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Influences of saturation ratios on crystallization of anatase titanium dioxide by a titanium alkoxide hydrolysis

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Abstract

Influences of supersaturation in a tetraethyl orthotitanate (TEOT) solution on the degree of crystallinity of product particles in the case of a hydrolysis reaction of TEOT were indicated and the crystallization phenomena of anatase titanium dioxide (TiO_2) were discussed. Changes in saturation ratios with experimental durations were examined for the various amount of acetylacetone added into a TEOT solution. At the initial stages of TEOT hydrolysis operations, the degree of crystallinity of product particles was lower for the longer hydrolysis durations but the degrees became almost constant in the later stages of TEOT hydrolysis operations, although the supersaturation of titanium oxide in a TEOT solution was remained. Rapid increase in supersaturation of titanium oxide in a TEOT solution and consequent nucleation of amorphous titanium oxide would be restrained by addition of acetylacetone into a TEOT solution because the concentrations of titanium oxide in a saturated TEOT solution increased with the amount of acetylacetone.
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Keywords: Degree of crystallinity; Saturation ratio; Hydrolysis operations; Anatase TiO_2 crystals; Acetylacetone; Amorphous titanium oxide

1. Introduction

Photocatalysts have been widely used for such applications as building materials, paint, glass, electrical appliances, automobiles and medicine. Photocatalysts are characterized by two properties, strong oxidation [1] and superhydrophilicity [2], and can be used in air and water purification, in anti-bacteria and anti-microbe, in the anti-fogging and the self-cleaning [3].

Anatase titanium dioxide (TiO_2) is one of the most representative photocatalysts. Crystals and thin films of anatase TiO_2 are produced by dry processes such as sputtering and chemical vapor deposition methods and by wet processes such as dip-coating, sol–gel, spray-coating, and spin-coating methods. Wet processing operations are easy and require no particular equipment. However, formation of uniform anatase TiO_2 thin films on specially shaped substrates are complicated because controlling size of the crystalline particles and thickness of thin films of anatase TiO_2 is difficult. Moreover, because annealing operations at several hundred celsius are necessary for conventional wet processing [4–7], a large amount of energy is consumed in forming crystals and thin films of anatase TiO_2 and it is impossible to produce anatase TiO_2 crystals or its thin films on the lower thermostability material substrate surfaces.

Crystallization methods of anatase TiO_2 under comparatively lower temperature conditions from titanium sulfate [8], ammonium hexafluorotitanate [9,10], or titanium fluoride solutions [11] have been reported. Anatase TiO_2 was also formed by soaking titanium plates into hydrogen peroxide (H_2O_2), H_2O_2–tantalum (V) chloride, sodium fluoride or sodium sulfate solution at 80 °C for 8 or 72 h and then the aging of their plates in distilled water or hydrochloric acid for 8 h [12–15]. And anatase TiO_2 precipitates were produced by a reaction between $TiOCl_2$ and NH_4OH solutions and then the treatment using NaOH solution or the aging in boiling water [16,17]. However, the formation of anatase TiO_2 crystals from a titanium sulfate or H_2O_2 solution must be conducted up to 60 °C which is higher than room temperature and requires several days. On the other hand, handling of ammonium hexafluorotitanate or titanium fluoride solutions is dangerous.

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Nomenclature

a	surface area (m^2)
A	constant ($m^{-3}\ s^{-1}$)
b	half bandwidth of characteristic peak for standard specimen (rad)
B	half bandwidth of characteristic peak for product particles (rad)
C	degree of crystallinity of product particle
c_{AA}	concentration of acetylacetone (mol/L)
c_{Ti}	remaining titanium oxide concentration (mol/L)
c^*_{Ti}	saturated titanium oxide concentration (mol/L)
D	size of crystal (m)
g	order of crystal growth process
J	nucleation rate ($m^{-3}\ s^{-1}$)
K	Scherrer's constant (rad)
k	Boltzmann constant
k_r	growth rate coefficient ($m\ s^{-1}$)
m	mass of crystal (kg)
r_{TEOT}	hydrolysis reaction rate of TEOT ($L^7\ mol^{-7}\ s^{-1}$)
S	saturation ratio
S_0	initial saturation ratio
t	duration (s)
T	temperature (K)
v	molecular volume (m^3)
w	solution concentration
w^*	saturated concentration
γ	interfacial tension ($J\ m^{-2}$)
λ	wave length of x-radiation (m)
θ	angle (rad)
ρ	density (kg/m^3)

