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Nucleation and Growth of TiO$_2$ Nanoparticles

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1. Introduction

Crystallization is one of the most important and interesting phenomena in human life. For instance, many purifications and productions of materials are based on crystallization. In pharmacology, more than 90% of all pharmaceutical products are used in the crystalline form of solid material. Hence, the controlling of the crystallization process has a critical role on the properties of products and allows manufacturers to prepare materials with desired and reproducible properties. The recent interest in nanocrystals and other types of nanomaterials is a further illustration of the crystallization importance in the science and technology (Mehranpour et al., 2010). It is well known that at the nanometer scale, the optical, the electronic, and the catalytic properties of nanomaterials are highly sensitive to their size and shape (Finney & Finke, 2008). Consequently, the crystallization process (nucleation & growth) plays an important role in determining the crystal structure, shape, size and size distribution of the nanomaterials. Therefore, a theoretical approach to understand the mechanism of nanocrystal formation provides a greater control over the size, shape, and composition of nanocrystals and results an ability to tune the abovementioned properties simply by varying the crystallization conditions. One of the main goals of this theoretical approach of the nanocluster science is the ability to prepare nanocrystals that have very narrow size distributions (so-called "near-monodisperse"). That is the main reason to know why the nucleation and the growth mechanism of nanocrystals in solution have been the subject of increasing study. On the other hand, the agreement between the theoretical models and experimental results is not very good. This is a general shortcoming of nucleation theories. As a result, the nucleation theories in general have a little predictive power. It seems that a main goal of nucleation study is to improve the accuracy of theory (Finney & Finke, 2008). Titanium dioxide (TiO$_2$) is one of the semiconductor materials with unique photocatalytic properties that make it an interesting candidate for different applications such as white pigment, cosmetics, catalysis support and a photocatalyst. During last two decades, this act has been highlighted that the physical and the chemical properties of nano-TiO$_2$ depend on its size, morphology and crystalline polymorph strongly. That is well known that these specifications of TiO$_2$ nanopowders are controlled by crystallization and phase transformation. Since the employed synthesis method has critical role on the crystallization and phase transformation of obtained material, many attempts have been done to use a procedure

which has enough potential to prepare TiO$_2$ nanopowders with designed properties. Researchers made a lot of efforts to innovate the best techniques that can be applied for this purpose. Despite the several attempts that have been served to prepare titanium oxide nanoparticles with very high uniformity in size and morphology, a deep understanding of nucleation and growth mechanism needs to make a better control on the physical and the chemical properties of synthesized TiO$_2$ nanomaterial. LaMer theory described the kinetic formation of particles which are controlled by diffusion of elements (particles, ions,..). In 1999 Tadao Sugimoto and his model described the formation of nanoparticles that their nucleation and growth comfort with LaMer diagram and controlled by diffusion. In this chapter, at first, the kinetic of nucleation and the growth of particles will be discussed generally and some of scientific reports will be analyzed. Then, the kinetic of nucleation and the growth mechanism of Titana nanoparticles will be studied on the basis of LaMer theory and Sugimoto model.

2. Nucleation

Generally, the nucleation is considered as a first stage of embryos formation from nuclei which have only nanometer in size and possible growth to the final particles. In fact, the nucleation is the first formation step of the solid phase from other phases such as solid, liquid and gas. Nucleation occurs and continues with aggregation and clustering of molecules or ions in a supersaturated melt, solution or vapor to form a stable size of solid phase. It seems that supersaturation of solute in the main matrix is the important key to nucleation of particle. Indeed, the driving force for nucleation and growth phenomena is supersaturation. After dissolving the chemical species in a solvent, whether or not of a predetermined nature, to observe the nucleation and growth process the solution must be supersaturated (Mangin et al., 2009) (Kashchiev, 2001). Supersaturation is the difference between the chemical potential of the solute molecules in the supersaturated (μ) and saturated (μ_s) states respectively. For one molecule, difference is explained by:

$$\Delta\mu = \mu - \mu_S = k_B T \ln \beta \qquad (1)$$

where k_B is the Boltzmann constant and T is the temperature. To simplify, we consider that the activities are equal to the concentrations and can be written as (Mangin, et al., 2009):

$$\beta = \frac{C_i}{C_s} \qquad (2)$$

Here β is the supersaturation ratio, C_i is the concentration of the solute in solution and C_s its saturated or equilibrium concentration. Obviously, this ratio is dimensionless . Moreover, if $\beta > 1$, the nucleus grows; if $\beta < 1$, the nucleus dissolves; and if $\beta = 1$, nuclei and solution are at equilibrium. However, in a crystallized system, not only there must be a supersaturation condition for the system but also the system must have a number of minute solid bodies, embryos, nuclei or seed which are acting as a core of nucleation to develop crystals. Therefore, nucleation may occur spontaneously or it can happen artificially. Nowadays there is no a general agreement on forming of particles. The term 'primary' is explained for the system that has unknown crystalline matter. On the other hand, nuclei are often generated in the vicinity of crystals presented in a saturated system; this is referred to as 'secondary' nucleation (Kashchiev, 2001) (Mangin et al,. 2009).

2.1 Primary nucleation

Scientists did not know exactly when and how a nucleus is become stable within a homogeneous solution. Actually, primary nucleation is the initial formation of a nucleus where there are no other solid phases. If the solid phases are present in the system, they do not have any influence on the nucleation process. The number of monomers in a stable nucleus is different about ten to several thousand, i.e., ice nucleus may contain about 100 molecules. The formation of nuclei can be explained by a successive addition of monomer (units A) according to the formation scheme (Mersmann et al,. 2001):

$$A_1 + A = A_2 \qquad A_2 + A = A_3;.....; A_n + A \underset{Kd}{\overset{Ka}{\leftrightarrow}} A_{n+1} \qquad (3)$$
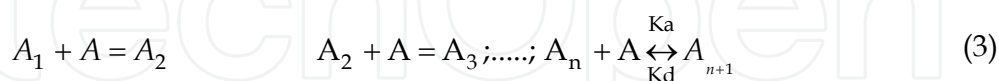
From above scheme, it can be found that the addition to the stable nucleus or part from it, would lead to growth or shrink which can be described by the rate constant of K_a and Kd. K_a is the monomer addition rate constant and K_d is the rate of monomer desorbstion which is parted from nucleus. So, addition to the stable nucleus would result in growth of the nucleus. Similarly, ions or molecules in a solution can make the short–lived clusters, which occurs very rapidly. These clusters can be considered as very high supersaturation in local region and many of these embryos or 'sub-nuclei' fail to growth (Mullin, 2001). They dissolve easily because they are extremely unstable. The classical nucleation theory (CNT) which was pioneered by Volmer and Decker (Maris 2006) , where the first to argue that the nucleation rate should depend exponentially on the reversible work of the formation of a critical cluster. The free energy of nucleus formation G is expressed by the two competing terms. One of them is free volume energy (G_V) and the other is free surface energy (G_A). The positive change in free surface energy (G_A) can be provided by increasing the interfacial tension μ_{CL} between the surface of the nucleus and the surrounding solution. On the other hand, the change in free volume energy (ΔG_V) is negative because it is set free. The ΔG_V is proportional to the volume of the nucleus and increased with increasing in energy $RT \times lnS$, where $S = a/a^*$ or in ideal systems, $S = C/C^*$. The concentration of the elementary units (C) changes to the lower equilibrium concentration as follows (Mersmann et al,. 2001):

$$C = C^* - \Delta C \qquad (4)$$

Fig 1 shows, the free energies of ΔG_A and ΔG_V and the total free energy $\Delta G = \Delta G_A + \Delta G_V$ against the nucleus radius. The nucleus free energy can expressed with the following equation which is obtained by the nucleus surface A_n, nucleus volume V_n, the degree of dissociation a, and the number of ions n:

$$\Delta G = \Delta G_A + \Delta G_V = A_n \gamma_{CL} - (1 - \alpha + un) V_n C_C R T \ln S \qquad (5)$$

