hydrolysis reactions because the K$_p$ value of oxidation is kept above the K$_p$ value of hydrolysis. Therefore, smaller nanoparticles will be obtained [16]. Xia et al. [16] stated that a K$_p$ value that exceeds $10^2$-$3$ is necessary for preparing nanoscale particles. As one can easily observe in Fig. 4, the K$_p$ value of oxidation is above $10^4$ up to a temperature of 1700 °C and the K$_p$ value of hydrolysis is above $10^2$ up to 1100 °C.

The particle diffusion coefficient, $\Gamma$, which is affected by the temperature is denoted by $\Gamma = \Gamma_b + \Gamma_t$, where $\Gamma_b$ is the Brownian diffusivity and $\Gamma_t$ is the turbulent diffusivity [26]. The Brownian diffusivity can be expressed as:

$$\Gamma_b = \frac{K_b T C_z}{3 \pi \mu d_a}$$  \hspace{1cm} (2)

where $C_z$ is the Cunningham correction factor, $K_b$ the Boltzmann constant, $\mu$ the viscosity of compound gas and $d_a$ the mean agglomerated particle diameter. Therefore, according to Eq. (2), Brownian diffusivity decreases at lower synthesis temperatures and thus smaller nanoparticles and clusters are obtained.

Eq. (3) defines turbulent diffusivity, which can be expressed as [27]:

$$\Gamma_t = \frac{\mu t}{\sigma \phi}$$  \hspace{1cm} (3)

where $\mu t$ is the turbulent viscosity and $\sigma \phi$ is the turbulent Schmidt number. The turbulent viscosity is defined by [27]:

$$\mu t = \frac{C_m (\rho) \kappa^2}{\varepsilon}$$  \hspace{1cm} (4)

where $C_m$ is a modeling coefficient in a standard two-equation $\kappa$-$\varepsilon$ turbulence model and is ascribed the value 0.09, $(\rho)$ is the density, $\kappa$ is the turbulent kinetic energy and $\varepsilon$ is the dissipation rate of turbulent kinetic energy [27].

The turbulent kinetic energy, $k$, is defined as [28,29]:

$$k = \frac{3}{2} (UT_u)^2$$  \hspace{1cm} (5)

where $U$ is the velocity magnitude and $T_u$ is the turbulent intensity [28,29].

The turbulent Schmidt number, $\sigma \phi$, is defined by [30]:

$$\sigma \phi = S_{\text{nf}} - \frac{\nu_t}{\nu_D}$$  \hspace{1cm} (6)

where $\nu_t$ is the turbulent kinematic viscosity and $\nu_D$ is the turbulent diffusion coefficient [30]. Valero et al. [28] showed that as far as turbulence arises, it is reasonable to assume that turbulent transport will prevail over molecular diffusion; hence $D_t \approx D_t$ where $D_t$ is the total diffusion (molecular and turbulent) coefficient [28].

In practical situations, small particles suspended in a flowing fluid are simultaneously subjected to Brownian diffusion and turbulent dispersion. For submicron particles, the Brownian diffusion effects may become quite important [31]. Hence the Brownian effect may become important only for very small particles. For particles larger than 5 μm the Brownian effects are negligible and turbulent diffusion is dominant. Ounis et al. [31] showed that turbulence effects generally dominate Brownian effects.

According to Eq. (5), by decreasing the temperature in an isotropic flow field, the turbulent kinetic energy, $k$, decreases due to lower velocity and lower turbulent intensity. Therefore, according to Eqs. (4) and (3) by decreasing the turbulent kinetic energy, the turbulent viscosity, $\mu_t$, and finally the turbulent diffusivity, $\Gamma_t$, decreases. Also, by decreasing the temperature the total diffusion decreases and due to $D_t \approx D_t$ [28] the turbulent diffusion coefficient, $D_t$, decreases and therefore the turbulent Schmidt number increases. By increasing the turbulent Schmidt number, $\sigma \phi$, the turbulent diffusivity, $\Gamma_t$, decreases. Finally, by decreasing the synthesis temperature either the Brownian diffusivity $\Gamma_b$ or the turbulent diffusivity, $\Gamma_t$, decreases and therefore the particle diffusion coefficient, $\Gamma$, decreases. By decreasing the particle diffusion coefficient, $\Gamma$, smaller nanoparticles would be obtained.

