Novel synthesis of microcrystalline titanium(IV) oxide having high thermal stability and ultra-high photocatalytic activity: thermal decomposition of titanium(IV) alkoxide in organic solvents

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Thermal decomposition of titanium(IV) tetra-tert-butoxide (TTB) in inert organic solvents at 573 K yielded microcrystalline anatase (titanium(IV) oxide, TiO_2) powders with a crystallite size of ca. 9 nm and a surface area of $> 100\ m^2\ g^{-1}$. Primary and secondary alkoxides of titanium(IV), however, were not decomposed under similar conditions, indicating that the thermal stability of C–O bonds in the alkoxides was a decisive factor for their decomposition. The TiO_2 prepared from TTB by this manner was thermally stable upon calcination in air and retained high surface area of ca. $100\ m^2\ g^{-1}$ even after calcination at 823 K. The as-prepared TiO_2 powders, without calcination, exhibited much higher rate of carbon dioxide formation than any other active photocatalysts such as Degussa P-25 and Ishihara ST-01 in the photocatalytic mineralization of acetic acid in aerated aqueous solutions. The higher activity of the present TiO_2 photocatalysts is attributed to both high crystallinity and large surface of the present product. The calcination of the as-prepared TiO_2 in air reduced the photocatalytic activity, but it was still higher than the other commercially available TiO_2's.

Keywords: titanium oxide, titanium alkoxide, thermal stability, organic solvent, photocatalyst, acetic acid, photodecomposition

1. Introduction

Titanium(IV) oxide (TiO_2) has been known to be an excellent catalyst support in industrial processes [1–3]; e.g., as a support in commercial vanadium(V) oxide catalyst for selective catalytic reduction of nitrogen oxides with ammonia. Generally, high surface area, as well as excellent thermal stability, is required for catalyst supports to disperse a catalyst material effectively and to increase the number of active sites of the catalyst. Another important characteristic of TiO_2 is its ability as a photocatalyst, which is originated from its semiconducting nature [4,5]. Some of the present authors (BO and SN) have shown that the overall rate of the photocatalytic reaction is expressed as a function of rates of recombination and capture of photoexcited electron (e^-) and positive hole (h^+) by substrates adsorbed on the surface [6]. On the basis of this finding, it has been suggested that TiO_2 having both high surface area and high crystallinity, leading to respectively enhancement of the capture and suppression of the recombination, should show high photocatalytic activity [6].

For preparation of catalysts, catalyst supports, and photocatalysts, metal alkoxides are widely used as the starting material to avoid contamination of the inorganic counter anion from the corresponding metal salts [7] which affects the activity and selectivity of the catalyst [8]. In most of the synthetic processes, the alkoxides are hydrolyzed in an alcoholic solution yielding amorphous (or hydrated) metal oxide with large surface areas; however, their surface areas are drastically decreased on calcination at the temperatures where corresponding oxides begin to crystallize [7]. This predicts that the conventional synthetic processes including the calcination of amorphous TiO_2 seldom satisfy the requisites for higher photocatalytic activity, large surface area and high crystallinity.

Recently, we have found that thermal decomposition of aluminum(III) and zirconium(IV) alkoxides in inert organic solvents, such as toluene, at 573 K yielded microcrystalline (average diameters of ca. 10 nm) χ-alumina [9] and tetragonal zirconia [10], respectively, and that they possessed large surface areas and exhibited excellent thermal stability. The latter fact suggests that these products had high crystallinity. Therefore, it was

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anticipated that if TiO_2 is prepared by this method, the two requisites for high photocatalytic activity will be satisfied. The present authors applied this novel method to the synthesis of TiO_2 and found that the product had extremely high photocatalytic activities as expected.

