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Hydrothermal synthesis of titanium dioxides from peroxotitanate solution using different amine group-containing organics and their photocatalytic activity

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Abstract

Nanosized TiO_2 particles were prepared by hydrothermal method of the amorphous powders which were precipitated in an aqueous peroxotitanate solution using different amine group-containing organics. The physical properties of prepared nanosized TiO_2 particles were investigated. We also examined the activity of TiO_2 particles as a photocatalyst for the decomposition of orange II. The TiO_2 particles calcined at 400 °C were shown to have a stable anatase phase which has no organic compounds. The particles size of titania particles decreased from 15 to 10 nm as the carbon chain length increased. The titania nanoparticles were shown to have a polygonal shape prepared using NH_4OH and tetramethylammonium hydroxide (TMAOH) as additives, however, the micrographs showed the spherical and narrow size distribution prepared using tetraethyl-ammonium hydroxide (TEAOH) and tetrabutylammonium hydroxide (TBAOH). The titania particles prepared using TEAOH as an amine group-containing organic showed the highest activity on the photocatalytic decomposition of orange II. In addition, the titania particles calcined at 500 °C showed the highest activity on the photocatalytic decomposition of orange II.

Keywords: Nanosized TiO_2; Hydrothermal synthesis; Peroxotitanate; Amine group-containing organics; Photocatalytic degradation of orange II

1. Introduction

Nanocrystalline powders of titania are widely used as catalysts in photocatalytic reactions, gas sensors, and white pigment materials [1]. Preparation of nanosized TiO_2 is mainly by the sol–gel method, whose main disadvantage is that costly organic solvents are required. Nanosized TiO_2 can be prepared by the direct hydrolysis of titanium salt and chemical vapor deposition procedure in which $TiCl_4$ vapor is oxidized at very high temperatures.

As for anatase TiO_2 nanaocrystalline, much attention has been paid to hydrothermal methods using amorphous TiO_2 [2], $TiCl_4$ [3], or $TiOCl_2$ aqueous solution [4], and sol–gel methods using titanium alkoxides [5–7], TiO_2 can be also obtained by hydrolysis of titanium compounds, such as titanium tetrachloride or titanium alkoxides [3,8], in solution. However, the use of starting materials containing of chlorine ligand usually resulted in the residue of chlorine in the as-prepared powder, which would increase the environmental problem. Therefore, chlorine-free route for preparation of high-purity TiO_2 nanoparticle is preferable for the practical application.

The different synthetic processes usually result in the as-prepared nanosized TiO_2 with distinct physiochemical properties. Organic modifiers, such as hydroxyl group-containing [9,10], carboxylate group-containing [11–13], and amine group-containing organics [14] are widely used in synthesis of nanosized TiO_2 to regulate their final morphology and hence their properties. The basis of such methods is the employment of organics with different types of functional groups to produce a desired product with the required shapes and interface structures of organic modifiers with crystal surface. Amongst the modifiers are amine group-containing organics widely used

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in the synthesis of nanosized TiO_2 particles. An unanswered question is how the nonpolar groups affect the crystal growth of nanosized TiO_2 particles in the synthetic process.

Wastewater produced from textile and other dyestuff industrial processes contain large quantities of organic dyes, which are difficult to degrade with standard biological methods. Within the overall category of dyestuffs, azo dyes constitute a significant portion and probably have the least desirable consequences in terms of surrounding ecosystems. Photocatalysis using TiO_2 semiconductors was irradiated by near UV-light. The complete mineralization of the organic compound with the absence of dangerous residual intermediate compounds and the possibility of working over wide ranges of operational conditions make the photocatalytic method preferable or, at least, competitive with the others.

In this study, we prepared nanosized TiO_2 particles by hydrothermal method from the amorphous powders which were precipitated in an aqueous peroxotitanate solution using different amine group-containing organics. The physical properties of prepared nanosized TiO_2 particles were investigated. We also examined the activity of nanosized TiO_2 particles as a photocatalyst for the decomposition of orange II.