The influence of the temperature on the morphology, coagulation, and agglomeration of the prepared TiO$_2$ nanoparticles was investigated by TEM. Fig. 5(a) and (b) shows TEM images of the TiO$_2$ nanoparticles synthesized at temperatures of
Fig. 5 – TEM images of TiO$_2$ nanoparticles formed due to simultaneous oxidation and hydrolysis reactions synthesized at (a) 400 °C and (b) 700 °C.

400 and 700 °C, respectively. In accordance with the theoretical prediction, larger particles are obtained at 700 °C.

The characteristic time for coagulation of TiO$_2$ nanoparticles, $\tau_c$, is [32]:

$$\tau_c = \frac{2}{\beta \rho g N}$$  \hspace{1cm} (7)

where $\beta$ is the collision frequency for Brownian coagulation in the transition regime, $\rho_g$ the density of the carrier gas and $N$ the particle number [32]. The thermal velocity increases with increasing temperature [10,32]. Therefore, the collision frequency of TiO$_2$ particles, $\beta$, and the particle number, $N$, increase and cause the reduction of $\tau_c$ and increment of coagulation. Therefore, lowering the synthesis temperature leads to a reduction of the coagulation. This is confirmed in Fig. 5, showing no coagulation at 400 °C.

Lehtinen and Zachariah [15] reported that the characteristic coalescence time, $\tau_f$, for volume diffusion is:

$$\tau_f = \frac{3kTN}{64\pi \rho g D}$$  \hspace{1cm} (8)
where $k$ is the Stefan-Boltzmann constant, $T$ the temperature, $N$ the number of TiO$_2$ molecules for each particle, $\sigma$ the surface tension and $D$ the diffusion coefficient. Hence, we can expect a decrease in nanoparticles size with decreasing temperature, which is confirmed by the experimental results as shown in the TEM images in Fig. 5.

The characteristic sintering time based on a surface diffusion neck growth model, $t_{\text{sinter}}$, was proposed as (SI units) [33]:

$$t_{\text{sinter}} = 7.4 \times 10^{16} d_p^4 T \exp \left( \frac{3.1 \times 10^4}{T} \right)$$

where $d_p$ is the primary particle diameter and $T$ the temperature. According to Eq. (9) in conventional CVS processes, the sintering rate increases with increasing synthesis temperature. In the case of the H$_2$O-assisted APCVS process, the primary and secondary H$_2$O particles significantly decrease the sintering neck and surface diffusion [22]. As shown in the TEM images in Figs. 3 and 5, no noticeable sintering necks were observed between the nanoparticles produced using the H$_2$O-assisted APCVS process.

Furthermore, theoretical studies [9,10,34] suggest that the secondary H$_2$O particles eliminate unreacted TiCl$_4$ particles which would otherwise condense on the TiO$_2$ nanoparticles and thus result in nanoparticles with unclear boundaries [9]. This is experimentally confirmed by the TEM images showing that the TiO$_2$ nanoparticles synthesized by the H$_2$O-assisted APCVS process are round with clear boundaries (cf. Figs. 3 and 5). It can be concluded, that due to the low activation energy of the TiCl$_4$ hydrolysis reaction and the low reaction temperature between TiCl$_4$ and H$_2$O [10,22], the synthesis temperature for TiO$_2$ nanoparticles decreases dramatically and pure round nanoparticles can be achieved.

While lowering the synthesis temperature has many advantages, a lower synthesis temperature has various problems in the case of the conventional CVS process. Therefore, it is important to point out that the present work demonstrates that the H$_2$O-assisted APCVS process enables to lower the synthesis temperature without facing those problems. In conventional CVS processes, the synthesis temperature cannot be reduced since no oxidation reaction occurs before thermal decomposition of TiCl$_4$ [19]. Johannessen et al. [35] showed that TiCl$_4$ oxidation is assumed to occur instantaneously once the gas temperature exceeds the decomposition temperature for the precursor, $T_D$. Nakaso et al. [9] showed that before 800 °C, no TiO$_2$ nanoparticles are produced and Rahiminezhad-Soltani et al. [10] showed that at atmospheric pressure the oxidation reaction does not occur before 700 °C. In addition, Nakaso et al. [9] showed that at low reactor temperatures only 5% of the precursor reacts, resulting in large and amorphous particles [9].