On the contrary, we proposed the crystallization method of anatase TiO_2 by a hydrolysis operation of titanium alkoxide at room temperature [18]. Since the reaction rate of a titanium alkoxide hydrolysis was controlled by addition of acetylacetone that is a hydrolysis reaction decelerated reagent and anatase TiO_2 crystals were added as seeds, seeded anatase TiO_2 crystals would be grown in a tetraethyl orthotitanate (TEOT) solution. Moreover, crystallization of anatase TiO_2 by a hydrolysis operation of titanium alkoxide is a human-friendly production method.

The purposes of this study are to examine the changes in the degree of crystallinity of product particles, the saturation ratios of titanium oxide in a TEOT solution with the amounts of acetylacetone, the durations of titanium alkoxide hydrolysis operations and to discuss the crystallization phenomena of anatase TiO_2 by a titanium alkoxide hydrolysis.

2. Experimentals

We used tetraethyl orthotitanate ($Ti(OC_2H_5)_4$) as a titanium alkoxide. One hundred millilitres of dehydrate ethanol (EtOH; Wako Pure Chemicals Industries), 1.37 g of TEOT (Tokyo Kasei Kogyo Co. Ltd.) and a specified amount of acetylacetone (Wako Pure Chemicals Industries) were mixed in the PVC vessel. Then, 0.10 g of commercial anatase TiO_2 crystals (AMT-100, Tayca Co.) was added into the solution after which 20.7 ml of EtOH solution in 3.60×10^{-2} mol of distilled water was added quickly. The mixed EtOH solution containing TEOT and water was agitated using a magnetic stirrer at about 20 °C. After a certain duration, the suspended solution was centrifuged and product particles were dried at 38 °C for a few days. The product particles were pounded well by an agate mortar and parts of the product particles were analyzed by a powder X-ray diffraction (XRD; RINT-2000, Rigaku Instruments Co.) Appearance of the product particles was observed by a field emission scanning electron microscopy (FE-SEM; S-4300, Hitachi High Technologies Co.).

The remaining titanium oxide concentration, that means the dissolving titanium oxide concentrations in the TEOT solution during or after the TEOT hydrolysis operations, was measured by a hydrogen peroxide method. Suspended solution was drawn out by a syringe and was filtrated by a membrane filter. One mililiter of its clear solution was added into a 50 ml volumetric flask including 10.0 g of (1 + 2) sulfuric acid (Sigma–Aldrich Co.) and 1.0 ml of 3% hydrogen peroxide (Mitsubishi Gas Chemical Company Inc.) and that mixture was diluted with distilled water. The absorbances of the solution at 410 nm were measured by UV–vis spectrometer (UV-2450, Shimadzu Co.).

The amount of acetylacetone ($0–1.80 \times 10^{-3}$ mol) added into the solution and the experimental durations (1–7 h) were changed in this study.

3. Results and discussion

3.1. Degree of crystallinity of product particles

The remaining concentrations of titanium oxide in a TEOT solution with experimental durations were measured for the various amount of acetylacetone when no seed crystal was added. The concentrations of titanium oxide when the duration of TEOT hydrolysis operations was 50000 s, i.e. the solubility of titanium oxide in an EtOH solution, depended on the amount of acetylacetone added into a TEOT solution, as seen in Table 1. The saturation ratio of titanium oxide in a TEOT solution, S, is defined as the ratio of titanium oxide concentration of the remaining TEOT solution, c_{Ti}, to the solubility of titanium oxide in a EtOH solution, c^*_{Ti}, and is indicated by the following equation [19]:

$$S = \frac{c_{Ti}}{c^*_{Ti}} \tag{1}$$

Influences of the durations of TEOT hydrolysis operations on the saturation ratios of titanium oxide are shown in Fig. 1. The saturation ratios of titanium oxide were rapidly decreased by the increase in the TEOT hydrolysis duration at the initial stages of TEOT hydrolysis operations. And the saturation ratios were higher for the smaller amount of acetylacetone added into a TEOT solution because the solubility of titanium oxide in an EtOH solution was lower.