The change in total enthalpy (ΔG), is regarding to the nucleus radius r passes through a maximum value. This is because the free volume energy (ΔG_V) is related to the volume of a cluster and therefore(Mersmann et al,. 2001):

$$\Delta G_v \approx V_n \approx r^3 \qquad (6)$$

whereas the free surface energy (ΔG_A) is proportion to the size of the nucleus with the following manner(Mersmann et al,. 2001):
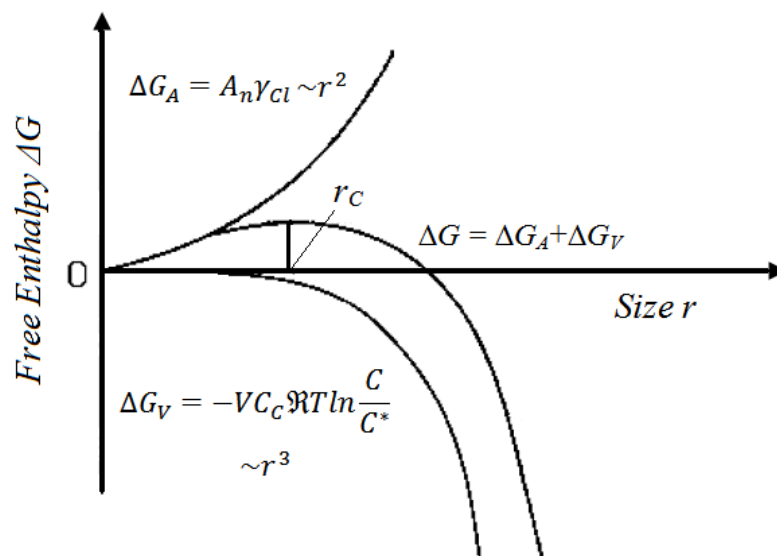
$$\Delta G_A \approx A_n \approx r^2 \qquad (7)$$

Fig. 1. Free enthalpy ΔG against nucleus size r (Mersmann et al,. 2001).

The maximum value of ΔG corresponds to the nucleus with critical radius (r_c). A thermodynamically stable nucleus exists when the radius of the nucleus reaches to r_c. Therefore, the slope of ΔG at critical radius of nucleus will be zerro(Mersmann et al,. 2001):

$$\frac{\partial \Delta G}{\partial r} = 0 \tag{8}$$

In that situation which the radius of nucleus is critical, the rate constant of addition (k_A) is equel to the desorbtion rate constant (k_D). Therefore, neither growth nor decomposition takes place. The critical radius of nucleus can be obtained by the above equations for the spherical nucleus:

$$r_{crit}^* = \frac{4\mu_{CL}}{(1 - a + an)RTC_c \ln S} \tag{9}$$

By considering the Boltzmann constant as $k_B = R / N_A$ and molecular volume as:

$$V_m = \frac{1}{C_C N_A} = \frac{M}{\rho_C N_A} \tag{10}$$

the critical radius(r_{crit}) is obtained by the following equation(Mersmann et al,. 2001):

$$r_{crit}^* = \frac{4\gamma_{CL}}{k_B T \ln S} V_m \tag{11}$$

The behavior of created crystalline particles in supersaturation solution depends on their size; they can be dissolved or grow, but the free energy of the particles determines the viable of particle. The critical size r_C represents the minimum size of stable nucleus. Particles with the radius smaller than r_C will dissolve because only in this way the particle can achieve a reduction in its free energy. Similarly, particles larger than r_C will grow to the final particle. The nucleus free energy can also be expressed in terms of the number of atoms in the nucleus; one such general expression is given by(Mersmann et al,. 2001):

$$\Delta G_n = -nk_B T \ln\left(\frac{C}{C_{sat}}\right) + \sigma b n^{2/3} \tag{12}$$

where, n is the number of atoms in the nucleus, k_B is the Boltzmann constant, T is the temperature, σ is the surface tension of the cluster, b is a geometric factor and hence the critical number of atom which create a stable nucleus at the supersaturation level is :

$$n_c = \left(\frac{2\sigma b}{3k_B T \ln\left(\frac{C}{C_{sat}}\right)}\right)^3 \tag{13}$$

Alternatively, the critical nucleus can be explained in terms of the number of atoms contained within it, n_C, by differentiating Eq. (12) and finding the maximum. For nucleus, containing less than n_C atoms or ions growth is not happened and the cluster dissolves. For nucleus containing more than n_C atoms, growth is favored. The *critical nucleus* is therefore the activated complex along the reaction coordinate of nucleation(Mersmann et al,. 2001).

3. Growth

It is well known that three basic steps are involving in the formation of crystal from an initially disordered phase. These stages are considered as achievement of supersaturation or supercooling, nucleation, and growth the nuclei into single crystals of distinct phase. When the crystallized particles are formed, the particles with size greater than critical size began to grow into final size. When, the equilibrium between crystallized phase and mother phase achives the free energy is at a minimum and the growth cannot occur. The equilibrium prevents the particle growth(Dhanaraj, et al. 2010). Therefore, a change in temperature or other effective parameters on the deriving force of crystallization must be applied to start the growth process again. Actually, supersaturation or supercooling of liquid increases the driving force of crystallization with respect to component whose growth is required. Several theories such as surface energy theory, diffusion theory, adsorption layer theory, and screw dislocation theory have been proposed to analyze the concept of particle growth. These theories evaluate the mechanism and the rate of crystal growth. Although, these theories cover the growth kinetic but high level accuracy remain elusive in the study of nucleation and growth process. For this reason, scientists try to fit experimental data and adjusting the theoretical parameter accordingly. In following, a brif presentation about these theories will be given.