2. Experimental

2.1. Preparation of catalysts

Peroxotitanate solution was prepared from H_2TiO_3 (80%, Mitsuwa) dissolved in the presence of H_2O_2 (30%, Junsei) and different amine group-containing organics (NH_4OH, tetramethylammonium hydroxide (TMAOH, 25 wt%, Aldrich), tetraethyl-ammonium hydroxide (TEAOH, 35 wt%, Aldrich), tetrabutylammonium hydroxide (TBAOH, 45 wt%, Aldrich)) in appropriate quantities. Specifically, 2 g of H_2TiO_3 was added to an ice-cooled solvent containing 20 ml of H_2O_2 and 3 ml of amine group-containing organics. After stirring for 90 min, a homogeneous pale yellow-green solution was obtained, which can be stable for several weeks at temperature of less than 5 °C.

Fresh aqueous peroxotitanate solution was diluted by deionized water to 100 ml and then was transferred to a 250 ml Teflon container held in a stainless-steel vessel. After the vessel was tightly sealed, it was heated at 120–200 °C for 5 h. After hydrothermal treatment, the TiO_2 particles were separated in a centrifuge at 10,000 rpm for 3 min and were then washed in distilled water. The particles were dried at 105 °C for 12 h and then were calcined at 200–900 °C for 3 h.

2.2. Characterization of catalysts

The dried fine powder of synthesized TiO_2 was subjected to thermogravimetric-differential thermal analysis (TG-DTA, Perkin-Elmer) to determine the temperature of possible decomposition and phase changes. The samples were heated at the rate of 10 °C/min from 50 to 800 °C.

The major phase of the obtained particles was analyzed by X-ray diffraction (Rigaku D/MAXIIC) using Cu Kα radiation. The average crystallite sizes of anatase and rutile were determined according to the Scherrer equation [15].

The chemical structure of the prepared particles was examined using the Fourier transform infrared spectrophotometer (FT-IR, Bruker, IFS-88) in the 400–4000 cm^{-1} frequency range KBr with as a reference. The particle size and external morphology of the prepared particles were observed on a transmission electron microscope (TEM, JEOL, JEM-2020) of 200 kV accelerating voltage.

2.3. Activity test

A biannular quartz glass reactor with a lamp immersed in the inner part of the reactor was used for all the photocatalytic experiments. The batch reactor was filled with 450 ml of an aqueous dispersion in which the concentration of titania and of orange II were 1.0 and 100 mg/l, respectively, and magnetically stirred to maintain uniformity both concentration and temperature. A 500 W high-pressure mercury lamp (Kumkang Co.) was used. The circulation of water in the quartz glass tube between the reactor and the lamp allowed the lamp to stay cool and warm the reactor to the desired temperature. Nitrogen was used as a carrier gas and pure oxygen was used as an oxidant. The samples were immediately centrifuged and the quantitative determination of orange II was performed by a UV–vis spectrophotometer (Shimazu UV-240).

3. Results and discussion

Fig. 1 shows the typical DTA and TGA thermodiagrams for the TiO_2 particles prepared using different amine group-containing organics. From the TGA analysis, the weight of particles sharply decreases at lower temperature with an increase of molecular weight of the additives. It is thought that they can be decomposed at lower temperature owing to weak molecular interaction according to the increase of molecular weight.

TiO_2 particles prepared using TEAOH and TBAOH as an amine group-containing organics show one endothermic peak at about 100 and 120 °C, respectively. It is thought that the endothermic peak is due to free adsorbed water. In the case of TMAOH, no endothermic peak is shown at low temperature. This result indicates that there is no adsorption of water on the surface of particles. In fact, it can be verified from the FT-IR result that no peak on stretching of water is shown in 3430 cm^{-1} range (Fig. 2).

