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Quantitative analysis of superoxide ion and hydrogen peroxide produced from molecular oxygen on photoirradiated TiO₂ particles

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Abstract

The reduction of molecular oxygen is the counter reaction of most photocatalytic reactions proceeding oxidatively on titanium dioxide particles. We have quantitatively analyzed the reductive production of hydrogen peroxide and superoxide ion from oxygen in an aqueous solution containing 2-propanol as the scavenger of positive holes. The rates for the production of hydrogen peroxide and superoxide ion were determined by colorimetry using iodide and nitroblue tetrazolium, respectively. In addition, the oxidation of 2-propanol to acetone was monitored. Based on a comparison of these production rates, it was concluded that the main product from oxygen is hydrogen peroxide when TiO_2 powder consisting mainly of anatase-form particles is used, whereas the main product is superoxide ion when TiO_2 powder consisting mainly of anatase-form particles is used. The difference in the photocatalytic activity between these powders can be attributed to the difference between the reduction paths of oxygen on these powders. It was also found that the superoxide ion generated from molecular oxygen spontaneously reacts with 2-propanol to produce acetone and hydrogen peroxide.

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1. Introduction

In recent years, studies of TiO₂ photocatalytic reactions have attracted much attention because these reactions are useful for the decomposition and mineralization of pollutants and undesirable compounds in the air and in waste water [1–9]. The TiO₂ photocatalytic reactions are also interesting from the viewpoint of organic syntheses [10–15]. In addition, the photochemical reactions on TiO₂ particles and on TiO₂ films are of interest due to their potential application for the conversion of solar energy into chemical energy [16–20] and electric energy [21,22]. In photocatalysis, light irradiation of TiO₂ powder with a photon energy larger than the band-gap energy produces electrons (e^-) and holes (h^+) in the conduction band and the valence band, respectively.

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These electrons and holes are thought to have the respective abilities to reduce and oxidize chemical species adsorbed on the surface of TiO₂ particles. In most photocatalytic reactions, oxidation processes are utilized for a variety of purposes, and the reduction of molecular oxygen is often used as a counter reaction. Hence, in the field of photocatalysis, most of the research interest has been focused on oxidation processes. However, the reduction of molecular oxygen is important because it is an essential part of the photocatalytic processes taking place on TiO₂ particles. In some cases, the reduction of molecular oxygen determines the efficiency of the overall photocatalytic reaction. This process is also essential because the products from molecular oxygen, i.e., superoxide ion (O_2^-) [23,24] and hydrogen peroxide [25], are considered to participate in subsequent reactions. However, few studies have focused on the quantitative analysis of these products from molecular oxygen.

In this paper, we discuss the reduction products from molecular oxygen in aqueous solutions containing 2-propanol as the hole scavenger. By using 2-propanol, we can neglect the oxidative production of hydrogen peroxide and superoxide ions, because the holes photogenerated in TiO_2

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particles are efficiently scavenged. In the discussion, the crystal structure effects of TiO_2 particles on the reduction of molecular oxygen are highlighted. In addition, we show that the high photocatalytic activity of anatase particles is correlated with the high yield of hydrogen peroxide from molecular oxygen on anatase particles.

2. Experimental

2.1. Materials

Titanium dioxide powders obtained from the Catalysis Society of Japan (TIO-1, TIO-2, TIO-3), Ishihara Sangyo Kaisha, Ltd. (ST-11, ST-21, CR-EL, PT-101), and Toho Titanium Co., Ltd. (NS-90) were used as the photocatalysts. Table 1 summarizes the physical properties of these TiO₂ powders. Nitroblue tetrazolium (NBT), which was used for the analysis of the superoxide ion, was obtained from Wako Pure Chemical as a guaranteed reagent. Potassium superoxide was obtained from Aldrich Chemical Co. All other chemicals used for this study were purchased from commercial sources as guaranteed-grade reagents and they were all used without further purification.

