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Photocatalytic reactivity for $O_2^{\bullet -}$ and $OH^{\bullet}$ radical formation in anatase and rutile TiO_2 suspension as the effect of H_2O_2 addition

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Abstract

Effect of crystalline structure, anatase and rutile, on the production of $OH^{\bullet}$ and $O_2^{\bullet -}$ by TiO_2 photocatalytic reaction was investigated. The $OH^{\bullet}$ radical free from the TiO_2 surface was monitored by the fluorescence intensity of 2-hydroxyl terephthalic acid produced by the reaction with terephthalic acid. Superoxide radical was detected by the chemiluminescence probe method with luminol. Formation rate of $OH^{\bullet}$ with rutile photocatalysts was significantly lower than that with anatase photocatalysts. By the addition of H_2O_2, the formation rate of $OH^{\bullet}$ was significantly increased for rutile and for anatase mixed with rutile by 10–20%, while pure anatase showed an opposite tendency. We suggest that the adsorption structure of H_2O_2 on the rutile TiO_2 surface is preferable to produce $OH^{\bullet}$. In photocatalytic production of $O_2^{\bullet -}$, rutile surpassed anatase in stabilizing the produced $O_2^{\bullet -}$. On H_2O_2 addition, anatase surpassed rutile in the photocatalytic activity to produce $O_2^{\bullet -}$ from H_2O_2.

Keywords: TiO_2; Photocatalytic reaction; Active oxygen species; Hydroxyl radical; Superoxide radical; Hydrogen peroxide; Luminol; Terephthalic acid

1. Introduction

TiO_2 photocatalytic reaction has been studied with much attention in recent years because it can be applied to the decomposition and mineralization of pollutant and/or undesirable compounds in air and wastewater [1–3]. In general, it has been reported that the TiO_2 photocatalytic reactions proceed mainly by the contributions of active oxygen species, such as hydroxyl radical, $OH^{\bullet}$, superoxide radical, $O_2^{\bullet -}$, and hydrogen peroxide, H_2O_2 [4–11]. Among them, $OH^{\bullet}$ radical is an extremely important species. Although the $OH^{\bullet}$ formation mechanism has been suggested as photocatalytic oxidation of water [4–11], the detailed mechanism on the TiO_2 surface is unclear so far, and a lot of efforts have been spent to elucidate the precise mechanism by many research groups [12–15].

Addition of H_2O_2 in the TiO_2 photocatalytic system accelerates the $OH^{\bullet}$ formation and then likely improves the reaction activity [16–19]. In this case, $OH^{\bullet}$ is formed on reduction of H_2O_2 with conduction band electron, e_{cb}^{-} (reaction (1)) or by $O_2^{\bullet -}$ (reaction (2)) [4]:

$$H_2O_2 + e_{cb}^{-} \rightarrow OH^{\bullet} + OH^{-} \tag{1}$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^{\bullet} + OH^{-} + O_2 \tag{2}$$

Furthermore, H_2O_2 is oxidized to $O_2^{\bullet -}$ by valence band hole, h_{vb}^{+} (reaction (3)) or by $OH^{\bullet}$ (reaction (4)):

$$H_2O_2 + h_{vb}^{+} + 2OH^{-} \rightarrow O_2^{\bullet -} + 2H_2O \tag{3}$$

$$H_2O_2 + OH^{\bullet} + OH^{-} \rightarrow O_2^{\bullet -} + 2H_2O \tag{4}$$

According to our previous studies, reaction (1) is the major reaction to produce $OH^{\bullet}$ from H_2O_2 [20,21], on the other hand the oxidation with h_{vb}^{+} (3) is the major reaction to increase $O_2^{\bullet -}$ concentration with H_2O_2 [20,21]. It has been widely reported that H_2O_2 is produced by disproportionation of $O_2^{\bullet -}$ and multiple reduction of O_2 in TiO_2 photocatalysis [4,16,20]. Since H_2O_2 is one of the intermediate species in TiO_2 photocatalytic reaction, it is important to study the behavior of H_2O_2 to understand the detailed mechanism of

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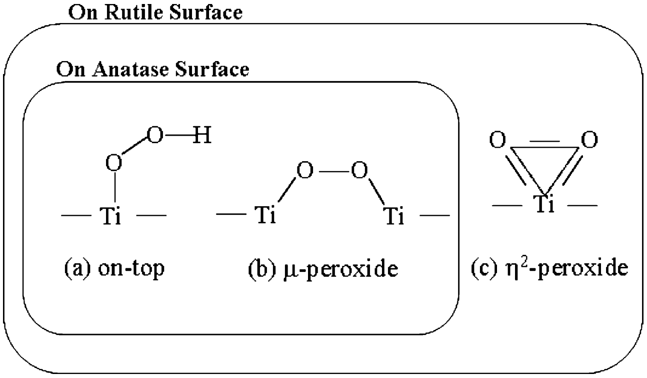

Scheme 1. Schematic diagram of H_2O_2 adsorption structure on the surface of anatase and rutile TiO_2 [23].

photocatalytic reaction, especially for clarifying the relationship with more reactive intermediates, $OH^•$ and $O_2^{•-}$.

