Analysis of Photocatalytic Reactions Using a TiO₂ Immobilized Microreactor

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We have developed an analysis system for photocatalytic reactions, which utilizes a TiO₂ immobilized micro-capillary and a detection technique for dye concentration at arbitrary positions. In this study, we investigated the reaction processes for the photocatalytic decomposition of rhodamine 6G. This system allows the distinction of direct and secondary photocatalytic reactions under the same experimental conditions. The direct reaction occurs between adsorbed species and photoexcited electrons or holes, while the secondary reaction is induced by radicals, such as $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, generated in water or ethanol. The entire reaction was studied by monitoring the dye concentration in the UV irradiated area, while only the secondary reaction was monitored outside the UV irradiated area.

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Introduction

Titanium oxide (TiO₂) is one of the most popular materials for photocatalysis.^{1,2} In the last 20 years, it has been used for practical purposes, especially for environmental cleanup.³ It exhibits two attractive properties upon UV irradiation, namely the decomposition of organic pollutants and superhydrophilicity.⁴ In the photocatalytic decomposition reaction, radical species generated by UV light irradiation cause the decomposition. Several types of radical species are known to be involved in the reaction, and their lifetime depends on conditions such as solution pH and temperature.⁵⁻⁸ Photocatalytic processes are classified into direct⁹⁻¹² and secondary¹³⁻¹⁵ reactions. Direct reactions occur between adsorbed species and photoexcited electrons or holes, while secondary reactions are induced by active oxygen species generated in the solvent after photoexcited electrons and holes react with solvent molecules. Most studies on photocatalytic reactions have not considered the two reaction processes within the overall reaction.

In this study, we developed a system to monitor a photocatalytic reaction inside a TiO₂ immobilized microcapillary reactor. Using a microreactor increases the surface ratio of TiO₂, accelerating the reaction speed.¹⁶⁻¹⁸ In addition, the photocatalytic reaction can be observed without the influence of concentration inhomogeneity due to the small reaction volume. The photocatalytic processes were monitored separately in UV and non-UV irradiated areas. Only the secondary reaction can be observed outside the UV irradiated area because photoexcited electrons and holes are generated only in the UV irradiated area, while the total reaction can be analyzed in the UV irradiated area.

Experimental

A dispersion solution of TiO₂ (CZL-523, Taki Chemical Ltd.) was used to coat the inside of a capillary (i.d. = 530 μm , o.d. = 660 μm). The dispersion solution included 5% TiO₂ particles with a diameter of 8 nm. A transparent capillary was treated with an alkali solution. The solution was introduced into the capillary using capillary action three times, and washed with water; this procedure was repeated three times. The capillary was dried at room temperature for 24 h. Rhodamine 6G (Rh6G) was used as a reactant and its concentration was 50 μM . The reasons why this dye was selected as a reactant is;

Fig. 1 Experimental setup for simultaneous UV light irradiation to induce photocatalytic reactions and measurement of the dye concentration.

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Fig. 2 Temporal changes in the rhodamine 6G concentration inside a microcapillary during UV irradiation. The numbers correspond to the ethanol volume fractions, which were varied from 0 to 100%.

the photocatalytic reaction was investigated in other papers, it is a well-known laser dye and has a strong light tolerance, and it should have absorption at around 532 nm for detection. The dyes were injected into the capillary using a syringe pump (Fig. 1). The photocatalytic reaction was initiated by UV light irradiation. The concentration change in the dye was monitored by a near-field heterodyne grating (NF-HDG) method.¹⁹ In this method, the signal intensity is proportional to the absorbance at the pump wavelength, and thus to the dye concentration in a microscale vessel. The error of this signal was less than 5%. The UV source was a UV-LED ($\lambda = 365$ nm) with an intensity of 3200 mW/cm² and a beam diameter of 3 mm. In the NF-HDG method, a Nd:YAG laser ($\lambda = 532$ nm) with an intensity of 15 mW was used as a pump light, and a He-Ne laser ($\lambda = 633$ nm) with an intensity of 2.0 mW was used as a probe light. The solvent was an ethanol/water mixture (0–100%), used to understand whether the reaction processes were affected by the viscosity.

In the direct reaction, photoexcited electrons and holes are generated by irradiating a TiO₂ surface, and adsorbed molecules react with electrons and holes, causing the molecules to decompose. On the other hand, in the secondary reaction, reactive radicals, such as O₂^{•-} and OH[•], are generated on a TiO₂ surface upon reactions of the surrounding oxygen and water with electrons and holes. These reactive radicals are the source for the decomposition. Although direct and secondary reactions occur at the UV irradiated position, only the secondary reaction proceeds at the UV non-irradiated position. During measurements performed outside at the UV irradiated area, the solution was maintained under flow conditions and the concentration of the dye was monitored at arbitrary positions from the UV irradiated position. Measurements at various positions give information on the temporal concentration changes because the reaction time at each position corresponds to the ratio of the distance from the UV irradiated position and the flow velocity. For this experiment, the flow rate was set at 9 mm/min, determined from the experimental result that the decomposition reaction at the UV-irradiated area does not proceed too much, and that sufficient active oxygen species are generated for the photocatalytic reaction during 20 s, which is the time for the sample passing through the UV irradiated area (3 mm).