TiO_2 particles prepared using TEAOH and TBAOH as an amine group-containing organics show two exothermic peaks after 300, 420, 280, and 450 °C, respectively. The first exothermic peaks at 280 and 300 °C are due to the decomposition of the residual organic compounds. In addition, the second exothermic peak at 420 and 450 °C corresponds to the crystallization of the amorphous phase into the anatase phase. In addition, it can be assumed that the product begins to transform the anatase phase into the rutile phase above 600 °C. It is reported that the transformation of the anatase phase into the rutile phase occurs between 450 and 800 °C and

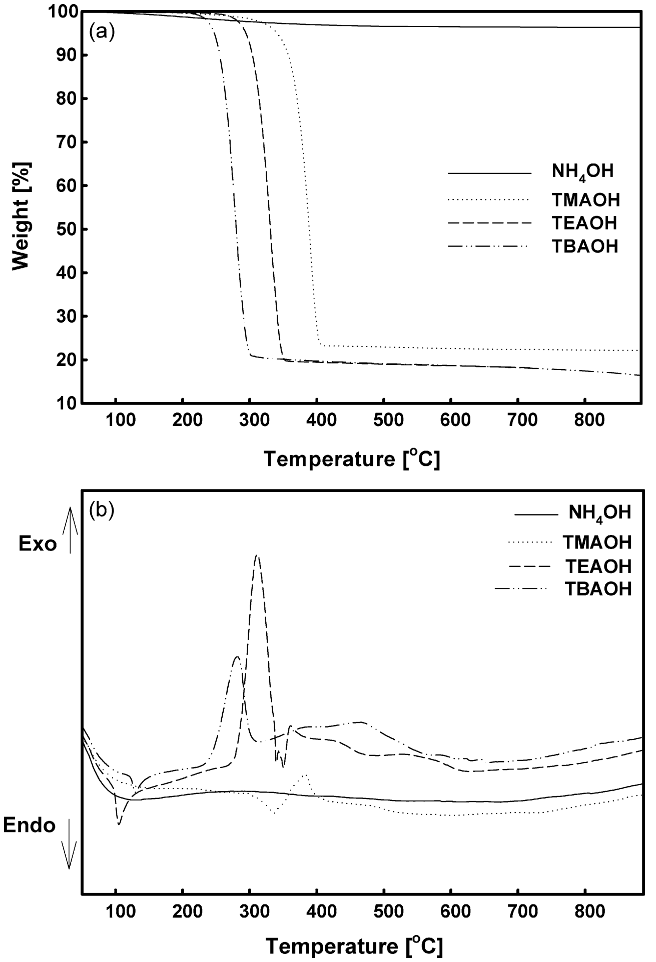

Fig. 1. TGA (a) and DTA (b) curves of nanosized TiO_2 particles prepared using different amine group-containing organics; initial pH of the solution 12, dried at 105 °C.

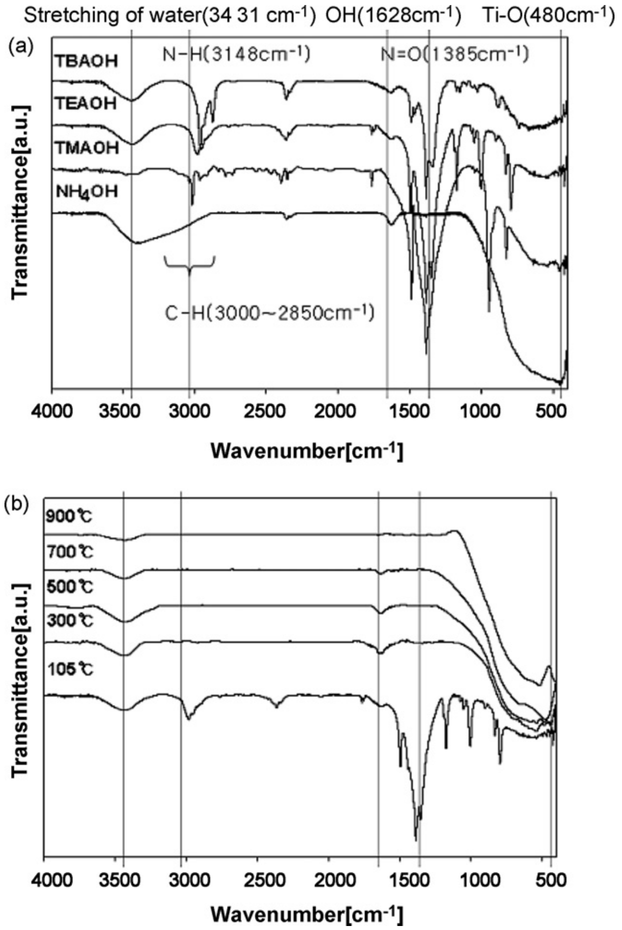

Fig. 2. FT-IR spectra of nanosized TiO_2 powders prepared using different amine group-containing organics (a) and calcined at different temperatures (b); initial pH of the solution 12, dried at 105 °C.

