

Factors Governing the Initial Process of TiO₂ Photocatalysis Studied by Means of in-Situ Electron Spin Resonance Measurements

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The ratio of the amount of carboxymethyl radicals to that of methyl radicals was measured in situ for the photocatalytic decomposition of acetic acid over platinized TiO₂ powder in deoxygenated aqueous solution at room temperature and discussed in connection with the contribution of •OH radicals in the oxidation process. Since carboxymethyl radicals are formed only by indirect oxidation, the radical ratio was used to measure the indirect oxidation via •OH radicals. Thus, ratios of the indirect oxidation were estimated for five commercially available TiO₂ photocatalysts, in addition to the several properties of the powders. The ratios were found to be sensitive to the characteristics of the TiO₂ catalysts. The larger the amount of surface OH group, the more likely the indirect oxidation via •OH radicals occurs. This could be attributed to the difference in the structures of the surface trapped holes elucidated by the ESR measurements of the corresponding TiO₂ powder at 77 K.

Introduction

Photocatalytic reactions with semiconductor powders have received much attention because of their applications to the cleanup of building materials and the mineralization of wastewater.¹ The initial process in the photocatalytic reactions, however, has not been clearly understood so far.² Most of the important issues concern the initial process of the oxidation of organic molecules. Since the photocatalytic reaction is performed usually in aqueous suspension, water can be oxidized to hydroxyl (•OH) radicals by photogenerated positive holes and then they react with organic compounds to form oxidized species or decomposed products. Another possible process is the direct oxidation of organic solute compounds at the surface by the photoproduced holes. The results of the analysis of the products revealed that these indirect and direct pathways are both plausible oxidation processes.² It has been pointed out, however, that distinct differentiation between two pathways would not be attainable directly from the product identification, since the products may be identical in both cases.² Hence, to investigate which pathway is facilitated in the initial process of the photocatalytic reactions, it is important to monitor the intermediate radicals formed during the reaction. The mechanism of the oxidation has been discussed mainly on the basis of the dependence of the various reactants on the photocatalytic reactions; however, the properties of TiO₂ have not been sufficiently discussed in connection with the two oxidation pathways.¹

In the previous report, we have shown that in-situ ESR (electron spin resonance) observation on the photocatalytic oxidation of acetic acid provides information of the ratio of the two pathways.³ In this reaction system, both the methyl (•CH₃) and carboxymethyl (•CH₂COOH) radicals can be detected.⁴ The methyl radicals are formed both from the direct hole oxidation and the indirect oxidation via •OH radicals, while the carboxymethyl radicals could be formed only by the indirect oxidation.³ In the present study, we confirmed that the reaction

pathways hold under various experimental conditions and extended the methodology to apply to several TiO₂ powders utilized commercially as photocatalysts. The results clearly indicate that the initial oxidation pathways are significantly affected by the properties of TiO₂ powders.

Experimental Section

A sample of platinized TiO₂ (Pt/TiO₂) powder was prepared as follows. One gram of TiO₂ and the desired amount of H₂-PtCl₆•6H₂O were mixed in 10 cm³ of 0.1 M HCl. The solution was neutralized with Na₂CO₃ and then adjusted to pH 5 with acetic acid. The mixture was irradiated for 9 h with a 500-W high-pressure Hg lamp under deoxygenated conditions with N₂ bubbling. The gray powder thus obtained was washed thoroughly with distilled water and dried for 8 h at 150 °C. The amount of platinum as a reactant was usually 0.3 wt % of TiO₂ as described later. The TiO₂ powders used were Degussa P25 (Japan Aerosil),^{5,6} Hombikat UV100 (Sachtleben Chemie),^{7–9} ST-01 (Ishihara Techno), and F-4 and F-6 (Showa Titanium).

To determine the primary particle size and the crystalline composition, X-ray diffraction (XRD) of the Pt/TiO₂ powders was measured with a Rigaku GeigerFlex RAD. For the estimation of the amount of surface OH group, thermogravimetry (TG) was measured with a TG-DTA meter (Seiko SSC/5200) for Pt/TiO₂ powders. Secondary particle size was measured as a mean diameter with a centrifugal size distribution meter (Shimadzu SA-CP3) for a Pt/TiO₂ suspension in 0.1 M acetic acid solution. Surface area was measured by the BET method with a micromesotechs flow sorb (Shimadzu 2300). The amount of Pt on TiO₂ was analyzed with an ICP (inductively coupled plasma) atomic emission spectrometer (Seiko SPS/4000) after the dissolution of Pt into aqua regia. Adsorption of acetic acid on Pt/TiO₂ powder was measured with an NMR spectrometer as follows. One-tenth gram of Pt/TiO₂ powder was dispersed in 2 cm³ of a D₂O solution of acetic acid. After standing for a day, the powder was removed with a centrifuge, then the concentration of acetic acid of the supernatant was measured with an NMR spectrometer (JEOL JLM-EX400) using dioxane as an internal standard.

