

Photocatalytic Activities of Pure Rutile Particles Isolated from TiO₂ Powder by Dissolving the Anatase Component in HF Solution

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We have found that anatase TiO₂ dissolves into an HF solution more easily than rutile TiO₂. Using this property, we succeeded in isolating pure rutile particles from TiO₂ powder consisting of rutile and anatase phases by the HF treatment. The isolation of pure rutile particles was confirmed by X-ray diffraction patterns and diffuse reflection spectra. The rutile particle showed much lower photocatalytic activity than the original powder, if compared for the oxidation of 2-propanol in aqueous solution using dissolved oxygen as the electron acceptor. On the other hand, when Fe(III) ions were used as the electron acceptor for oxidation of 2-propanol and water, the activity scarcely changed after the HF treatment. These results indicate that rutile TiO₂ has poor activity for the reduction of oxygen, and the presence of a small amount of an anatase component is crucial for an efficient photocatalytic reaction on TiO₂ particles using oxygen as the electron acceptor.

Introduction

Semiconductor photocatalysts have attracted much attention because of their applicability in treatment of wastes and pollutants in air and water.^{1–9} They are also interesting from the viewpoint of application to chemical conversion of solar energy, for example, by splitting of water.^{10,11} For these purposes, TiO₂ particles have been used most often as a photocatalyst because of their chemical stability and high activity. In treatment of pollutants in air, anatase TiO₂ particles with small sizes have been commonly used. Their large surface area is especially effective for capturing low-concentration chemicals. In addition, the large band gap of anatase TiO₂ has been considered to be related to its high activity.^{12,13} However, in photooxidation of water, we have found that rutile TiO₂ particles with large particle sizes are more active than anatase particles.^{14–16} Similar results have been reported by Sato et al.¹⁷ The effectiveness of large particles in this reaction is understandable from the properties of TiO₂ photoelectrodes, which indicate that band bending is necessary to oxidize water.^{18,19} To develop the band bending in particles, their size and donor density are important. For example, if the donor density is about $3 \times 10^{17} \text{ cm}^{-3}$, a space charge layer of 100 nm is necessary to develop a potential drop of 0.3 eV. Usually, rutile TiO₂ powders have larger particle sizes than anatase powders, because they are produced at higher temperature, and thus are advantageous for band bending.

In most nominal rutile TiO₂ powders, the content of the anatase phase is a few percent or higher. On the other hand, pure rutile TiO₂ particles prepared at very high temperature show low photocatalytic activity because of their extremely small surface area. Therefore, it is not easy to get information about the intrinsic photocatalytic properties of pure rutile TiO₂ particles. It should also be noted that in some typical TiO₂ photocatalysts, such as Degussa P-25, which show high activity for many reactions, the contents of both anatase and rutile phases are high. This Degussa P-25 powder is reported to be effective

for splitting water quantitatively when carbonate is added to the solution.²⁰ On the basis of these experiences, it has been suggested that a synergetic effect may exist between the anatase and rutile phases.²¹ To confirm such an effect, however, it is necessary to get information regarding the pure rutile particles. Here, we report that pure rutile particles can be isolated from TiO₂ powders containing both rutile and anatase phases by treatment with an HF solution. In addition, some photocatalytic properties of pure rutile TiO₂ isolated from the powder are reported.

Experimental Section

Materials and Instruments. Typical titanium dioxide (TiO₂) powders used in the present study are Degussa P-25 and a standard sample supplied from Catalyst Society of Japan (JRC-TIO-5). The content of the rutile phase and the surface area of these powders are as follows: Degussa P-25, 26%, 48 m² g⁻¹; JRC-TIO-5, 91%, 2.1 m² g⁻¹. For some experiments we also used other TiO₂ powders obtained from commercial sources. Hydrogen fluoride used for the treatment of TiO₂ powders was obtained from Morita Chemical Industries as an electronics-grade reagent. Other chemicals were purchased from commercial sources as guaranteed-grade reagents and used without further purification.