In our previous study, P25 was mainly used as a photocatalyst [20,21], which is a mixture composed of 20% of large rutile crystallites and 80% of small anatase crystallites [22]. Ohno et al. have reported that the adsorption of H_2O_2 on the rutile surface with a specific structure (in Scheme 1(c)) increased the photocatalytic activity [23]. They also reported that the anatase TiO_2 produced mainly H_2O_2 while rutile TiO_2 produced $O_2^{•-}$ from O_2 [24]. This difference was explained by the higher photocatalytic activity of anatase TiO_2 and by the difference in the surface conditions of two crystalline structures. Since rutile TiO_2 has lower activity than anatase TiO_2 in general, a synergy effect was reported for the high photocatalytic activity by mixing rutile TiO_2 into anatase TiO_2 [25]. The mixture of anatase and rutile crystal has photocatalytic activity against the kind of photocatalytic reaction [26]. The reports mentioned above suggest that anatase and rutile will have characteristic properties on the reduction and oxidation of H_2O_2. By observing the difference in the reactivity of anatase and rutile, we can expect to utilize TiO_2 photocatalyst with H_2O_2 for treating wastewater under solar light, since the H_2O_2-adsorbed TiO_2 can absorb visible light.

In the present report, we investigated the ability of anatase and rutile to produce $O_2^{•-}$ and $OH^•$ by means of the luminol chemiluminescence (CL) method [20] and terephthalic acid (TA)–fluorescence (FL) probe method [13,20,21]. From the effect of the addition of H_2O_2, we verified the characteristic properties of anatase and rutile TiO_2 to produce the active oxygen species.

2. Experimental

2.1. Materials

Ten kinds of TiO_2 powders commercially available were employed as TiO_2 photocatalysts: Degussa P25 (Japan Aerosil), F4 (Showa Titanium) consisting of anatase–rutile mixture, ST-21 (Ishihara) and AMT600 (TAYCA) as anatase, and MT500B, MT-600B, MT-150W (TAYCA), HPC (High Purity Chemetal), Aldrich rutile (Aldrich) and PT101 (Ishihara) as rutile. All TiO_2 powders were generous gifts from corresponding manufacturers.

Table 1
Characteristics of TiO_2

Name	Anatase component (%)[a]	Primary particle size (nm)[a]	Supplier
ST-21	100	20	Ishihara Techno
AMT600	100	30	TAYCA
F4	92	28	Showa Taitania
P25	79	32	Japan Aerojir
MT-500B	1	35	TAYCA
MT-500B(H)[b]	0	52	–
MT600B	0	67	TAYCA
NT-150W	0	18	TAYCA
PT101	0	67	Ishihara Techno
AR	5	64	Aldrich
HPC	0	54	High Purity Chemetal

[a] Anatase component and primary particle size was calculated from XRD spectrum. Anatase component was calculated by using χ_A (%) = 100/(1 + 1.265I_R/I_A). Here, I_R and I_A were $2\theta = 27.42°$ and 25.25° as XRD peak intensity. Primary particle size was calculated by using Scherrer equation as $D = (k\lambda)/(\beta \cos \theta)$. Here crystal shape constant $k = 0.89$ and X-ray wavelength $\lambda = 0.15418$ nm on Cu Kα were used. β is half width of XRD peak intensity.

[b] MT-500B was sintered at 1073 K for 72 h.

MT500B powder was heat-treated at 1073 K in an electric furnace for 72 h and named MT500B(H). The primary particle size and the content of anatase crystallites of these TiO_2 powders are listed in Table 1.

2.2. Terephthalic acid (TA)–fluorescence (FL) probe method

Aqueous solution containing 0.01 M NaOH and 3 mM TA (Nacalai Tesque) was prepared and then 15 mg of TiO_2 powder was suspended in 3.5 cm^3 of the TA solution placed in a 1 cm × 1 cm Pyrex glass cell. In some cases, H_2O_2 was added up to 0.5 mM. The cell was placed in a dark box and the suspension was stirred by magnetic stirrer for 10 min prior to the UV irradiation. The light source for the excitation of TiO_2 was a 150 W Xe lamp (Hamamatsu Photonics, C2499). The excitation wavelength was confined to 387 ± 11 nm and light intensity was 40 mW cm^{-2}. The irradiation periods were varied to evaluate the growth rate. The intensity of fluorescence peak at 426 nm with 312 nm excitation, which is attributed to 2-hydroxyterephthalic acid (TAOH), was measured with a fluorescence spectrophotometer (Shimadzu RF-5300PC). The concentration of $OH^•$ was estimated by comparing the fluorescence intensity to that of the known concentration of TAOH [20]. The other experimental details have been described previously [20]. In this method, similar sizes of TiO_2 powders, P25, F4, ST-21 AMT600, MT500B and MT500B(H), were used to avoid the effect of particle size. In addition, PT-101 was also used as rutile because of the same size as the rutile part in P25.

2.3. Luminol chemiluminescence (CL) probe method

The formation of $O_2^{•-}$ was observed by using the luminol CL probe method with photon-counting system. Fifteen milligrams of TiO_2 powder was added into 3.5 mL of