3.1 Crystal growth theories
3.1.1 Surface energy
In surface energy theory, the particle growth happens through the plane which has the lowest surface energy based on the thermodynamic principle. In 1878 Gibbs proposed that the growth of a crystal depends on the total free energy of a crystal in equilibrium with surrounding at constant temperature and pressure. For the stable nuclei If the free energy per unit volume is assumed to be constant in the crystal, then the surface energy must have a minimum for a given volume (Mullin, 2001; Jones, 2002):

$$\sum_{1}^{n} a_i g_i = \min. \qquad (14)$$

In a crystal which is bounded by n faces, a_i is the area of the ith face and gi is the surface free energy per unit area of the ith face. Therefore, if crystal grows in supersaturated system, its shape must have an equilibrium with surrounding medium. Many scientists used this idea in their research. Wulff (Suzuki, et al. 2007) studied the relationship between growth rate at different faces and the surface free energies. He showed that the excess surface free energy $\sigma_{ijk}dA_{ijk}$ is minimum for crystal with its {hkl} faces when it is in equilibrium with surrounding medium. The value of σ_{hkl} could determine on the basis of the shape of crystal. For example if σ is isotropic; the form of the crystal is spherical. Also Marc and Ritzel (Dhanaraj, et al. 2010) indicated that different faces have different values of solubility. When the difference in solubility is small, the surface energy has an imposrant role on the growth of nucleus. The rate of growth can be measured by the outward rate of monemer movement in the direction perpendicular to the face. In a crystal with geometrically shape, the velocity of growth will different from face to face. The ideal case of a crystal that has geometrical shape is called 'invariant'. In this crystal, any face with equal area grow at same rate. But, the smaller faces grows faster while the smallest face grows fastest of all. A similar, but, reverse behavior would be seen in the crystal in this type in a solvent. The face with faster growth rate dissolves at a faster rate than the other faces, but the sharp outlines of the crystal are soon lost ones dissolution commences (Mullin, 2001; Jones, 2002).

3.1.2 Diffusion theory

The main work on diffusion theory backs to the researches of Noyes and Whitney (1897). They proposed that the deposition of solid monomer on the surface of crystal was essentially a diffusion process. The base of this idea has two following assumptions. At first, it can be hypothesed that a concentration gradient exists in the near layer of the growing surface. Secondly, it can be considered that the crystal growth is the reversible process (Mullin, 2001; Jones, 2002). Consequently, on the basis of these assumptions, an equation can be written between the amounts of solute that are getting to solid surface and in the bulk of the supersaturated solution, which is as follows:

$$\frac{dm}{dt} = \left(\frac{D}{\delta}\right) A (C - C_0) \qquad (15)$$

where m is the mass of solid deposited in a small time t; A is the surface area of crystal; C is the solute concentration in the solution; C_0 is the equilibrium saturation concentration; D is the diffusion coefficient of the solute and δ is the length of diffusion path. The thickness δ of the torpid layer would obviously depend on the relative solid-liquid velocity, in the system without any agitation, the film thickness would be around of 150 nm but in agitation system this thickness maybe less than 100 nm. The importance of nucleation site during growth of crystals was the main consideration of Volmer. He suggested that in growth mechanism the monomers when reached to a surface, they are not attached immediately to the lattice but migrate over crystal face to find a suitable site for attachment (Mullin, 2001; Jones, 2002).

3.1.3 Adsorption layer theory

In 1939 Volmer proposed the crystal growth mechanism based on adsorption layer theory. Volmer theory or Gibbs-Volmer theory explained the growth of particles when the units of solute arrive at the crystal face they do not attract immediately into surface but they migrate over the crystal face. Consequently, there is a loosely adsorption layer of the monomers at the interface and a dynamic equilibrium is established between the layer and the bulk solution. Kossle considered that crystal is in equilibrium with the solution when it is just saturated (Dhanaraj, et al. 2010). Also the energy of attachment unit on surface is a simple function of distance only. The thickness of the adsorption layer does not exceed 10nm and may even be near 1nm. The places in the lattice surface which have the greatest attractive energy are the best place for ions, molecules or monomers to attach. After that the suitable places with less energy attract these pieces. Under the standard condition this step-wise build-up will continue till the monomers cover the surface and will create a new layer on surface completely. Before the crystal faces can continue to grow or before creating the additional layer, a center of crystallization must exist on the surface plane. Gibbs-Volmer theory suggested that there is a monolayer island on the crystal surface which is called a two-dimensional nucleus (Mullin, 2001; Jones, 2002). Kossle (Dhanaraj, et al. 2010) also showed that the attachment energy depends on the kind of crystal. If the crystal is homopolar the attachment energy is due to Van Der Wals while if the crystal is heteropolar (ionic) the energy is due to electrostatic forces. The important specific feature of new phase nucleation on substrate surfaces, as compared to homogeneous nucleation in the bulk, is the presence of various defects on the substrate. Defects are typically divided into point and linear ones; the latter include kinks, surface dislocations, and vacancies. It seems that the sites like terraces, ledge, and kinks are the suitable place to unit arriving at a crystal to attach. The attachment energy of atoms, molecules or ions is maximum when it is correlated into a kink site in a surface ledge, whilst at any point on the ledge it is greater than that for an atom attached to the flat surface. Consequently, when a monomer reaches to a crystal surface, it does not go around and integrated into the lattice immediately. Instead, it goes to find to a step and moves along it to a kink sites, where it is finally incorporated. A crystal grow fastest when have lots of kink on its face (Mullin, 2001; Jones, 2002).

4. Kinetic models

4.1 LaMer model

One of the most famous and widely used nucleation theories is the work done by LaMer in the 1950s. LaMer and Dignae (1954) described the formation of sulfur sols from the decomposition of sodium thiosulfate in hydrochloric acid. Fig. 2, shows the concentration changing profile of nucleating species (sulfur in this case) via time. The contest of the nucleation mechanism is as follows. At first, the concentration of elemental sulfur increase slowly(stage I). In this stage no appreciable nucleation occurs even if the concentration level exceed the solubility level which is called as critical concentration (Moon et al., 1998; Finney & Finke, 2008; Keshmiri & Kesler, 2006; Tovstun & Razumov, 2010). When the concentration reaches to a critical level (critical supersaturation level) the nucleation process can be started (stage II). In the second stage, because some of the solute monomer is consumed to form particles the concentration of the solute species continues to increase but in lower slope. However, as the concentration still increases, the nucleation is drastically accelerated and,

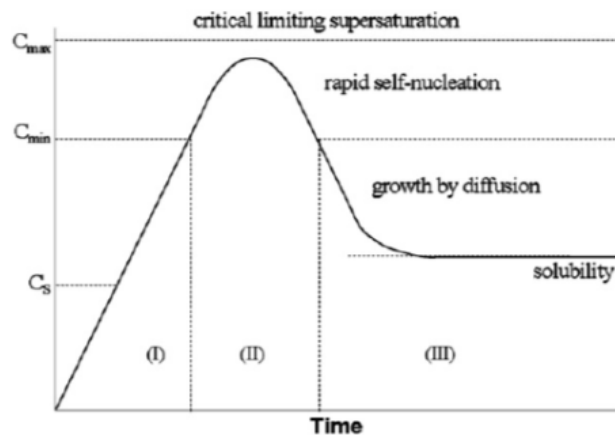finally, the concentration of the monomeric species reaches the maximum level (maximum supersaturation).

Fig. 2. The LaMer mechanism of nucleation of sulfur shows the changing pattern of sulfur concentration as a function of time(LaMer & Dignae, 1954).

