

Efficient Dihydroxylation of Naphthalene on Photoirradiated Rutile TiO₂ Powder in Solution Containing Hydrogen Peroxide

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We report on enhanced dihydroxylation of naphthalene on photoirradiated TiO₂ particles by addition of H₂O₂ to the reaction solution. The rate was enhanced by 6–40 times by the addition of H₂O₂, and the quantum yield reached as high as 76% for rutile TiO₂ powders. On the other hand, no such enhancement was observed for anatase TiO₂ powders.

TiO₂-mediated photocatalytic reactions have recently been the subject of many works due to their potential applications to environmental cleanup,^{1–3} and solar energy conversion.^{4–6} Utilization of photocatalysts for organic syntheses is also an interesting application.^{7–13} In the previous letter, we reported that naphthalene is converted to dihydroxynaphthalene on photoirradiated TiO₂ powder in a mixed solvent of water/acetonitrile.¹⁰ This reaction is interesting because 1) the main products are 1,3- and 1,8-dihydroxynaphthalenes, and no monohydroxynaphthalenes are produced, 2) the quantum yields reach as high as 2.9% and 7.3% for 1,3- and 1,8-dihydroxynaphthalenes, respectively, 3) the presence of both molecular oxygen and water is essential to obtain these products, 4) the yield of dihydroxynaphthalenes reaches about 90% based on the amount of naphthalene consumed. These results indicate that the reaction is fairly efficient and specific. Such properties are in contrast to many photocatalytic reactions in aqueous solutions, where organic substances are randomly oxidized by •OH radical to produce finally carbon dioxide.¹⁴

The efficiency of the production of dihydroxynaphthalene is fairly high compared with many other photocatalytic reactions. However, for the application to organic syntheses it is preferable to raise the efficiency further. To enhance the efficiency, the addition of chemical oxidants has been reported to be useful for many kinds of reactions.^{15–20} However, the roles of the oxidants and the reproducibility are still controversial.

In this letter, we report that the dihydroxylation of naphthalene on photoirradiated TiO₂ particles is strongly enhanced by the addition of H₂O₂ to the solution containing rutile TiO₂ particles. However, the reaction was not enhanced when anatase TiO₂ particles were employed.

The photocatalytic reactions of naphthalene were carried out in 5 mL of mixed solution (acetonitrile : water = 94 : 6 by volume). Acetonitrile has sometimes been used as an inert solvent for photocatalytic reactions using TiO₂.¹² To this solvent 0.015 g of TiO₂ and 0.1 g of naphthalene were added. The solution was bubbled with O₂ gas, magnetically stirred, and externally photoirradiated using a 500-W Hg lamp. The irradiation intensity was lowered to ca. 1.4% using stainless meshes, and deep UV light was eliminated by passing the light beam through a cut-off glass filter ($\lambda < 340$ nm). Reaction products were analyzed by a high-performance liquid chromatograph (HPLC) equipped with an ODS column. Different kinds of

TiO₂ powders, which were obtained from the Catalysis Society of Japan (TIO-2,3,5) and commercial sources (P25, CR-EL, ST-11, ST-01, PT-101), were used as the photocatalysts. The quantum yield of the reaction was determined at a wavelength of 365 nm, which was chosen from the Hg lamp using band-pass filters, on the assumption that all the irradiated photons were absorbed by TiO₂ particles. The number of irradiated photons was determined using a potassium tris(oxalato)-ferrate chemical actinometer. The details of the experimental conditions were described previously.¹⁰

1,8- and 1,3-dihydroxynaphthalenes were always obtained as the main products of the photocatalytic reaction, as shown in Figure 1a. Small amounts of 1,4-dihydroxynaphthalene and unknown compounds were also produced, but no monohydroxylated naphthalenes, i.e., 1- and 2-naphthols, were obtained.¹⁰ As shown in Figure 1b, by the addition of H₂O₂ to the solution containing rutile powders, the production of dihydroxynaphthalenes was enhanced by 6–40 times. In contrast, practically

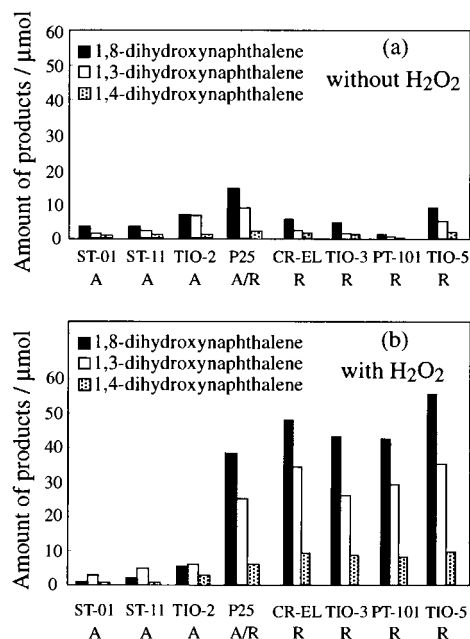


Figure 1. Photocatalytic dihydroxylation of naphthalene on various kinds of TiO₂ in solutions without (a) and with (b) H₂O₂ (0.2 mmol). The reaction was carried out for 1 h in mixed solution (5 ml) of CH₃CN and H₂O (6% in volume) containing TiO₂ (0.015 g) and naphthalene (0.78 mmol). The solution was bubbled with O₂. The main crystalline structure of each TiO₂ powder is denoted by A (anatase) and R (rutile).

