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Effects of aging on nanocrystalline anatase-to-rutile phase transformation kinetics

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Abstract

The effects of aging on the kinetics for nanocrystalline anatase-to-rutile phase transformation were investigated. The agglomeration and crystallite sizes for TiO_2 gels decreased with increasing aging treatment. For unaged samples, the agglomeration number was high, so that there are a larger number of anatase crystallites and crystallite–crystallite anatase contacts in each cluster. This promotes interfacial nucleation. Therefore, the activation energy of nucleation calculated for unaged samples was smaller than that for those found for the aged ones.

Keywords: Kinetics; Rutile; Anatase; Phase transformation; Aging

1. Introduction

TiO_2 is widely used as a catalyst, pigment and in electronics [1–3]. However, these applications demand high purity titania with controlled crystallite size, definite phase composition and surface properties. Therefore, it is important to control the particle size, morphology, and crystalline phase of the TiO_2 system.

Many different methods have been used in preparing nanosized TiO_2 powders. Among these, the thermal treatment of precursors obtained using sol–gel [4,5], $TiCl_4$ precipitation [6], and $Ti(SO_4)_2$ precipitation [7] have been widely investigated because of the easily controlled process. There are three well-known TiO_2 crystalline types: anatase, rutile, and brookite. The phase transition of anatase to rutile takes place during calcination [8]. The phase transformation, which occurs during calcination, gives rise to a transformed rutile powder that has undergone considerable aggregation and grain growth [9]. The above characteristics are detrimental for nanosized TiO_2 powders.

The kinetics of anatase to rutile phase transformation has been studied extensively. The activation energy values reported in the literature for anatase to rutile phase transformation are very diverse, ranging from 147 to 837 kJ/mol [10–13]. Recently, Zhang and Banfield [14] proposed an interface nucleation model for the phase transformation in anatase samples with denser particle packing and a surface nucleation model for those with less dense particle packing.

Aging is a process in which the physical properties of the gels can be changed through polymerization, coarsening and phase transformation [15]. The changes in the gel structure and properties which occur during aging have a profound effect on the subsequent sintering process [16]. In our previous study [17], we found that the aging treatment of TiO_2 decreased the hydroxyl ions existing in the anatase and resulted in lowering surface area reduction rate and promoting densification. However, the aging treatment mechanism effects on the anatase to rutile phase transformation of TiO_2 powders during calcination have not been well understood.

The aim of this study was to investigate the aging effects on the kinetics of anatase to rutile phase transformation of TiO_2 gels obtained from $TiCl_4$.

2. Experimental

2.1. Sample preparation

Titanium chloride (reagent grade) was dissolved in distilled water to prepare Ti^{4+} solution with concentration of 1.5 mol/kg. The TiO_2 gel was prepared by adding Ti^{4+} solution, drop by

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drop to a NH_4OH solution at pH 9.5 under vigorous stirring. The pH was maintained at 9.5 by adding 10% NH_4OH solution. After precipitation, the gels were refluxed in a boiling solution, kept at pH 9.5 for various periods (0, 12, 24, 48 h). Distilled water was used for filtering and washing three times. The gel was then washed with ethanol. The washed gels were dried at 80 °C and then calcined at 200–1100 °C for 2 h. However, the powder calcined at 600 °C without soaking was used as the precursor for the study of the kinetics of anatase to rutile phase transformation. The powders were annealed in air at temperatures between 800 and 850 °C for different durations.

2.2. Characterization

The crystalline phases of the samples were identified using the XRD powder method using Ni-filtered Cu Kα radiation (Siemens D5000). Quantitative X-ray diffractometry (Siemens D5000) was used to determine the amount of the rutile phase. The intensity ratio of rutile phase in the matrix was determined from [18]:

$$X = \frac{1}{1 + 0.8(I_A/I_R)}$$

where X is the fraction of rutile phase; I_A the integrated (1 0 1) intensity of anatase; I_R is the integrated (1 1 0) intensity of rutile. The crystallite sizes of the TiO_2 in these specimens were determined using the Scherrer equation. The specific surface areas of the TiO_2 powders were measured using the conventional nitrogen absorption (BET) technique (Gemini 2360, Micromeritics).