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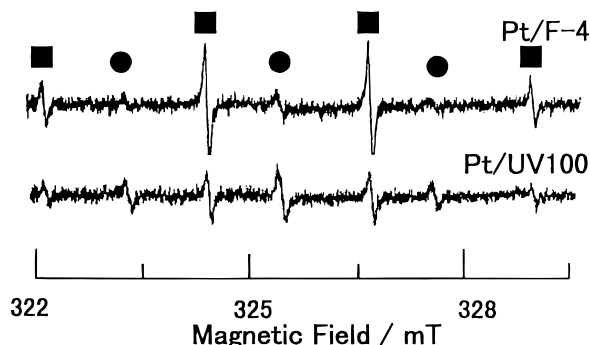


Figure 1. Typical ESR spectra observed for 0.3 wt % platinized TiO₂ (F-4 and UV100) during photocatalytic reaction in deaerated aqueous acetic acid: (■, ·CH₃; ●, ·CH₂COOH).

In-situ ESR spectra were measured with a JEOL JES RE-2X spectrometer. A flat flow cell with an internal cross section of 0.3 mm × 5 mm was placed in the microwave cavity of the spectrometer and irradiated with a 500-W Hg lamp through a U-330 (Hoya) glass filter. An aqueous solution (40 cm³) of 0.1 M acetic acid (Nacalai Tesque) suspending 0.16 g of Pt/TiO₂ powder was circulated with a tube pump at the flow rate of 0.8 cm³ min⁻¹. In some experiments the concentration of acetic acid was varied. The solution was agitated with an ultrasonic vibrator to disperse the powder and then it was deoxygenated by N₂ bubbling for 20 min before and during the ESR measurements.

Results

Figure 1 shows the ESR spectra observed during the photocatalytic reaction with two kinds of Pt/TiO₂ in an aqueous acetic acid solution. The quartet and triplet signals are a response to ·CH₃ and ·CH₂COOH radicals, respectively.⁴ This assignment of the signal has been confirmed from the experiment with deuterated acetic acid.³ Figure 1 shows that the relative peak intensities for the two catalysts differ from each other. The signal intensity was reproducible within 8% among the repeated measurements for the same catalyst. From the signal intensities, the relative concentrations of the two radicals can be calculated. Namely, for the ·CH₂COOH radicals the height of the central peak of the 1:2:1 triplet was multiplied by its width and then by 4/2. Similarly, for ·CH₃ radicals the height of the second peak in the 1:3:3:1 quartet was multiplied by its width and by 8/3. Thus, the amount of the two radicals could be compared among the catalysts, though the absolute amount of the radicals was not evaluated in the present study.

Figure 2 shows the amounts of ·CH₃ and ·CH₂COOH radicals for two kinds of Pt/TiO₂ as a function of the amount of platinum loaded. The amount of Pt in this figure is determined from the ICP analysis. At higher platinum loading, the amount of radicals tends to decrease as typically shown in the ·CH₃ radicals for UV100 Pt/TiO₂. This observation indicates that the large amount of platinum provides a site at which the photoinduced holes recombine with the photoinduced electrons, because the photoinduced electrons are trapped at the platinum-loaded surface. The amount of ·CH₃ showed a maximum value at 0.04 wt % Pt for UV100 and at 0.11 wt % Pt for P25. This difference is explained by the difference in the size of the particle, because usually the recombination easily occurs in a small particle. Since the amounts of radicals were almost constant at about 0.15 wt % Pt, this amount of platinum, which corresponds to 0.3 wt % Pt on the reactant basis, was used in the following experiment.

In Figure 3 are plotted the amounts of ·CH₃ and ·CH₂COOH radicals observed in the photocatalytic reaction with Pt/TiO₂ of ST-01 and P25 as a function of acetic acid concentration.