2.2. Photocatalytic reactions

Photocatalytic reactions were carried out in Pyrex glass tubes (15 mm i.d.) containing TiO₂ particles (100 mg) and 5 ml of a mixed solution (water:2-propanol = 96:4 by volume; hereafter referred to as "4% 2-propanol") at room temperature. Some of the experiments were carried out in 2% 2-propanol. A 500 W high-pressure mercury lamp (Wacom, BMO-500DY) was used as the light source. The light beam was passed through a UV34-filter (Kenko Co.) to exclude the deep UV components ($\lambda < 340$ nm), and the light intensity was controlled using fine stainless-steel meshes. The intensity of UV light falling on the reaction tube was approximately 0.6 mW/cm² and the area was approximately 4 cm². During photoirradiation, the TiO₂ particles were suspended in the solution with a magnetic stirrer, and oxygen

Table 1 Physical properties of some TiO₂ powders used in this study

•		•	
TiO ₂ powder	Anatase component (%)	Surface area (m^2/g)	Purity [*] (%)
NS-90	< 1.0	0.9	> 99
CR-EL	< 0.1	7.1	> 99
PT-101	< 0.1	25	> 99
TIO-3	< 1.0	48	> 99
TIO-2	> 99.9	18	98.5
ST-21	> 99.9	56	95
ST-11	> 99.9	71	95
TIO-1	> 99.9	72.6	95

* The purity indicates the weight content of TiO₂ in the powder and the remainder is mostly water, except for TIO-2, which contains a total of about 0.5 wt% impurities, such as Nb₂O₅ and P₂O₅.



Fig. 1. Reaction of NBT with superoxide ions.

was introduced into the reaction solution at a rate of about 5 ml/min.

2.3. Analyses of products

Acetone generated as a result of the photocatalytic reaction was analyzed by gas chromatography (Shimadzu GC-6A) using a PEG-1000 column. For the analysis of superoxide ion, the photocatalytic reaction was carried out in 4% 2-propanol, to which NBT had been added at a concentration of 1 mM. Fig. 1 represents the chemical reaction between superoxide ion and NBT. This reaction leads to the formation of purple formazan [26]. Although formazan is soluble in aprotic solvents, it is insoluble in aqueous solutions. Hence, when formazan is produced during photocatalytic reactions in aqueous solutions, it precipitates on the surface of TiO₂ particles, rendering them purple. We determined the amount of superoxide ion generated as a result of the photocatalytic reaction by detecting the decreased intensity of the absorbance of NBT in the solution. These measurements proceeded as follows: after the TiO₂ powder had been removed from the solution by centrifugation, the supernatant solution was poured into a 1-cm quartz cell. The UV-Vis absorption spectra were measured with a Shimadzu UV-2500PC spectrophotometer. The amount of hydrogen peroxide photocatalytically produced was determined by the addition of starch as the indicator, after the addition of 1 ml of 1×10^{-2} M KI to the photoirradiated solution. The concentrations of the aqueous solutions of hydrogen peroxide used for the calibration were standardized by using sodium thiosulfate. For the analysis of hydrogen peroxide produced by the photocatalytic reaction, the reaction was performed in solution at a pH of about 2; the pH level was controlled by the addition of a small amount of an aqueous solution of H₂SO₄. It was necessary to maintain a low pH in the reaction solution, otherwise it would have been difficult to quantitatively analyze the amount of the concentration of hydrogen peroxide, because the hydrogen peroxide gradually decomposed in the reaction solution, especially in the presence of the TiO₂ particles.

2.4. Blank tests in the dark

The reactivity of the superoxide ion with 2-propanol was evaluated using potassium superoxide as the reagent. For the quantitative analysis, potassium superoxide was dissolved in dimethyl sulfoxide (DMSO) containing 0.3 M 1,4,7,10,13,16-hexaoxacyclooctadecane (or 18-crown-6) according to the reported method [27], and the solution was added to 4% 2-propanol. In addition, the reactivity of hydrogen peroxide with 2-propanol was also measured.

