

Research Article

Study on the Phase Transformation Kinetics of Sol-Gel Driven TiO_2 Nanoparticles

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Titanium dioxide nanopowders were synthesized by the diffusion controlled sol-gel process (LaMer model) and characterized by DTA-TG, XRD, and SEM. The prepared TiO_2 nanoparticles have uniform size and morphology, and the phase transformation kinetics of obtained material was studied by interpretation of the X-ray diffraction patterns peaks on the base of Avrami equation. The starting point of anatase-rutile phase transformation temperature in the prepared nanoparticles was found between 100 and 200°C. A decreasing trend on the intensity of X-ray peaks of anatase phase was observed up to 600°C when the presence of the rutile phase became predominant. Results indicated that the transition kinetics of the diffusion controlled prepared nanoparticles was begun at low temperature, and it can be concluded that the nucleation and growth sites in these particles were more than other. However, it has been found that the nucleation activation energy of rutile phase was 20 kJ/mol, and it is the lowest reported activation energy.

1. Introduction

Titania (TiO_2) continues to attract much interest, because of its wide variety of applications such as optical devices, sensors, and catalysis or photocatalysis [1, 2]. There are several key factors in determining the properties of the final materials and their applications. For example, anatase 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 [3–5]. On the other hand, rutile phase exhibits a higher refractive index and hiding power, as well as good chemical stability, and is becoming a candidate material for high-temperature separation and catalysis applications [6, 7]. Recently, it has been found that a mixture of anatase and rutile demonstrates better hot catalysis activity than does the single TiO_2 phase [8, 9]. As a sequence, studying the kinetics of the phase transformation of TiO_2 nanomaterial is fundamentally important to control its properties and seems to be essential for special applications. During last decade, phase transformation of

titanium oxide nanoparticles was a subject of scientific efforts and it has been proved that the intrinsic parameters such as particle size [10, 11], purity [12], powder compaction [13], aging [14], as well as peptization [15] can affect the temperature and the energy of phase transition of TiO_2 nanoparticles. Banfield et al. [16, 17] purposed that a critical size may also be important and concluded that anatase is thermodynamically stable and the phase transformation will not begin with heating until the critical size is reached. It means that the nucleation and the growth have critical roles on the phase transformation of TiO_2 nanoparticles. In sol-gel process, the formation of nanoparticles is explained on the base of two important theories that are called LaMer and Turkevich. The most famous and widely cited example of nucleation theory for cluster formation is the pioneer work of LaMer and Dinegar in 1950s [18]. LaMer theory is based on the diffusion controlled nucleation and growth of the same-size particles. By contrast, in the second theory (Turkevich theory) the nucleation and the growth of particle are controlled by chemical reaction of reactants in the gel [19]. In this paper, a diffusion controlled sol-gel process

has been employed to obtain TiO₂ nanoparticles with the uniform size and morphology and the phase transformation kinetics of synthesized material was studied by interpretation of the X-ray diffraction patterns peaks on the base of Avrami equation.

2. Experimental

In this investigation, the raw materials contain Titanium isopropoxide (TTIP) (98%), Triethanolamine (TIPO), Ethanol, HNO₃ (98%) which have been purchased from Merck. The established controlled conditions for the preparation of TiO₂ nanoparticles were as follows. First, a stock solution of Ti⁴⁺ was prepared by mixing titanium isopropoxide (TIPO: Ti[OCH(CH₃)₂]₄) with triethanolamine (TEOA: N(CH₂CH₂OH)₃) at a molar ratio of TIPO:TEOA=1:2 under dry air to form a stable Ti⁴⁺ 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 Ti⁴⁺ is near to $5 \times 10^{-4} \text{ mol}\cdot\text{l}^{-1}$. Then, 10 mL of the stock solution was mixed with the same volume of doubly distilled water. In order to have TiO₂ nanoparticles with uniform size and morphology alkaline regime has been selected and pH (~9.6) was controlled by addition of HClO₄ or NaOH solution. The final solution was placed in a screw-capped Pyrex bottle and aged at 100°C for 36 hours. Finally, the resulting highly viscous gel was mixed with 80 mL (2×10^{-3} molar) nitric acid and stirred at 25°C for 3 hours to dissolve the gel. The solution was set in pool water at 70°C. After 4 minutes a sample has been taken from prepared solution, and TiO₂ particles were separated from the resulting Ti⁴⁺ suspension by centrifugation. This work has been repeated several times and every time the concentration of the Ti⁴⁺ was measured by the atomic adsorption. The products were washed with distilled water and observed using a JEM-1200EX II transmission electron microscope (SEM) with an acceleration voltage of 80 kV. For the identification of the products, X-ray diffractometry (XRD) was conducted using a Rigaku RAD-B system with a CuK α beam.