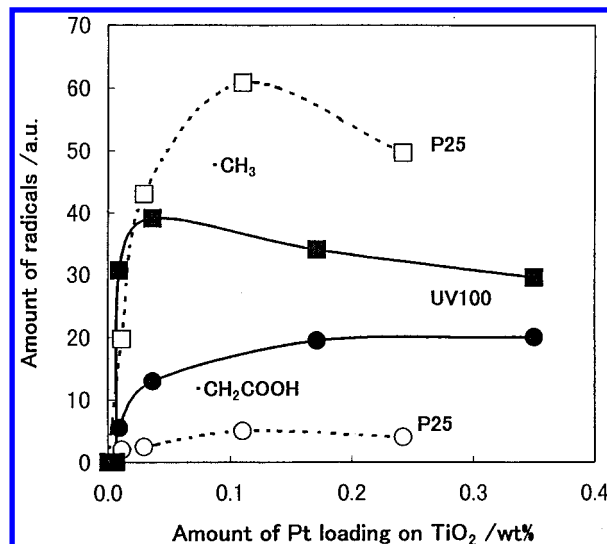


Figure 2. Relative amounts of ·CH₃ (■, □) and ·CH₂COOH (●, ○) radicals formed with Pt/TiO₂ of UV100 (■, ●) and P25 (□, ○) as a function of the amount of platinum loaded.

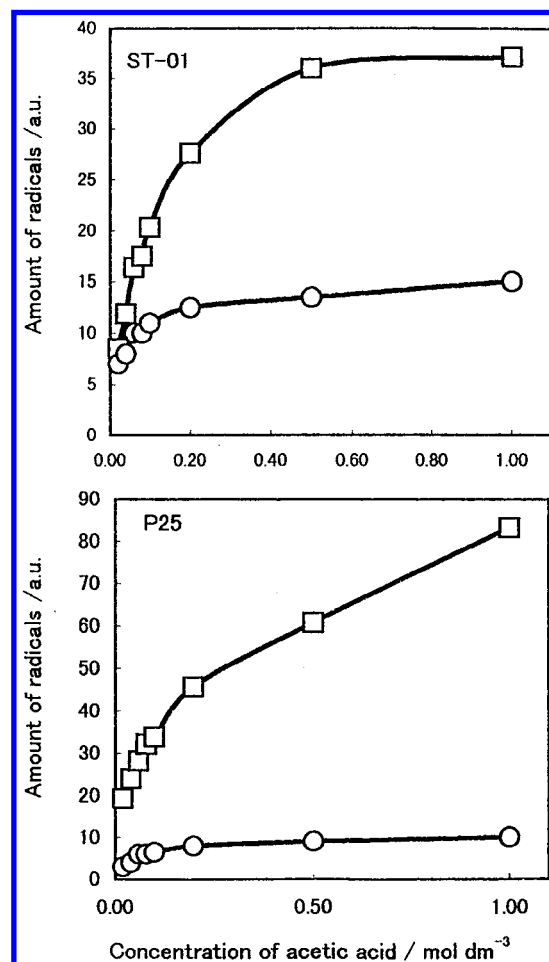
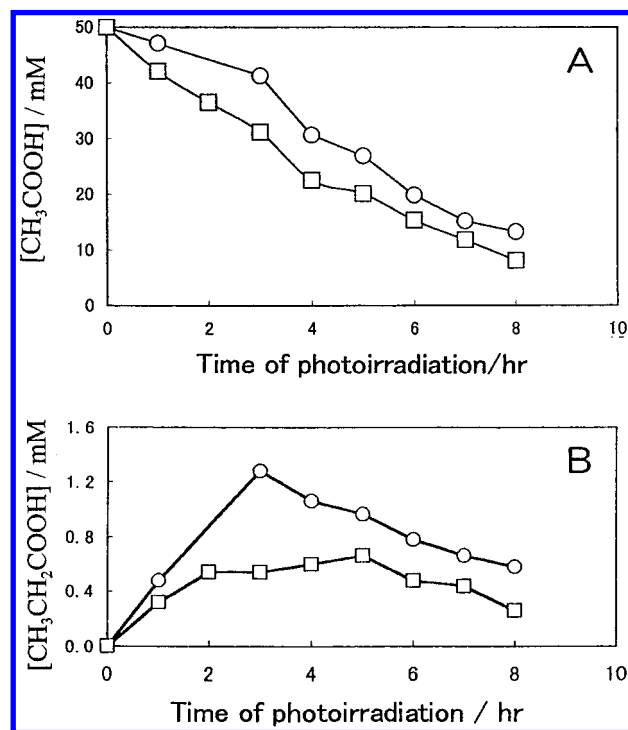


Figure 3. Relative amounts of ·CH₃ (□) and ·CH₂COOH (○) radicals formed with Pt/TiO₂ photocatalysts of ST-01 and P25 as a function of the concentration of acetic acid in the solution.