X-ray diffraction patterns of the TiO₂ powders were measured with a Philips X'Pert-MRD X-ray diffraction meter. The diffuse-reflectance spectra of the powders were obtained using a Shimadzu UV-2500PC spectrophotometer with an integrating sphere.

Photocatalytic Reactions Using TiO₂ Powder. For photocatalytic reactions, a 500-W high-pressure Hg lamp (Wacom, BMO-500DY) was used as the light source. The light beam was passed through a stainless steel mesh filter and a UV-34 filter to adjust the light intensity and cut off the deep UV light of wavelengths shorter than 340 nm, respectively. Photocatalytic oxidation of 2-propanol was carried out in a Pyrex flask (100 mL) containing an aqueous solution (25 mL) of 2-propanol (13.0

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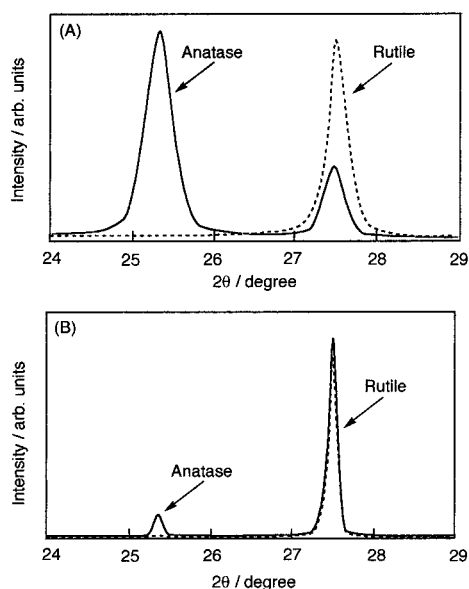


Figure 1. XRD patterns of TiO_2 powders: (A) Degussa P-25; (B) JRC-TIO5. The patterns obtained before and after treatment with a 10% HF solution are shown by solid lines and broken lines, respectively.

mmol) and TiO_2 powder (250 mg). As an electron acceptor, oxygen gas was passed through the solution at a rate of 30 mL min^{-1} during photoirradiation. The reaction was also carried out using Fe(III) ions as electron acceptor at a concentration of $8.0 \times 10^{-3} \text{ M}$. Acetone produced in the solution as a result of the photocatalytic reaction was determined by gas chromatography using a silicone DC-550 column. Photocatalytic oxidation of water was carried out in a Pyrex flask containing a solution (25 mL) of iron(III) chloride (200 μmol) and TiO_2 powder (200 mg). The TiO_2 powders had been photoirradiated overnight in deionized water to decompose organic contaminants. Concentrations of Fe(II) ions in solutions before and after the photocatalytic reactions were determined from the UV-vis absorption spectra. Before the spectroscopic measurements, Fe(II) ions were colored by complexing with 2,4,6-tris(2-pyridyl)-*s*-triazine (TPTZ) in solutions at pH 4.6.¹⁴

Results and Discussion

Isolation of Rutile TiO_2 Particles by Treatment with a 10% HF Solution. TiO_2 powder (1.5–3.0 g) was suspended in a 10% HF aqueous solution (100 mL) and stirred for 24 h at room temperature. After filtration, the TiO_2 powder was washed with deionized water. The fluoride ions in the wash liquid were monitored with a pH meter (TOA, HM-60S) equipped with a fluoride-ion electrode, and the wash was continued until the fluoride ions were not observed. Then, the TiO_2 powder was dried under reduced pressure successively at 50°C for 1 h and at 100°C for 2 h. After the treatment, the XRD patterns of Degussa P-25 and JRC-TIO-5 powders drastically changed, as shown in Figure 1. It is seen that the peak due to the anatase phase completely disappeared. This result suggests that the anatase is less stable than rutile, which is in agreement with the results of energy calculations for anatase and rutile phases.²²

The diffuse reflectance spectra of Degussa P-25 shifted to longer wavelengths after treatment with a 10% HF solution, as shown in Figure 2A. This shift is attributable to the disappearance of anatase particles, which have a larger optical band gap than rutile particles.²¹ It should be noted that the reflectance at wavelength longer than 400 nm decreases after treatment with the HF solution. In practice, the isolated rutile particles look

