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Photooxidation of organic compounds in a solution containing hydrogen peroxide and TiO_2 particles under visible light

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Abstract

Cyclohexane was oxidized under visible light in a titanium dioxide suspension containing hydrogen peroxide. Cyclohexanol and cyclohexanone were detected as products. Under similar experimental conditions, nonyl aldehyde was oxidized to nonylic acid. The reaction rate for the oxidation on rutile particles was faster than that on anatase particles. When hydrogen peroxide was added to suspensions of these particles, both rutile and anatase particles became yellow-colored due to the formation of peroxide complexes on their surfaces. The difference between the reaction rates for rutile and anatase particles suggests that the properties of the peroxide complexes formed on these particles are different. The properties of these complexes were studied by UV–vis spectroscopy.

1. Introduction

Photocatalytic reactions have attracted much interest with regard to decomposition and mineralization of pollutants and undesirable compounds in air and waste water [1–10]. The reactions are also interesting from the viewpoint of organic syntheses [11–17]. In most of these reactions, TiO_2 particles have been utilized as the photocatalyst. Photogenerated electrons and holes in the TiO_2 particles reduce and oxidize species adsorbed on the TiO_2 particles, respectively. UV irradiation is necessary to generate electrons and holes in TiO_2 particles. The threshold wavelengths are about 410 nm for rutile particles and about 390 nm for anatase particles at room temperature. Extension of the photoactive wavelength region of photocatalysts into the visible region is desirable for increasing the activity of photocatalysts, especially when they are used under room light or sunlight. For this purpose, CdS [18, 19], WO_3 [20, 21], and some other semiconductor particles with band gaps of less than 3.0 eV have been utilized. Recently, TiO_2 photocatalyts doped with N-atoms [22, 23] or S-atoms [24] have been demonstrated to react under visible light. However, TiO_2 particles are still used most frequently for practical applications due to their chemical stability, non-toxicity and high activity.

Utilization of complexes formed on the surfaces of TiO_2 particles provides another approach to the extension of the photoactive absorption region of TiO_2 photocatalysts into the visible region. Ikeda et al. [25] reported that TiO_2 photocatalysts showed activity under visible light when complexed with an aromatic diol. Li et al. [26] and we [27] have reported that TiO_2 shows activity under visible light when hydrogen peroxide is adsorbed on the surfaces of particles. When complexed with H_2O_2, colorless Ti(IV) ions or TiO_2 particles change to yellow owing to the specific interaction with hydrogen peroxide. The coloration of TiO_2 particles by hydrogen peroxide is thought to be related to their photocatalytic activity under visible light. However, we found from the results obtained for the photocatalyzed epoxidation of olefin that the strength of the coloration was not straightforwardly correlated with activity under visible light [27]. In this case, anatase particles showed a low level of activity even though they were colored intensively by H_2O_2, whereas rutile particles showed a high level of activity when colored by H_2O_2. We attributed the difference in their activities to the formation of different complexes. However, further study is required to clarify the exact reason. For this purpose, the effect of hydrogen peroxide must be studied in other types of reactions.

In this study, we focused on the photoreaction under visible light and investigated the oxidation of cyclohexane, nonyl aldehyde and naphthalene, which were used as model compounds. The interaction between TiO_2 and

Table 1. Physical properties of TiO_2 powders used in this study

TiO_2 powder	Crystal structure	Anatase component /%	Surface area /$m^2 g^{-1}$	Purity[a] /%
CR-EL	Rutile	<0.1	7.1	99.8
PT-101	Rutile	<0.1	25	99.9
TIO-3	Rutile	<1.0	48.1	99.1
MT-150W	Rutile	<0.1	94.7	>91.0
ST-21	Anatase	>99.9	56.1	95
ST-01	Anatase	>99.9	236	95

[a] The purity indicates the weight content of TiO_2 in the powder. The remainder is mostly water.

H_2O_2 was also studied by UV-vis spectroscopy. It should be noted that H_2O_2 is photocatalytically produced from oxygen on photoirradiated TiO_2 [28, 29] and that photocatalytic oxidation of some compounds is activated by addition of H_2O_2 [30]. Hence, in order to obtain insights into many kinds of TiO_2-photocatalyzed reactions, it is important to study the effect of the addition of H_2O_2 to the reaction solution.