3. Results

3.1. General properties of the photocatalytic reaction of 2-propanol on TiO_2 particles

When molecular oxygen is reduced on the surface of TiO₂ particles, the reduction products can be either superoxide ions or hydrogen peroxide. Although no experimental result has been reported, it is theoretically possible that molecular oxygen is reduced to water. The purpose of the present study was to quantitatively examine these reduction products obtained from molecular oxygen in TiO2-photocatalyzed reactions. For the analysis of the reduction products, the oxidation processes must be considered, because OH radicals may be oxidatively produced from hydroxide ions or water, if the holes are not scavenged. In turn, the OH radicals produce hydrogen peroxide, interfering in the analysis of hydrogen peroxide produced reductively from molecular oxygen. In order to circumvent this problem, we used 2-propanol as the hole scavenger. In the presence of 2-propanol, the generation of hydrogen peroxide in the oxidation process is inhibited because 2-propanol is known to capture holes from TiO₂ very efficiently [28].

The oxidation product from 2-propanol is acetone, and the amount of acetone has often been used as a measure of the photocatalytic activity of TiO₂ photocatalysts. However, it is known that acetone is finally oxidized to carbon dioxide, if the reaction is allowed to continue for a long period of time. Hence, we measured the relationship between the amount of acetone produced and 2-propanol consumed by the TiO₂ photocatalytic reaction carried out under our experimental conditions. The results suggested that the produced amount of acetone and the consumed amount of 2-propanol show good agreement when the conversion of 2-propanol remained under 4% (50 µmol), as shown in Fig. 2. In addition, we obtained no products other than acetone, such as 2,3-dihydroxy-2,3-dimethylbutane. Hence, we concluded that the produced amount of acetone could serve as a good measure of the extent of a photocatalytic reaction on TiO₂, provided that the conversion of 2-propanol is lower than 4%. In the following experiments, we performed reactions in the conversion range below 1%.

Another important aspect of the properties of the reaction of 2-propanol is the dependence of the reaction rate on



Fig. 2. Relationship between the amount of 2-propanol consumed and acetone produced by a photocatalytic reaction carried out in 2% 2-propanol for different time periods using a TiO₂ powder (ST-21) as the photocatalyst.



Fig. 3. pH dependence of the amount of acetone produced by the photocatalytic reaction in 4% 2-propanol for 1 h. A TiO₂ powder (ST-21) was used as the photocatalyst, and the pH was controlled by the addition of a small amount of aqueous H_2SO_4 solution.

the pH of the solution. We had to use acidic solutions for the quantitative analysis of hydrogen peroxide, which was gradually decomposed in neutral and alkaline solutions, especially when TiO_2 was present. On the other hand, the neutral condition was necessary for the analysis of superoxide ion using NBT as the colorimetric reagent. Hence, we compared the reaction rates observed in solutions with different pH values, and we found that the amount of acetone produced after photoirradiation for 60 min showed practically no pH dependence in the pH range from 1.5 to 7, as shown in Fig. 3. This result warrants the comparison of the reaction rates determined in acidic and neutral solutions without taking into account the pH differences.

3.2. Production rates for acetone using various kinds of TiO_2 powders

The amount of acetone produced as a result of the photocatalytic reaction was nearly proportional to the irradiation time under our experimental conditions, in which the conver-

Table 2 Production rates (including dark reactions) of acetone, hydrogen peroxide, and superoxide ion using different TiO₂ powders^{*}

TiO ₂ powder	Acetone (10 ⁻⁷ mol/min)	H_2O_2 (10 ⁻⁷ mol/min)	O_2^- (10 ⁻⁷ mol/min)
NS-90	1.0	0.9	1.0
CR-EL	1.2	1.0	0.9
TIO-3	1.6	1.6	1.6
TIO-2	3.5	3.3	0.4
ST-21	5.5	5.5	0.2
ST-11	3.0	3.2	0.5