the difference in the transformation temperature depends on the kind of precursors, the preparation conditions of particles, and the property of particles [6].

Fig. 2 shows the IR spectra for the TiO_2 particles prepared using different amine group-containing organics: (a) without any calcination and calcined at different temperatures using TEAOH as an amine in the range of 400–4000 cm^{-1} (b).

The wave number of 480 cm^{-1} in Fig. 2(a) indicates the absorption band for Ti–O bond. The wave number of 1385 cm^{-1} relates to a stretching vibration N=O [16]. In addition, the strong bands from 750 to 1300 cm^{-1} due to residual organic compounds are observed and the C–H bands at 2850–3000 cm^{-1} are also shown. As shown in Fig. 2(b), however, these peaks disappeared on the TiO_2 particles calcined at 400 °C. This result suggests that the TiO_2 particles calcined at 400 °C have a stable anatase phase which has no organic compounds. In addition, the broad absorption peak appearing near 3400 cm^{-1} relates to a stretching vibration of O–H group. At 1620 cm^{-1}, a band assigned to water also appears. The OH band intensities show significant decrease when titania particles are calcined at high temperature.

Fig. 3(a) shows the XRD patterns of the TiO_2 particles prepared using different amine group-containing organics. These particles are only dried at 105 °C without any calcination.

The anatase structure appears at $\theta = 25.3°$ when NH_4OH is used as an amine group-containing organics. However, a lot of complicated peaks are shown instead of anatase structure when other amines are used. These peaks are assumed to have tetraalkyl-ammonium nitrate [17]. When these particles are calcined at 400 °C, however, these peaks disappear and the anatase structure is shown at 25.3° for all TiO_2 particles (Fig. 3(b)). From the IR result (Fig. 2), adsorption bands due to organic compounds of TiO_2 particles prepared without any calcination are shown. Therefore, the titania sol can be successfully crystallized to the anatase phase through calcining above than 400 °C.

The crystallite size of the particles prepared using different amine group-containing organics can be determined by the Scherrer's equation [15] and is listed in Table 1.

The particles size decreases from 15 to 10 nm as the carbon chain length increases. It is thought that TBAOH, with the longest carbon chain, exhibits the weakest basicity because of the strongest association of TBN^+ with OH^-. The probability of OH^- replacing the H_2O ligand with TiO_2 to form anatase nuclei decreased [18], and thus, the growth rate of anatase crystal was slower in comparison with two other amines.