2. Experimental section

Various kinds of titanium dioxide (TiO_2) powders containing either anatase or rutile crystal structures were obtained from the Catalysis Society of Japan (JRC-TIO-3), Ishihara Sangyo Co. (ST-01, ST-21, PT-101, and CR-EL), and TAYCA Co. (MT-150 W). The properties of these TiO_2 powders are summarized in Table 1. Cyclohexane, cyclohexanol, cyclohexanone, hydrogen peroxide and acetonitrile were purchased from Wako Pure Chemical Industries Co. Nonyl aldehyde, nonylic acid, and butyronitrile were purchased from Tokyo Kasei Co. They were all guaranteed-grade reagents and used without further purification.

Photocatalytic reactions were carried out in Pyrex glass tubes (ϕ = 10 mm) that contained TiO_2 powder (50 mg), 30% hydrogen peroxide and butyronitrile. In the case of oxidation of cyclohexane, cyclohexane (0.5 g) and butyronitrile (1.5 g) were added to the reaction tube. In the case of oxidation of nonyl aldehyde, nonyl aldehyde (0.1 g) and butyronitrile (1.9 g) were added to the reaction tube. During the photocatalytic reaction, the TiO_2 particles were suspended in the solution using a magnetic stirrer. The suspension was photoirradiated using a 500-W Xe lamp (Wacom R&D) or a 1-kW Xe lamp (XDS-501I). To evaluate the photocatalytic reactivity under visible light a cutoff filter (Kenko Co., Y-44) that eliminates light of wavelengths shorter than 440 nm was used. The products were analyzed with a gas–liquid chromatograph (Shimadzu GC-8A). A Silicone DC-550 column was used for analysis of the products from cyclohexane, and a TC-WAX column was used for analysis of the products from nonyl aldehyde. The products were identified by co-injecting the corresponding authentic samples into the columns. UV–visible diffuse reflection spectra were obtained using a Shimadzu 2450 spectrophotometer with an integrating sphere, and the spectra were converted to the Kubelka–Munk (K–M) function [31].

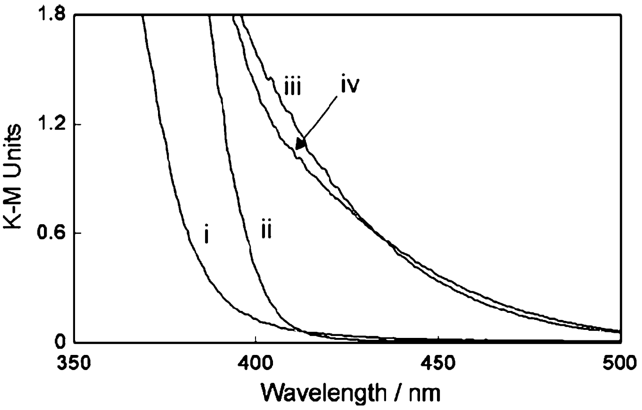

Fig. 1. Diffuse reflection spectra of TiO_2 powders displayed using the K–M function: (i) ST-01 (anatase), (ii) MT-150W (rutile), (iii) ST-01 treated with 15% H_2O_2 solution, and (iv) MT-150W treated with 15% H_2O_2 solution.

3. Results and discussion

3.1. *Coloration of TiO_2 particles by treatment with H_2O_2*

It is well known that TiO_2 is colored by treatment with H_2O_2. We experimentally observed that both anatase and rutile powders became yellow-colored after soaking in an aqueous solution of 15% H_2O_2. Figure 1 shows the diffuse reflection spectra of TiO_2 powders before and after treatment with H_2O_2. It can be seen that both rutile and anatase powders show red shifts in the photoabsorption into the visible region. Generally, stronger coloration was observed for samples with a larger specific surface area, suggesting that the coloration is due to the formation of a complex on the particle surface.

