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An approach to estimating photocatalytic activity of TiO_2 suspension by monitoring dissolved oxygen and superoxide ion on decomposing organic compounds

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Abstract

We proposed a novel method to analyze photocatalytic reaction of TiO_2 suspension by measuring the consumption process of dissolved oxygen (DO). The decay rates for DO consumption could be analyzed with Langmuir–Hinshelwood (L–H) kinetics as the effects of reactants such as ethanol and *iso*-propanol. Two parameters in the L–H kinetics, the maximum consumption rate r_{max} and adsorption equilibrium constant K_D were obtained. The rate constants, k_t and k_p, which express O_2 consumption and O_2 reproduction, respectively, could be estimated from dependence of r_{max} on excitation intensity. Participation of $O_2^{\bullet -}$ in the decomposition of alcohols was examined by measuring the amount of $O_2^{\bullet -}$. An increase of $O_2^{\bullet -}$ concentration was observed by the addition of a small amount of the reactants, and a decrease was observed for the reactant concentration of more than few mM. Based on these results, we analyzed the DO consumption process and suggested the applicability that the DO consumption efficiency can be used as a relative photonic efficiency to compare the differences in the photocatalytic activities and in the stabilities of reactants.
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1. Introduction

TiO_2 photocatalysis is developing into a popular technology to decompose and mineralize undesirable compound and pollutant in our surroundings [1]. On these decomposition and mineralization, TiO_2 photocatalysis consumes O_2. In earlier study on photocatalysis, this O_2 consumption was studied as "photo-adsorption" of O_2 [2]. The photo-adsorption of O_2 has been a general term of the consumption of O_2 by photocatalytic reaction. Actually, photocatalytic reaction should proceed simultaneously by reduction and oxidation. In general photocatalysis, O_2 in air is reduced to give $O_2^{\bullet -}$, while organic compounds are oxidized to form organic radicals which consume O_2 as well for further oxidation [3–5].

The formation of $O_2^{\bullet -}$ contributes to improving the photocatalytic activity to promote e^-–h^+ charge separation [6,7]. The details of the behavior of $O_2^{\bullet -}$ have been studied by luminol chemiluminescent (CL) probe method [8,9] and ESR spectroscopy [10]. According to the studies, the produced $O_2^{\bullet -}$ is adsorbed at the surface of TiO_2 and it becomes a steady amount during the irradiation [8,9]. The lifetime of $O_2^{\bullet -}$ after stopping UV irradiation was few seconds in air and several hundred seconds in water [8e, 9a,b] Some of the $O_2^{\bullet -}$ decay processes in different pH solution were observed by MIR-IR spectroscopy technique [11].

On disproportionation of $O_2^{\bullet -}$ and/or further reduction of $O_2^{\bullet -}$, H_2O_2 is produced from O_2 in the TiO_2 photocatalysis [7–14]. In addition, H_2O_2 can be also produced by a chain reaction of O_2 with the intermediate radicals of alcohol [3,4]. Details of the formation and reaction processes of H_2O_2 in TiO_2 photocatalysis have been studied more extensively than the behavior of O_2 and $O_2^{\bullet -}$. The produced H_2O_2 is oxidized to form $O_2^{\bullet -}$ and reduced to $OH^{\bullet}$. Although H_2O_2 has relatively

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high reactivity, $OH^{\bullet}$ is likely more considerable species to oxidize organic compounds [7,8,10,12–15].

As introduced above, despite we know that O_2 is necessary species as an electron donor to promote charge separation and as an oxidant to decompose organic molecules in TiO_2 photocatalysis, the behavior of O_2 has not been correlated with the photocatalytic activity of TiO_2 suspension. Although, oxygen consumption focusing on O_2 reduction was kinetically studied [16], the study on the kinetics of O_2 consumption process under whole photocatalysis with a reactant has not been fully carried out yet. In addition, since the behavior of active oxygen species in the photocatalytic oxidation with a reactant has not been analyzed from the quantitative points of view, the detailed reaction mechanism involving O_2 and active oxygen species in photocatalysis carries still unclear points.

In the present study, the amount of dissolved oxygen (DO) in TiO_2 photocatalytic system with a reactant is kinetically analyzed to obtain the information of reaction mechanism including O_2. Furthermore, we also report here the reaction of $O_2^{\bullet -}$ with the organic reactant as one of the DO consumption processes by observing the amount of $O_2^{\bullet -}$ produced in the TiO_2 photocatalysis. As model organic compounds, we employed ethanol and *iso*-propanol because the reaction mechanism of these alcohols has been widely studied [17–21] and their oxidation processes are different; ethanol oxidation process contains a chain reaction with O_2, whereas no chain reaction takes place in *iso*-propanol decomposition process [3,17–21].

