Application of Sugimoto model on particle size prediction of colloidal TiO_2 Nanoparticles

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Abstract:
In this paper, Sugimoto model has been employed to study the nucleation and the growth of TiO_2 nanoparticles. On the base of this model some parameters of the nucleation and the growth of nanoparticles such as supply rate of the solute (Q_0), molar volume of the solid (Vm), and mean volumic growth rate of the stable nuclei during the nucleation period ($\dot{v}$) were determined. For this approach, TiO_2 nanoparticles were synthesized in two stages in an aqueous solution by using HNO_3 and TTIP and TIPO as starting materials. In this experiment, it was obviously observed that the changing of Ti^{+4}concentrations was followed with LaMer diagram. Typical obtained results were $\dot{v}=2.93\times10^2$ $nm^3.s^{-1}$ and r_0=8.2nm under the standard conditions at 70°C. The maximum supersaturating ratio (Sm) was found to be 3.07. It has been concluded that the size of TiO_2 nanoparticles can be predict by Sugimoto model. The LaMer diagram was used as a fundamental principle of monodispersed particles formation.

Keywords: Titanium Dioxide, Sugimoto model, Nucleation, Monodispersed particles, LaMer diagram.

Introduction

Nanostructured titanium dioxide (TiO_2) is widely applied as a white pigment for paints or cosmetics, a support in catalysis, and a photocatalyst [1]. The performance of TiO_2 nanocrystals are strongly influenced by the crystallinity, morphology and the particle size. During three last decades many attempts have been done to prepare nanocrystalline TiO_2 particles with improved their properties [2]. It is well known that the preparation method has a critical role in performance of obtained TiO_2 nanomaterials [3]. Among all methods which are employed to synthesis TiO_2 nanocrystals, sol-gel is the best due to its controllability and low cost [4, 5]. The formation of nanostructures by sol-gel method consist a chemical process which is initiated by the reactions of molecules or ions that serve as precursors to nuclei. Nuclei undergo growth or further reactions to form nanostructures. Detailed understanding of the associated mechanism with nuclei formation and growth is important in controlling the size, shape and the physical properties of nanostructures [6, 7]. Many researches have been focused on the preparation and study on nucleation and growth of TiO_2 nanoparticles. For example, the synthesis of uniform anatase TiO_2 nanoparticles by gel–sol method and mechanisms in size control of uniform nanoparticles has investigated by Sugimoto [8,9]. In 1999, Sugimoto pointed out that the nucleation and growth of silver nanoparticles can be conformed to the LaMer theory [10]. Using Lamer mechanism, Sugimoto developed the nucleation model and verified it experimentally and described the nucleation and growth of AgCl and AgBr [10,11]. In the present work, we have tried to evaluate the nucleation and growth of TiO_2 nanocrystals on the base of Sugimoto approach. At first we need to present a brief description about LaMer Theory. In that theory the formation of sulfur sols has been described on the base of the decomposition of sodium thiosulfate in hydrochloric acid [10,11]. The essence of the mechanism was illustrated in Fig. 1; the time variation of nucleating species concentration (sulfur in this case) has three steps. The concentration of elemental sulfur builds up slowly until some critical concentration is reached, or more specifically a critical supersaturation level, C/C_{eq} where C_{eq} is the solubility of sulfur in the solution (stage I in Fig. 1).

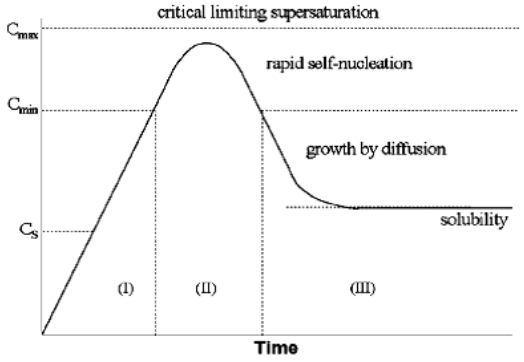

Fig.1 .The LaMer mechanism of nucleation of sulfur. The (theoretical) curve shows sulfur concentration as a function of time.

