Efficient TiO_2 Powder and Film Photocatalysts with Rutile Crystal Structure

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Efficient TiO_2 powder and film photocatalysts with the rutile structure were prepared. Their photocatalytic properties were assessed by measuring the photooxidative decomposition of gaseous acetaldehyde. The rutile powder showed much higher photoactivity than Degussa P-25 powder, both in degradation rate and in quantum efficiency. Moreover, the rutile film prepared by sintering the rutile sol at 450 °C also showed rather high photocatalytic activity.

Heterogeneous photocatalytic processes using semiconducting oxide catalysts in powder form have been gaining increasing attention for the detoxification of both air and water. Titanium dioxide, because of its high photoactivity and chemical stability, has been the most extensively employed in such photocatalytic reactions. In recent years, TiO_2 films have been gaining much attention as useful photocatalysts in various photocatalytic reactions.[1] These film photocatalyst systems have been widely proven to offer practical benefits that are not available with the powder ones. We have recently succeeded in preparing a highly photocatalytically active TiO_2 film with the anatase structure by sintering an anatase sol on a substrate.[2] It was found that the photocatalytic activity of the film is higher than that of one of the most photoactive commercial TiO_2 powder catalysts, Degussa P-25.

In general, it has been shown that anatase is photocatalytically more active than rutile.[3-5] This difference is often attributed to the differences in surface area and/or particle size.[6] Anatase powders usually have larger surface areas and smaller partice sizes in comparison with rutile powders. It has also been proposed that the larger bandgap for anatase (3.2 eV *vs.* 3.0 eV for rutile)[5] and its more negative flatband potential[6] lead to higher photoactivity. However, here we report on highly photoactive rutile powder and film, whose activities are, respectively, higher than and almost as great as that of Degussa P-25 anatase powder.

The rutile photocatalysts were prepared by the following method. Titanium tetrachloride was hydrolyzed in an aqueous sodium carbonate solution to give a titanium hydroxide solution. After being filtered and washed, the resultant was dispersed by adding nitric acid to yield a rutile sol. In order to enlarge rutile crystal, the sol was then autoclaved for 15 min at 180 °C. The transmission electron micrograph (TEM) of the sol is presented in Figure 1(a); the particles are nearly cubic in apparance with an average size of ca. 20~40 nm. To obtain powdered rutile (rutile powder A), the sol was dried at 110 °C in air for 5 h. For the preparation of the film, polyethylene glycol was then added to the sol so that its concentration was 40 wt%. Finally, the TiO_2 sol was smeared on a glass plate substrate (5 cm x 10 cm) followed by sintering at 450 °C in air for 30 min. The thickness of the semitransparent film was ca. 10 μm. The scanning electron micrograph (SEM) of the film surface is given in Figure 1(b). The film is rather porous and consists of small crystalline particles with diameters of ca. 40~50 nm. The X-ray diffraction of the powder and the film were measured, and the pattern for the film is given in Figure 2. All diffraction peaks can be attributed to rutile phase. The Raman spectrum of this film shown in Figure 3 also exhibited only bands that were attributable to rutile: 231, 443 and 613 cm^{-1}. These observations show that, within the detection limits of the measurements, both the powder and film consist of only rutile.

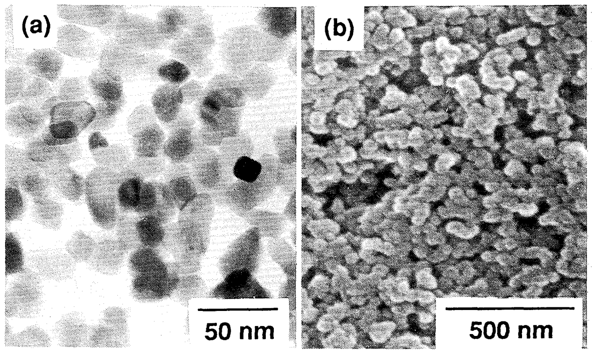

Figure 1. The transmission electron micrograph of the TiO_2 sol (a) and the scanning electron micrograph of the surface of the TiO_2 film (b).

The photocatalytic activities of both photocatalysts were evaluated according to the procedure reported previously.[2,7,8] Figure 4 shows the change in concentration against irradiation time for the photocatalytic degradation of acetaldehyde with rutile powder A and the rutile film as well as with commercial anatase powder (Degussa P-25), commercial rutile powder (Wako Chem. Ind. Ltd.), rutile powder B prepared by the procedure described in the literature[9] (thermal hydrolysis of titanium tetrachloride and this powder was reported to show a very high photocatalytic activity), and the anatase film which we reported previously.[2] The initial concentration of the reactant was 300 ppm, and UV illumination from black-light bulbs, with an intensity of 2.1 mW cm^{-2}, was used for the above experiments. Under the conditions of the experiments, the reaction proceeded approximately with

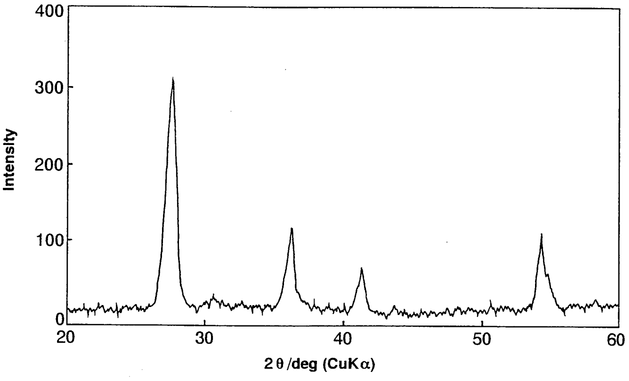

Figure 2. X-Ray diffraction pattern of the TiO_2 film.

