Photocatalytic Mineralization of Acetic Acid in Aerated Aqueous Suspension of Ultra-highly Active Titanium(IV) Oxide Prepared by Hydrothermal Crystallization in Toluene

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(Received September 2, 1996)

Anatase titanium(IV) oxide synthesized by high-temperature hydrolysis of titanium(IV) tetrabutoxide in toluene was used for photocatalytic mineralization of acetic acid in aerated aqueous solutions, and showed the rate of carbon dioxide production much higher than representative active photocatalysts (Degussa P-25 and Ishihara ST-01). The catalyst of the larger crystallite size showed the higher activity, suggesting the importance of reduction of crystal defects.

In the previous paper, we have shown that microcrystalline anatase TiO_2 of both high surface area and sufficient crystallinity could be synthesized by high-temperature hydrolysis of titanium alkoxides with a limited amount of water dissolved in organic solvents and concomitant crystallization (HyCOM; Hydrothermal Crystallization in Organic Media).[1] The HyCOM TiO_2's have exhibited remarkably higher activities for photocatalytic reaction under deaerated conditions such as dehydrogenation of 2-propanol,[2] silver metal deposition,[2] and N-cyclization of (S)-lysine.[3] However, the applicability toward the mineralization, i.e., oxidation of organic compounds under aerated conditions has not yet been examined. This paper shows the superior photocatalytic activity of HyCOM TiO_2's toward complete mineralization of acetic acid in an aqueous solution[4] and the effects of the preparation conditions and physical properties on the photocatalytic activity.

The HyCOM TiO_2 was synthesized in the reported manner[1] with a little modification of the amount of titanium(IV) tetrabutoxide (25 g) and water (25 cm^3) in feed. 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 wavelength at > 300 nm by a high-pressure mercury lamp (100 W) under oxygen with magnetic stirring until carbon dioxide (CO_2) did not evolve any more (e.g., total amount of CO_2 was ca. 8 μmol for E in Table 1). After the pre-treatment, air was bubbled into the suspension for 15 min, and then acetic acid (19 or 175 μmol) was injected. The resulting aerated aqueous suspension with acetic acid was irradiated again at room temperature. Amount of CO_2 in the gas phase was measured by GC.

All the catalysts examined in this paper showed appreciable activity for photocatalytic CO_2 formation from acetic acid (Table 1). A typical time dependence of CO_2 yield from the thinner acetic acid (19 μmol) solution (Catalyst E) is shown in Figure 1. The photoirradiation produced CO_2 linearly with time to give stoichiometric amount (38 μmol) by ca. 2 h, indicating complete mineralization of acetic acid ($CH_3COOH + 2O_2 = 2CO_2 + 2H_2O$) proceeds efficiently. The linear time course (22.3 μmol h^{-1} in Figure 1), which continued just before the complete consumption of acetic acid, suggests a zero-order kinetics with the acetic acid concentration. In fact, the ca. 9-times thicker acetic acid solution gave almost same initial rate for each TiO_2 powder used in this study (Table 1). A possible reason for this is that adsorption of acetic acid on the TiO_2 surface is saturated at the lower concentration and therefore amount of acetic acid reacting with photogenerated positive hole (h^+) is constant. Another interpretation is also plausible; rate of reduction by photoexcited electron (e^-), as well as recombination of e^- and h^+, dominantly

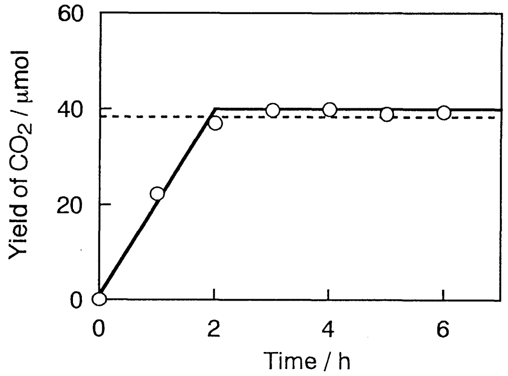

Figure 1. Time course of CO_2 yield from aqueous acetic acid (19 μmol) solution by suspended HyCOM TiO_2 powder (E in Table 1). The concentration corresponding to the complete decomposition of acetic acid is shown by dashed line.

Table 1. Physical properties of TiO_2 samples prepared under various conditions and their photocatalytic activities for mineralization of acetic acid in aqueous solutions

Catalyst	T_{syn}[a] / K	t_{syn}[a] / h	T_{ann}[b] / K	d_{101}[c] / nm	S_{BET}[d] / m^2g^{-1}	S_{calc}[e] / m^2g^{-1}	CO_2[f] / $\mu molh^{-1}$
A	423	2	-	5.1	280	306	3.5
B	473	2	-	7.1	243	214	9.4
C	523	2	-	9.4	167	166	14.4
D	573	2	-	12	140	130	19.8
E	573	8	-	16	103	98	23.6
F	573	24	-	18	91	87	27.2
G	573	8	823	16	85	98	14.2
H	573	8	973	16	71	98	11.7
I	573	8	1123	25	40	63	9.3
P-25[g]				24	50[h]	—	8.5
ST-01[g]				7[h]	320[h]	223	11.6

[a] Synthesized at T_{syn} for t_{syn}. [b] Annealed at T_{ann} for 1 h. [c] Crystallite size calculated from the 101 peak of anatase. [d] BET surface area. [e] Surface area calculated from crystallite size using 3.84 g cm^{-3} as the density of anatase. [f] Rate of CO_2 evolution from acetic acid (175 μmol) solution evaluated from the slope for initial 6 h. [g] P-25; Degussa, ST-01; Ishihara. [h] Data reported by the suppliers.

determines the overall reaction rate under the present reaction conditions where O_2 acts as an efficient e^- scavenger. At present we have no mechanistic information enabling us to distinguish them. Anyway, the initial rate of CO_2 formation may be a good indication of photocatalytic activity of TiO_2 powders, because of both that the reaction is less sensitive to the conditions, e.g., concentration of acetic acid and that stoichiometric complete decomposition proceeds by TiO_2 photocatalysts.

