Isolation of Anatase Crystallites from Anatase-Rutile Mixed Particles by Dissolution with Aqueous Hydrogen Peroxide and Ammonia

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Pure anatase crystalline phase was isolated from Degussa P25, a frequently used titanium(IV) oxide (TiO₂) photocatalyst containing both anatase and rutile crystallites, by dissolving rutile phase selectively through treatment with aqueous hydrogen peroxide (H_2O_2)-ammonia (NH_3). X-ray diffraction analyses revealed that pure crystallites have almost the same particle sizes in original P25, indicating that the purification process did not change their size distribution. Specific surface area measurement and scanning electron microscopic analysis also suggest that relatively smaller anatase crystallites were left undissolved by the H_2O_2 -NH₃ treatment.

Key words: titanium(IV) oxide, anatase-rutile mixture, X-ray diffraction analysis, selective dissolution

1. INTRODUCTION

Titanium(IV) oxide (TiO₂) is one of the most promising materials, or even the sole material, of a photocatalyst that drive various redox reactions by their photoabsorption with light of energy greater than their bandgaps.¹ Although the bandgap of TiO₂, ca. 3 eV, is too large to absorb only ultraviolet light and visible light included largely in solar radiation can not be used for its bandgap photoexcitation, its photostability, availability, non-toxicity and low cost are the reasons why TiO₂ is used widely in laboratory research and practical applications. Another reason, actually the main one, especially for laboratory study, is that almost all samples of TiO₂, whatever be purchased or synthesized, exhibit photocatalytic activity more or less; appreciable photocatalytic reaction can be observed when one examines, and there have therefore been many reports on TiO₂ photocatalysis. In those reports, photocatalytic activities have been discussed in relation to physical properties, such as crystalline phase, particle size and Crystalline phase has been specific surface area. believed to be a predominant factor determining the photocatalytic activity, and it is often claimed that anatase has better photocatalytic activity than that of rutile. However, it should be emphasized that, as far as the authors know, there have been very few reports showing clearly a specific relation between photocatalytic activity and a physical property of a photocatalyst; the order of photocatalytic activity, anatase > rutile, seems to be an empirical expression without any scientific evidence.

Among the many TiO_2 samples reported so far, Degussa P25 (code name in Degussa: AEROXIDE TiO_2 P 25) is the most well-known photocatalyst and is frequently used as a reference TiO_2 photocatalyst. One of the reasons why Degussa P25 has been used as a reference is that it exhibits relatively high, in fact the highest in most of the photocatalytic reactions, photocatalytic activity under ultraviolet irradiation. A characteristic feature of this TiO_2 sample is that it contains both anatase and rutile crystallites, as indicated by the fact that X-ray diffraction peaks assignable to anatase and rutile are observed (see Figs. 1 and 2). Based on this crystal structural feature, many scientists in the field of photocatalysis have suggested that the co-existence of anatase and rutile crystallites gives P25 its higher photocatalytic activity and that electron and positive hole transfer from anatase to rutile or vice versa induces efficient charge separation. To prove this, it is necessary to obtain direct evidence of this electron and hole transfer between particles.

Another important point is that, to our knowledge, the precise crystalline composition of P25 has not been determined, though the crystalline content is an indispensable parameter in the characterization of solid materials. It is believed that crystal content can be determined quantitatively through powder X-ray diffraction (XRD) analysis using a calibration curve of standard sample(s).² While it is reasonable to assume that intensity of a peak assigned to a given crystalline phase is proportional to its content considering the theoretical background of XRD, there seems to be at least two problems.

One is how can we obtain a standard sample for making calibration curves. There are many samples, for example TiO_2 , for which the crystalline structure is characterized by XRD analyses. In the study of crystallization of amorphous TiO_2 , we have found that the XRD peak intensity of anatase crystallites depends on their size; when the particle size is smaller than ca. 40 nm, the peak intensity becomes drastically small. This suggests that for such small particles, the calibration curves differ depending on particle size.³

Another problem is the existence of amorphous phase in the powder samples, especially of small particles. Since such amorphous phase does not give any peak in XRD patterns, it is impossible to determine its content. For P25, while a report claiming that there is no such amorphous phase was published,⁴ Ohno et al. have proved the presence of amorphous phase in P25 by transmission electron microscopic analyses.⁵

It should be emphasized that the reported content

(or anatase/rutile ratio) of P25 has often been calculated based on a paper⁶ published a long time ago and this reported procedure can not give any solution to the above-mentioned problems; home-made anatase and rutile samples, which had not been well characterized, were used in that study, and the probability of the presence of amorphous was not assumed.