* The error range of the data is approximately ± 0.1 .

sion of 2-propanol to acetone was less than 1% and oxygen gas was continuously supplied during the reaction. Hence, we determined the rate of the photocatalytic reaction by dividing the amount of acetone by the irradiation time. The reaction rates for the production of acetone using different TiO_2 powders are shown in the second column of Table 2. As it is often reported for some photocatalytic reactions [25,29], anatase powders (TIO-2, ST-21, and ST-11) were associated with generally higher activity than rutile powders (NS-90, CR-EL, and TIO-3).

3.3. Production rates for hydrogen peroxide using various kinds of TiO₂ powders

We carried out experiments for the quantitative analysis of hydrogen peroxide in acidic solution using 2-propanol as the hole scavenger. The production rates obtained by using 6 different types of TiO₂ powder are shown in the third column of Table 2. The same rate was obtained for the production of both acetone and hydrogen peroxide in the case of each powder, and each rate was dependent on the type of powder used. However, this agreement between the production rates of acetone and hydrogen peroxide does not necessarily indicate that the counterreaction for the oxidation of 2-propanol is the production of hydrogen peroxide from molecular oxygen, as will be discussed later.

3.4. Qualitative analysis of the production of superoxide ion

When NBT is added to an aprotic solution containing superoxide ion, formazan is formed (Fig. 1) and the solution assumes a purple hue. In the aqueous suspension of TiO₂ particles, if superoxide ions are photocatalytically produced in the solution, the particles are purple due to the deposition of formazan on these particles. We confirmed from the control tests that no formazan was produced by the reaction between NBT and hydrogen peroxide or by the addition of NBT to an aqueous suspension of TiO₂ in the dark. However, on photoirradiating TiO2 in 4% 2-propanol containing 1 mM NBT, some of the TiO₂ powders turned purple, as shown in Fig. 4. Generally, rutile powders acquired strong pigmentation, whereas the pigmentation of anatase powders was weak. However, the anatase powders were also pigmented after irradiation for a prolonged period. These results suggest that superoxide ion is produced at a higher rate on rutile particles than on anatase particles. It is important to note that, even by using rutile powders, the formation of formazan was negligible when nitrogen instead of oxygen was supplied to the solution. The production of formazan was also negligible when the TiO₂ particles were irradiated in the solution without 2-propanol. In the absence of 2-propanol, the production of hydrogen peroxide was also negligible, indicating that the net reaction proceeds only slightly on photoirradiated TiO₂ in the absence of electron donors. This finding is consistent with the fact that the oxidation of water on photoirradiated TiO₂ particles is very inefficient without the use of strong electron acceptors [30,31]. It should also be noted that when the irradiation time was shorter than 3 min, the production rate of acetone on photoirradiated TiO₂ powders was only slightly affected by the addition of NBT. When ir-



Fig. 4. Photographs of TiO₂ powders after photoirradiation in 4% 2-propanol containing 1 mM NBT for 30 s. The following powders are depicted (left to right): NS-90, CR-EL, PT-101, TIO-3, TIO-2, ST-21, ST-11, and TIO-1. The first four powders consist of rutile particles and the latter four powders consist of anatase particles.



Fig. 5. Change in the absorption spectra of 1 mM NBT in 4% 2-propanol as the photocatalytic reaction continued using TiO_2 powder (NS90) as the photocatalyst. The photoirradiation times are shown in the figure. Optical length of the cell: 1 cm.

radiation continued for longer time periods, the production rate gradually decreased due to the deposition of formazan on the particles.

3.5. Quantitative analysis of the production of superoxide ion

Since formazan is insoluble in aqueous solutions, the amount of superoxide ion produced by the photocatalytic reaction was determined from the lowering of the absorption spectra of NBT. An example of such a change in the spectra is shown in Fig. 5. The extent of the lowering of the absorption spectra was proportional to the irradiation time during the initial a few minutes, even in the case of the rutile powders, which were strongly colored as the irradiation proceeded. Hence, the rate of production of superoxide was determined from the slope of the relationship between absorbance vs irradiation time in the range of the initial 3 min. The rates determined using different TiO_2 powders are summarized in the fourth column of Table 2.