3.2. *Photocatalytic reaction of cyclohexane and nonyl aldehyde under visible light*

Many organic compounds in solution undergo oxidation under UV light in the presence of oxygen, whereas no reaction proceeds under visible light. Like many compounds, cyclohexane added to a TiO_2 suspension can be oxidized under UV light [32, 33]. However, when the suspension contained hydrogen peroxide, the reaction did proceed under visible light, and we detected cyclohexanol and cyclohexanone in the solution after photoirradiation for a certain time period. Even when both hydrogen peroxide and TiO_2 powders were present, no reaction proceeded without photoirradiation. The amounts of these products obtained after photoirradiation for 1 h using different TiO_2 powders as

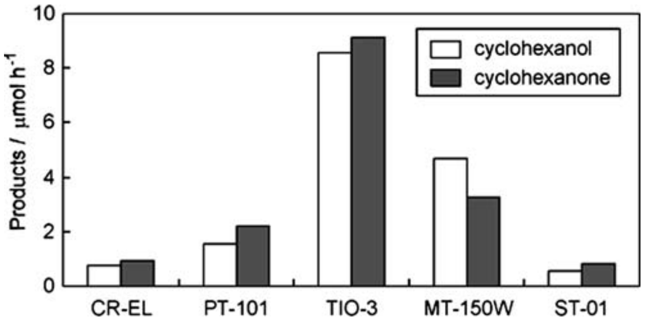

Fig. 2. Amounts of cyclohexanol and cyclohexanone produced from cyclohexane in different kinds of TiO_2 suspension by visible light irradiation for 1 h. The suspension consists of TiO_2 powder (50 mg), 30% H_2O_2 (0.2 g), and butyronitrile (1.5 g). A 1-kW Xe lamp was used as the light source.

photocatalysts are shown in Figure 2. It is clearly seen that the activity for the oxidation is low for the ST01 powder, which consists of anatase particles. Other anatase particles we studied also showed low levels of activity under visible light (not shown in Figure 2), although these anatase powders usually show high levels of photocatalytic activity under UV light. On the other hand, rutile powders (CR-EL, PT-101, TIO-3, MT-150W) showed higher levels of activity than did anatase powders for the reaction of cyclohexane under visible light.

In order to further clarify the effect of hydrogen peroxide on the reaction under visible light, changes in the concentrations of the reactant (cyclohexane) and the products (cyclohexanol and cyclohexanone) under visible light were compared, as shown in Figure 3. The total molar amount of the products was less than the molar amount of the consumed reactant, probably because the products are oxidized more easily than the reactant. In the case of anatase powders, not only the production rate but also the consumption rate was low, as shown in Figure 3b for the case of ST-01 powder. This result indicates that anatase powders are less active than rutile powders under visible light.

It is notable that the reaction with organic reactants decelerates with prolongation of visible light irradiation. When the reaction almost stopped, the yellow-colored TiO_2 powder changed to pale yellow. However, when H_2O_2 was added to the solution after the reaction had stopped, coloration of TiO_2 reoccurred and the reaction restarted. Therefore, we conclude that the peroxide complexes formed on the surfaces of TiO_2 particles are responsible for the photochemical reaction under visible light.

The reaction under visible light was also investigated for the oxidation of nonyl aldehyde to nonanoic acid, as shown in Figure 4, It is clearly seen that the rutile powders show higher levels of activity than do the anatase powders, as was observed in the reaction of cyclohexane. In the case of nonyl aldehyde, the reaction proceeded to some extent even in the dark. Hence, in Figure 4, the amount of the product obtained over a period of 1 h is shown after subtraction of the amount produced over a period of 1 h in the dark.