The XRD crystallite size ratio to the BET particle size gives an estimate of the average number of primary particles in each agglomerate. Assuming that the particle shape is spherical, the agglomeration number can be derived from the following relationship:

$$\mathrm{AN}(50) = \frac{D_{\mathrm{BET}}^3}{D_{\mathrm{XRD}}^3}$$

where D_{BET} is the BET particle surface area; D_{XRD} is the crystallite size measured by XRD line broadening.

The morphology of the calcined powder was observed by TEM (HF-2000, Hitachi, Tokyo, Japan).

3. Results and discussion

3.1. Effects of aging on the characteristics of TiO_2 starting powders

Fig. 1 shows the crystallite sizes of the calcined TiO_2 gels as a function of calcination temperature. The growth of anatase crystallite for the unaged sample was faster than for the aged sample. The variations in rutile ratio with various calcination temperature for samples aged for various times are shown in Fig. 2. For the unaged sample, the anatase to rutile phase transformation occurred at around 800 °C. In contrast, the

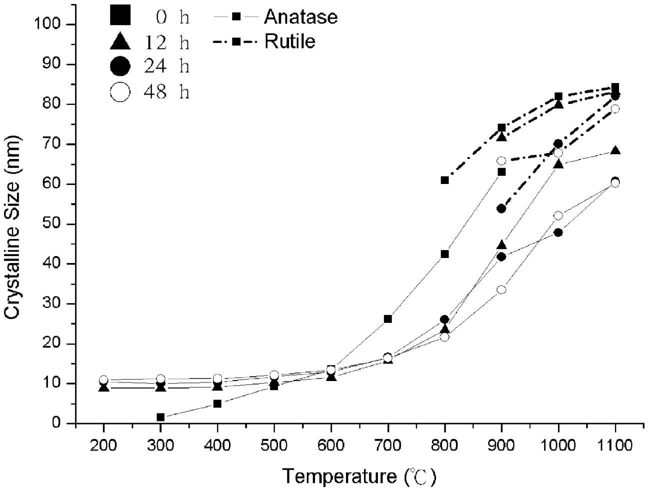

Fig. 1. The crystallite sizes of the calcined TiO_2 gels as a function of calcination temperatures.

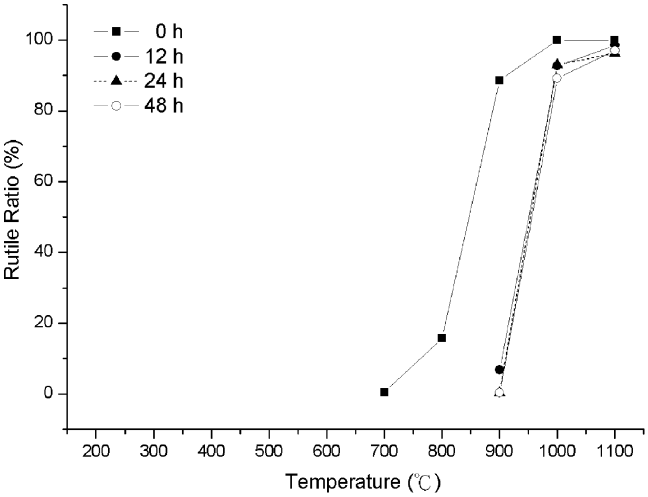

Fig. 2. The variations in rutile ratio with various calcination temperatures for samples aged at various times.

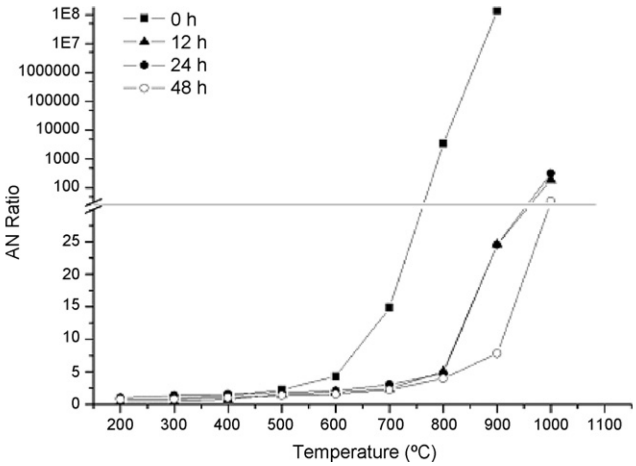

Fig. 3. The agglomeration numbers for TiO_2 gels calcined at various temperatures.

temperatures of anatase to rutile phase transformation for the aged specimens are shifted upward by 100 °C.