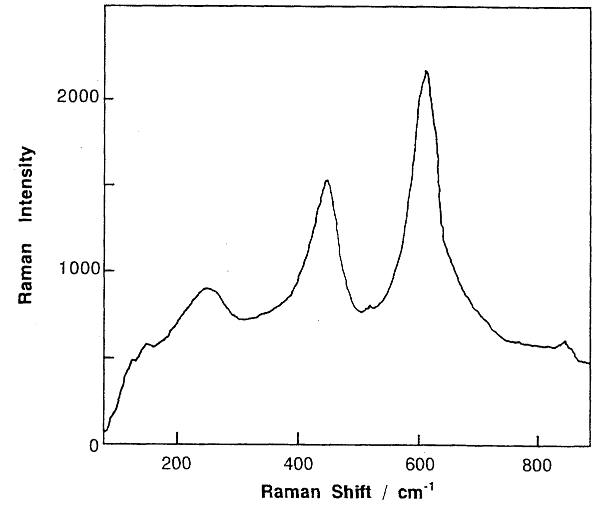

Figure 3. The Raman spectrum of the TiO_2 film.

first-order reaction kinetics. As was reported previously,[2] the anatase film showed much higher photoactivity than P-25 powder. Suprisingly, however, the rutile powder A showed the photoactivity comparable with that of the anatase film. This activity is clearly much higher than those of Wako rutile powder and rutile powder B. Moreover, the rutile film prepared by sintering our rutile sol at 450 °C also showed rather high reaction rate.

Table 1. Quantum yields (QY) for the photodegradation of 1000 ppm acetaldehyde gas with various TiO_2 photocatalysts under UV illumination of 0.5 mW cm^{-2} intensity

Photocatalyst	QY, %		
	CH_3COOH	CO_2	Total
Rutile Powder A[a]	27.7	16.7	44.4
Rutile Film[a]	21.6	9.0	30.6
Anatase Film (Ref. 2)	37.5	49.1	86.6
Anatase Powder (Degussa)	26.1	8.1	34.2
Rutile Powder B (Ref. 9)	11.6	8.1	19.7
Rutile Powder (Wako)	5.6	1.0	6.6

[a] This work.

We have shown that acetaldehyde oxidation would lead to the intermediate, CH_3COOH, before to the final product, CO_2.[2] It was shown that the amounts and/or ratios of CH_3COOH and CO_2 produced depend remarkably on the initial concentration of acetaldehyde, the light intensity used, and the activity of each catalyst. Table 1 lists the quantum yields for the production of CH_3COOH and CO_2 as well as the total quantum yields in the photodegradation of 1000 ppm acetaldehyde over the above catalysts under UV illumination of 0.5 mW cm^{-2} intensity. Under the experimental conditions, the reaction initially proceeded with nearly zero-order reaction kinetics. The quantum yield was then evaluated from this initial decomposition rate, and the calculation was performed under the assumption that only photogenerated holes take part in the oxidation.[2,7,8] The total quantum yields calculated for rutile powder A, the rutile film, the anatase film, and Degussa P-25 powder were 44.4, 30.6, 86.6 and 34.2%, respectively. Thus, the quantum yields for rutile powder A and the rutile film were almost equivalent to that for the P-25 powder and higher than those of rutile powder B (19.7%) and the commercial one (6.6%).

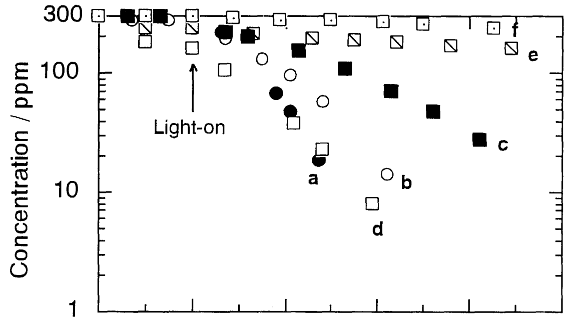

Figure 4. The plots of the concentration *vs.* irradiation time on the photodegradation of acetaldehyde over various TiO_2 photocatalysts. The catalysts used are the anatase film[2] (a), Degussa P-25 powder (b), the rutile film (c), rutile powder A (d), rutile powder B[9] (e), and Wako rutile powder (f).

Although anatase powders are usually recognized to be more active than rutile ones, it is sometimes reported that their photoactivity is lower than that of rutile powders. In such cases, however, they compared with low-activity anatase powders. On the other hand, we compared here the rutile powder and *film* with the P-25 *powder*, which is one of the most active anatase powders. It is important to recall that the photocatalytic activity of films is usually smaller than that of powders. One of the main reasons is because of the difference in surface area. In general, the surface area would decrease drastically by the calcination processes, especially at high temperatures. And according to the literature 6, rutile powder B with its large surface area lost its photoactivity drastically by heat treatment. On the other hand, a remarkable decrease in photoactivity of rutile powder A was not observed even by heating at 450 °C. Therefore, the rutile film we obtained is rather active. This is probably because the crystal in the rutile has been grown by the autoclaving process before being subjected to the calcination. The reasons for high photocatalytic activity of our rutile are not elucidated yet; however, one of the possible reasons is that although it is well crystallized, it has a relatively large surface area. The BET surface area of the rutile powder was 45 m^2 g^{-1}, which is comparable to that of P-25 powder, 50 m^2 g^{-1}. Detailed analysis based on Langmuir-Hinshelwood kinetics is now in progress.

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