For ST-01, the formation of ·CH₃ radicals became constant at 0.5 M acetic acid, while for P25 it still increased at 1.0 M acetic acid. As shown experimentally in the previous report,³ the formation of ·CH₃ radicals by direct oxidation involves a slower process than the formation of ·CH₂COOH radicals by indirect oxidation with short-lived ·OH radicals. When this slow process stems from the diffusion of acetic acid molecules to the surface

TABLE 1: Relative Amount of Unstable Intermediates and Several Properties for Various Pt/TiO₂ Photocatalysts

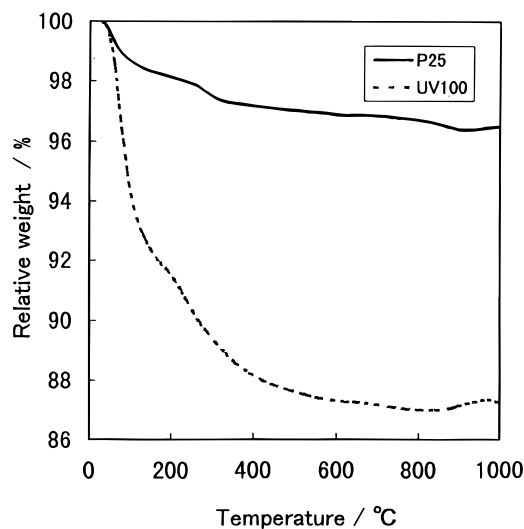
name of TiO ₂	anatase component (%)	primary particle size (nm)	BET surface area (m ² g ⁻¹)	secondary particle size (μm)	adsorption of CH ₃ COOH (10 ⁻⁴ mol/ g-cat)	amount of OH group (wt %)	relative amount of radicals			ratio of indirect oxidation ^a
							•CH ₃	•CH ₂ COOH	total	
UV100	100	9	275	0.5	5.8	4.5	21	20	41	0.93
ST-01	100	9	315	1.3	4.7	4.3	16	8	24	0.51
F-6	95	10	94	0.8	3.1	4.0	24	7	31	0.29
F-4	86	16	56	0.4	1.0	2.8	60	8	68	0.13
P25	80	32	49	2.6	0.6	1.3	24	6	30	0.25

^a Calculated as [\cdot CH₂COOH]/[\cdot CH₃].**Figure 4.** Time profile of the amount of acetic acid (A) and propionic acid (B) during photocatalytic degradation of acetic acid with Pt/TiO₂ of UV100 (O) and P25 (□).

of TiO₂, the large concentration dependence can be explained. Since the pH of the solution is about 2, the surface of the TiO₂ grain is positively charged. Then, anionic acetate ions are adsorbed on the surface under an equilibrium with a certain amount of maximum adsorption. Similar concentration dependence to that of ST-01 was observed for F-6 and UV100; on the other hand F-4 behaves as observed for P25. Since the amount of \cdot CH₂COOH radicals became almost constant at 0.1 M, we used 0.1 M acetic acid solution in the following experiments involving ESR measurement.

Table 1 shows the amount of radicals observed in situ for the five kinds of Pt/TiO₂ photocatalysts. For UV100, a large amount of \cdot CH₂COOH radicals was produced. To see whether this ESR observation represents the photocatalytic characteristics, products in the solution were analyzed in a separate experiment. Figure 4 shows the decomposition of CH₃COOH and the formation of CH₃CH₂COOH. The latter is the product of the radical reaction between \cdot CH₂COOH and \cdot CH₃. Although the decomposition of CH₃COOH for P25 is faster than that for UV100, the amount of produced CH₃CH₂COOH was larger for UV100. This observation in the product analysis is consistent with the ESR observation in which a larger amount of \cdot CH₂COOH radicals was observed for UV100 than for P25.