2. Experimental

Titanium(IV) tetra-tert-butoxide (TTB) (Merck), 4 g, was dissolved in a 70 cm^3 portion of an organic solvent in a test tube which was then set in a 200 cm^3 autoclave. An additional 30 cm^3 of the solvent was placed in the gap between the test tube and the autoclave wall. The autoclave was thoroughly purged with nitrogen, heated to the desired temperature (453–573 K) at a rate of 2.7 deg min^{-1}, and kept at that temperature for 2 h. Autogenous pressure gradually increased as the temperature was raised and usually reached ca. 6 MPa at 573 K. After the autoclave treatment, the resulting powders were washed repeatedly with acetone and dried in air. In the present paper, the TiO_2 samples prepared by this method will be called TD-TiO_2 (thermal decomposition). A part of the TD-TiO_2 powders was calcined in a box furnace for 1 h in air.

Powder X-ray diffraction (XRD) (RINT 2500, Rigaku, Tokyo, Japan) was measured using Cu Kα radiation and a carbon monochromator. The crystallite size of TiO_2 was calculated from the half-height width of the 101 diffraction peak of anatase using the Sherrer equation; the value of the shape factor, K, was arbitrarily taken to be 0.9. The specific surface area was calculated using the BET single-point method on the basis of the nitrogen uptake measured at 77 K using a gas chromatograph. Morphologies of the particles were observed with a transmission electron microscope (TEM) (JEM-3010, Jeol, Tokyo, Japan) operated at 300 kV.

The photocatalytic activity of TiO_2 for mineralization of acetic acid in aerated aqueous suspension was examined [11–13]. Prior to the photocatalytic reaction, pre-treatment was carried out to decompose contaminated organic moieties on the TiO_2 surface; TiO_2 (50 mg) was suspended in 5 cm^3 of water and photoirradiated at a wavelength of > 300 nm by a high-pressure mercury arc (100 W) under oxygen with magnetic stirring until carbon dioxide (CO_2) was not liberated any more. After the pre-treatment, air was bubbled into the suspension for 15 min, and then acetic acid (19 or 175 μmol) was injected through a rubber septum. The resulting aerated aqueous suspension was irradiated again at room temperature. The amount of CO_2 in the gas phase was measured at every 1 h with a Shimadzu GC-8A gas chromatograph with a Porapak QS column. Photocatalytic dehydrogenation of 2-propanol (500 μmol) in aqueous solution (5 cm^3) was also examined as another model system under deaerated conditions; the TiO_2 powders were calcined at 823 K, platinized (0.5 wt%) followed by hydrogen (H_2) reduction at 773 K, and then used for the photocatalytic reaction where a 400 W mercury arc was used. The details of platinization, photoirradiation, and product analyses were reported elsewhere [14,15].

3. Results and discussion

An XRD pattern of TD-TiO_2 prepared in p-xylene at 573 K is depicted in figure 1 (a), which shows that anatase was formed without contamination of any other phases such as rutile or brookite. Addition of water to the supernatant after the autoclaving gave no precipitates, indicating that TTB was completely decomposed. The crystallite size of the as-prepared sample was calculated to be 8.8 nm from the line-broadening of the diffraction peak. TEM observation of the sample revealed that the average particle size was 13 nm (figure 2). This value was larger than the XRD crystallite size but is in good agreement with the particle size (14 nm) calculated from the surface area (111 $m^2\ g^{-1}$) by assuming the density of anatase to be 3.84 g cm^{-3} [16]. Anyway, it should be noted that TD-TiO_2 consists of quite small TiO_2 microcrystals. Kondo et al. [17] examined hydrothermal crystallization of alkoxide-derived amorphous TiO_2 and reported that the thus-formed anatase had a relatively large crystallite size (25 nm by the treatment at 523 K). The smaller crystallite size of TD-TiO_2 can be interpreted by the inhibition of crystal growth due to the smaller solubility of TiO_2 microcrystals in the organic solvent under the present autoclaving conditions than in water during the hydrothermal treatment.