Fig. 2 shows the powder XRD patterns of seeded anatase TiO_2 crystals (a) and product particles obtained when the

Table 1
Solubilities of titanium oxide for various amount of acetylacetone

Acetylacetone (mol)	Solubility (mol/L)
0.00	1.09×10^{-2}
6.00×10^{-4}	1.41×10^{-2}
1.20×10^{-3}	1.73×10^{-2}
1.80×10^{-3}	2.14×10^{-2}

amount of acetylacetone added into a TEOT solution was 1.80×10^{-3} mol (b) and 6.00×10^{-4} mol (c), respectively. The characteristic peaks of anatase TiO_2 crystals are $2\theta = 25.3°$, 37.8° and 48.1° and the corresponding Miller indices are (1 0 1), (0 0 4) and (2 0 0), respectively [20]. For comparison, the powder XRD pattern of particles obtained when the TEOT hydrolysis operation was carried out without additions of seed crystals and acetylacetone is shown in Fig. 2(d). The peaks of its XRD pattern were very broad. Since it is said that metastable amorphous titanium oxide (Ti_xO_y) is formed by the hydrolysis reactions of titanium alkoxide under the ordinary sol–gel methods, these particles would be amorphous Ti_xO_y. The powder XRD peaks of product particles obtained by TEOT hydrolysis operations (Fig. 2b and c) were smaller than those of seed crystals (Fig. 2a). Moreover, as the amount of acetylacetone added into a TEOT solution was larger, the intensities of the characteristic peaks of anatase TiO_2 crystals were larger. Appearances of seed crystals and product particles observed by a FE-SEM are indicated in Fig. 3. Two types of particles were observed in the product particles obtained by TEOT hydrolysis operations, as shown in Fig. 3(b and c).

It is said that the peaks of a powder XRD of the particles are broader or smaller when the particles are amorphous or the particle size is very small [21]. The product particles were, however, larger than seed crystals as seen in Fig. 3. Therefore, the reason why the peaks of a powder XRD of the product particles were smaller than those of seed crystals would be that the product particles were the mixtures of anatase TiO_2 crystals and amorphous Ti_xO_y.

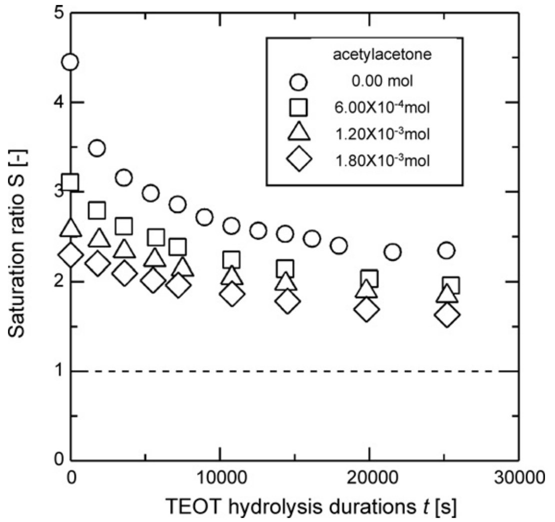

Fig. 1. Changes in saturation ratios of TiO_2 with duration of TEOT hydrolysis for various amount of acetylacetone.