At this point, "self-nucleation" (i.e., homogeneous nucleation) occurs at a rate that has been called "effectively infinite". This step has pointed out as stage II in figure 1. That stage is the origin of the idea of "burst" nucleation.
The burst of nucleation immediately lowers the super-saturation level of monomers in the solution; as a result, nucleation essentially stops at this time. Growth then occurs by diffusion of sulfur atoms throughout the solution, stage III

[10,11]. The Sugimoto nucleation model can be briefly explained as follow.
When C reaches to C_{max}, the steady state of a mass balance between the supply rate of solute (R_S), consumption rates for nucleation (R_N), and growth rate of the generated nuclei (R_G) is established, and the following relationship can be given as [12,13,14]:

$$R_N + R_G - R_S = 0 \quad (1$$

This mass balance equation may be replaced by a corresponding differential equation for the number of the generated stable nuclei, n_∞, as:

$$v_0 \frac{dn_\infty}{dt} + \dot{v} n_\infty - Q V_m = 0 \quad (2$$

Where $v_0$the minimum particle volume of the stable nuclei is, $\dot{v}$ is the mean volume growth rate of the stable nuclei, Q is the supply rate of solute in mol per unit time, and V_m is the molar volume of the solid. The stable nuclei are sufficiently large to be grown to the final product particles, and they are defined as nuclei whose each particle volume is over the maximum particle volume of the stationary nuclei. One may regard Q as being kept constant at Q_0 during the short nucleation period, and $\dot{v}$ may be regarded as a constant. In the initial time (t=0) n_∞ is equal to 0 and C reaches to C_{max}. Therefore the n_∞ can be treated as a function of time as follows [12,13,14]:

$$n_\infty = \frac{Q_0 V_m}{\dot{v}} \left[1 - \exp\left(\frac{-\dot{v} t}{v_0}\right)\right] \quad (3$$

When t→∞ the final number of generated stable nuclei is equal to:

$$n_\infty = \frac{Q_0 V_m}{\dot{v}} \quad (4$$

On the other hand, since particles are known to grow by diffusion control, the linear growth rate (dr/dt) in the growth stage may be given by [9,10,15]:

$$\frac{dr}{dt} = \frac{D V_m}{r} \left[C - C_\infty exp\left(\frac{2\gamma V_m}{rRT}\right)\right] \quad (5$$

In this equation D is the diffusivity of the solute including free ions and their halide complexes, C is the molality of the solute, C_∞ is the solubility of the bulk solid in terms of total molality of solute, and γ is the specific surface energy of the solid. By considering the initial particle radius as radius of the stable nuclei during the nucleation stage, the below equation is established between r_0, D and $\dot{v}$:

$$\dot{v} = 4\pi r_0 D V_m C_\infty \left[S_m - \exp\left(\frac{2\gamma V_m}{r_0 RT}\right)\right] \quad (6$$

In this experiment the radius and the formation free energy of nucleus can be determined by Gibbs-Thomson relations [12,13,14].

In our work, the application of Sugimoto model for formation of TiO_2 nanoparticles was evaluated. At first, it was shown that the nucleation and growth of TiO_2 nanoparticles is conform with LaMer diagram and after that the parameters were obtained by Sugimoto Model for this approach we use the size of final particles from TEM photo. Comparison of our work with results of other researches shows that our results were obtained in high accuracy.

Experimental

In this investigation, the raw materials contain Titanium isopropoxide (TTIP) (98%), Triethnolamine (TIPO), Ethanol, HNO3 (98%) which have been purchased from Merck. The established controlled conditions for the preparation of TiO_2 nanoparticles were employed as follows. First, a stock solution of Ti^{4+} was prepared by mixing titanium isopropoxide (TIPO:$Ti[OCH(CH_3)_2]_4$) with triethanol amine (TEOA : $N(CH_2CH_2OH)_3$) at a molar ratio of TIPO: TEOA=1 : 2 under dry air to form a stable Ti^{4+}compound against the hydrolysis reaction at room temperature. The process followed by addition of doubly distilled water to make an aqueous stock solution that the concentration of Ti^{4+} is near to 5×10^{-4} mol^{-1}. Then, 10 ml of the stock solution was mixed with the same volume of doubly distilled water. The pH was controlled by addition of $HClO_4$ or NaOH solutions. The final solution (pH=9.6) was placed in a screw-capped Pyrex bottle and aged at 100°C for 36 h. Finally, the resulting highly viscous gel was mixed with 80 ml (2×10^{-3} molar) nitric acid and stirred at 25°C for 3 h to dissolve the gel and so prepared a dark solution with pH=1. The solution was set in pool water at 70°C.