As clearly seen in Table 1, the HyCOM TiO_2 powders exhibited the activity much higher than those of commercial TiO_2's. Exceptionally lower activity was observed for TiO_2's prepared at the temperature < 500 K, though they consist of small anatase crystallites (< 10 nm, from X-ray diffraction (XRD)) with large surface area (> 200 m^2 g^{-1}). Consequently, relatively larger surface area, corresponding to larger amount of adsorbed substrate(s), is not a sole decisive factor of photocatalytic activity. With raising the synthesis temperature from 423 to 573 K, the crystallite size was increased from 5 to 12 nm and surface area was decreased (Catalysts A-D). Further increase in crystallite size was induced by prolonging the time for synthesis. For these samples, the BET surface area (S_{BET}) was in good agreement with that calculated (S_{calc}) from the crystallite size on the assumption that TiO_2 crystals were spherical and their density is 3.84 g cm^{-3}.[5] Moreover, transmission electron microscope (TEM) observation of Catalyst D showed that it consisted of agglomerates of primary particles having an average diameter of 12 nm (Figure 2), which was in good agreement with the crystallite size. These results support that the HyCOM TiO_2 comprised agglomerates of anatase single crystals.[1]

With increasing crystallite size, i.e., the more forceful thermal treatment in the synthesis procedure, the photocatalytic activity was markedly improved; catalyst synthesized at 573 K for 24 h (Catalyst F) showed the highest CO_2 production rate of 27.2 μmol h^{-1}.[6] These facts show that the intenser thermal condition enhances the photocatalytic activity despite that the surface area is reduced. Decrease in crystal defects, which possibly induce the e^--h^+ recombination, is attributable. Amorphous-like surface moiety, having many crystal defects, of TiO_2 particles formed by the hydrolysis of alkoxide would undergo crystallization to anatase phase during the synthesis process in toluene.[7] Enhancement of photocatalytic activity by the crystallization to anatase from amorphous TiO_2 has been reported.[8]

Table 1 also shows the effect of heat-treatment (annealing) of synthesized TiO_2 in air. As expected, S_{BET} was reduced with the increasing annealing temperature (while yet larger than those of the usual commercial TiO_2 powders). However, in contrast to the case of above mentioned synthesis conditions, the photocatalytic activity was drastically diminished. It should be noted that S_{calc} was less sensitive to the annealing temperature; S_{calc} was much larger than S_{BET}. As one of possible reasons, sintering of TiO_2 particles, being small single crystals before annealing, to polycrystalline ones is attributed to this phenomenon; the sintering may cause the decrease in S_{BET} but give negligible influence on the crystallite size since each crystallite in polycrystalline particles behaves independently in XRD analyses. Under such circumstance, the TiO_2 particles have grain boundaries which induce the e^--h^+ recombination[9] and thereby reduce the photocatalytic activity. We tried to confirm this by TEM, but yet have not distinguished whether particles were sintered or not. Further detailed TEM observation is now in progress.

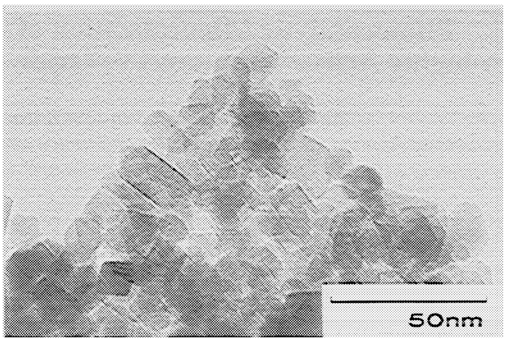

Figure 2. A transmission electron micrograph of HyCOM TiO_2 powder (D in Table 1).

In an usual manner, TiO_2 is synthesized by calcination of titanium(IV) hydroxide ($Ti(OH)_4$) or oxyhydroxide ($TiO(OH)_2$) to dehydrate and crystallize.[10] In such procedure, the higher calcination temperature induces the crystallization but, at the same time, drastic decrease in surface area and transformation into rutile crystallites may occur, i.e., it is rather difficult to synthesize the highly crystallized (but not sintered) anatase small particles by the conventional methods. As shown above, the HyCOM method could produce crystallized, i.e., of less crystal defects, anatase particles of relatively high surface area; such properties satisfy the requisites of a highly active photocatalyst utilizing the photogenerated e^--h^+ pairs efficiently.[11]

This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture of Japan (07805077). The authors are grateful to Kinki University and Tayca Corp. for their financial supports. Mr. Hideki Yamagiwa (Kinki University) and Dr. Keiji Hashimoto (Osaka Municipal Technical Research Institute) are acknowledged for help for TEM analysis and useful suggestions, respectively.

References and Notes

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6 Quantum efficiency for Catalyst F was roughly estimated to be 40%. Synthesis with longer time (96 h) gave 19 nm-sized anatase particles, but their S_{calc} (82 m^2 g^{-1}) larger than S_{BET} (69 m^2 g^{-1}) suggested the sintering of crystallites as observed by annealing (see next paragraph).

7 Decreasing the amount of water in feed (15 cm^3) resulted in reduction of activity (13.7 μmol h^{-1}) compared with catalyst D. The decrease in water in feed may cause decrease in autogenous pressure and thereby decrease in amount of water dissolved in toluene. Both of these decreases might account for leaving amorphous-like surface moiety during the synthesis process to result in the diminished photocatalytic activity.

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