3. Results and Discussion

As has been mentioned, the diffusion controlled of nucleation and growth process has been selected to prepare TiO₂ nanoparticles with uniform size and shape. Therefore, the nanoparticles must be formed on the base of LaMer theory that is not very simple. Figure 1 shows the scanning electron microscopy (SEM) image of the TiO₂ nanostructured material. The average particle size of TiO₂ nanostructured material was near to 50 nm. These particles were took out after centrifugation of solution. Figure 2 shows the TGA curve of TiO₂ nanopowder. This curve essentially shows that the complete weight loss is due to removal of water occurred in 150°C. Also, there are two exothermic peaks on the DTA curve which correspond to the decomposition of the probably existing organic species (250°C) and the completed anatase-rutile phase transition (500°C). In order

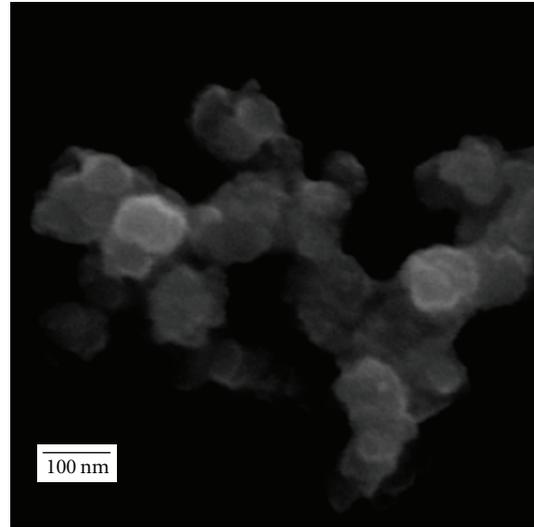


FIGURE 1: SEM micrographs of TiO₂ particles after seeding.

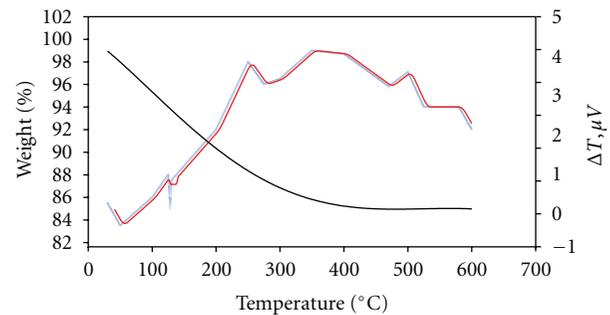
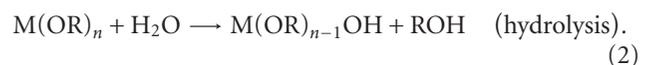


FIGURE 2: DTG analysis of prepared TiO₂ nanoparticles.

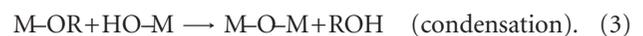
to know the source of water and kind of organic species, we need to have a brief introduction about sol-gel process. As has been explained in our last paper [20], two chemical processes, which are called hydrolysis and polycondensation, are involved in the formation of the metal oxide (M–O–M) from the metal alkoxide precursor (M(OR)ⁿ). The hydrolysis and polycondensation of metal alkoxide can be generally represented as the reaction of the alkoxide with X–OH species as follows:



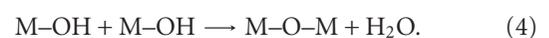
where R is an alkyl group. (I) For X = H, and m = 1 it can be written as