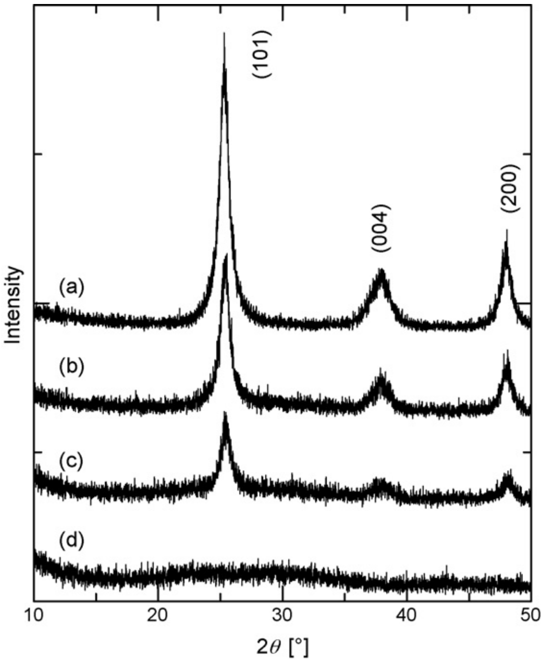

Fig. 2. Powder XRD patterns of seed crystals (a), product particles for case the amount of acetylacetone was 1.80×10^{-3} mol (b) and 6.00×10^{-4} mol (c) and amorphous Ti_xO_y (d).

Since the powder XRD pattern was broader for Fig. 2(c) and a number of larger particles were observed for Fig. 3(c), amorphous Ti_xO_y particles were larger than anatase TiO_2 crystals. Therefore, the growth rates for anatase TiO_2 crystals were lower than those for amorphous Ti_xO_y and the differences in growth rates between anatase TiO_2 crystals and amorphous Ti_xO_y might have depended on the structures of their particles.

Comparing Fig. 2(b) with Fig. 2(c), the half bandwidth of characteristic peak for $2\theta = 25.3°$ in case that the amount of acetylacetone added into a TEOT solution was 1.80×10^{-3} mol was narrower than that for 6.00×10^{-4} mol. Correlation between size of crystals, *D*, and the half bandwidth of characteristic peaks obtained by a powder XRD, *B*, is indicated by the Scherrer's equation [22]:

$$D = \frac{K\lambda}{(B - b)\cos\theta} \tag{2}$$

where *b* and K are a half bandwidth of the characteristic peak for standard specimen and Scherrer's constant, respectively. Since size of crystals is larger for the narrower half bandwidth of characteristic peaks, it is found that anatase TiO_2 crystals grown from seeds were larger for 1.80×10^{-3} mol than those for 6.00×10^{-4} mol. On the contrary, size of the smaller product particles, i.e. anatase TiO_2 crystals, was larger for 1.80×10^{-3} mol than that for 6.00×10^{-4} mol, as seen in Fig. 3. This tendency agreed with the result obtained from Fig. 2.

The crystallinities of product particles were evaluated by the differences of absolute peak intensities of powder XRD patterns. Since the experimental procedures and the analyzing conditions of product particles such as thickness of powder