Several physical properties of the TD-TiO_2 synthesized under the various conditions are summarized in table 1. TTB was decomposed in toluene even at 473 K to give anatase having a quite large surface area. Since the BET surface area of a sample synthesized at 523 K (339 $m^2\ g^{-1}$) was larger than that (295 $m^2\ g^{-1}$) calculated from its crystallite size, it is strongly suggested that the products synthesized at lower temperatures were contaminated with the amorphous-like hydrated phase. This may be attributed to insufficient thermal energy for dehydration and crystallization of TiO_2. Upon raising the synthesis temperature to 573 K, the crystallite size was increased and the amorphous fraction, as indicated by a difference in surface area by XRD and BET methods, seemed to become negligible. These facts show that temperature at > 573 K is necessary for the synthesis of crystalline TiO_2 via the TD method.

The effect of the structure of the alkyl group in the starting alkoxide was also examined. Primary and secondary alkoxides of titanium(IV) were not decomposed even at 573 K giving no appreciable amounts of solid products. This suggests that the process requires direct cleavage of the C–O bonds in alkoxides, and therefore the thermal stability of the C–O bond may be a decisive

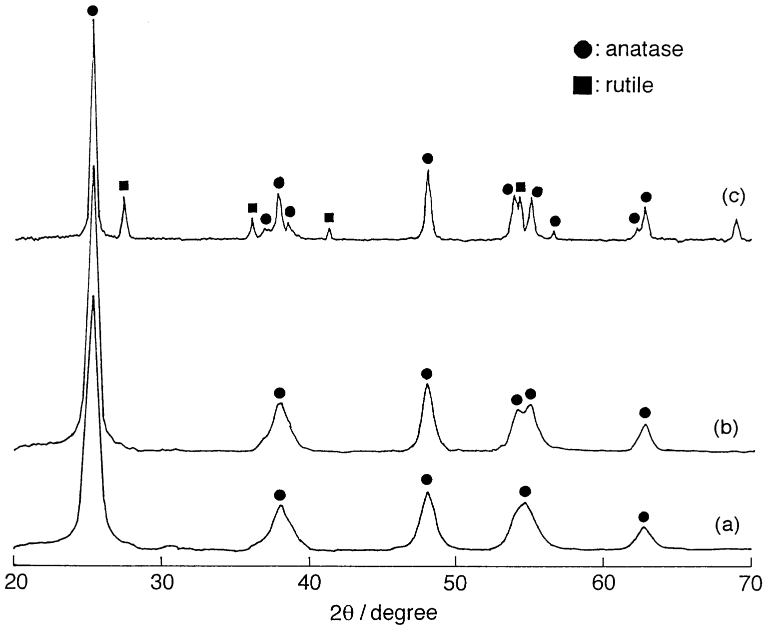

Figure 1. XRD patterns of: (a) a TiO_2 product prepared by the thermal decomposition of titanium tetra-tert-butoxide in *p*-xylene at 573 K for 2 h; (b) and (c), the samples obtained by calcination of the TiO_2 product at 823 and 973 K, respectively.