Fig. 3 Dependence of the reaction rates on the ethanol volume ratios in solution. The rates were calculated from the results given in Fig. 2.

Fig. 4 Dependence of the EtOH solution viscosities (25°C) on the mixture ratios.

Results and Discussion

Reaction in the UV irradiated area

The change in the Rh6G concentration was monitored at the UV-irradiated position under a stop-flow condition. Figure 2 shows decay curves for the NF-HDG signal intensity resulting from the photocatalytic decomposition of Rh6G in the ethanol/water solvent mixture. The decomposition time was found to depend on the ethanol/water mixing ratio. The decay curves were fitted with a single exponential function, suggesting that the concentration decreased according to a pseudo-first-order reaction scheme.

The reaction rate (r), equal to the inverse of the decay time, is shown in Fig. 3. The reaction rate took a minimum at around a mixing ratio of 50% and increased for all other ratios, except for a ratio of 0%. The inverse of the viscosity for the solvent mixture (Fig. 4) took a maximum around a mixing ratio of 50%, showing a similar profile as the one displayed in Fig. 3. If the reaction rate does not depend on the viscosity of the solvent, it is considered that the reaction takes place not in the liquid phase, but at solid/liquid interfaces, and thus the viscosity dependence implies that the reaction occurred in the liquid phase. If this reaction is assumed to occur between the dye and an active oxygen species, the reaction rate may be explained using a two-body reaction mechanism. The reaction rate is expressed as

$$r(t) = -\frac{dC_{\text{dye}}(t)}{dt} = kC_{\text{dye}}(t)C_{\text{AOS}}(t), \quad (1)$$

where k is the rate constant, and C_{dye} and C_{AOS} are the

Fig. 5 Signal intensity for rhodamine 6G solutions as a function of the distance from the UV irradiated position. The distance was measured from the edge of the UV light. Open circles represent the signal intensities for the rhodamine 6G solutions before passing through the UV-irradiated area and the filled circles represent the signal intensities just after passing through the UV-irradiated area. The longitudinal axis for each solution has the same intensity scale.

concentrations for the dye and active oxygen species, respectively. $C_{AOS}(t)$ was considered to be constant (C_{AOS}) due to the rapid equilibrium between the generation and deactivation of this species. C_{dye} follows

$$C_{dye}(t) = A \exp(-t/kC_{AOS}), \quad (2)$$

and therefore, the decay time is constant and equal to kC_{AOS} . The rate constant of the two-body reaction is proportional to the diffusion coefficients of the two species. It is thus inversely proportional to the viscosity because the diffusion coefficient is inversely proportional to the viscosity. The similarity in the profiles shown in Figs. 3 and 4 support this assumption. Therefore, the secondary reaction was found to be the dominant process for Rh6G decomposition. The reaction rate for a mixing ratio of 0% is slower than expected, but the reason is not yet clear.

Reaction outside the UV irradiated area

Changes in the Rh6G concentration were monitored at UV non-irradiated positions to study secondary reactions involving active oxygen species only. In this experiment, the solution was kept under flow conditions, and the dye concentration was monitored at a defined distance from the UV-irradiated position (0–20 mm). The solvent was an ethanol/water mixture (0–100%). Figure 5 shows the signal intensity before (open circle) and after passing the solution in the UV irradiated area for a distance of 0 mm. The concentration of Rh6G gradually decreased, even outside the UV irradiated area. For ethanol/water mixture ratios of 3 and 10%, the dye concentration decreased up to a distance of 2.5 mm, but the decomposition did not proceed further for greater distances. In contrast, for mixture ratios of 50 and 100%, the concentration decreased up to a distance of

10 mm. As mentioned above, the reaction time at each position corresponds to the ratio of the distance from the UV irradiated position with the flow velocity. Therefore, for ethanol/water mixture ratios of 3 and 10%, the decomposition continued for 15 s after passing through the photoirradiated area, while for mixture ratios of 50 and 100%, the decomposition continued for 60 s.

Because the reported lifetimes of $OH\cdot$ and $O_2^{\cdot-}$ are 1 s and several tens of seconds,⁵ respectively, it is supposed that the decomposition in water-rich solvents (ethanol ratio: 3 and 10%) is caused by $O_2^{\cdot-}$. However, there may be another reactive species in ethanol-rich solvents because of the longer lasting decomposition. It was reported that alcohol solvents are changed into reactive radical species by being oxidized by photoexcited holes,^{20,21} and thus the ethanol radical generated in the photocatalytic reaction would cause decomposition.

In summary, the results show that the decomposition reaction of Rh6G occurred in a solvent. In the UV-irradiated area, the photocatalytic reaction originated due to the active radical species, and long-lived radical species were involved in the reaction outside of the UV irradiated area.

Conclusion

We combined a TiO_2 immobilized microreactor and a detection technique inside a microchannel to develop an analytical method for photocatalytic reactions. Although photocatalytic reactions have usually been characterized as simple pseudo-first-order reactions, actual reactions simultaneously proceed in the liquid phase and on the solid surface depending on the reactants and various radical species involved. The actual reaction steps are therefore difficult to follow, and this analytical system may be helpful for the explanation.

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