Fig. 3 shows the agglomeration numbers for TiO_2 gels calcined at various temperatures. Apparently, the agglomeration numbers for TiO_2 gels with and without aging treatment increased rapidly as the calcination temperature increased above 600 and 800 °C, respectively. In addition, the agglomeration numbers for TiO_2 aged gels were much lower than those for TiO_2 gels without aging treatment as the calcination temperature was raised above 600 °C. Fig. 4 shows the morphology of anatase obtained by calcining TiO_2 gels with different durations at 800 °C. Apparently, the agglomeration and crystallite sizes for TiO_2 unaged gels were higher than those for TiO_2 aged gels. Hebrard et al. [19] investigated the surface area reduction in a TiO_2 anatase powder under various partial water and oxygen pressures. They proposed that surface diffusion of hydroxyl ions was the rate-limiting step in surface area reduction. During the surface diffusion process, material from the particle surface region with positive curvature diffused along the particle surface and then precipitated at the region with negative curvature in the neck between the particles. This process leads to neck development between particles, which is characteristic of hard agglomerates. It is likely that the hydroxyl ions existing in the anatase lattice decreased with increasing aging time, which resulted in decreasing the agglomeration after calcination.

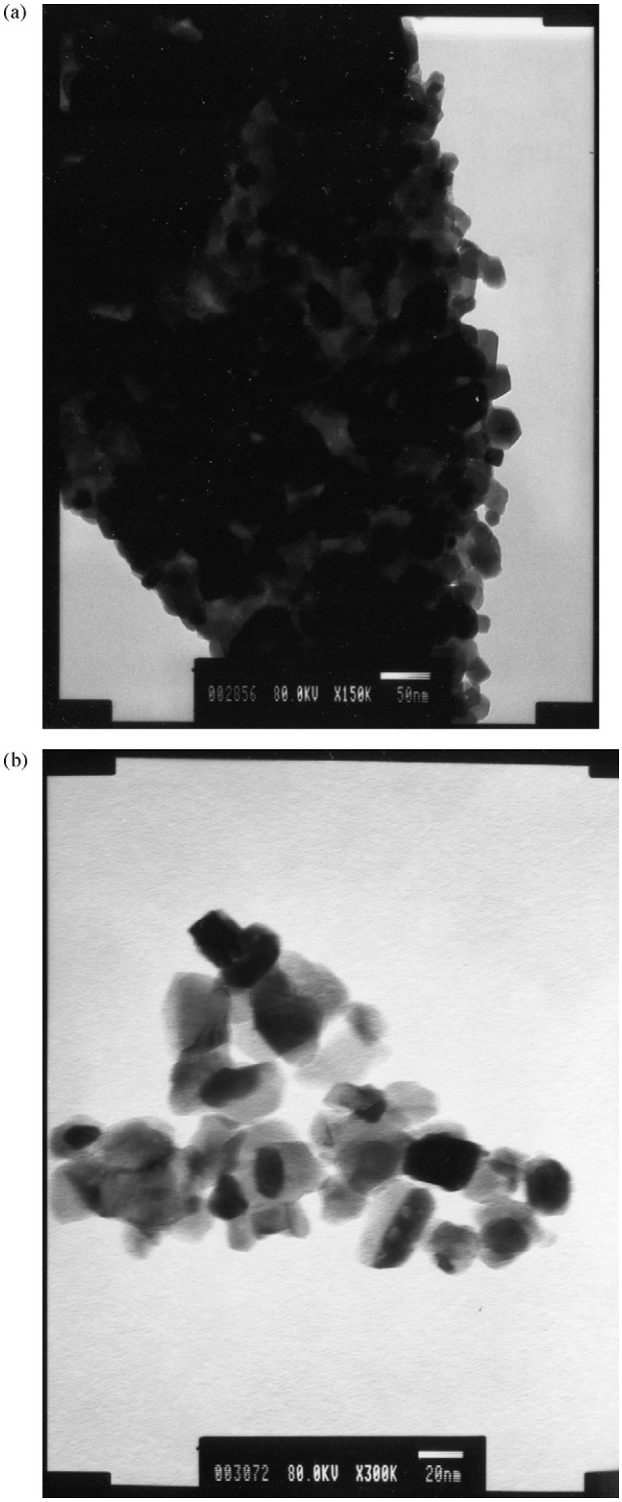

Fig. 4. Morphology of anatase obtained by calcining TiO_2 gels with various aging time at 800 °C: (a) 0 h and (b) 48 h.