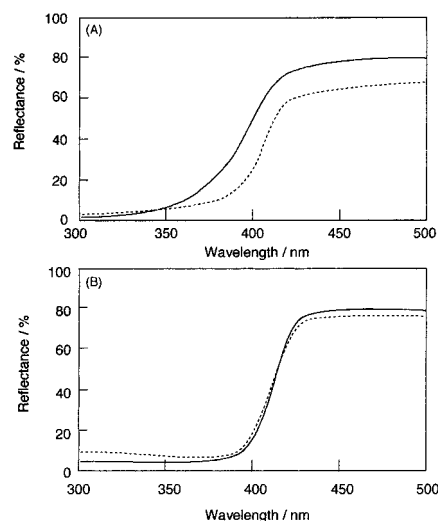


Figure 2. Diffuse reflectance spectra of TiO_2 powders: (A) Degussa P-25; (B) JRC-TIO5. The spectra of the powders before and after the treatment with a 10% HF solution are shown by solid lines and broken lines, respectively. Barium sulfate powder was used as the reference.

grayish, like the TiO_2 particles treated with hydrogen at about 600°C . This may have something to do with the high activity of Degussa P-25 for many photocatalytic reactions. In the case of JRC-TIO-5, which contains only 9% anatase, practically no change in the spectra is observed at wavelengths near the band gap of TiO_2 after the treatment with the HF solution, as shown in Figure 2B.

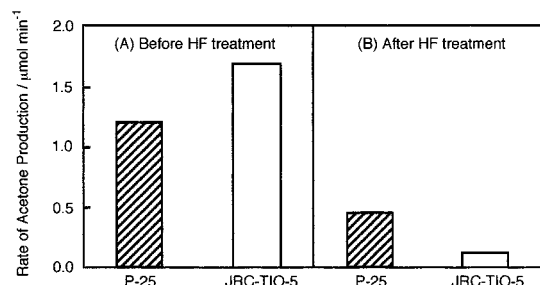
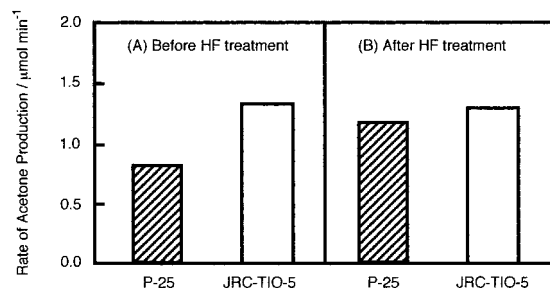
The change in the surface areas of these powders with HF treatment was measured by the BET method using helium gas as the adsorbate. In the case of Degussa P-25, the surface area was decreased from 48 to $28 \text{ m}^2 \text{ g}^{-1}$ by treatment with a 10% HF solution. The decrease in the surface area is due to the fact that the anatase particle, which was dissolved by the treatment, has a larger surface area than the rutile particle. On the other hand, the change in the surface area was small in the case of JRC-TIO-5 (from 2.1 to $2.2 \text{ m}^2 \text{ g}^{-1}$), because the content of anatase particles in this powder is small. The small increase in the surface area suggests that rutile particles are also dissolved to some extent by the treatment, although the dissolution rate is very slow. By the analysis of scanning electron micrography, we saw only a small decrease in the size of rutile particles after the treatment. The content of anatase phase, the BET surface area, and the particle size of the Degussa P-25 and JRC-TIO-5 powders before and after treatment with HF solution are summarized in Table 1.

Photocatalytic Oxidation of 2-Propanol on TiO_2 Powder.