At this time, the consummation of monomers to form the particles is balanced with increasing in their concentration. After that, the concentration of the monomeric species starts to be reduced. Due to the increasing in consumption of the monomeric species by growth of a number of the preformed nuclei, the concentration of the monomeric species decrease until reach to the supersaturation level. At this stage the nucleation is stopped (the end of the nucleation stage) and the remaining stable nuclei continue to grow with a supersaturation below the critical level for nucleation (Stage III). When the concentration of monomeric species becomes close to the solubility level of the bulk solid, the particle growth finishes (Finney & Finke, 2008; Keshmiri & Kesler, 2006; Tovstun & Razumov, 2010). There is another nucleation and growth theory, which is called as Turkevich model. In this model, it can be found that the particle formation followed kinetics consisting of an induction period, fast and linear increase particles number and then a rapid decrease in the rate.

4.2 Experimental models

Although, nucleation and growth process have a lot of interests to study, the highest levels of accuracy and precision have not made just by theoretical approach. It seems that, the theoretical approach would be come out by fitting experimental data with adjusting theoretical parameters simultaneously. Oxtoby (Oxtoby, 1992) has observed that the nucleation theory is one of the few areas of science in which the agreement of predicted and measured rates to within several orders of magnitude is considered a major success. Recently, some nucleation and growth studies based on experiment are developed. Becker and Doring (Toralff & Marro, 1987) evaluated and formulated the growth kinetic of particles as a steady-state process. The main goal of a theoretical description is to explain the size selection mechanism, the formation kinetic of monodisperse and the shape of the precipitated solids. There are approaches describing thermodynamic and dynamical growth mechanisms have been proposed by a lot of researchers (Privman, et al., 1999a; Privman and Mozyrsky, 1999b; Park, et al., 2001; Gorshkov & Privman, 2010; Libert, et al.

2003; Kulkarni & Zukoski 2002a; Dixit & Zukoski 2001; Dixit & Zukoski, 2002b). Dmitri V. Talapin in 2001 evaluated the evolution of an nanoparticle and presented a model allowing to calculate the progressed size of an nanoparticle under reaction, diffusion, and mixed reaction-diffusion control. The assumed model describing a place with a solution and durable concentration of monomer. The monomers can add to the nanoparticle surface and help it to growth or it can remove from the surface. It seems that the most probable for nanoparticles colloidal growth is polynuclear-layer ,so , the flux of monomer J_g^{react} toward the particles surface is described by a first order surface reaction (Talapin, et al. 2001, 2002):

$$J_g^{react} = 4\pi r^2 k_g^{flat} [M]_r \exp\left[-a\frac{2\gamma V_m}{rRT} \right] \tag{16}$$

where $[M]_r$ is the concentration of the monomer near the particle surface and k_g^{flat} is the growth rate constant for growth of a flat $(r = \infty)$ surface (Talapin, et al. 2001, 2002). If the rate of the dissolution of a solid does not depend on the monomer concentration in solution, it can be said that the flux of the monomer toward the particles is as follows:

$$J_g^{react} = -4\pi r^2 k_d = -4\pi r^2 k_d^{flat} \exp\left[\beta \frac{2\gamma V_m}{rRT} \right] \tag{17}$$

where

$$k_d^{flat} = B_d \exp\left(-\frac{\Delta\mu_d^\infty}{RT} \right) \tag{18}$$

is the dissolution rate constant for a flat $(r = \infty)$ interface. The equilibrium constant for the dissolution of the bulk material gained by the ratio between and :

$$K_{eq} \cong \frac{k_d^{flat}}{k_g^{flat}} = C_0^{flat} \tag{19}$$

Considering of the Fick low for the diffusion of the monomers from the bulk solution toward the particle surface and neglecting the size of the nanoparticle compare to the thickness of the diffusion layer under real condition the following equation can be written:

$$J_{diff} = 4\pi Dr\left([M]_{bulk} - [M]_r \right) \tag{20}$$

Where $[M]_{bulk}$ is the concentration of the monomer in the bulk of the solution and D is the diffusion coefficient. The number of monomers remove and add to the particles surface equal to those diffused toward the bulk of the solution, so:

$$J_g^{react} - J_d^{react} = J_{diff} \tag{21}$$

Now with substitution of the equations (18), (19), (20) and (21) the following equation for determination of the stationary concentration of the monomer near the particle surface can be expressed (Talapin et al., 2001, 2002):

$$[M]r = \frac{D[M]_{bulk} + rk_d^{flat} \exp\left[\beta \frac{2\gamma V_m}{rRT}\right]}{rk_g^{flat} \exp\left[-a \frac{2\gamma V_m}{rRT}\right] + D} \tag{22}$$

The size dependent rate of the particle radius is obtained from the combination of the Equations (20) and (22) :

$$\frac{dr}{dt} = VmDC_0^{flat} \left\{ \frac{\frac{[M]_{bulk}}{C_0^{flat}} - \exp\left[\frac{2\gamma V_m}{rRT}\right]}{r + \frac{D}{k_g^{flat}} \exp\left[-a \frac{2\gamma V_m}{rRT}\right]} \right\} \tag{23}$$

If the process is the pure diffusion control i.e. $D \langle\langle k_g^{flat}$ and $r^* >> 1$, equation (23) can be simplified to equation obtained by Sugimoto which is explained in the next part. In 1999, Tadao Sugimoto developed a model to explain the nucleation and the growth of nanoparticles which is based on LaMer model. This model described the formation of nanoparticles that their nucleation and growth comfort with LaMer diagram and controlled by diffusion (Sugimoto, 2001; Sugimoto et al., 2000a; 200b). The Sugimoto model is briefly explained as follow. When C reaches C_{max},(Fig. 2) the steady state of a mass balance between the supply rate of solute (R_S), its consumption rates for nucleation (R_N), and the growth of generated nuclei (R_G), is established, and the following relationship may be held:

$$R_N + R_G - R_S = 0 \tag{24}$$

This mass balance equation may be replaced by a corresponding differential equation for the number of the generated stable nuclei, n_∞ (Sugimoto, 2001; Sugimoto et al., 2000a; 2000b):

$$\upsilon_0 \frac{dn_\infty}{dt} + \dot{\upsilon} n_\infty = Q V_m \tag{25}$$

In Eq.(25) the generation of stable nuclei shows itself as the first term in the left-hand and similarly, the second term indicates the growth of the generated stable nuclei. Where υ_0 is the minimum particle volume of the stable nuclei, $\dot{\upsilon}$ is the mean volume growth rate of the stable nuclei, n is the their number density, 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 (Sugimoto, 2001; Sugimoto et al., 2000a; 200b). It's assumed that Q is constant during the short nucleation period (Q_0), and may be regarded as a constant during nucleation stage and shortly after growth. If it's assumed that there is a time-averaged mean volume growth rate of the stable nuclei during the nucleation stage, the behavior of n as a function of time by using the time-averaged growth rate is as follows:

$$n(t) = \frac{Q_0 V_m}{\dot{\upsilon}} \left[1 - \exp\left(\frac{-\dot{\upsilon} t}{\upsilon_0}\right) \right] \tag{26}$$