Stage1. Solution was heated to achieve super saturation of Ti in solution. Each 4 min a sample has been taken from prepared solution and analyze by Atomic Adsorption.

Stage2. Using condenser to stop evaporation of solution and Each 4 min a sample has been taken again among this process TiO_2 particles was separated from the resulting Ti^{4+} suspension by centrifugation. This work has been repeated several times and every time the concentration of the Ti^{4+} was measured by the atomic adsorption. The products were washed with distilled water and observed using a transmission electron microscope using Germany ZEISS Em-900.

Results

3.1 *Formation of TiO_2 particles*

The basic alkoxide precursor used in this study, can be hydrolyzed and condensed, where an oxygen link between two Ti atoms is formed through several steps that can be written as follows:

$$Ti\text{-}OR + H2O \leftrightarrow Ti\text{-}OH + ROH \quad (1)$$

Depends on the pH of the solution, the present of titanium (IV) compounds in aqueous solutions are TiO^{2+}, $TiOH^{3+}$, $Ti(OH)_2^{2+}$, and $TiO(OH)^+$ [15,16]. In this experiment the

pH=1, and the TiO^{2+} is the dominant complex in solution. Therefore, TiO_2 can be nucleate by the below equations:

$$...Ti\text{-}OH + OR\text{-}Ti... \leftrightarrow ...Ti\text{-}O\text{-}Ti... + ROH \quad (2)$$

$$...Ti\text{-}OH + OH\text{-}Ti... \leftrightarrow ...Ti\text{-}O\text{-}Ti... + HOH \quad (3)$$

Thus, the growth of particles occurs by addition of Ti^{4+} to the existing particles. It was shown that the TiO_2 surfaces has enough number of O− or −OH sites which are available in appropriate positions to create octahedral coordination for the incoming Ti^{4+} ions. Moreover, after the attachment of Ti^{4+} ion along the planes, equal number of new O− or −OH sites are created for further attachment of Ti^{4+} ions [17].

3.2 *Nucleation of unstable particles under the standard conditions*

The time variation of Ti^{4+} supersaturation was recorded clearly and illustrated in Fig. 2. It is like the LaMer diagram. This diagram is divided in two stages under the standard conditions. In the first stage, when the liquid in the solution was evaporated, the concentration of titanium increases. It is believed that the evaporation of liquid has directly affected on changing the mass balance and so, the titanium concentration increased. The concentration of titanium increase until the C=3510ppm which can be considered as the maximum supersaturation of Ti^{+4} in solution, at this time the unstable particles are create, this particles can be solute or remain until the starting of the second stage. The radius of these particles can be found by the Gibbs-Thomson equation. In contrast, in the second stage after maximum supersaturation the concentration of titanium decrease and it was also observed that TiO_2 particles were precipitated and could separate after centrifuging the samples. Also, it can be found that the obtained supersaturation ratio (S) from the analysis of the [Ti]-curve leads to determination of the nucleation start point that is equal to 37.5 min. From the curve of the supersaturation, the maximum supersaturation ratio (S_m) can be measured as high as 3.19.

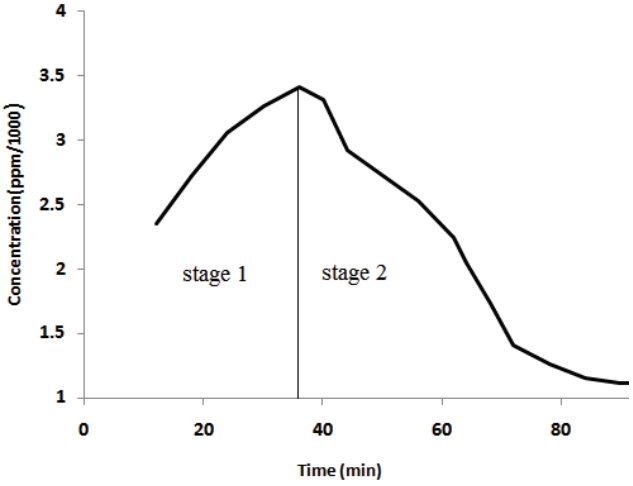

Fig2. Time evolutions of Ti^{4+} concentration in the standard system, stage1: [Ti] concentration increasing, stage 2: [Ti] concentration decreasing

The equilibrium nucleus radius r^* and ΔG^* at the maximum supersaturation (unstable particles), r_m^* and ΔG_m^*, are calculated from Gibbs-Thomson equation and are r_m=4.01*nm* and $\Delta G_m^*=1.16\times10^{-16}$ *J* (=343*kT*), where V_m =20.9 cm^3 mol^{-1} and γ=350 mJ/m^{-2} [18].