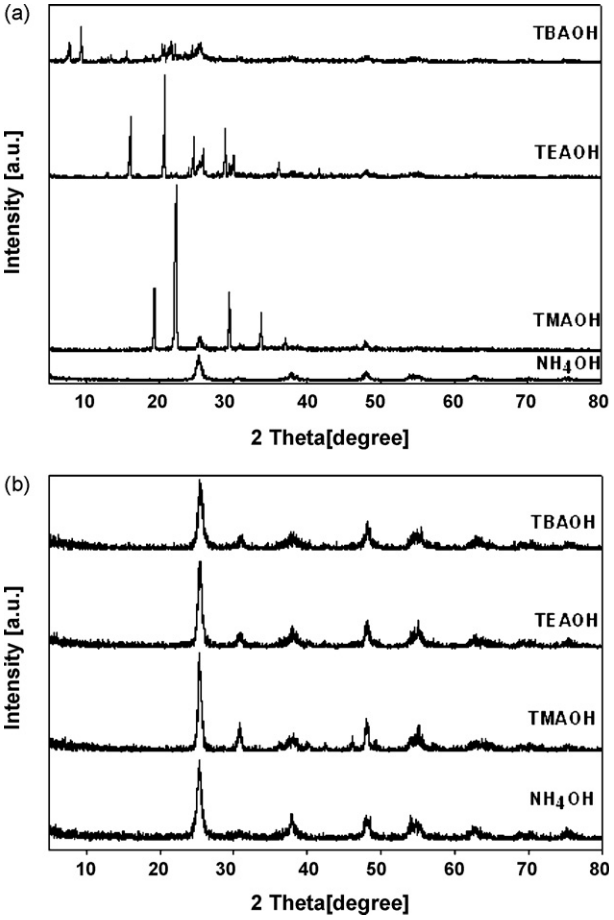

Fig. 3. XRD patterns of nanosized TiO_2 powders prepared using different amine group-containing organics before calcination (a) and calcined at 400 °C (b); initial pH of the solution 12, dried at 105 °C.

Table 1
Physical properties of nanosized TiO_2 powders prepared using different amine group-containing organics and their photocatalytic activity

Type of amine group	XRD		Activity[b], k' ($\min^{-1}$) $\times 10^{-2}$
	Structure	Crystallite size (nm)[a]	
NH_4OH	Anatase	15	2.0
TMAOH	Anatase	15	1.9
TEAOH	Anatase	12	4.5
TBAOH	Anatase	10	3.9

Synthesis temperature = 180 °C, initial pH of the solution 5, calcined at 400 °C.

[a] Obtained by Scherrer equation.

[b] Apparent first-order constants (k') of orange II.

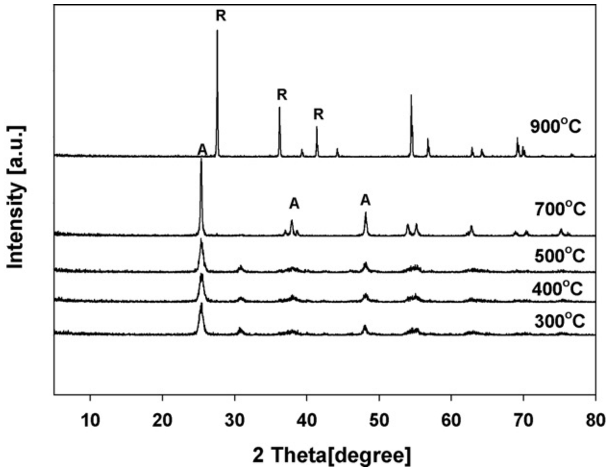

Fig. 4. XRD patterns of nanosized TiO_2 powders calcined at various temperatures; TEAOH is used as amine group-containing organics, dried at 105 °C.

Fig. 4 shows the XRD patterns of the TiO_2 particles prepared using TEAOH calcined at different temperatures. The major phase of all the prepared particles is an anatase structure and a rutile peak was observed above 900 °C.

It is well known that the calcination improves the crystallinity of the particle, and the amorphous TiO_2 changes into the anatase phase and the anatase phase changes into the rutile phase with an increase of calcination temperature. It is reported that the transformation of the anatase phase into the rutile phase occurs above 600 °C and the difference in the transformation temperature depends on the kind of precursors, the preparation conditions of particles, and the property of particles [12]. As shown in Fig. 4, the particles calcined at 600–700 °C were identified as nanocrystalline anatase. It is also confirmed that the titania prepared by hydrothermal method has high thermal stability, which results in the suppression of phase transformation of titania from anatase to rutile. In addition, this high thermal stability made it possible to calcine the TiO_2 particles at higher temperature without forming the rutile phase.

Fig. 5 shows the TEM micrographs of the nanoparticles prepared using amine group-containing organics. The titania nanoparticles are shown to have a polygonal shape when they are prepared using NH_4OH and TMAOH as amine group-containing organics, however, the micrographs of titania particles prepared using TEAOH and TBAOH are shown to have spherical and a narrow size distribution. In addition, TiO_2 particle size decreases with an increase of carbon chain length and this result shows the same tendency with that from XRD analysis. This result indicates that the particle size and shapes can be affected by the preparation conditions, such as, synthesis temperature, the pH value, and the nature of additives [13].