Little has been known of the photocatalytic activity of pure rutile particles, because most nominal rutile powders contain small amounts of anatase particles. On the other hand, pure anatase particles are easily obtained, and it has been reported that anatase TiO_2 powders show higher photocatalytic activity than nominal rutile TiO_2 powders for the oxidation of organic compounds.^{12,13} When we measured the reactivity of different TiO_2 powders for the oxidation of 2-propanol in water using dissolved oxygen as the electron acceptor, we also found that anatase powders show high activity. However, using nominal rutile powders with anatase content higher than 5%, we also observed high activity. In contrast, the activity was very low for those with anatase content lower than 2%. It is still difficult, on the basis of these results, to explicitly determine whether the activity of TiO_2 photocatalysts is dependent on the crystal phases or on the particle size.

TABLE 1: Content of Anatase Phase, BET Surface Area, and Particle Size of the Degussa P-25 and JRC-TIO-5 Powders before and after Treatment with an HF Solution

		before HF treatment	after HF treatment
Degussa P-25	content of anatase, %	74	0
	BET surface area, m ² /g	48	28
	particle size, nm	anatase (25), rutile (85)	rutile (80)
JRC-TIO-5	content of anatase, %	9.0	0.7
	BET surface area, m ² /g	2.1	2.2
	particle size, nm	anatase (350), rutile (950)	rutile (900)

**Figure 3.** Photocatalytic production of acetone using Degussa P-25 and JRC-TIO-5 powders before and after the treatment with a 10% HF solution. Oxygen was supplied to the solution as the electron acceptor.**Figure 4.** Photocatalytic production of acetone using Degussa P-25 and JRC-TIO-5 powders before and after the treatment with a 10% HF solution. Fe(III) ions at a concentration of 8 mM were added to the solution as the electron acceptor.

The photocatalytic acetone production by oxidation of 2-propanol in water using dissolved oxygen as the electron acceptor was studied for Degussa P-25 and JRC-TIO-5 powders before and after the treatment with a 10% HF solution. Before the treatment, both powders show nearly the same activities, as shown in Figure 3 A. This result suggests that the particle size or the surface area does not play an important role in this reaction. The quantum efficiency for the reaction on the JRC-TIO-5 powder before the HF treatment was estimated to be about 70%. The quantum efficiency was calculated from the result obtained using 365-nm light on the assumption that the irradiated photons are all absorbed by TiO₂ particles, and the intensity of the light was determined by using an Fe(III) oxalate actinometer.²³ By the HF treatment, the activities of both powders are lowered, as shown in Figure 3 B, suggesting that rutile particles are inefficient in this reaction. The effect of the HF treatment is especially significant for JRC-TIO-5.

Figure 4 shows the activity of these two powders before and after treatment with an HF solution for the oxidation of 2-propanol using Fe(III) ions as the electron acceptor. In this case, there was no significant effect from the treatment for JRC-TIO-5. On the other hand, the activity of Degussa P-25 was improved by about 40% by the treatment. This improvement is attributable to the enhanced photoabsorption over the wavelength region from 360 to 400 nm due to the dissolution of the anatase phase, as seen in Figure 2A.

The above results shown in Figures 3 and 4 indicate that the presence of an anatase phase is important for the reaction using oxygen as the electron acceptor. The ineffectiveness of rutile particles for some other reactions using oxygen as the electron acceptor has also been observed.^{24,25} As for the photoabsorption, more light is absorbed by the rutile phase even when the anatase phase is present in the powders, because light at wavelengths longer than 340 nm was used in our measurements and photoabsorption by the anatase phase in this wavelength region is weak. This is typically the case for JRC-TIO-5 powder, which has only 9% anatase. Although photoabsorption by the anatase phase is very low, the activity was drastically lowered by removing the anatase phase, as shown in Figure 3. These results suggest that a synergetic effect is present between the rutile and anatase phases. It is expected that the electrons generated in the rutile phase by photoabsorption are transferred to the anatase phase across an energy barrier of about 0.2 eV²⁵ and then donated to oxygen. From preliminary analysis of Degussa P-25 by transmission electron microscopy, we found that fine anatase particles are loaded on the relatively large rutile particles. This supports the above model.

In contrast to the electron transfer to oxygen, the result shows that pure rutile particles are effective for the oxidation of 2-propanol using Fe(III) ions as the electron acceptor. This suggests that rutile particles can donate electrons to the Fe(III) ions effectively.