Table 1 also shows several properties of Pt/TiO₂ powders. To calculate crystalline size and anatase content, X-ray diffraction was measured for Pt/TiO₂ powders. The full width at half-

**Figure 5.** Change in the weight of Pt/TiO₂ (UV100 and P25) with heating.

maximum for the anatase peak at $2\theta = 25.28^\circ$ was used to estimate primary particle size with Scherrer's equation. The anatase component was calculated with the following equation:¹⁰

$$\text{anatase component (\%)} = 100 / (1 + 1.265 I_R / I_A)$$

where I_A represents the intensity of the anatase peak and I_R is that of a rutile peak at $2\theta = 27.42^\circ$.

The amount of surface OH group listed in Table 1 was calculated as the relative decrement of the weight from 150 to 600 °C. Figure 5 represents experimental observations in the thermogravimetry for UV100 and P25, which shows the change in the weight as a function of temperature. The rapid decrease of the weight at temperatures up to 150 °C is a result of the release of physisorbed water, and the next decrease up to 600 °C is for that of surface OH groups.¹¹ It is known that there are two types of surface OH groups, i.e., terminal Ti—OH and bridge Ti(OH)Ti. Dissociation temperatures of these surface OH groups differ from each other, and each temperature also could be affected by the chemical structure of the surroundings. Thus the decrease in the weight appears in the wide range of temperatures from 150 to 600 °C. A small increase at 900 °C corresponds to the oxidation of loaded Pt metal.

To investigate the effect of the surface OH group, Pt/TiO₂ (UV100) powder was calcined at various temperatures under a H₂ atmosphere. With this treatment, the surface OH group is known to be almost irreversibly removed or to take a long time to return in aqueous media.¹² Figure 6 shows the amount of intermediate radicals observed by using these treated Pt/TiO₂ powders. The amount of \cdot CH₂COOH radicals decreased markedly with the increase in the calcination temperature, while the amount of \cdot CH₃ radicals remained unchanged, although the

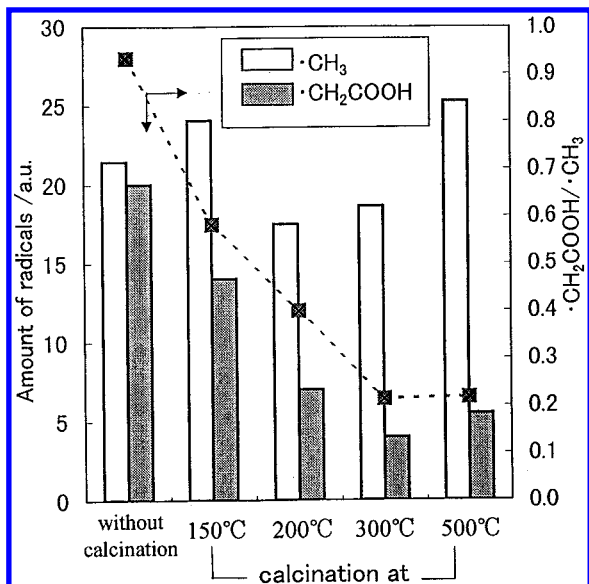


Figure 6. Effect of calcination up to 500 °C under a H₂ atmosphere on the amount of radicals for Pt/TiO₂ (UV100).

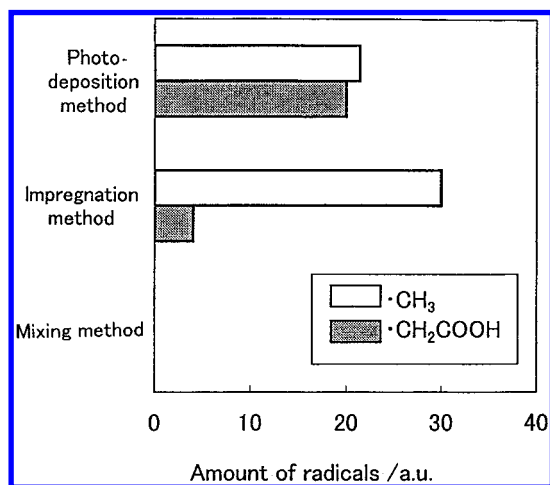


Figure 7. Relative amount of radicals for various methods of platinum loading on TiO₂.

values fluctuated. The decrease of ·CH₂COOH radicals with the calcination is responsible for the decrease of the surface OH group.