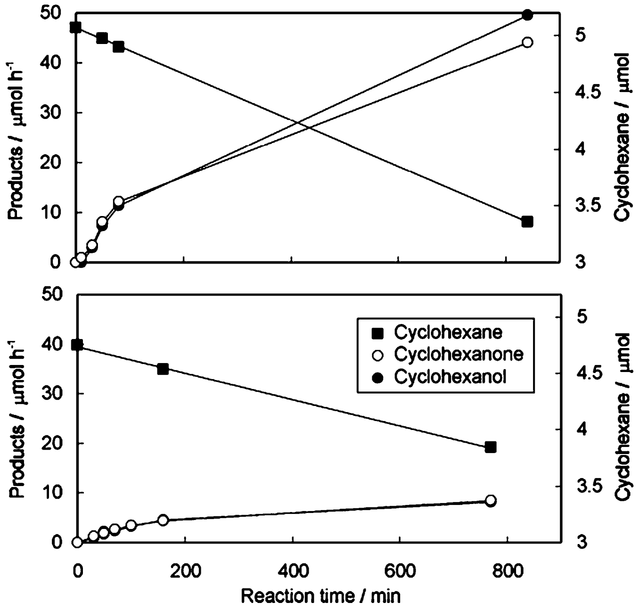

Fig. 3. Changes in concentrations of the reactant (cyclohexane) and the products (cyclohexanol and cyclohexanone) under visible light in TiO_2 suspension: (a) TIO-3 powder (rutile) and (b) ST-01 powder (anatase). The experimental conditions were the same as those described in the legend to Figure 2.

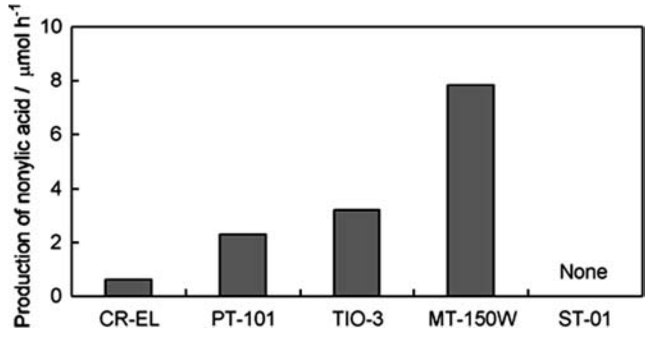

Fig. 4. Amounts of nonanoic acid produced from nonanal in different kinds of TiO_2 suspension by visible light irradiation for 1 h. The suspension consisted of TiO_2 powder (50 mg), 30% H_2O_2 (0.1 g), and nonanal (1.9 g). A 500-W Xe lamp was used as the light source.

We previously investigated the photocatalytic oxidation of naphthalene in an acetonitrile solution containing a small amount of water [14]. When this reaction was carried out under UV light, 2-formylcinnamaldehyde was obtained at high efficiency on rutile TiO_2 particles. The reaction rate under UV light was greatly enhanced by the addition of H_2O_2. However, 2-formylcinnamaldehyde was not produced under visible light even in the presence of H_2O_2. For the photocatalytic production of 2-formylcinnamaldehyde under UV light, we found that oxygen atoms were introduced into the product from water molecules but not from oxygen molecules. This finding suggests that reactive oxygen species for the oxidation of naphthalene are produced as intermediates

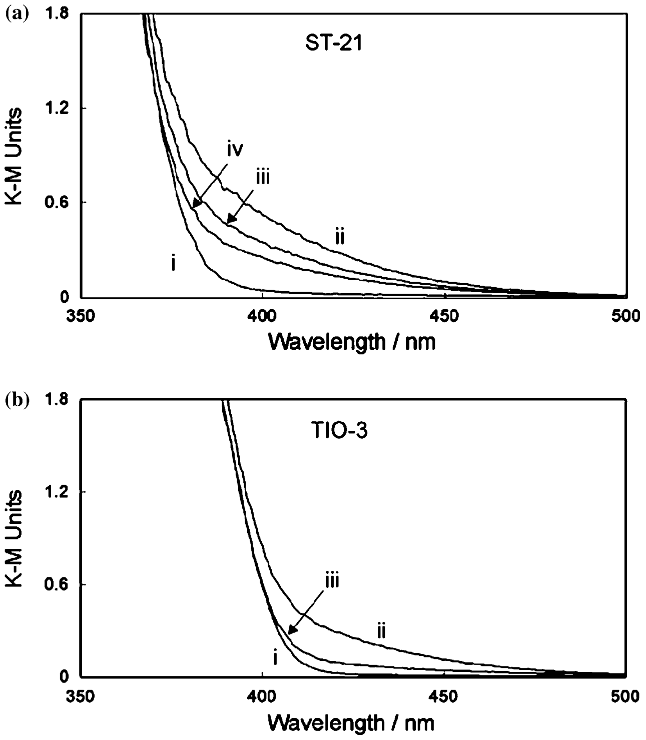

Fig. 5. Diffuse reflectance spectra of (a) ST-21 and (b) TIO-3 powders displayed using the K–M function. The spectra were obtained (i) without any treatment, (ii) after treatment with 15% H_2O_2 solution, and (iii) and (iv) after visible light irradiation for 5 and 20 min, respectively, for H_2O_2-treated samples.