It is well known that photocatalytic oxidation of organic pollutants follows Langmuir–Hinshelwood kinetics [5,19], with the rate being proportional to the coverage θ

$$r = -\frac{\mathrm{d}c}{\mathrm{d}t} = k\theta = k\frac{KC}{1+KC} \tag{1}$$

where k is the true rate constant which is dependent upon various parameters such as mass of catalyst, the flux of efficient, the coverage in oxygen, etc., K the adsorption coefficient of the reactant, and C is the reactant concentration. When C is very small, the product KC is negligible with respect to unity so that Eq. (1) describes a first-order kinetics. Setting Eq. (1) at the initial conditions of the photocatalytic procedure, $t = 0$, the concentration transforms to $C = C_0$, which gives Eq. (2).

$$-\ln\left(\frac{C}{C_0}\right) = k_{\mathrm{app}}t \tag{2}$$

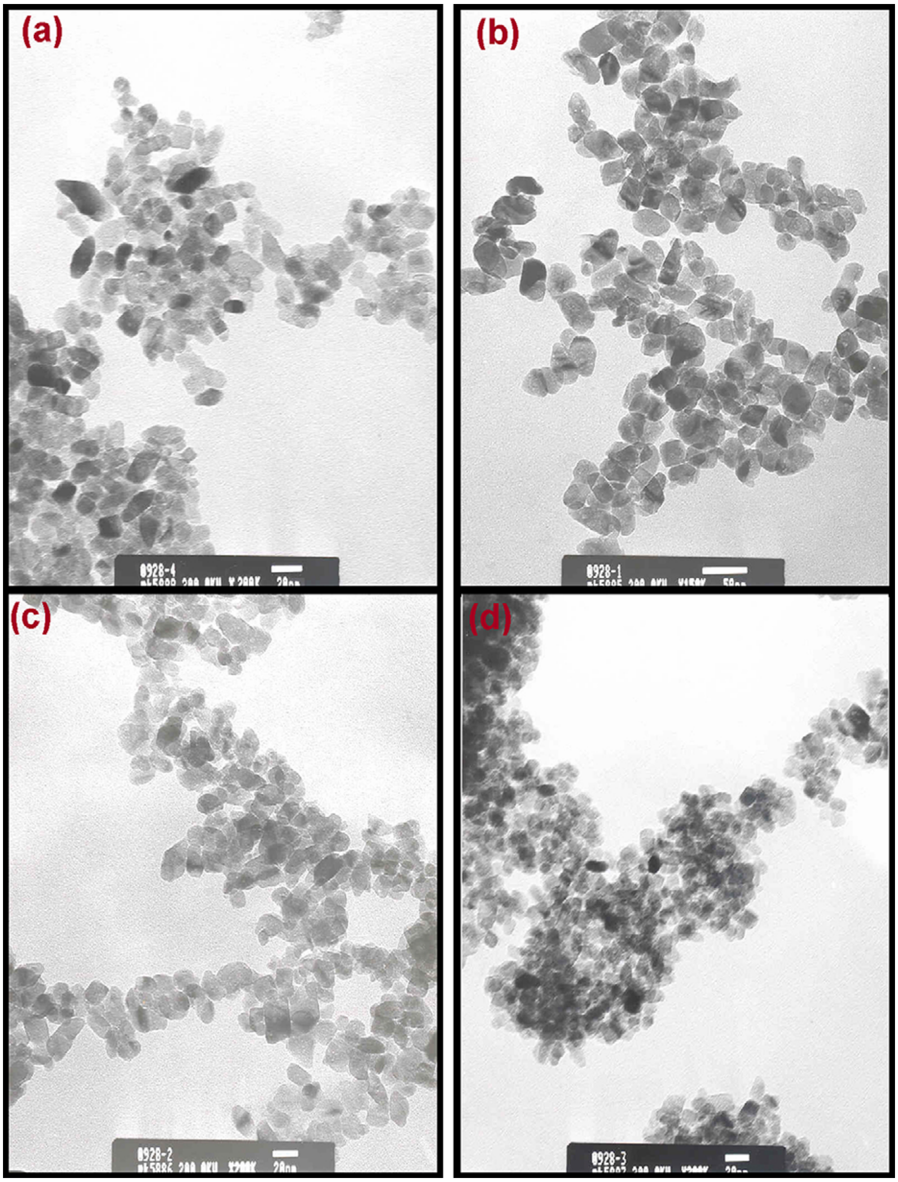

Fig. 5. TEM micrographs of nanosized TiO_2 particles prepared using different amine group-containing organics; dried at 105 °C and calcined at 400 °C; (a) NH_4OH, (b) TMAOH, (c) TEAOH, and (d) TBAOH.

where k_{app} is the apparent first-order reaction constant.

When blank test in the absence of TiO_2 photocatalyst was carried out, orange II was decomposed to about 10% after 3 h reaction by photolysis reaction. However, the presence of TiO_2 prepared at 180 °C and calcined at 500 °C decomposed completely orange II within 2 h.

The photocatalytic activity of titania particle prepared different amine group-containing organics was examined and the result is shown in Table 1. The titania particles prepared using TEAOH as an additive show the highest activity on the photocatalytic decomposition of orange II. In the case of TBAOH, however, the photocatalytic activity shows lower value than TEAOH owing to the aggregation of the particles even though the particle has the smallest size. This result suggests that the photocatalytic activity of the decomposition of orange II depends on the particle size. That is, the activity increases with a decrease of particle size. It is consistent with the result that the photocatalytic reaction has a small particle-size effect, wherein the photocatalytic activity increases with a decrease of particle size [6]. It can also be confirmed that a small particle has a large illuminated surface area by the reason that the particles have a constant density at the same structure.

Table 2 shows the photocatalytic activity of the titania particles calcined at different temperatures.