Therefore, the number of final particles is given by:

$$n_\infty = \frac{Q_0 V_m}{\dot{\upsilon}}$$ (27)

On the other hand, it has been assumed that the growth of nanoparticles is controlled by diffusion, the linear growth rate, *dr/dt*, in the growth stage may be given by (Sugimoto, 2001; Sugimoto et al., 2000a; 200b):

$$\frac{dr}{dt} = \frac{DV_m}{r}\left[C - C_s \exp\left(\frac{2\gamma V_m}{rRT}\right)\right]$$ (28)

In Eq. 28, *D* is the diffusivity of the solute including free ions or their halide complexes, *C* is the molality of the solute, *C$_\infty$* is the solubility of the bulk solid in terms of total molality of solute and *γ* is the specific surface energy of the solid For maximum supersaturation. With having $\dot{\upsilon}$ and *S$_m$(=C$_{max}$/C$_s$)*, the initial particle radius of the stable nuclei during the nucleation stage *r$_0$*, the below equation is established between *r$_0$, D, $\dot{\upsilon}$* :

$$\dot{\upsilon} = 4\pi r_0 DV_m C_s\left[S_m - \exp\left(\frac{2\gamma V_m}{r_0 RT}\right)\right]$$ (29)

5. Nucleation and growth of TiO$_2$ nanoparticles

When TiO$_2$ powder was comerically produced in the early of twenty centery, it was used widely in a lot of applications such as membrane, sensor devices, photocatalyst. These applications can be classified in two major categories which are named as energy and enviromental. The employment of TiO$_2$ powders in these applications depends on the properties of the titania material which are affected by particle size, morphology, kind of polymorphe. Anatase, brookite and rutile are the main polymorphes of the TiO$_2$ and each of its phase has its own properties. In the nanoscale, the difference between properties of titanium is more considrelable. For example, anatase nanopowder shows advantages in applications such as photocatalytic material or dye-sensitized solar cells, and the particle size, shape and the morphology of TiO$_2$ nanomaterial have an important role in the performance of prepared material (Behnajady et al., 2008; Lee et al., 2009; Ni et al., 2006). On the other hand, rutile phase exhibits a higher refractive index, hiding power, good chemical stability. It is becoming a candidate material for high-temperature separation and catalysis applications (Li et al., 2006). Consequently, phase stability is very important for advanced application of TiO$_2$ nanomaterial. The phase transformation occurs during calcinations which is effected by the particle size and morphology. It is well known that the particle size and morphology are controlled by nucleation and growth procedure of TiO$_2$ nanoparticles. Therefore, it is necessary to have a detailed understanding of the nucleation and growth mechanism, as well as processes such as aggregation and coarsening. Nowadays, several methods such as flame reactor (Mehta et al., 2010), melt-phase separation technique (Zhaoa & Zhang, 2011), atomic layer deposition (King et al., 2009), combustion of TiCl$_4$ (West et al. 2007), atmospheric pressure CVS process (Rahiminezhad-Soltani et al., 2011), solvothermal (Wang & Xiao, 2006), thermal hydrolysis

(Santacesaria et al., 1985), sol-gel (Mahshid et al., 2007; 2008) have been developed to prepare TiO_2 nanoparticle with designed and controlled properties (crystalline phase, size, shape, etc.). Formation of TiO_2 nanoparticles have been studied in many papers with different approaches and aspects. For example, the influence of synthesis condition on preparation of TiO_2 by the hydrothermal method has shown that the size of particle increases from 18 to 26 nm when the synthesis temperature rise from 140 to 200°C (Ryua et al., 2008). But, the nucleation and growth kinetic study of nanaocrystalline TiO_2 formation from aqueous solutions and sol-gel methods have attracted many attentions (Courtecuisse et al., 1996; Mizukami, 1999; Baek et al., 2009; Kim et al., 1999; Gaoa et al., 2004; Jiaa et al., 2009; Nishidea & Tieng et al., 2011). Demopoulo and his co-workers (Charbonneau et al., 2009) produced the nanostructured TiO_2 particles by precipitation from forced hydrolysis of aqueous Ti(IV) chloride solution. The kinetic study of precipitation was shown that the nucleation rate is slow while growth rate is fast and follows Avrami model equation. They reported that the formation of nanostructure spherical particles is based on two steps. In the first step, the nuclation and aggregation of elementary nanocrystallite (≈ 10 – 2 nm) is acquired and in the second step the growth of elongated self –assembled nanofibers along rutile (110) atomic planes (Charbonneau et al., 2009). Oskam et al., (2003) reported that the average size of primary particles, depends on the parameters such as like coarsing time, temperature and solution chemistry. Solution chemistry can be modified by using different anions, solvent, pH or concentrations. He prepared precipitated anatase nanoparticles from the homogeneous acidified solution (pH=1) using titanium(IV) isopropoxide as precursor and using water-to-titanium mole ratio of about 200. It was shown that the secondary particles could be formed by epitaxial self-assembly of primary particles when longer time and higher temperature were used. The formation of secondary particles increases at higher temperatures because the tendency of primary particles to attend in the attachment process rises. It was indicated that the average particles radius increases linearly with time on the basis of the Lifshitz-Slyozov-Wagner model for coarsening (Oskam, et al. 2003). One of the complete research for studying of the nucleation and growth kinetic of titania nanoparticles was done by Zhang (Zhang et al., 2008). In his research titnium dioxid particles produced by the hydrolysis of a titanium tetrachloride ($TiCl_4$) precursor in aqueous solution at temperature below 100°C. They studied on the formation of TiO_2 particles in the three periods; induction, initial growth and saturated growth. Induction time depends extremely on the concentration of $TiCl_4$ and pH. Induction time was shorter with higher pH or [$TiCl_4$]. Higher supersaturation was made by increasing the solution temperature, [$TiCl_4$], and pH which results in shorter induction time for nuclation and a faster growth rate. The growth rate can be represented by the following power-low relationship:

$$d = Cs^P \tag{30}$$

which d is the growth rate and is equal to 0.6 at lower pH. The growth rate is equal to 3.9 nm/min at higher pH in 25°C. The particle critical size for growth was 0.44nm. In addition, the particle growth rate has the parabolic behavior relationship with the degree of supersaturation (Zhang, et al. 2008). As it has been mentioned above another appropriate technique for preparation of titanium oxide nanoparticles is sol-gel process. Sol-gel is a one the best techniques that can be applied to prepare and analyze the