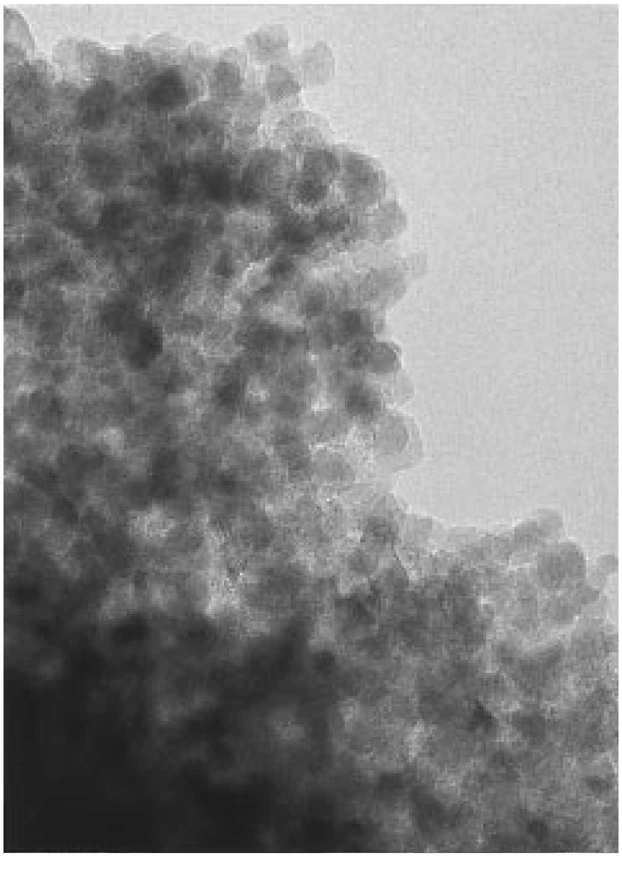

Figure 2. TEM photograph of the TD-TiO_2 whose XRD pattern is shown in figure 1 (a).

factor for the formation of TiO_2 lattice. A similar effect of the alkyl group in alkoxides has been observed for thermal decomposition of aluminum and zirconium alkoxides in inert organic solvents [11,12]. However, because of the difference in strength of the C–O bonds with metals, sec-alkoxides of these elements were decomposed and yielded the corresponding oxides, whereas *n*-alkoxides were not decomposed [11,12].

As shown in table 1, the crystallite size of TD-TiO_2 depended markedly on the kind of organic solvents. Komiyama et al. [18] synthesized TiO_2 powder by chemical vapor deposition (CVD) of titanium alkoxide and found that porous amorphous TiO_2 was formed at temperatures < 593 K. Although the thermal decomposition of titanium alkoxide similar to the present method took place in the CVD process, the presence of organic solvent in the autoclave might facilitate the crystallization of anatase.

As shown in figure 1 (b), an XRD pattern of TiO_2 calcined at 823 K was almost identical to that before calcination except for the fact that the peaks were slightly sharpened. As expected from this pattern, the TD-TiO_2 calcined at that temperature still possessed small crystallite size (10–16 nm) and large specific surface area (ca. 100 m^2 g^{-1}) (table 1). Even after calcination at 973 K, the TD-TiO_2 (prepared in *p*-xylene at 573 K) was predominantly composed of the anatase phase and maintained its large surface area (43 m^2 g^{-1}) though partial transformation into rutile took place (figure 1 (c)). As shown in table 1, the products with relatively large crystallite size (> 8 nm) before calcination showed negligible crystal growth and slight decrease in surface area by calcination at 823 K. This is presumably because the as-prepared

Table 1
Some physical properties of TiO_2 powders prepared under various conditions and their photocatalytic activities for mineralization of acetic acid in aqueous solutions

Titanium alkoxide	Organic solvent	Reaction temp. (K)	Product				After calcination at 823 K		
			phase	d_{101} [a] (nm)	S_{BET} [b] ($m^2\ g^{-1}$)	CO_2 [c] ($\mu mol\ h^{-1}$)	d_{101} [a] (nm)	S_{BET} [b] ($m^2\ g^{-1}$)	CO_2 [c] ($\mu mol\ h^{-1}$)
tert-butoxide	toluene	573	anatase	9.0	117	22.3	10	100	13.8
tert-butoxide	toluene	523	anatase	5.3	339	6.0	12	108	13.4
tert-butoxide	toluene	473	anatase	< 5	420	4.6	12	85	12.3
tert-butoxide	toluene	453	no reaction						
tert-butoxide	benzene	573	anatase	7.0	172	10.0	12	95	ND
tert-butoxide	*p*-xylene	573	anatase	8.8	111	17.5	11	97(43) [d]	ND
tert-butoxide	cyclohexane	573	anatase	(8.1) [e]	ND	7.5	16	73	ND
n-butoxide	toluene	573	no reaction						
isopropoxide	toluene	573	no reaction						
(P-25) [f]			anatase, rutile	24	50 [g]	8.5	ND	ND	ND
(ST-01) [f]			anatase	7 [g]	320 [g]	11.6	ND	ND	8.3
n-butoxide	(ethanol) [h]	r.t.	amorphous	–	452	< 1	18	29	2.6

[a] Crystallite size calculated from the 101 diffraction peak of the anatase phase.

[b] BET surface area.