Figure 7 shows the difference in the amount of radicals for various platinumization methods. In the impregnation method, UV-100 TiO₂ powder was soaked in H₂PtCl₆ solution and then the powder was dried and calcined under H₂ atmosphere at 500 °C for 4 h. The Pt/TiO₂ powder obtained by the impregnation method produced amounts of two kinds of radicals similar to that for the photodeposited Pt/TiO₂ powder calcined at 500 °C (Figure 6). This observation shows that a similar catalyst could be prepared with both methods. When TiO₂ was platinumized by the mixing method, no radicals were observed in in-situ ESR measurements. Since this method of platinumization was performed by grinding TiO₂ powder with Pt black in an agate mortar, the platinumization should not be effective.

Discussion

In the previous report, we proposed a reaction scheme based on the flow-rate dependence of the radical formation³ combined with the reported mechanism^{13–16} for photocatalytic decomposition of acetic acid under deoxygenated condition. In this scheme, ·CH₃ radicals are formed via two reaction pathways. One is

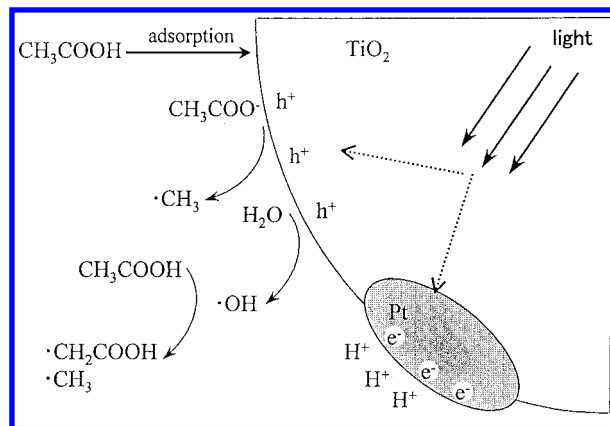
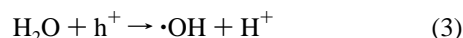


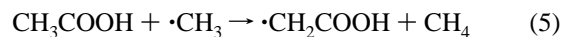
Figure 8. Schematic illustration of the initial decomposition of acetic acid under deaerated condition by using a Pt/TiO₂ photocatalyst.

direct hole oxidation (eq 1) of adsorbed molecules with photoinduced holes (h⁺) at the valence band. The other is indirect oxidation (eq 2) via ·OH radicals which are formed by the oxidation of water (eq 3). On the other hand, ·CH₂COOH radicals are formed only via ·OH radicals (eq 4). The proposed reaction scheme is illustrated in Figure 8.



In the present study the experimental observation showed that the ratio of the amounts of two radicals markedly changes for different kinds of TiO₂. Therefore, the properties of TiO₂ must control the initial process in the photocatalytic oxidation. That is, the oxidation starts directly by the surface trapped holes or proceeds indirectly via ·OH radicals. Since ·CH₃ radicals are formed from ·OH radicals as much as ·CH₂COOH,³ the ratio of the amount of radicals, [·CH₂COOH]/[·CH₃], is regarded as the ratio of the indirect oxidation. This ratio is listed in Table 1.

The formation process for ·CH₂COOH radicals via ·CH₃ radicals (eq 5) has been applied by Kaise et al. for in-situ ESR observations.^{4a}



On the basis of a careful review of the literature,^{14,15} however, we did not adopt this process in the previous report³. If this process is dominant in the formation of ·CH₂COOH radicals, the amount of ·CH₃ radicals should be parallel to that of ·CH₂COOH, because of the high concentration of CH₃COOH. In the present observations, however, the amount ratio of ·CH₂COOH to ·CH₃ varied significantly with the properties of Pt/TiO₂ photocatalysts. This supports our previous conclusion that ·CH₂COOH radicals are formed only by the reaction of ·OH radicals with CH₃COOH. This conclusion is also supported by a report¹⁷ in which an exclusive formation of ·CH₂COOH radicals by ·OH radicals was indicated for the photocatalytic decomposition of some chlorinated acetic acids.

Table 1 shows that the anatase content of Pt/TiO₂ ranging from 80% to 100% does not affect the oxidation pathways. A similar observation was reported for CH₂ClCOOH decomposi-

tion, where the photocatalytic decomposition rate is reported to be independent of the anatase content down to 15%.¹⁸

Photocatalytic activity has been usually considered to increase with decreasing crystalline size.¹⁹ The decomposition rate, however, is reported to be independent of the size in the case of decomposition of CH₃CICOOH.¹⁸ In the present research, no clear dependency on the total amount of radicals was presented as shown in Table 1, where TiO₂ is listed in the order of the primary particle size or crystalline size. The BET surface area also does not systematically affect the amount of radicals. The surface area which is measured by adsorbing N₂ molecules correlates naturally with the primary particle size, and then the surface area causes no effect on the total amount of radicals in the case of the primary size.