If we consider that n = 1 and X = M, it can be regarded as



The sol-gel process can be finally finished by



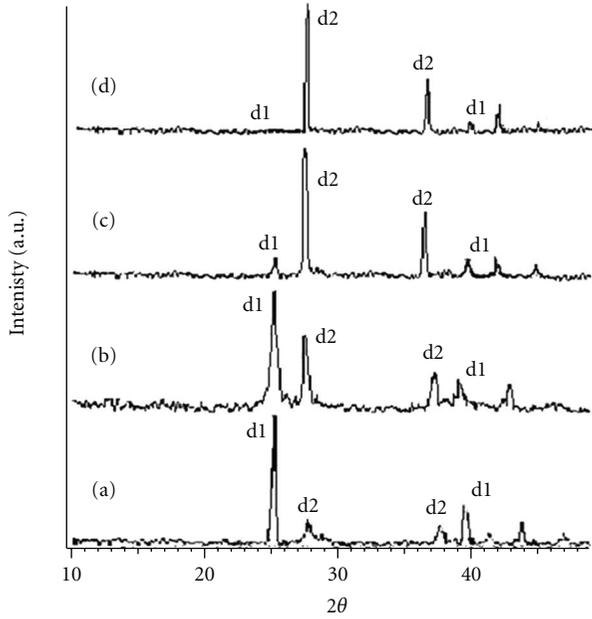


FIGURE 3: XRD patterns of samples reacted in the temperature range 200–800°C for 2 hours (a) 200°C, (b) 400°C, (c) 600°C, (d) 800°C.

The sol-gel process resultant materials contain water, oxides and organic species. The absorption of water on the surface sites of oxide powder is physically, and organic species are absorbed chemically. Therefore, different temperatures need to desorb them from oxide surface. Figure 3 shows that the XRD patterns of 4 samples of TiO_2 nanoparticles were thermally heated at 200, 400, 600, and 800°C for 2 hours. In Figure 3 the peaks of d1, d2 show anatase and rutile peaks, respectively. Also, there are not any corresponding peaks to confirm the crystallization of brookite in the temperature range of heat treatment. The obtained results indicated that the process is involved with the phase transformation of anatase to rutile in the starting material and the formation of rutile was begun from initial heat treatment process and the temperature, at which the anatase-rutile transformation becomes significant, is 200°C. The phase content of a sample can be calculated from the integrated intensities of the above-mentioned anatase, rutile, and brookite peaks. If a sample contains only anatase and rutile, the weight fraction of rutile (X_R) can be calculated from

$$X_R = \frac{1}{1 + 0.8(I_A/I_B)}, \quad (5)$$

where X_R is the transformation fraction of rutile and I_A represents the integrated intensity of the anatase (101) peak and I_R the integrated intensity of rutile (110) peak. The intensity of the 2θ degree positions of 101 peak of the anatase phase and those of the 110 peak of rutile are given as a function of the treatment temperature. For the anatase reflection, a decrease of the Bragg (2θ) positions and the increase of the corresponding d values in the Bragg reflection equation ($n\lambda = 2 \cdot d \cdot \sin\theta$) were observed up to 600°C.

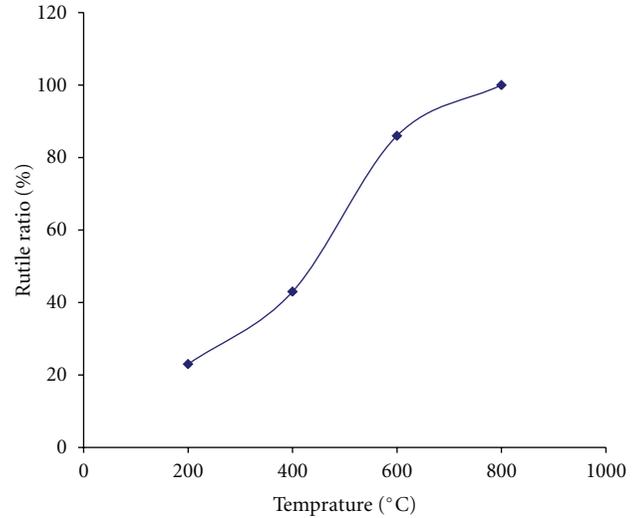


FIGURE 4: Evolution of the amount of Rutile phases in the various temperatures.