3.3 *stable particle size and growth*

In the second stage, the concentration of Ti^{+4} decreases that is due to formation of TiO_2 particles and are precipitated during this stage. The end of the Ti^{+4} reduction, was observed after about 90 min, as shown in Fig.2. After that, the concentration of Ti^{4+} was constant at the level of C = 1180ppm. When reduction starts, at first Ti ions decrease rapidly but after a while (about 5 min) it is observed that Ti ions reduce with a less speed than before. It is believe that at this time the nucleation period of particles finished and the stable particles was created and after that this particles were grown to compose the final particles.

At this level, Gibbs-Thomason equation was used again to obtain the size of stable particles which is equal to r_0=8.2*nm*. TEM analysis was used to check the agreement between theory and experiment. It has been found that the synthesized TiO_2 particles in this time have a size of r =10nm which are nearly to our theoretical size. These particles are the particles which turn into final particles.

Fig. 3 shows a TEM image of TiO_2 particles prepared under the standard conditions and after 100 min. it can be found that the obtained mean particle diameter is equal to 0.200 mm and the final particle density was obtained which is $n_\infty = 4.8\times10^{13}$ dm^{-3} [12,13,14].

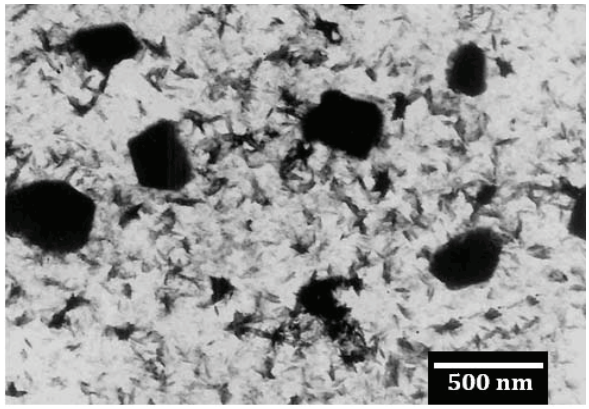

Fig3.The TEM image of uniform TiO_2 particles prepared under the standard condition.

On the other hand The supply rate of the monomer in the nucleation period, Q_0, is obtained from the product of the tangential slope of the curve of [Ti] vt *t* at $[Ti]^{max}$ in Fig. 3 and hence Q_0= d[Ti]/dt=7.03×10^{-8} mol dm^{-3} s^{-1}. The amount of mean volumic growth rate of the stable nuclei obtained $\dot{v}=Q_0V_m/n_\infty=2.93\times10^2$ nm^3s^{-1}.

The growth rate of stable nuclei examine with TEM photos which was got every 10 min after the nucleation of stable particles. We expected that the size of particles will be around of 25, 35 and 45 nm in approximately 10, 15 and 20 min after

supersaturation respectively. Our TEM images shows that the particle dimensions have good adaptability with our theoretical calculations. And finally, from the equation (6) diffusion coefficient of [Ti] is $D = 6.18\times10^{-5}$ cm^2s^{-1}. This *D* value is in a reasonable range for diffusion of ions or complexes in an aqueous solution. Moreover, this coefficient is approximately equal with the diffusion coefficient of Ti ions which and was obtained by Shingyouchi [19].

Conclusion

Tadao Sugimoto formulated a new model for studying the nucleation and growth of nano particles. The base of this model is on the nucleation and growth of particles which controlled by diffusion and the particles which their growth follows the LaMer diagram. With this model he studied the nucleation and growth of AgCl and AgBr nano particles in standard condition. At the present work an effort was made to study on nucleation and growth of TiO2 nano particles nano particles with this model the important factors obtain as follows:

S_m=3.19, r_m=4.01*nm* and ΔG_m*=1.16×10^{-16}*J*, r_0=8.2*nm*, Q_0=7.03×10^{-8} mol dm^{-3} s^{-1}, $\dot{v}$= 2.93×10^{2} nm^3s^{-1} and $D = 6.18\times10^{-5}$ cm^2s^{-1}.

It is believe that with these parameters we can predict the size of TiO_2 nano particles in different time in growth part.

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