[c] Rate of photocatalytic CO_2 production from acetic acid (175 μmol) solution evaluated from the slope for initial 6 h.

[d] After calcination at 973 K.

[e] This value included a large error due to the less intense XRD peak.

[f] P-25; Degussa P-25, ST-01; Ishihara ST-01.

[g] Data reported by the suppliers.

[h] Alkoxide was hydrolyzed in ethanolic solution under atmospheric pressure.

TiO_2 is well-crystallized having smaller tendency toward sintering and contains lesser amount of amorphous-like phase to be crystallized into anatase upon calcination. To confirm this, an amorphous TiO_2 sample, which can be regarded as particles with the smallest crystallite size, was prepared by hydrolysis of titanium *n*-butoxide in an alcoholic solution (table 1). The thus-obtained sample possessed quite a large surface area larger than 450 $m^2\ g^{-1}$ but its surface area drastically decreased when calcined at 823 K. Similarly, Komiyama et al. [18] reported that the large surface area (300 $m^2\ g^{-1}$) of amorphous TiO_2 prepared by the CVD method decreased to 11 $m^2\ g^{-1}$ on calcination at 723 K as a result of crystallization into the anatase phase.

In the previous papers, we reported that microcrystalline TiO_2 synthesized by the similar but distinguished method, hydrothermal crystallization in organic media (HyCOM) [19], had remarkably high photocatalytic activities for dehydrogenation of 2-propanol [15], silver metal deposition [15], and N-cyclization of (S)-lysine [20]. In addition to these reactions under deaerated conditions, mineralization of acetic acid in aerated aqueous solutions was also investigated and the HyCOM-TiO_2 exhibited much higher rate for photocatalytic CO_2 formation from acetic acid [13]. This reaction was found to be less sensitive to the conditions, e.g., concentration of acetic acid, and stoichiometric decomposition proceeded by TiO_2 photocatalysts.

Time dependencies of CO_2 yield from acetic acid (19 or 175 μmol in 5.0 cm^3) in an aqueous suspension of TD-TiO_2, synthesized in toluene at 573 K without further thermal treatment in air, are shown in figures 3 and 4, respectively. From the dilute solution of acetic acid, a stoichiometric amount (38 μmol) of CO_2 was formed by ca. 2 h photoirradiation, indicating that the acetic acid was completely decomposed according to the following equation ($CH_3COOH + 2O_2 \rightleftharpoons 2CO_2 + 2H_2O$). At the initial stage of the reactions, the molar amounts of CO_2 increased linearly in both solutions with photoirradiation time and, irrespective of the concentration of acetic acid, almost the same rates (21.9 and 22.3 $\mu mol\ h^{-1}$ for

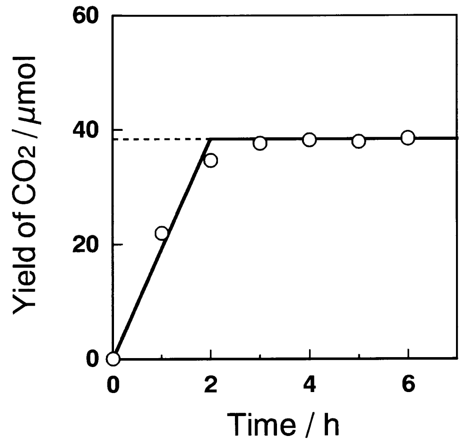

Figure 3. Time course of CO_2 yield from an acetic acid (19 μmol) solution by suspended TD-TiO_2. The catalyst was prepared by the thermal decomposition of titanium tetra-tert-butoxide in toluene at 573 K for 2 h. The CO_2 yield corresponding to the complete decomposition of acetic acid is shown by a dashed line.