by the photogenerated holes in the TiO_2 particles during the oxidation of water. Hence, the reactions that proceed under visible light in the presence of hydrogen peroxide are considered to be mechanistically different from the reaction of naphthalene. On the other hand, all of the reactions activated under visible light are mono-oxygenation, i.e., epoxides from olefines, cyclohexanol and cyclohexanone from cyclohexane, and nonanoic acid from nonyl aldehyde.

3.3. *Photoreaction of the peroxide complex formed on TiO_2 particles*

The coloration of TiO_2 particles after treatment with H_2O_2 indicates that a peroxide complex is formed on the surfaces of TiO_2 particles. The photocatalytic reaction proceeding under visible light is probably caused by photoreaction of the complex. Li et al. [26] suggested that an electron is transferred from the photoexcited complex to the conduction band of TiO_2 by photoexcitation with visible light and that the electron is then transferred to H_2O_2, leading to the generation of an OH^- ion and an OH radical, which is assumed to be the reactive species. However, it is also possible to assume that the O–O bond of the peroxide is directly cleaved by visible light. In the case of H_2O_2, UV light of wavelength up to about 370 nm is absorbed by H_2O_2 and the O–O bond is cleaved to form OH radicals. If the O–O bond is weakened in the complex, the active wavelength for the formation of the radicals can be extended to the visible region. In any case, the important product from peroxide under visible light is probably these radicals formed on the surfaces of TiO_2 particles.

In order to clarify the reason why rutile powders are more active than anatase powders under visible light, we compared the spectral changes in the colored powders under visible light. As a result of photoirradiation with visible light, the color of both rutile and anatase TiO_2 powders became pale. In addition, we found that the yellow-colored rutile powders faded much faster than did the anatase powders, as shown in Figure 5. This difference in the fading rate suggests that the peroxide formed on rutile particles is photodecomposed more easily, generating more radicals under visible light. This result explains the high activity level of rutile powders for oxidation of organic compounds under visible light. We previously reported IR spectra of peroxides formed on anatase and rutile films are slightly different [27]. This may reflect the different reactivities of the peroxide complexes formed on rutile and anatase powders under visible light.

The reactions so far observed under visible light are all reactions via a mono-oxygenation pathway. On the other hand, the oxidation of naphthalene to 2-formylcinnamaldehyde, which is a di-oxygenation product, was not observed under visible light. These results can be explained by assuming that the species generated under visible light are radicals, each of which donates an O atom to the compounds. Previously, we assumed that Ti-η^2-peroxide is preferentially formed on rutile TiO_2 [27]. According to this model, the mono-oxygenation proceeds under visible light, as shown in Figure 6.

4. Conclusions

Hydrogen peroxide is an important oxidizing agent from the viewpoint of green chemistry. Reaction with hydrogen peroxide usually requires an external driving force such as other oxidants or UV irradiation. We found that an active oxidant can be produced from hydrogen peroxide by visible light in the presence of TiO_2. For the reaction, rutile TiO_2 particles are more effective than antase TiO_2 particles. This method may be applicable to the treatment of pollutants and wastes and to syntheses of organic compounds under visible light.

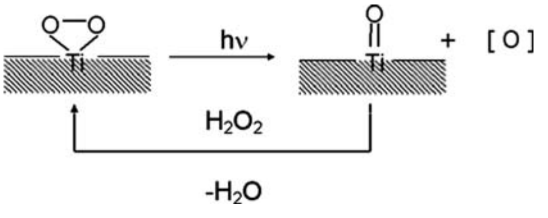

Fig. 6. Proposed mechanism for mono-oxygenation under visible light through a Ti^{-2}-complex formed on the surfaces of TiO_2 particles.

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