To solve this problem in the crystalline content analyses of P25, it is necessary to obtain pure anatase and rutile crystallites by separating them from the mixture. The separation of rutile, i.e., selective dissolution of anatase from P25, has been reported.⁷ In this study, we tried to separate anatase crystallites by selective dissolution of rutile.

2. EXPERIMENTS

2.1 Materials

The starting material Degussa P25 was supplied as one of the Reference Titania Catalysts (JRC-TIO series), TIO-4(2), by the Catalysis Society of Japan. This sample had been prepared by Nippon Aerosil Co. Ltd. The sample was used without any pre-treatment. The other chemicals were supplied by Wako Pure Chemical. Water was purified by a Yamato-Millipore Autopure WQ 501 water purification system to produce Milli-Q water.

2.2 Procedure

A representative procedure for selective rutile dissolution was as follows. To aqueous hydrogen peroxide (H₂O₂, 30%; 50 mL) in a flask set in an ice-cooled bath was added dropwise aqueous ammonia (2.5%; 5.0 mL) under magnetic stirring. A 0.500-g portion of P25 powder was added to the H₂O₂-NH₃ mixed solution and stirred in air at ambient temperature for 12 h. The remaining precipitate was separated by centrifugation at 10,000 rpm for 5 min (Kokusan H-201F High Speed Centrifuge), washed with water several times, and dried at 393 K in air. For some of the samples, the solution part, sol, of the H₂O₂-NH₃ mixture was treated with a platinum mesh to decompose the remaining H₂O₂ and evaporated to obtain dried gel.

2.3 XRD analyses

XRD patterns of samples were recorded on a Rigaku Rint 2000 powder X-ray diffractometer using copper K_{α} radiation (40 kV, 30 mA) with a scanning rate of 1 degree min⁻¹ (0.010-degree step). Peak intensity was measured by integration of a given peak, 101 (25.3 degrees) and 110 (27.4 degrees) for anatase and rutile, respectively, after baseline correction. Crystallite size was estimated by Scherrer's equation.⁸

$$D=\frac{K\lambda}{\beta\cos\theta},$$

where D, K, λ , β , and θ are size in nm, a constant (0.89), wavelength of X-ray radiation (0.1542 nm), full width at half-maximum (FWHM) of a diffraction peak, and diffraction angle (For anatase, 101 diffraction at 2θ =25.3 degrees was used.), respectively. The FWHM was calculated with correction for peak broadening due to K_{a2} radiation and X-ray divergence.

2.4 Specific surface area measurement

Specific surface areas of samples were estimated from the nitrogen adsorption at 77 K (Yuasa Ionics NOVA 1200e gas adsorption measurement instrument) using the BET equation.

2.5 SEM observation

Scanning electron microscopic analysis was performed using a JEOL JSM-7400F field-emission scanning electron microscope (SEM). A powder sample was fixed on a sample holder by graphite paste, Colloidal Graphite (Ted Pella) and introduced to a sample chamber.

3. RESULTS AND DISCUSSION

3.1 Dissolution of P25 in H₂O₂-NH₃ mixture

Stirring of P25 in H2O2-NH3 mixed solutions led to the dissolution of solid to give light yellow sol and white or off-white precipitate as shown in Table I. Use of aqueous H₂O₂ only, without NH₃, caused slight change in the anatase-rutile intensity ratio, $I_{\rm R}/I_{\rm A}$, but > 98% recovery was observed even after 24-h treatment. Addition of NH₃ accelerated the dissolution of samples; 20-40% recovery, i.e., 80-60% dissolution, was observed. In the case of a mixture containing 5.0 mL of aqueous NH₃, the dissolution proceeded rapidly in the initial 2 h and gradually afterward. Along with the dissolution, XRD peak ratio I_R/I_A was decreased to less than 10%. This suggests that both anatase and rutile crystallites were dissolved in the H2O2-NH3 mixture, while the rate of rutile dissolution as calculated by percent disappearance seems faster than that of anatase. The rutile-anatase peak-intensity ratio becomes small by the addition of a larger amount of NH₃, when comparing the data for 12-h treatment. As a result, a part of anatase was left undissolved, while rutile crystallites disappeared almost completely when an 8.0-mL portion of aqueous NH₃ was added. With higher NH₃ concentration (10 mL), however, the recovery was dissolved almost negligible; anatase was also completely.