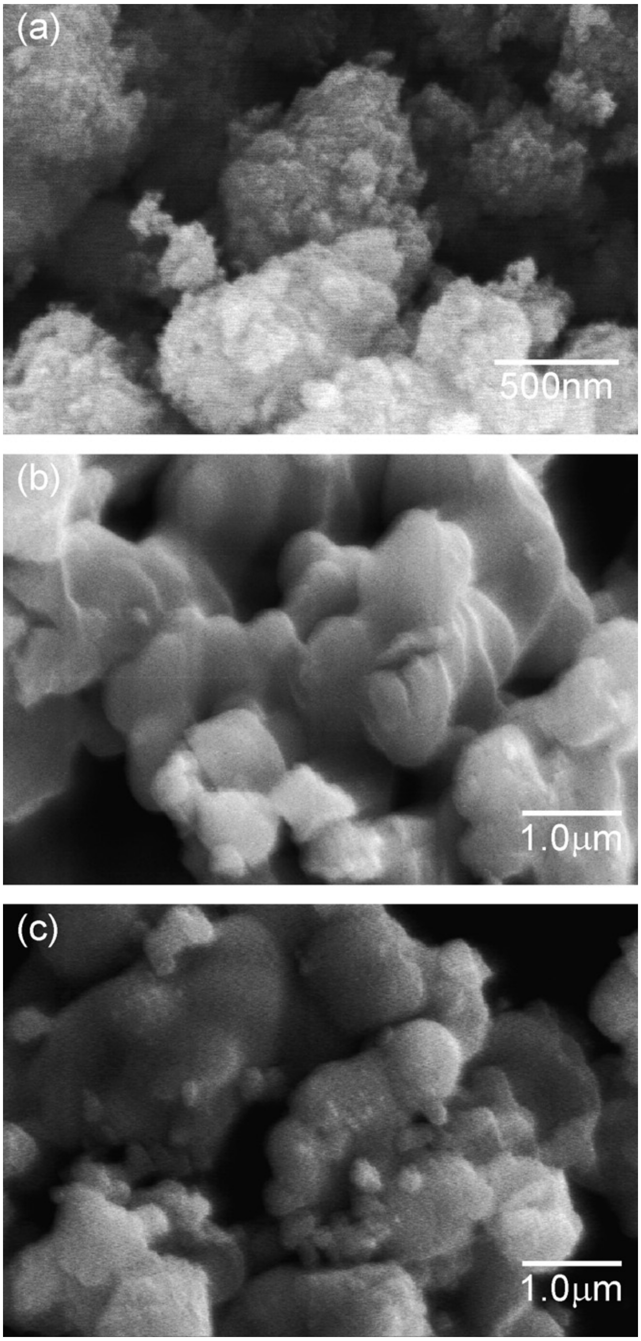

Fig. 3. Appearances of seed crystals (a) and product particles for case the amount of acetylacetone was 1.80×10^{-3} mol (b) and 6.00×10^{-4} mol (c).

films were the same every time in this study, the absolute peak intensities of powder XRD patterns would depend on the characteristics of product particles. The degree of crystallinity of product particles, C, is defined as the following equation:

$$C = \frac{\sum \text{characteristic peak intensities for product particles}}{\sum \text{characteristic peak intensities for seed crystals}}, \qquad (3)$$

where numerators and denominators are the sum of absolute intensities of three characteristic peaks of anatase TiO_2 crystals ($2\theta = 25.3, 37.7, 48.1°$) for product particles and for seed crystals, respectively. The influences of the durations of TEOT hydrolysis operations on the degree of crystallinity of product particles are plotted in Fig. 4, where the degree of crystallinity of product particles, when the duration is 0, is unity (the solid dot) because commercial anatase TiO_2 crystals were seeded into a TEOT solution at the beginning of TEOT hydrolysis operations. The degrees of crystallinity of product particles were lower for the longer durations at the initial stages of TEOT hydrolysis operations but they became almost constant after 2 or 3 h, as shown by the dotted or the broken lines in Fig. 4. And, as the amount of acetylacetone added in a TEOT solution was larger, the degree of crystallinity of product particles was higher.

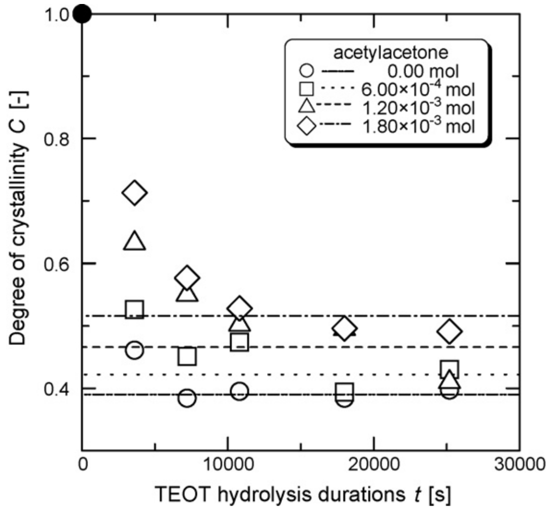

Fig. 4. Degree of crystallinity of product particles.