The particle diameter, $D$, of TiO$_2$ nanoparticles synthesized by gas-phase reactions is proportional to the number of nuclei, $N$, as shown in Eq. (10) [36]:

$$D = \left( \frac{C_0 N}{N} \right)^{1/3}$$

where $C_0$ is the concentration of metal halide and $N$ the number of nuclei. According to Eq. (10), the particle size of TiO$_2$ decreases with increasing nuclei. Therefore, in conventional CVS processes, a decrease in synthesis temperature leads to an increase in particle diameter for the TiO$_2$ nanoparticles, due to the lower number of nuclei, $N$.

As an estimate of the degree of agglomeration in a suspension, the average agglomeration number (AAN) was calculated. AAN is the average number of primary particles contained within an agglomerate. AAN can be calculated as [37]:

$$AAN = \left( \frac{d_{\text{DLS}}^{\text{3}}}{d_{\text{BET}}^{\text{3}}} \right)^{3} (1 - \varepsilon)$$

where $\varepsilon$ is the estimated fractional porosity of the agglomerates, approximated as 0.4; $d_{\text{DLS}}$ the surface-volume diameter from particle size distribution of dilute dispersions measured with the DLS method, $d_{\text{BET}}$ is the surface-volume diameter calculated from BET analysis of nitrogen adsorption isotherms.

The $d_{\text{DLS}}$ can be calculated using particle size analysis data as follows [37]:

$$d_{\text{DLS}} = \frac{\sum x^3 dN}{\sum x^2 dN}$$

where $x$ is the particle size and $N$ is the number of particles [37]. According to Eqs. (7)–(9) by increasing the synthesis temperature, the particles size increases. Hence, according to Eqs. (11) and (12) by increasing the particles size, the average agglomeration number (AAN) as an estimate of the degree of agglomeration increases. Therefore, by increasing the synthesis temperature, the agglomeration of nanoparticles increases.

The pathway of particle formation in high-temperature processes can often be characterized by nucleation of condensable material and subsequent particle growth by coagulation. Depending on the temperature, particles formed in this way may have different morphological structures. Spherical particles are produced when the colliding particles coalesce. However, when coalescence is quenched, agglomerates are formed. The size of the primary particles composing the agglomerates depends on the temperature history of the particle-formation process and on the temperature dependence of the material properties determining particle coalescence [38].

Fig. 6 shows the TG-DTA diagram of the samples synthesized at different synthesis temperatures. TG-DTA was carried out to assess the purity of the H$_2$O-assisted APCVS-synthesized nanoparticles and their thermal stability. A small endothermic peak was observed in the DTA curves at a temperature of around 100 °C. This peak is attributed to dehydration of the titanium hydrates [16]. The weight loss below 200 °C is caused by the adsorbed water as the result of the exposure of the samples to air [10,22]. As one can easily observe, the DTA curve of synthesized TiO$_2$ at 200 °C, shows a small exothermic peak at 325 °C corresponding to the crystallization of the amorphous nanoparticles.

A very small exothermic peak around 337 °C can be observed also for the sample synthesized at 700 °C, confirming the presence of some amorphous nanoparticles in this specimen. Apart from this small peak, no exothermic peak can be observed in the DTA curves of the samples produced in the
Fig. 6 – TG-DTA results for TiO₂ nanoparticles formed due to simultaneous oxidation and hydrolysis reactions at different synthesis temperatures.

range of 400–800 °C, showing that no crystallization or phase transition occurs in this temperature range.