3.2 Dissolution of anatase-rutile mixture

Commercial pure anatase and rutile samples supplied by Merck (BET surface area: ca. 10 m² g⁻¹) and JRC-TIO-3 (40 m² g⁻¹) were mixed in the weight ratio of 7:3 and subjected to H_2O_2 -NH₃ treatment. Table II

Table I Dissolution of P25^a by aqueous H₂O₂.^b

additive	time/h	$I_{\rm R}/I_{\rm A}^{\rm c}$	% recovery
none	0	0.31	
none	12	0.29	98
none	24	0.30	98
$NH_3 2.0 mL^d$	12	0.088	36
$NH_3 5.0 mL$	2	0.091	37
NH_3 5.0 mL	4	0.058	35
$NH_3 5.0 mL$	6	0.020	31
$NH_3 5.0 mL$	12	0.013	30
NH_3 5.0 mL	24	0.015	31
NH_{1} 8.0 mL	12	0	29
NaOH 0.30 g	12	0.035	20

^a0.50 g. ^b50 mL. ^cPeak area ratio of rutile-anatase. ^dAqueous NH₃ solution (2.5%).

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additive	time/h	I _R /I _A c	% recovery
none	0	0.093	
NH3 ^d 8.0 mL	12	0.045	74
NH ₃ 16 mL	12	0.059	60
NH ₃ 24 mL	12	0.038	62
NH ₃ 200 mL	12	0	50

Table II Dissolution of a 7:3 mixture^a of Merck (anatase) and JRC-TIO-3 (rutile) TiO₂s by aqueous $H_2O_2^{b}$ -NH₃.

^a0.50 g. ^b50 mL. ^cPeak area ratio of rutile-anatase. d Aqueous NH₃ solution (2.5%).

shows the results. The mixture was also dissolved, while the rate was relatively slow, presumably due to the larger particle size. Complete removal of rutile required a large amount of aqueous NH_3 . On the basis of these results, it is expected that the present H_2O_2 - NH_3 treatment can be applied for the separation of pure anatase phase from anatase-rutile mixed powder samples.

3.3 Mechanism of dissolution

It is well known that reaction of H_2O_2 with titanium(IV) cation (Ti⁴⁺) produces a peroxo complex,⁹ and its visible photoabsorption has been applied to the quantitative analysis of Ti⁴⁺ or H_2O_2 . The yellow color of the solution during and after treatment also suggests the formation of Ti⁴⁺-H₂O₂ complex. Taking into account the fact that in the absence of NH₃ practically no dissolution occurs and addition of sodium hydroxide (NaOH) instead of NH₃ also accelerates the dissolution (Table I), extraction of Ti⁴⁺ by H_2O_2 may proceed at relatively high pH. Since aqueous H_2O_2 is weakly acidic, the addition of NH₃ or NaOH neutralizes the solution. Actually, pH of the solution containing 8 mL of aqueous NH₃ was ca. 7.8. Aqueous H_2O_2 whose pH was adjusted by the addition of an appropriate amount of aqueous NaOH to 7.8 did not give pure isolated anatase crystallites, indicating that the pH of solutions is not a



Fig. 1 XRD patterns of powders of original P25, after HF treatment, and dried gel from H_2O_2 -NH₃ (8.0 mL) reaction mixture after and before calcination at 773 K.



Fig. 2 XRD patterns of powders of original P25 and those after treatment with H_2O_2 -NH₃ (5.0 mL) mixture.