formation of nano titania. Some effective parameters on the nature of the sol–gel process are metal precursor, temperature, pH of solution and the presence/absence of catalyst. Proposed benefits of the sol gel process are considered as easy control of formation process (nucleation and growth), high stability, better homogeneity, and high purity. The sol-gel process has been widely employed for preparing of titanium dioxide particles because the control of hydrolysis and polycondensation reactions can be easily stablished and gotten the appropriate properties (Zhang et al., 2009). TiO₂ nanomaterial can be synthesized by sol gel process with different titanium precursors. Typically, synthesizing of TiO₂ nanoparticles via sol-gel process include an acid-catalyzed hydrolysis step of titanium (IV) alkoxide followed by condensation. The development Ti-O-Ti is favorite with low water. Present of large excess of water lead to develop polymetric Ti-O-Ti chains (Mahshida et al., 2007; 2009). The study on nucleation and growth kinetic of titana nanoparticles prepared by sol gel method shows that the rate constant for coagulation of particles increases with temperature because the velocity of monomer through the particles has high dependency of temperature. Secondary particles were formed and the growth of particles incresed when they passed critical radius and became stable (Chenl & Mao, 2007). Jean and Ring (1986) studied on the growth kinetic of titania monospheres and noticed that the data fitted with theoretical curve for growth under diffusion control (LaMer diagram). They used the curve and determined the diffusion coefficient of particles which was $\approx 10^{-9}$ cm^2/s (Jean & Ring, 1986). Keshmiri and Troczynski (2002) syntheszied the ultra-fine and spherical of TiO₂ nanoparticles with a controlled precipitation of sol-gel technique. They found that the nucleation period was limited to a short period of time and the growth process was induced by another step. On the basis of this idea it can be possible to make nucleation through supersaturation phenomena (refer to LaMer diagram), and it is possible to produce almost perfect monodispersed particles (Keshmiri & Troczynski 2002). Li et al., (2002) prepared TiO₂ nano powder by sol-gel method. They used tetra-n-butyl-titanate and dionized water as the starting materials. The grain size of powder as a function of calcination temperature was studied and they found out that the grain size increase with the increasing of calcinations temperature. The following equation was used to explain the growth rate (Li, et al. 2002):

$$u = a_0 \dot{\upsilon}_0 \left[\exp\left(\frac{-Q}{kT} \right) \right] \left[1 - \exp\left(-\frac{\Delta F_\upsilon}{kT} \right) \right] \qquad (31)$$

where a_0 is the particle diameter, $\dot{\upsilon}_0$ the atomic jump frequency, Q the activation energy for an atom to leave the matrix and attach itself to the growing phase, ΔFv the molar free energy difference between two phases. For non-crystallization $\Delta Fv >> KT$. So Eq. (31) can be reduced as (Li, et al. 2002):

$$u = a_0 \dot{\upsilon}_0 \left[\exp\left(\frac{-Q}{kT} \right) \right] \qquad (32)$$

When the calcination temperature is high, the activation energy is very small, therefore, the growth rate is large. So the grain size increases very quickly as the calcination temperature increases. When the calcination temperature is low, the activation energy is very large and the growth rate becomes slow. So the grain size increases very slowly (Li, et al. 2002). A series of complete experiment on formation of TiO₂ particles have been assembled by Sugimoto

(Sugimoto, et al. 2002; Sugimoto & Zhou, 2002; Sugimoto, et al. 2003a). Using the sol-gel method for synthesis of TiO_2 nanoparticles, different sizes and shapes can be obtained by changing the reaction parameters. In his experiments, uniform anatase TiO_2 nanoparticles were formed by the gel–sol process from a condensed $Ti(OH)_4$ gel preformed by the hydrolysis of a Ti–triethanolamine (TEOA) . the titanium complex is hydrolyzed by degrees in water and completely converted to a rigid gel of $Ti(OH)_4$ after aging at 100°C for 24 hr (first aging). Then, the $Ti(OH)_4$ gel is totally transformed into anatase TiO_2 nanoparticles by additional aging at 140°C in an autoclave for 3 days (second aging) . In his experiment, the deposition process hydroxo complexes of titanium ion onto the growing TiO_2 determined the step for the formation of TiO_2 particles and not the dissolution of the $Ti(OH)_4$ gel. Consequently, the supply rate of the solute is equivalent to the dissolution rate of the gel and is increased with the consumption rate of solute and the particles of TiO_2 grow to keep the equilibrium concentration level (Sugimoto, et al. 2003b; 2007). His results showed that, however a mass balance exists between the rates of supply and consumption of solute toward the particles, the nucleation rate is related and a function of solute concentration which is equilibrium with the gel and also is independent of the consumption rate increase of solute for the particle growth. In this way, LaMer mechanism doesn't work in this situation because the nucleation of TiO_2 will not be finished until the precursor gel remains. Sogimoto pointed out that in such situation it is hard to separate the nucleation and growth process (Sugimoto et al., 2003b; Sugimoto, 2007). But, he defined a different way to separate nucleation and growth stage. Fig(3), shows the changing pattern of the time evolution of the concentration vs. time during the first aging at 100°C and the second aging at 140°C. Under the standard condition a different way of separation can be distinguished. In stage 1, the concentration of titanium ion isdecreased by a factor of about 2 orders of magnitude for the precipitation of $Ti(OH)_4$ gel. But, in second stage its order factor is one. He suggested that the factor is lowered probably because the progress of hydrogen bonding throughout the gel hydroxide groups when temperature raised to 140°C. He observed that at the earlier of the second aging, the nucleation
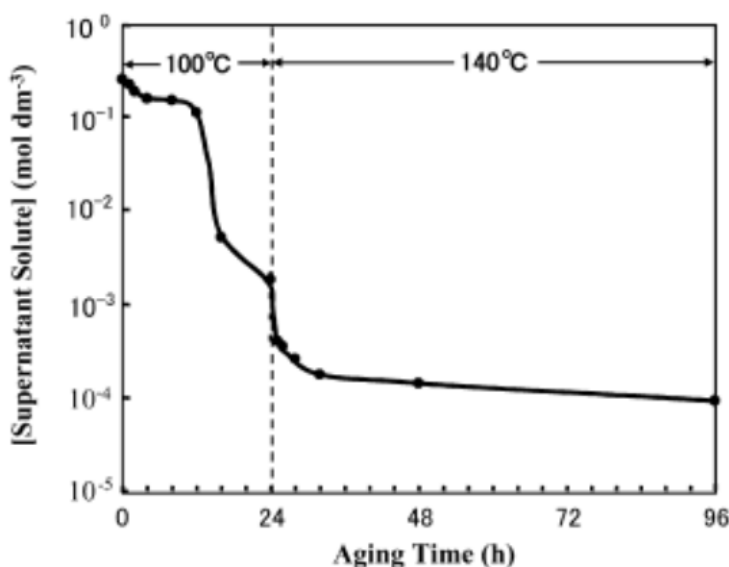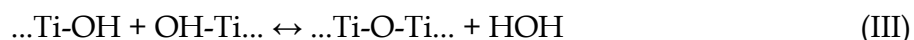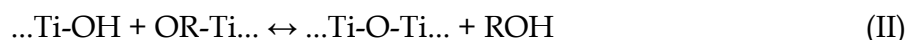

Fig. 3. Time evolution of the concentration vs. time during the first aging at 100°C and the second aging at 140°C under standard sol-gel system for TiO_2 nanoparticles (Sugimoto, 2007).

of TiO$_2$ particles happend, but it was completed soon with the drop of the supernatant concentration, followed by the growth of the nuclei under the supersaturation below the critical level for nucleation (Sugimoto et al., 2003b; Sugimoto, 2007).