The degree of crystallinity of product particles was lower for the higher initial saturation ratios, as seen in Fig. 5. Amorphous Ti_xO_y would be nucleated more frequently in a TEOT solution when the initial supersaturations in the solution were higher.

3.2. Formation of amorphous Ti_xO_y and anatase TiO_2 crystals

Fig. 6 shows schematic drawing of changes in the saturation ratios of titanium oxide in a TEOT solution with the durations of TEOT hydrolysis operations. Since the saturation ratio became very high immediately after mixing a TEOT and a H_2O solution, both nucleation of amorphous Ti_xO_y and growth of their amorphous Ti_xO_y and seeded anatase TiO_2 crystals would occur in the mixed solution. On the contrary, since the saturation ratio was lower in the latter stages of TEOT hydrolysis operations, only growth of anatase TiO_2 crystals and amorphous Ti_xO_y suspended would happen in the mixed solution.

In case of no acetylacetone added into a TEOT solution, the degree of crystallinity of product particles became almost constant 2 h after mixing a TEOT and a H_2O solution, and the saturation ratio of titanium oxide was about 2.7, as seen in Figs. 1 and 4. Therefore, when the saturation ratio of titanium

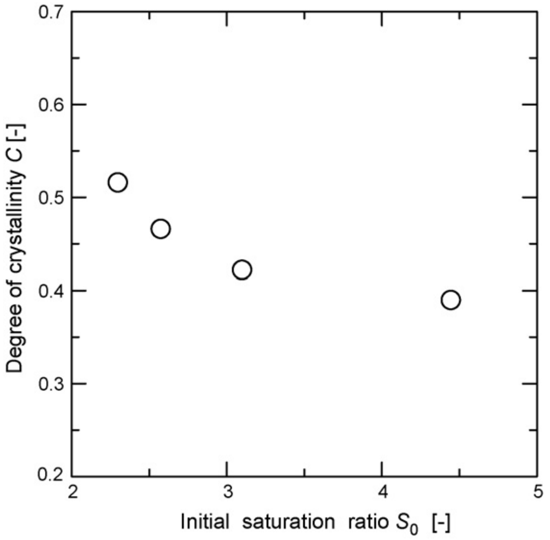

Fig. 5. Relations between degree of crystallinity of product particles and initial saturation ratios.

oxide in a mixed solution was lower than 2.7, primary nucleation of amorphous Ti_xO_y would be restrained in case that no acetylacetone was added into a TEOT solution.

As the amount of acetylacetone added into a TEOT solution was larger, the degree of crystallinity of product particles was higher. When acetylacetone is added into a TEOT solution, a $Ti(OC_2H_5)_3$–acetylacetone complex is formed [23,24] and its complex is dissolved into an EtOH solution more easily than titanium oxide. Since the saturation ratios of titanium oxide in a TEOT solution decreased by addition of acetylacetone into a TEOT solution because the solubility of titanium oxide in a TEOT solution increased, primary nucleation of amorphous Ti_xO_y was restrained, and consequently, the degree of crystallinity of product particles became higher.

In general, the rate of primary nucleation for crystalline particles is indicated by the following equation [19]:

$$J = A\exp\left[-\frac{16\pi\gamma^3 v^2}{3kT^3(\ln S)^2}\right] \tag{4}$$

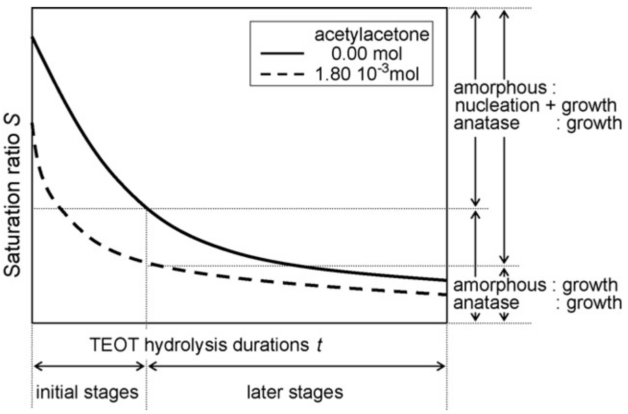

Fig. 6. Schematic drawing of changes in saturation ratios with duration of TEOT hydrolysis.