Photocatalytic Oxidation of Water on TiO₂ Particles. We have reported that rutile powders show higher activity for oxidation of water than anatase particles, when Fe(III) ions are used as the electron acceptor.¹⁴ More precisely, pure anatase powders show very poor activity for oxidation of water, and the activity is especially high for rutile particles with large particle sizes. Although JRC-TIO-5 powder contains 9% anatase, it is one of the most efficient powders for this reaction, probably because of its large particle size (about 0.95 μm). The quantum efficiency of the oxidation of water on this powder reaches as high as 17%.¹⁵ When this powder was treated with an HF solution, the photocatalytic activity for oxidation of water slightly decreased, as shown in Figure 5. The lowered activity may be due to the decrease of the particle size by partial dissolution of rutile particles. The effect of the dissolution of rutile particles is considered to be stronger for Degussa P-25 than for JRC-TIO-5, because the size of the rutile particles of Degussa P-25 (about 85 nm) is much smaller than that of JRC-TIO-5 (about 0.95 μm). This is consistent with the result shown in Figure 5. On the other hand, the small size of the rutile particles in Degussa P-25 suggests the presence of a high density of kink or step sites on the surface, which are active sites for many reactions. This may be responsible for the higher activity of this powder for the reduction of oxygen than that of JRC-TIO-5 after HF treatment, seen in Figure 3.

The high activity of pure rutile particles for oxidation of water using Fe(III) ions as the electron acceptor is partly because the electron transfer from the rutile surface to the Fe(III) ions is effective as discussed above concerning the oxidation of

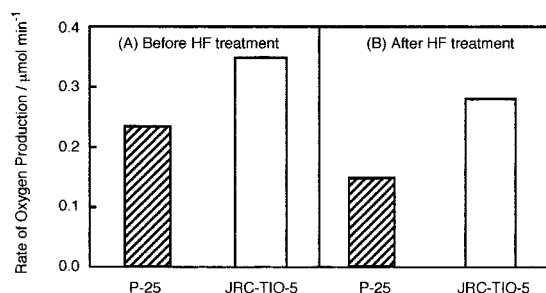


Figure 5. Photocatalytic production of oxygen from water using Degussa P-25 and JRC-TiO-5 powders before and after the treatment with a 10% HF solution. Fe(III) ions at a concentration of 8 mM were added to the solution as the electron acceptor. The production rate of oxygen is defined as one-fourth of the rate of the generation of Fe(II) ions. Before the reaction, TiO₂ powders were photoirradiated overnight to decompose organic impurities.

2-propanol. In contrast, it is known that reduction of oxygen is very sensitive to the materials and surface properties in the field of fuel cells.^{26,27} The surface structure of rutile and/or its lower energy level of the conduction band are considered to be responsible for the low activity for the reduction of oxygen.

As to the low activity of anatase particles for the oxidation of water, there are two possible explanations: (1) the anatase surface has low catalytic activity for oxidation of water and (2) the small particle size of the anatase particles is unable to form the band bending which is necessary for the reaction. However, there has been no information to determine the reason, especially regarding the properties of large-size anatase TiO₂ particles for the photooxidation of water, except the information obtained using single crystalline electrodes.¹⁹

Conclusions

We found that the anatase phase included in TiO₂ powders is selectively dissolved by the HF treatment. This method is useful to isolate pure rutile particles from TiO₂ powders and elucidate the relationship between crystal structures and photocatalytic activities. For the oxidation of 2-propanol using oxygen as the electron acceptor, the photocatalytic activity of pure rutile particles was much lower than that of the original powder consisting of rutile and anatase. In contrast, the photocatalytic activities for the photooxidation of water and 2-propanol using Fe(III) ions as the electron acceptor were changed slightly by the HF treatment. These results indicate that the rutile surface is ineffective for reduction of oxygen. Importantly, based on these results, the synergetic effect by a

mixture of the rutile and anatase phases for the reaction using dissolved oxygen as the electron acceptor is clearly demonstrated.

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