Recently, we studied on the nucleation and growth of TiO$_2$ nanoparticles which were synthesized in two stages in an aqueous peroxotitanate solution by using HNO$_3$, TTIP, and TIPO as starting materials. The established controlled conditions for the preparation of TiO$_2$ nanoparticles were as follows: First, a stock solution of Ti^{+4} was prepared by mixing titanium isopropoxide with triethanol amine (TEOA) 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. 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 solution. The 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 various temperatures ranging from 60 to 80°C. Solution was heated to achieve super saturation of Ti in solution. In each 4 min time interval, a sample has been taken from prepared solution and analyzed by atomic adsorption. A condenser was used to stop the evaporation of solution and each 4 min a sample has been taken throughout the process. TiO$_2$ particles were separated from the resulting Ti^{4+} suspension by centrifugation. This procedure has been repeated for several times and every time the concentration of Ti4+ ions was measured via atomic adsorption. Titanium alkoxide can be hydrolyzed and condensed through following steps:

$$\text{Ti-OR} + \text{H}_2\text{O} \leftrightarrow \text{Ti-OH} + \text{ROH} \qquad\qquad\qquad (\text{I})$$

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

$$...\text{Ti-OH} + \text{OH-Ti}... \leftrightarrow ...\text{Ti-O-Ti}... + \text{HOH} \qquad\qquad\qquad (\text{III})$$

Depending on the pH of solution, several compounds of titanium (IV), e.g. TiO^{2+}, TiOH^{+3},Ti(OH)$_2^{+2}$, and TiO(OH)$^+$, can be formed. Experimental results have shown that the uniform nanoparticles can be obtained in solution with more acidic condition (pH~1) (Sugimoto & Zhou 2002; Sugimoto et al., 2002a). Therefore, it is reasonable that an acidic solution is suitable to choose for our theoretical approach. When the pH of solution is near to 1, the TiO^{+2} ions are the dominant complex in the solution and TiO$_2$ can be nucleated by the aforementioned equations (II and III). It can be found that the growth of particles occurs by the addition of Ti^{+4} to the growing particles. It has been shown that the sufficient number of O$^-$ or OH$^-$ sites are available along the TiO$_2$ particle planes, which are appropriate positions to create octahedral coordination for the incoming Ti^{+4} ions. Moreover, after the attachment of Ti^{4+} ions along the planes, equal number of new O$^-$ or OH$^-$ sites are created for further attachment of Ti^{4+} ions (Baek, et al. 2009). In Fig. 4, the concentration-changing pattern of [Ti] ions in the solution under the standard condition in 70°C can be observed, which is similar to the LaMer diagram. For better explanation, the diagram is divided in two different stages. In the first stage, the liquid in the solution evaporates slowly which leads to the increase in the concentration of titanium ions. In contrast, in the second stage, the concentration of titanium ions starts to decrease as TiO$_2$ particles start to precipitate. The supersaturation ratio, S, was obtained from the LaMer

diagram (Fig. 4). The maximum value of supersaturation ratio, S_m, is equal to 3.19. The radius and free energy of formation of the nucleus at the supersaturation, r_m^* and ΔG_m^* respectively, are calculated from Gibbs-Thomson equation which are $r_m^*=4.42nm$ and $\Delta G_m^* =1.16\times10^{-16}J$ (=343K). At the supersaturation level, the high driving force is available (Fig. 4). Therefore, the nucleation process is easiest and continues until the radius of the nucleus of stable particles reaches (r_0).
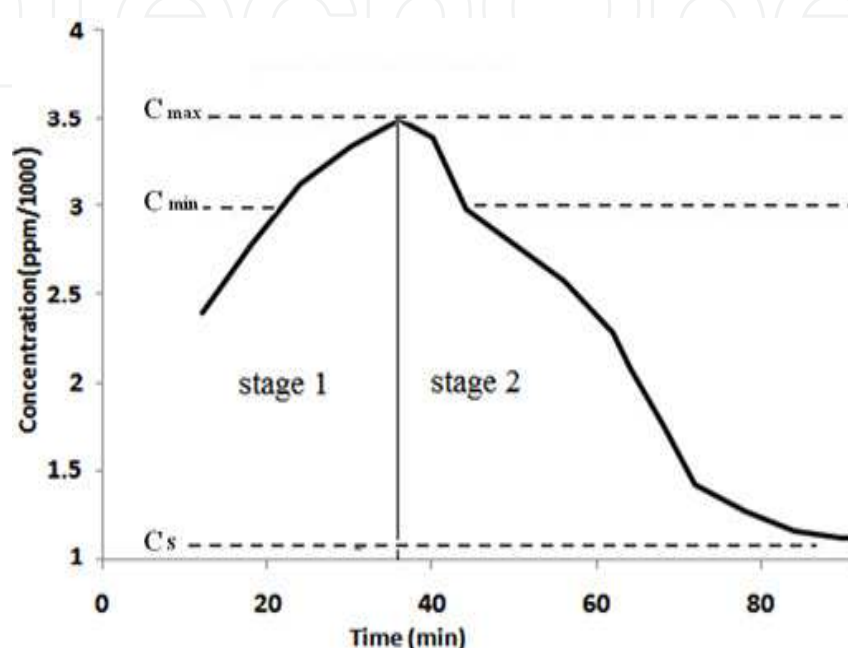
Fig. 4. Time evolutions of Ti^{4+} concentration in the standard system: stage 1;[Ti] concentration increasing. stage 2; [Ti] concentration decreasing (Mehranpour et al., 2010).