In order to restrain primary nucleation of amorphous Ti_xO_y and to grow anatase TiO_2 crystals seeded into a TEOT solution, it is necessary to decrease the saturation ratio. The saturation ratios of titanium oxide decrease by decreasing of the solution concentration in addition to increasing of the concentration of saturated solution, as seen in Eq. (1). In this study, since TEOT hydrolysis operations were carried out in the suspended solution, growth of amorphous Ti_xO_y and anatase TiO_2 crystals would be controlled by surface-integrated process. In general, the growth rates of crystalline particles in case of the controlling surface-integrated processes are indicated by the following equation [19]:

$$\frac{dm}{dt} = ak_r\rho(w - w*)^g \tag{5}$$

When the larger amount of seed crystals was added into the solution, the consuming rates of solution concentration by growth of seed crystals suspended in a TEOT solution become faster because the surface areas, *a*, of seed crystals become larger.

Moreover, the hydrolysis reaction equation of TEOT is indicated by the following equation:

$$Ti(OC_2H_5)_4 + 2H_2O \rightarrow TiO_2 + 4C_2H_5OH \tag{6}$$

and the reaction rates of TEOT hydrolysis were indicated by the following equation [18]:

$$-r_{\mathrm{TEOT}} = 9.3\times10^5\,e^{-1.45\times10^4 c_{\mathrm{AA}}}c_{\mathrm{Ti}}^8 \tag{7}$$

Therefore, when the initial concentration of TEOT was lower and the amount of acetylacetone added into a TEOT solution was larger, the formation rates of titanium oxide became slower, and consequently, nucleation of amorphous Ti_xO_y is expected to be restrained.

Since the saturation ratio of titanium oxide became lower by the decrease in the solution concentration or by the increase in the saturated concentration, i.e. solubility, in a TEOT solution, primary nucleation of amorphous Ti_xO_y would be restrained and the degree of crystallinity of product particles is expected to become higher by controlling operating conditions.

4. Conclusions

Influences of saturation ratio of titanium oxide in a TEOT solution on the degree of crystallinity of product particles in the case of a hydrolysis reaction of TEOT were indicated and the crystallization phenomena of anatase TiO_2 by a hydrolysis reaction of TEOT were discussed.

From the powder XRD patterns and appearances of product particles obtained by TEOT hydrolysis operations, the product particles were the mixtures of anatase TiO_2 crystals and amorphous Ti_xO_y. At the initial stages of TEOT hydrolysis operations, the saturation ratio of titanium oxide in a TEOT solution and the degree of crystallinity of product particles were lower for the longer TEOT hydrolysis durations, but the degree became almost constant in the later stages of TEOT hydrolysis operations, although the supersaturation of titanium oxide in a

TEOT solution was remained. Both nucleation of amorphous Ti_xO_y and growth of their amorphous Ti_xO_y and seeded anatase TiO_2 crystals would occur in the mixed solution at the initial stages of TEOT hydrolysis operations, but only growth of anatase TiO_2 crystals and amorphous Ti_xO_y suspended in the mixed solution would happen in the latter stages. When the amount of acetylacetone added into a TEOT solution was larger, the concentration of titanium oxide in a saturated solution, i.e. solubility of titanium oxide in an EtOH solution, and the degree of crystallinity of product particles were higher.

Because the $Ti(OC_2H_5)_3$–acetylacetone complex is formed in the solution, the concentration of titanium oxide in a saturated solution was higher and consequently, nucleation of amorphous Ti_xO_y would be restrained by addition of acetylacetone into a TEOT solution. Controlling of the amount of acetylacetone was expected to crystallize the anatase TiO_2 by a hydrolysis reaction of titanium alkoxide.

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