3.2. Effect of the heat capacity of the H₂O particles

In previous studies [10,22] we showed that H₂O particles have extraordinary effects on the characteristics of the TiO₂ nanoparticles synthesized through the gas-phase APCVS process [10,22]. Our hypothesis is that the high heat capacity of H₂O particles is the major factor affecting the nanoparticles. This hypothesis is based on two observations: Firstly, a decrease in the size of the nanoparticles is observed when H₂O particles are introduced [10]. Therefore, H₂O particles have decreased the temperature of TiO₂ monomers and primary particles. Secondly, introducing the liquid-phase H₂O particles reduced the coagulation, coalescence, agglomeration, and sintering of the nanoparticles [10]. Since the specific heat capacity of water is high, the heat loss due to the collisions with water molecules increases and thus the nanoparticles’ temperature decreases significantly, leading to lower coalescence and particle size growth. Therefore, much smaller nanoparticles are obtained. In addition, decreasing the nanoparticles’ temperature reduces agglomeration, coagulation, and sintering of the nanoparticles. Therefore, it seems reasonable to assume that the change in nanoparticles characteristics is caused by the heat capacity of H₂O particles. However, Akhtar et al. [34] and Jang [39] stated that the changes in particle characteristics in the presence of H₂O particles are still not well understood because of the complex collisions and reactions occurring during synthesis.

The only way to confirm our hypothesis is to carry out experiments comparing H₂O particles with different heat capacities. Therefore, H₂O particles were introduced to the reactor in the liquid and in the gas phase. The heat capacity of gas-phase H₂O particles is about half of the heat capacity of liquid-phase H₂O particles. Based on our hypothesis, using gas-phase H₂O particles should lead to an increase in size, coagulation, agglomeration, and coalescence of the TiO₂ nanoparticles as compared to using liquid phase H₂O particles.

Fig. 7(a and b) shows a comparison of TEM images of TiO₂ nanoparticles synthesized using gas-phase and liquid-phase H₂O particles, respectively. The nanoparticles synthesized using gas-phase H₂O particles have larger sizes than those using liquid-phase H₂O particles. Furthermore, coagulation, coalescence, and agglomeration of the nanoparticles increase significantly, when using gas-phase H₂O particles. Fig. 8(a and b) shows XRD profiles of the TiO₂ nanoparticles synthesized with liquid-phase H₂O particles and gas-phase H₂O particles, respectively. Both XRD patterns clearly show the TiO₂ anatase phase, showing that the heat capacity of the H₂O particles has no effect on the phase structure of the synthesized TiO₂ nanoparticles. In addition, the average TiO₂ nanoparticles size was calculated from the XRD profiles using the Scherrer
equation (cf., Eq. (1)) [17]. For gas-phase H$_2$O particles the average TiO$_2$ nanoparticle size was 41 nm and for liquid-phase H$_2$O particles 13 nm.

As resulted in theoretical studies, introducing H$_2$O particles in the gas phase leads to an increase in the average nanoparticle size. The experimental results thus confirm the predicted hypothesis: the heat capacity of the H$_2$O particles used in the H$_2$O-assisted APCVS process is the major factor affecting the synthesis and the characteristics of the TiO$_2$ nanoparticles. Increasing the heat capacity leads to a decrease in size, coagulation, coalescence, agglomeration, and aggregation because it lowers the temperature of the TiO$_2$ nanoparticles and monomers during synthesis.
4. Conclusion

The H$_2$O-assisted APCVS method allows to decrease the synthesis temperature dramatically. The minimum synthesis temperature for TiO$_2$ nanoparticles was reduced to 200 °C, resulting in amorphous nanoparticles. The minimum synthesis temperature for crystalline anatase TiO$_2$ nanoparticles was reduced to 400 °C in atmospheric pressure. The synthesis temperature of 400 °C is the best temperature for the gas-phase synthesis of anatase TiO$_2$ nanoparticles by H$_2$O-assisted APCVS process. In addition, the present work demonstrates that the formation of TiO$_2$ nanoparticles is determined by a temperature reduction mechanism caused by the high heat capacity of the H$_2$O particles. The importance of high heat capacity of H$_2$O particles has not been shown experimentally to date. Therefore, experiments comparing H$_2$O particles with different heat capacities were carried out. The results support the hypothesis that the formation and characteristics of the TiO$_2$ nanoparticles are linked to the ability of H$_2$O particles to reduce the temperature of the TiO$_2$ nanoparticles. The size of the TiO$_2$ nanoparticles is significantly reduced and coagulation, coalescence, agglomeration, and aggregations decrease with increasing heat capacity of the H$_2$O particles.

Conflicts of interest

The authors declare no conflicts of interest.

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References


Fig. 8 – XRD patterns of TiO$_2$ nanoparticles prepared using: (a) liquid-phase and (b) gas-phase H$_2$O particles.