When, the stable particles are present, the nucleation stops and particles start to grow until the final product is produced. To obtain the primary radius of stable embryo, the Gibbs-Thomson equation was used and the determined radius is equal to $r_0=6.1nm$. Fig. 5 shows the TEM image of the TiO$_2$ particles. It is clear that the size of formed TiO$_2$ nanoparticles is equal to $7.1nm$ ($d=14.2nm$) and has a good agreement with the theoretical size. The supply rate of the monomer in the nucleation period, Q_0, was obtained from the tangential slope of the [Ti]-t diagram (Fig. 4) at [Ti]$_{max}$ which is equal to $7.03\times10^{-7}mol.dm^{-3}.s^{-1}$. Using the supply rate of monomer and the final particle density, the amount of mean volumic growth rate of the stable nuclei are calculated from Equ. 27 as 2.98×10^2 nm^{3}s^{-1}. Finally, from equation 29 the diffusion coefficient of ions in solution is $D = 6.18\times10^{-8}$ cm^{2}s^{-1}. The effect of temperature on the formation of particles was investigated in the diffrent temperature. The results show that the nucleation and growth of TiO$_2$ nanoparticles is Extremely dependent on the temperature. It can be observed the increase in temperature has caused a shift in the LaMer diagram to the left side. So, the maximum supersaturation can be reached in higher temperatures. In fact, temperature has a major effect on the diffusion coefficient of monomers. According to Arrhenius equation, the rise in temperature causes an increase of the diffusion coefficient which effects on the acceleration of hydrolysis of Ti in solution and the supply rate of the monomer in the nucleation period, Q_0, rises.
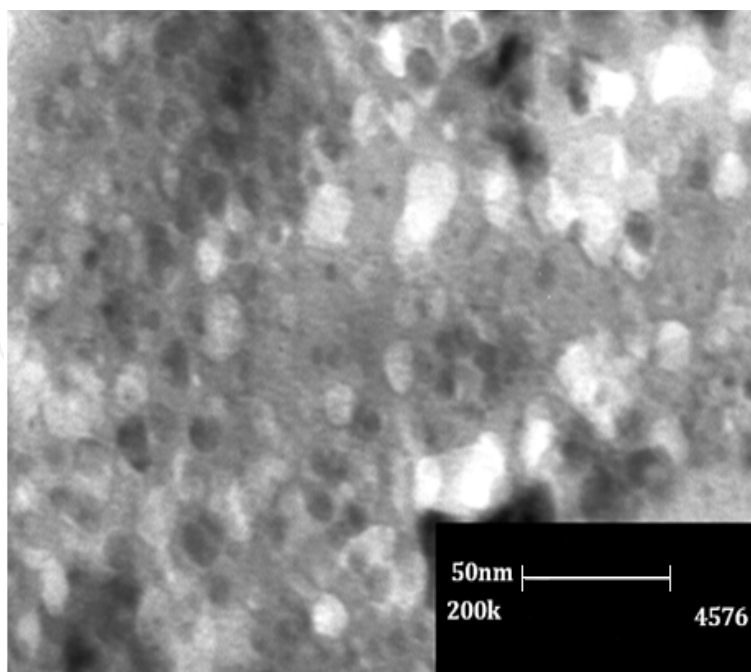
Fig. 5. TEM image of TiO₂ nanoparticles at the end of nucleation and start of growth stage. The radius is large enough to be stable and growth to the final particles ($r^* = r_0$).

Therefore, it was predictable that the nucleation and growth of particles occurred earlier in upper temperature. As we mentioned above, TiO₂ phases have their own properties and the phases transformation which is associated by the nuclation and grain growth of new phase inside the old phase has attracted a considerable attention (Delogu 2009; Gole et al., 2008; Napolitano et al., 2010). The activation energy of anatase to rutile phase transformation has been reported from 147 to 837 kJ/mol (Hsiang & Lin, 2006; 2008). Zhang and Banfield (2000) suggested that in anatase samples with denser particle packing, rutile nucleates primarily at interfaces between contacting anatase particles. But in anatase samples with less dense particle packing, rutile nucleates at both interfaces and free surfaces of anatase particles (Gribb & Banfield, 1997). To analyze, the phase transformation of synthesized titania nanoparticles, they were thermally heated at 200, 400, 600, and 800°C for 2 hours. Figure 6 shows the phase contents of rutile in samples which were treated isochronally at 2 hours within the temperature range 200 to 800°C. The results indicate that the process involves the transformation of anatase in the starting material to rutile from its initial 23% at 200°C to 100% at 800°C. Rapid reaction rate of phase transformation shows that there is high driving force for the transition (free energy change for phase transformation). It means that a lot of nucleation and growth site for transformation are available in prepared sample. The kinetics of anatase-rutile phase transformation is followed by Avrami equation as follows (Hsiang and Lin 2006):

$$X = 1 - \exp{(-kt)^n} \tag{33}$$

where X is the fraction of transformation, t is the time, k is the kinetic constant. From the Arrhenius plot of various kinetic constants, and with calculation of slop, activation energy is obtained as -20 kj/mol.
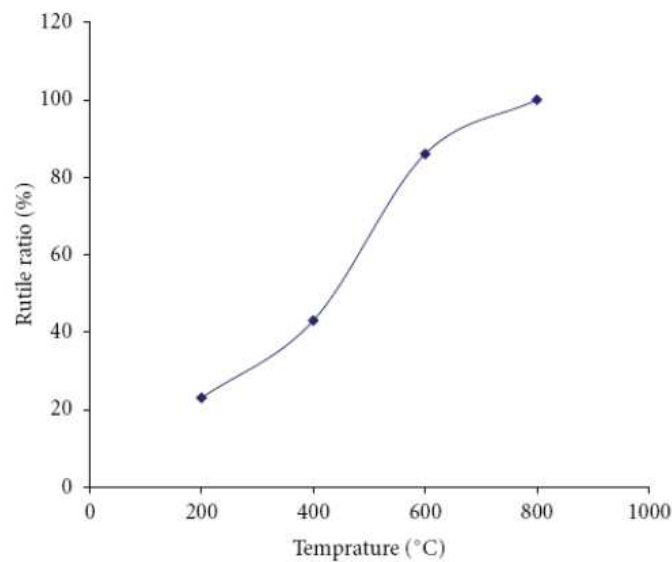
Fig. 6. Evolution of the amount of Rutile phases in the various temperatures (Mehranpour et al., 2010).

6. Conclusion

Nowadays, titanium oxide nanoparticles have the most interest due to their properties. These properties make them to use in a wide range of advance. It is well known that the size of nanoparticles plays an important role in electrical and optical characteristic (Miao et al., 2004; Oskam et al., 2003). Also the other factor effecting on properties of nano powder is the phase composition and the particle size of each phase. Hence, it is essential to have completely control on forming of particles to achieve the favorite particle size, shape, and size distribution. Therefore, a theoretical approach to understand the mechanism of TiO_2 nanocrystal formation provides a greater control over the size, shape, and composition and results an ability to tune the abovementioned properties simply by varying the crystallization conditions. In this chapter, at first, the kinetic of nucleation and growth of particles have been generally discussed and some of scientific reports have been analyzed. Then, the kinetic of nucleation and the growth mechanism of Titana nanoparticles were studied on the basis of LaMer theory. In comparison with other synthesized TiO_2 nanoparticles the kinetics of phase transformation of our sample is very fast and so proposes that the activation energy of nucleation and growth is more than other prepared nanoparticles. It is concluded that the lowering of activation energy is due to diffusion controlled synthesis process and the uniformity of size and shape of resultant material.

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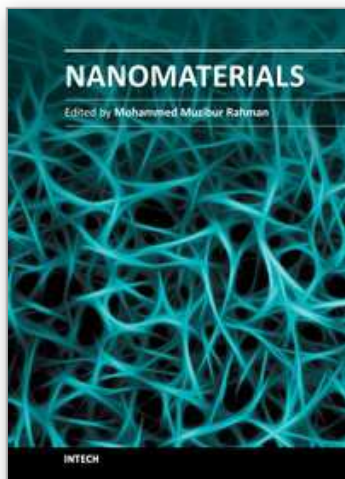
Nanomaterials

Edited by Prof. Mohammed Rahman

The book "Nanomaterials" includes all aspects of metal-oxide nano-structures, nano-composites, and polymer materials instigating with materials survey and preparations, growth and characterizations, processing and fabrications, developments and potential applications. These topics have utilized innovative methods of preparation, improvement, and continuous changes in multidimensional ways. The innovative frontiers are branching out from time to time to advanced nanotechnology. It is an important booklet for scientific organizations, governmental research-centers, academic libraries, and the overall research and development of nano-materials in general. It has been created for widespread audience with diverse backgrounds and education.

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