Since, the height of the rutile peak is longer enough than anatase peak, and so rutile phase is the dominant phase and becomes important from phase transformation point of view. Normally, the phase transformation of anatase to rutile is started at 500°C. But, in heat-treated sample at 600°C, the rutile is dominant phase and more than 80% of anatase is transformed to rutile. Figure 4 shows the phase contents of rutile in samples which were treated isochronally at 2 hours in the temperature range 200–800°C. The percentage of rutile phase has been calculated by (5). 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. High rapid reaction rate for this transformation shows that there must be lots of nucleation and growth site for transformation and also there is high driving force for the transition (free energy change for phase transformation). In summary, the main factor determining the rate for transformation of phase a to phase b by a nucleation and growth mechanism is $\Delta G_{a \rightarrow b}$, which is the difference in free energy between a and b . So it seems that the free energy between rutile and anatase phase in this transformation is low. To clarify this inference the Avrami equation is used. It has been shown that kinetics of anatase-rutile phase transformation is followed by Avrami equation as follows:

$$X = 1 - \exp(-kt)^n, \quad (6)$$

where X is the fraction of transformation, t is the time, k is the kinetic constant, and $n = 0.9 \sim 1.2$ for TiO_2 . The kinetic constant can be calculated for each transformation fraction. Activation energy for the transformation can be obtained using Arrhenius equation as given by

$$\ln k = -\frac{E_a}{RT} + \ln k_0, \quad (7)$$

where E_a is the activation energy, k is the kinetic constant, k_0 is a material properties constant, R is the universal gas

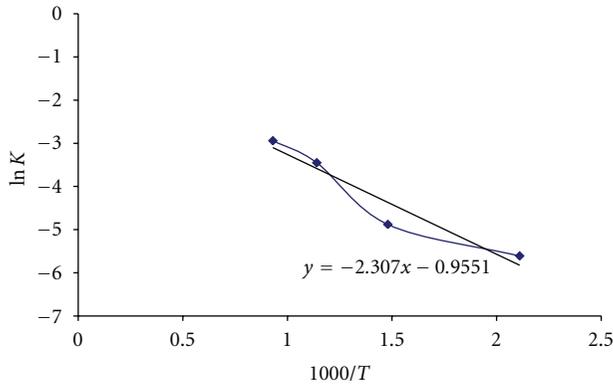


FIGURE 5: Arrhenius plot for samples aged at various times.

constant (8.314 J/mol·K), and T is the absolute temperature. From the Arrhenius plot of various kinetic constants (Figure 5), and with calculation of slope, activation energy is obtained as -20 kJ/mol. Numerous researchers, such as Kumar et al. [21, 22] and Zhang and Banfield [17], have investigated the kinetics of the anatase-to-rutile phase transformation, and the activation energy from their experiment was 147 and 248 kJ/mol, respectively. We believe that the high activation energy is due to nonuniformity of morphology and wide size distribution of the prepared TiO_2 nanoparticles using sol-gel method. Therefore, the understanding of sol-gel-derived nanoparticles phase transition kinetics needs to have a uniform shape, morphology, and narrow size distribution. Also, the activation energy for the nuclei growth has been reported by Hsiang and Lin [15]. They showed that the activation energy depends on the experimental conditions and changes from 205 to 506 kJ/mol. Density functional theory [23] and tight binding [24] model have been employed to evaluate the routes of phase transformation mechanism in titanium oxide. According to these approaches, it has been found that the point defects have an important role in the phase transition of TiO_2 material. On the other hand, the thermodynamically stable shape of TiO_2 nanoparticles is very different from spherical and rod shapes of TiO_2 nanomaterials [25]. It means that the spherical or rod shape of titanium oxide nanoparticles has different surface state density (point defects or surface dangling bond) with respect to thermodynamically stable shape of TiO_2 nanoparticles, and the density of surface state in these synthesized materials will be high. As has been argued in our last paper [26], the phase transformation of anatase to rutile depends to surface state. Therefore, the lowering of calculated activation energy of nucleation for samples prepared by this experiments is due to high surface state density and the uniformity of size and shape of resultant material that were caused from diffusion controlled synthesis process.

4. Conclusion

Prior treatment of synthesized titanium oxide nanopowders has remarkable effects on their properties as well as on the structural transitions observed under heating. At the present

work, we have prepared 50 nm TiO_2 nanoparticles by sol-gel method based on LaMer theory. The particles were treated in different temperatures. The XRD pattern of particles indicated that the rutile phase transition phase was begun at lower than 200°C . 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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