The titania particles calcined at 500 °C show the highest activity on the photocatalytic decomposition of orange II and the photocatalytic activity decreases according to an increase of calcination temperature. It is also consistent with the result that the photocatalytic reaction has a small particle-size effect, wherein the photocatalytic activity increases with a

Table 2
Physical properties of nanosized TiO_2 powders calcined at different temperature and their photocatalytic activity

Calcination temperature (°C)	XRD		Activity[b] k' (min^{-1}) × 10^{-2}
	Structure	Crystallite size(nm)[a]	
105	Amorphous	–	–
300	Anatase	12	3.1
400	Anatase	12	4.5
500	Anatase	14	5.0
700	Anatase	35	2.6
900	Rutile	69	0.8

Synthesis temperature = 180 °C, TEAOH was used as amine group-containing organics.

[a] Obtained by Scherrer equation.

[b] Apparent first-order constants (k') of orange II.

decrease of particle size. It is thought, on the contrary, the titania particles have low crystallinity and relatively unstable structure at the low calcination temperature below 400 °C. Titanium dioxide can take on any of the following three crystal structures: rutile, anatase, or brookite. Anatase-type titanium dioxide generally exhibits a higher photocatalytic activity than the other types of titanium dioxide as regards the decomposition of organic pollutants by suppressing the electron–hole recombination [5]. In the case of titania particle calcined at 900 °C, the rutile phase is shown and then it shows low photocatalytic activity.

4. Conclusions

We have prepared nanosized TiO_2 particles by hydrothermal method of the amorphous powders which were precipitated in an aqueous peroxotitanate solution using different amine group-containing organics. The physical properties of prepared nanosized TiO_2 particles were investigated. We also examined the activity of TiO_2 particles as a photocatalyst for the decomposition of orange II. The TiO_2 particles calcined at 400 °C were shown to have a stable anatase phase which has no organic compounds. The particles size of titania particles decreased from 15 to 10 nm as the carbon chain length increased. The titania nanoparticles had a polygonal shape prepared using NH_4OH and TMAOH as additives, however, the micrographs showed that spherical and a narrow size distribution prepared using TEAOH and TBAOH. The titania particles prepared using TEAOH as an additive showed the highest activity on the photocatalytic decomposition of orange II.

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