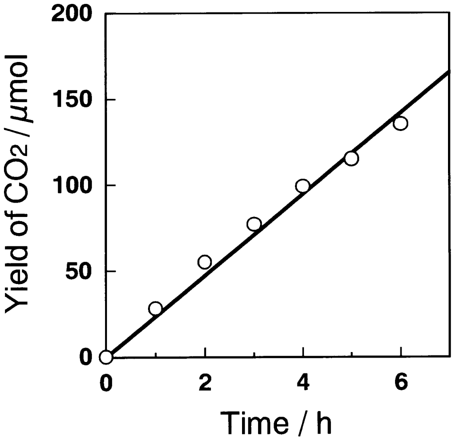

Figure 4. Time course of CO$_2$ yield from an acetic acid (175 μmol) solution by suspended TD-TiO$_2$, the same as that for figure 3.

19 and 175 μmol, respectively) were obtained, indicating a zero-order kinetics on the acetic acid concentration [13].

The rates for photocatalytic CO$_2$ formation from the acetic acid (175 μmol) solution by various uncalcined TD-TiO$_2$ samples are also shown in table 1. For comparison, results for the amorphous and some commercial TiO$_2$ samples known to have high photocatalytic activities are also shown. As clearly seen from table 1, the TD-TiO$_2$ samples with larger crystallite sizes, which were prepared in toluene and *p*-xylene at 573 K, exhibited much higher production rate of CO$_2$ than the commercial TiO$_2$ samples. Since these TD-TiO$_2$ samples satisfied the basic requirements for active TiO$_2$ photocatalyst, i.e., both large surface area and sufficient crystallinity [6], the present results can be reasonably accepted. The negligible activity of the amorphous TiO$_2$ powders, maybe due to defective part (like a crystal defects for crystalline materials) leading to the e^-–h^+ recombination, was also consistent with the hypothesis.

Photocatalytic activity of TD-TiO$_2$ strongly depended on the synthesis conditions, especially synthesis temperature. Poorly-crystallized TD-TiO$_2$ samples, e.g., those synthesized at lower temperatures, showed relatively lower activity although they have quite large surface area. As mentioned above, these samples possibly contained the amorphous-like phase with many crystal defects which act as sites for e^-–h^+ recombination.

The effect of heat-treatment (calcination) on the photocatalytic activity for TD-TiO$_2$ samples synthesized in toluene at various temperatures is also shown in table 1. The TD-TiO$_2$ sample synthesized at 573 K drastically lost its activity on calcination at 823 K. Similar behavior was also observed for microcrystalline TiO$_2$ prepared by the HyCOM method [13]. It should be noted that the activity of the calcined sample, although it was lower than that of the uncalcined sample, was larger than that of the commercial TiO$_2$ samples. In contrast to the well-crystallized TiO$_2$ samples, activities of the TiO$_2$ samples synthesized at lower temperatures were greatly improved on calcination. Such behavior has been commonly observed for amorphous TiO$_2$ powders [21] and is attributed to the decrease in number of recombination sites. However, as clearly seen in table 1, the annealed TD-TiO$_2$ had much higher activities than the sample obtained by calcination of amorphous TiO$_2$. Sufficient surface areas more than 80 m^2 g^{-1} of the former samples and, on the other hand, small surface area less than 30 m^2 g^{-1} of the latter sample could reasonably account for the higher photocatalytic activities of the TD-TiO$_2$.

Photocatalytic activity of platinized TD-TiO$_2$ under deaerated conditions (dehydrogenation of 2-propanol: $CH_3CH(OH)CH_3 \rightleftharpoons H_2 + CH_3COCH_3$) were also examined. Two TD-TiO$_2$ samples synthesized in toluene and *p*-xylene at 573 K showed H$_2$ production rates of 239 and 259 μmol h^{-1}, respectively, with almost equal rates of acetone formation, which were much larger than that for P-25 (125 μmol h^{-1}). It is obvious that, in addition to the aerated condition, TD-TiO$_2$ has a potential for photocatalytic reaction under the deaerated condition. The details on this reaction will be reported elsewhere.

In conclusion, microcrystalline TiO$_2$ could be synthesized by a novel method, thermal decomposition of titanium alkoxides in inert organic solvents, and the thus-obtained TiO$_2$ exhibited high thermal stability on calcination and superior potential for photocatalytic reactions under both aerated and deaerated conditions.

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