2. Photocatalytic reaction model for oxygen consumption

The DO decay process in TiO_2 photocatalysis with a reactant was considered to obey the following reaction steps as illustrated in Scheme 1. Firstly, conduction band electron (e^-) and valence band hole (h^+) are induced by UV-light excitation (reaction (1)). Though some of them recombine each other in a TiO_2 particle (reaction (2)), the produced e^- and h^+ react with O_2 (reaction (3)) and alcohols (ROH) (reaction (4)), respectively:

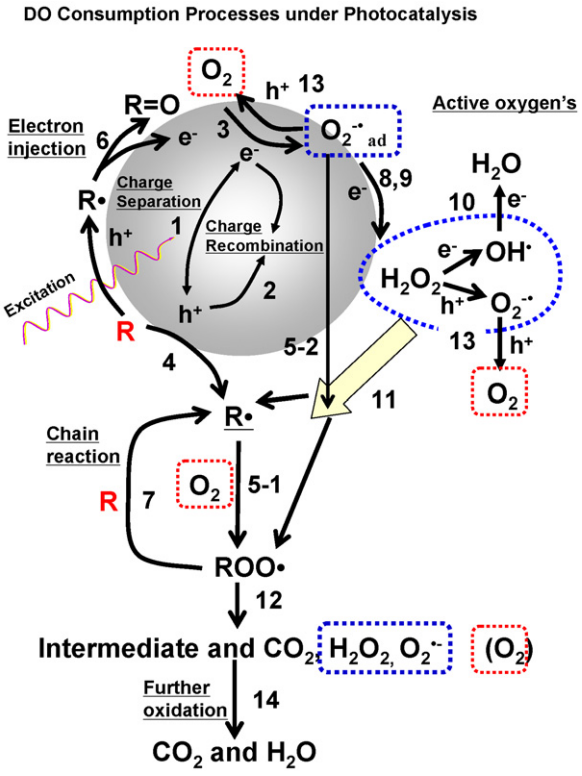
$$TiO_2 + h\nu \rightarrow Ti^{3+}(e^-) + h^+ \quad (1)$$

$$Ti^{3+}(e^-) + h^+ \rightarrow h\nu\,(\text{heat}) \quad (2)$$

$$O_2 + Ti^{3+}(e^-) \rightarrow Ti^{4+}\text{–}O_2^{\bullet -} \quad (3)$$

$$h^+ + ROH \rightarrow R^{\bullet}OH \quad (4)$$

where $R^{\bullet}OH$ is an intermediate radical of the reactant and reacts with O_2 to produce oxygenated radical intermediate, $ROO^{\bullet}$ (reaction (5.1)) [2–5]. Though a lot of researchers consider so-called OH radical reaction path, the formation of $OH^{\bullet}$ radical was not supported from EPR [22,23], and IR measurements [24]. We have also discussed the detection method of $OH^{\bullet}$ radicals previously [25]. Then we think that in TiO_2 photocatalytic reactions, $OH^{\bullet}$ radical is minor oxidative reaction species, and instead, valence band hole and trapped hole are major oxidative reaction species, especially, in the present condition as ethanol adsorption at the surface of TiO_2.



Scheme 1. DO consumption processes under photocatalysis.

It has been suggested that the reaction of $O_2^{\bullet -}$ with ROH is relatively disregarded. However, the $O_2^{\bullet -}$ produced by reaction (3) can react with $R^{\bullet}OH$ directly (reaction (5.2)) as has been reported [2–5]:

$$R^{\bullet}OH + O_2 \rightarrow ROO^{\bullet} \quad (5.1)$$

$$R^{\bullet}OH + O_2^{\bullet -} \rightarrow ROO^{\bullet} \text{ or other oxygenated radical intermediate} \quad (5.2)$$

Actually, radical intermediates $R^{\bullet}OH$ on TiO_2 photocatalytic oxidation of ethanol and *iso*-propanol produce $CH_3(CH^{\bullet})OH$ and $(CH_3)_2C^{\bullet}OH$, respectively [3,17–26]. The reaction rate of these radical intermediates with O_2 (reaction (5.1)) is very fast. That is, the bi-molecular rate constants are of diffusion limit; k ($^{\bullet}CH_2OH + O_2$) $= 4.9 \times 10^9\ M^{-1}\ s^{-1}$ and k ($(CH_3)_2C^{\bullet}OH + O_2$) $= 4.2 \times 10^9\ M^{-1}\ s^{-1}$ [26]. This reaction may compete with an electron injection into TiO_2 solid as expressed by reaction (6):

$$R^{\bullet}OH + TiO_2 \rightarrow R{=}O + H^+ + TiO_2\,(e_{CB}^-) \quad (6)$$

The redox potential $E_{1/2}$ for $CH_3CH^{\bullet}OH$ and $(CH_3)_2C^{\bullet}OH$) are -0.94 and -1.06 V (versus NHE: at pH 7) [27], respectively, while the potential of the conduction band of TiO_2 is -0.81 V (versus NHE) calculated from -0.13 to 0.059 pH with a pH of 11.5 [28]. Then, the radical intermediates could inject an electron to the conduction band. The electron injection from intermediate radical is much faster than the reaction with O_2 since the surface of photocatalysts locates near the radical. In the present study, we supposed that the injected electrons increase the reduction of O_2

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