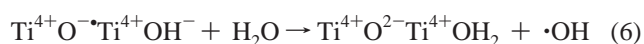
On the other hand, the secondary particle size correlates well with the total amount of radicals. One should keep in mind that photocatalytic reactions are initiated by the absorption of photons in the semiconductor grains. Penetration depth of light into the TiO₂ semiconductor is estimated to be 25 nm ($= \lambda/4\pi k$) based on the value of imaginary refractive index k of 1.0 at the wavelength λ of 320 nm.²⁰ This depth is far shorter than the secondary particle size of 0.4–2.6 μm , and only a part of the surface of the aggregated powder is illuminated. Therefore, not all parts over the surface of the photocatalytic particles contribute to the photocatalytic reaction. When the secondary particle size becomes smaller, the more illuminated part on the grain surface is exposed to the bulk solution. This is the reason for the observed correlation between the activity and the secondary particle size. Since the absorbed amount of photons is proportional to the mass of the powder, it seems appropriate to describe the properties on the basis of mass. Then, in Table 1 adsorbed CH₃COOH and surface OH group are expressed as the amounts per weight of Pt/TiO₂.

Although the amount per weight for the adsorption of CH₃COOH molecules changes more than 1 order of magnitude, the corresponding amount per BET surface area is almost constant (1.2–3.3 $\mu\text{mol}/\text{m}^2$). The small variation can be explained with the difference in the secondary particle sizes. That is, P-25 with the largest secondary particle size carries the smallest amount of CH₃COOH per surface area. The amount of adsorbed CH₃COOH shows no clear correlation with the amount of produced $\cdot\text{CH}_3$ radicals. As mentioned above, since $\cdot\text{CH}_3$ radicals are formed by a rather slow reaction of surface trapped holes with adsorbed CH₃COOH, the lifetime of the surface trapped holes may also contribute to the amount of $\cdot\text{CH}_3$ radicals. For F-4 Pt/TiO₂, the lifetime of holes would be longest among the TiO₂ powders used, because this photocatalyst produces a large amount of $\cdot\text{CH}_3$ radicals. It is reported that mixed anatase/rutile structure of the TiO₂ photocatalysts promotes charge-pair separation and inhibits recombination.⁶

The difference in the amount of surface OH group shows some correlation with the observed ratio of indirect oxidation. This observation is consistent with the experimental result in Figure 6, where the effect of calcination for UV100 Pt/TiO₂ is shown. These observations suggest that the TiO₂ powders having a large amount of surface OH group are apt to produce $\cdot\text{OH}$ radicals. The present authors estimated relative amounts of $\cdot\text{OH}$ radicals for these photocatalysts, by measuring the amount of O₂^{•−}.²¹ In this case, nonplatinized TiO₂ powders were suspended in pure water containing oxygen, and a chemiluminescence probe method²² was used for estimating the amount of O₂^{•−}. In the comparison with P25, UV100 TiO₂ showed the formation of a large amount of $\cdot\text{OH}$ radicals, which was deduced from the experimental result of the competitive reaction with

halide ions.²¹ This observation is consistent with the fact that UV100 prefers indirect oxidation for the acetic acid decomposition.

Recently, we have measured photoinduced ESR spectra at 77 K under vacuum for heat-treated UV100 TiO₂ powders.⁹ For the treated powders, photoinduced holes were trapped as Ti⁴⁺O^{2−}–Ti⁴⁺O^{•−} radicals at the surface, while for the untreated powder these holes were trapped at the subsurface forming Ti⁴⁺O^{•−}–Ti⁴⁺OH[−] radicals. When this observation is considered in connection with the ratio of indirect oxidation or $[\cdot\text{CH}_2\text{COOH}]/[\cdot\text{CH}_3]$ in Figure 6, the former trapped holes prefer the formation of $\cdot\text{CH}_3$ radicals and the latter is suitable for the $\cdot\text{OH}$ radical formation. The surface OH group seems to prevent the chemical adsorption which leads to the direct oxidation. However, since the amount of apparent adsorption per surface area was almost constant for the Pt/TiO₂ photocatalysts used, the water oxidation of eq 6 may occur rather more easily than that of eq 7.



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