3.2. Aging effects on the kinetics of the anatase to rutile phase transformation

Fig. 5 shows the variation in rutile ratio with various calcination temperatures and soaking times for samples aged at various times. It indicates that the aging treatment inhibited the anatase to rutile phase transformation.

The phase transformation kinetics generally follows the Avrami equation [20]:

$$x = 1 - \exp(kt)^n$$

where x is the fraction of rutile phase; k the rate constant; t the holding time; n is a constant which depends on the mechanism.

Fig. 6 shows a plot of $\ln\ln(1-x)$ versus $\ln t$ with a regression line fitted. The activation energy for the anatase to rutile transformation can be determined from the slope of an Arrhenius plot of $\ln k$ versus $1/T$ (Fig. 7) where T is the testing temperature. Table 1 shows the n values and activation energies of anatase to rutile phase transformation of powders with various aging time.

The phase transformation of nanocrystalline anatase particles proceeds by anatase crystal growth followed by nucleation and nuclei growth. Therefore, the activation energy for phase transformation calculated from Fig. 7 involves: (1) the activation energy of coarsening of anatase particles; (2) the activation energy of nucleation; (3) the activation energy for the growth of nuclei.

The activation energy for the nuclei growth is nearly zero reported by Zhang and Banfield [14]. Consequently, the activation energy of nucleation could be obtained by subtracting the activation energy of anatase particle coarsening reported in our previous study (as shown in Table 1) [17] from the calculated phase transformation activation energy from Fig. 4 and summarized in Table 1. In our previous study [17], we observed that the agglomeration number for aged samples

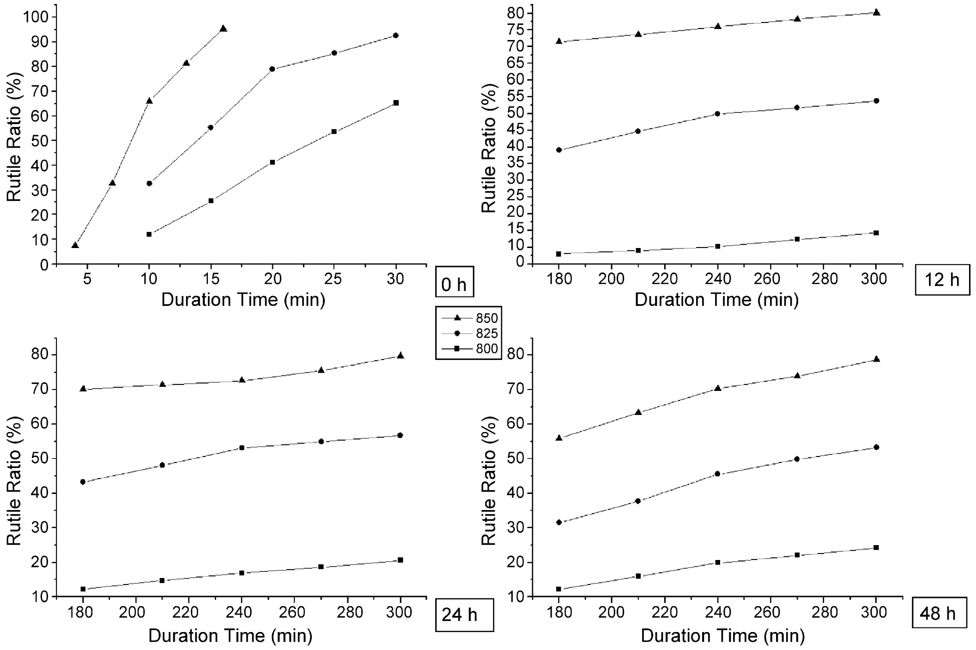

Fig. 5. The variation in rutile ratio with various calcination temperatures and soaking times for samples aged at various times.