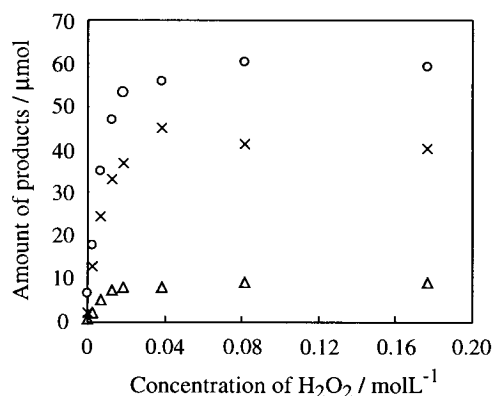


Figure 2. Influence of H₂O₂ concentration on production of 1,8-dihydroxynaphthalene (○), 1,3-dihydroxynaphthalene (×), and 1,4-dihydroxynaphthalene (△) on rutile TiO₂ powder (TiO-5). Reaction conditions are the same as those shown in Fig. 1.

no enhancement was observed for anatase TiO₂ powders. In the case of P25, which has 30% rutile phase and 70% anatase phase, the reaction was enhanced by 2.6 times by the addition of H₂O₂.

The influence of H₂O₂ concentration on the photocatalytic reaction is shown in Figure 2, where TiO-5 (rutile) was used as the photocatalyst. The reaction rate was drastically enhanced by the addition of H₂O₂ at concentrations higher than 0.02 M. The quantum efficiency of the production of dihydroxylated compounds (1,8- and 1,3-dihydroxynaphthalenes) reached as high as 76% at an H₂O₂ concentration of 0.058 M. The efficiency was determined on the assumption that 4 holes are necessary to form one dihydroxynaphthalene molecule. When H₂O₂ was added to the solution, this high reaction efficiency was obtained without bubbling oxygen. From the analysis of the reaction products, it was found that 55 and 35 μmol of 1,8- and 1,3-dihydroxynaphthalenes were generated after photoirradiation for 1 h, during which 127 μmol of naphthalene (17% of the initial amount) was consumed.

Enhancement of photocatalytic reactions by the addition of H₂O₂ has generally been attributed to the formation of •OH radicals as the result of the reaction with electrons in the conduction band of TiO₂.¹⁸ However, in the present case, these •OH radicals are not considered to be the main oxidant, judging from the absence of 1- and 2-naphthols in the products. The enhancement may be attributable to the strong electron accepting ability of H₂O₂. This leads to efficient separation of electrons and holes, and to the improved oxidation of the reactants. However, this model is not sufficient to explain why the reaction is enhanced only in the case of rutile particles. To discuss the effect of H₂O₂, the energy levels and oxidation power of rutile and anatase TiO₂ powders are the important criteria.

The conduction band edge of anatase TiO₂ is reported to be at ca. -0.7 V vs NHE at pH 7, and that of rutile TiO₂ at ca. -0.5 V vs NHE.²¹ On the other hand, the reduction potential of molecular oxygen at this pH is at -0.563 V vs NHE.²² Because of the higher (more negative) energy level of the conduction band of anatase TiO₂, the electron transfer to oxygen is considered to be an efficient process, and there may be no room for

further enhancement by the addition of H₂O₂ to the solution. Contrarily, in the case of rutile TiO₂, the rate can be enhanced by the addition of H₂O₂, because the electron transfer to oxygen is an uphill process in energetics.

As regards the oxidation power of holes generated in photoirradiated TiO₂ particles, we have evidence indicating that the holes in rutile particles are more reactive than those in anatase particles as follows. On rutile particles, water can be efficiently oxidized to oxygen in the presence of suitable electron acceptors, such as Fe(III) and Ag(I) ions.^{4,5} In contrast, the oxidation of water hardly proceeds on anatase particles even when these electron acceptors were added to the solution. On anatase particles as well as on rutile particles, alcohols, which are chemically reactive, are easily photo-oxidized. These results suggest that the hole transfer from the valence band of anatase TiO₂ to a species in solution is not an easy process, if it is hard to oxidize. Since naphthalene is rather difficult to oxidize, the hole transfer from the valence band of anatase particles is probably a slow process, which controls the reaction rate. Hence, in this case no enhancement is expected by the addition of H₂O₂.

In conclusion, we found that dihydroxylation of naphthalene on photoirradiated TiO₂ powder is enhanced by the addition of H₂O₂ when rutile TiO₂ is used as the photocatalysts. This effect is considered to be applicable to other organic synthetic reactions on TiO₂ photocatalysts, especially to hydroxylation reactions.

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