Table III Crystallite sizes of anatase in P25 and isolated pure anatase and specific surface areas before and after the isolation

sample	D _A ª/nm	$S_{\text{BET}}^{b}/\text{m}^2 \text{g}^{-1}$	
P25	24	57	
anatase	25	67	

^a Crystallite size of a	natase estimated by Scherrer's
equation.	^b BET surface area.

unique parameter predominating the rate of dissolution; NH₃ or ammonium cation (NH₄⁺) may participate in the selective dissolution of rutile. The influence of NH₄⁺ on the stability of a peroxo complex anion of Ti⁴⁺, Ti₂O₅(OH)_x^{(2-X)-} (x>2), has been discussed, ¹⁰ and it was suggested that NH₄⁺, but not alkali metal cations such as Na⁺, stabilizes the complex. Assuming the formation of similar complex in the present treatment, NH₃ might enhance the dissolution of TiO₂, especially rutile crystallites, by stabilizing the dissolved titanium(IV) species. Mechanistic studies using infrared spectroscopy are now in progress. Ohno et al. have also reported that similar H₂O₂ treatment using an alkali not including NH₃ gave anatase crystallites from P25.¹¹

After the H_2O_2 -NH₃ treatment, by which pure anatase crystallites were obtained, the solution part was gelated to obtain powder. Figure 1 shows XRD patterns of the thus-obtained powder before and after calcination at 773 K. Dried gel did not give any peaks, and calcination at 773 K led to crystallization into anatase. It is plausible that both anatase and rutile crystallites are dissolved into the atomic level to give homogeneous solutions without retaining the crystal structure by the H_2O_2 -NH₃ treatment.

3.4 Isolated anatase crystallites

Figure 2 shows the change in XRD patterns caused by H_2O_2 -NH₃ treatment. A characteristic rutile 110 peak at 27.4 degrees almost disappeared after 12-h treatment. At this NH₃ concentration (5 mL in 50 mL



Fig. 3 SEM images of original P25 (upper panel) and isolated anatase particles (lower panel). Gray plate-like structures are of the surface of graphite paste used for sample fixation.

aqueous H_2O_2), a negligible but appreciable rutile peak was observed, but no such peak was detected at a higher concentration (8 mL/50 mL) treatment. Thus, pure anatase crystallites were isolated from P25.

Table III shows a comparison of crystallite sizes of anatase and BET surface areas of original P25 and the isolated pure anatase. The crystallite size, D_A , of the pure anatase from P25 was practically the same considering the experimental error. The fact that the size of anatase was not changed in the isolation process indicates that the anatase crystallites were isolated without change in distribution of their particle size. Specific surface area of the pure anatase was a little larger than that of P25. This seems reasonable considering the fact that the size of rutile crystallites in P25 is a little larger than that of anatase.⁵

The smaller size of anatase crystallites than rutile ones in P25 was confirmed by SEM observation. Figure 3 shows that the isolated pure anatase crystallites have a size of 20—40 nm, while original P25 contained larger particles, presumably rutile crystallites.

4. CONCLUSION

A pure anatase phase has been separated from P25 without changing its particle size distribution by a newly developed selective dissolution technique using aqueous H_2O_2 -NH₃ mixed solutions. As has been reported,⁷ a pure rutile phase can be separated from P25. This rutile separation has been successfully reproduced in our laboratory; powder obtained by hydrofluoric acid (HF) as shown in Fig. 1. The characterization of this pure rutile sample is now under investigation. These pure anatase and rutile samples enable construction of intrinsic calibration curves of each component and determination of their content independently (if the isolated pure rutile has a size distribution the same as

that of rutile in P25). Although there is currently no method for detection and separation of amorphous phase in P25, its content, if present, can be determined as a remainder of anatase and rutile phases, the contents of which can be evaluated independently as described above.

Thus, the results shown in this paper provide a way for complete crystalline-phase content analysis of anatase-rutile (with amorphous) samples such as P25. Furthermore, P25 as a mixture of anatase and rutile can be reconstructed using pure anatase and rutile samples. Comparison of photocatalytic activities of original and reconstructed P25 samples with pure components will provide information on absence or presence of electronic interaction between anatase and rutile crystallites during the course of photocatalytic reactions. Study along this line is now in progress.

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