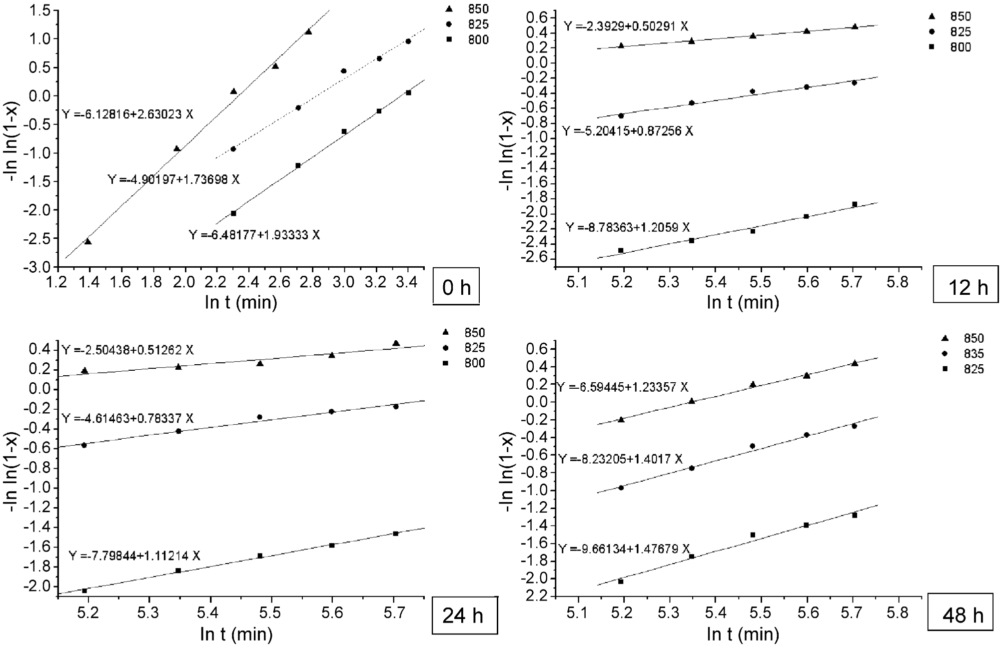

Fig. 6. Plots of ln ln(1 − x) vs. ln t for samples aged at various times.

Table 1

The n values and activation energies of anatase to rutile phase transformation, crystallite growth [17], and nucleation of powders with various aging time

Aging time (h)	0	12	24	48
n	1.7–2.6	0.5–1.2	0.5–1.1	1.2–1.5
Activation energy of phase transformation (kJ/mol)	205	506	426	481
Activation energy of crystallite growth (kJ/mol)	53	250	220	206
Activation energy of nucleation (kJ/mol)	152	256	206	275

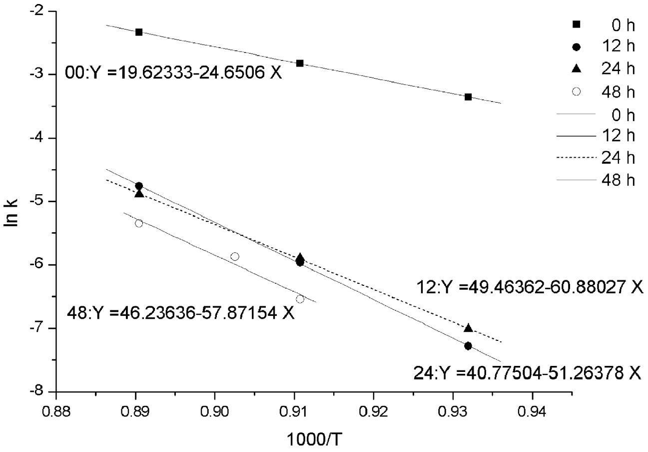

Fig. 7. Arrhenius plot for samples aged at various times.

was lower than for unaged samples. The higher the agglomeration numbers for the powder, the smaller the distance between the nanocrystallites and the greater the chance for the nanocrystallites to make contact with each other. This promotes rutile to nuclei at the interfaces [14]. Therefore, the activation energy of nucleation calculated for unaged samples (mean value: 152 kJ/mol), which is close to the previous observation reported by Zhang and Banfield [14] who analyzed the phase transformation kinetics based on interfacial nucleation (activation energy = 156.6 kJ/mol), was smaller than for aged samples (206–275 kJ/mol).

4. Conclusions

The agglomeration and crystallite sizes for TiO_2 gels decreased with increasing aging treatment. For unaged samples, the agglomeration number was high, inducing a larger number of anatase crystallites and crystallite–crystallite anatase contacts in each cluster, which promotes interfacial nucleation. Therefore, the activation energy of nucleation calculated for unaged samples (mean value: 152 kJ/mol) was smaller than for aged samples (206–275 kJ/mol).

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