3.6. Analysis of superoxide ion produced in solution without NBT

Regarding the rate of production of superoxide ion, the possibility must be considered that NBT is directly reduced to formazan on photoirradiated TiO_2 . In order to obtain information about the reaction with NBT, we carried out the photocatalytic reaction in the absence of NBT, and added NBT to the solution just after stopping photoirradiation. As a result, we detected a slight coloration of the rutile powders due to the formation of formazan. In addition to this finding, the fact that the formation of formazan is inhibited by changing the bubbling gas from oxygen to nitrogen strongly suggests that formazan is formed from NBT not by its direct reduction on TiO_2 , but by the reaction with superoxide ions.

3.7. Comparison of the production rates of acetone, hydrogen peroxide, and superoxide ion

The production rates of acetone, hydrogen peroxide, and superoxide ion are summarized in Table 2. It can be seen from these data that the production rate of hydrogen peroxide is close to the production rate of acetone for all of the TiO₂ powders used as photocatalysts, whereas the ratio of the production rate of superoxide ion to that of acetone greatly depends on the powder; i.e., the ratio is close to unity for rutile powders and is less than 0.2 for anatase powders. Unexpectedly, the sum of the production rates of hydrogen peroxide and superoxide ion exceeded the production rate of acetone. Even by taking into account the fact that production of superoxide ion is a one-electron process and the other reactions are two-electron processes, their production rates are inconsistent, especially in the case of the rutile powders.

The above inconsistency among the production rates can be explained in terms of reactions in solution that take place in the dark. Hydrogen peroxide hardly reacted with 2-propanol under our experimental conditions in the dark. On the other hand, superoxide ion oxidized 2-propanol in the dark. This reaction was confirmed by the results of the reaction between KO₂ and 2-propanol as carried out under dark conditions. More precisely, by the addition of 2.5×10^{-5} mol of KO₂ to an aqueous solution of 4% 2-propanol, approximately 1.2×10^{-5} mol (48% of the molar amount of KO₂) of acetone and 2.5×10^{-5} mol of hydrogen peroxide were obtained. This result indicates that the oxidation of 2-propanol by superoxide ions [Reaction (1)] occurs efficiently under the experimental conditions of the photocatalytic reaction.

$$2\text{-propanol} + 2O_2^- + 2H^+ \rightarrow \text{acetone} + 2H_2O_2. \tag{1}$$

In parallel with Reaction (1), the superoxide ions may suffer disproportionation to hydrogen peroxide and oxygen [Reaction (2)] [32]:

$$2O_2^- + 2H^+ \to H_2O_2 + O_2.$$
 (2)

The above result that nearly stoichiometric amounts of acetone and hydrogen peroxide were obtained by the addition of superoxide ion to 4% 2-propanol indicates that Reaction (1) is faster than Reaction (2) under our experimental conditions. Hence, we concluded that the superoxide ions generated by the photocatalytic reaction were mostly consumed by the reaction with 2-propanol in the solution. However, this reaction was prevented in the presence of NBT, because NBT effectively reacted with the superoxide ions at a rate constant of approximately $6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ [33]. This interpretation gains support from the observation that, when KO₂ was added to the solution of 4% 2-propanol containing 1 mM NBT, we did not obtain acetone in the solution. Taken together, these findings indicate that the reaction between the superoxide ions and NBT took place much faster than Reactions (1) and (2) under our experimental conditions.

The above results also indicate that in order to evaluate the respective amounts of acetone and hydrogen peroxide, which are photocatalytically produced on TiO_2 , it is necessary to subtract the amounts produced via superoxide ion by Reaction (1) from the amounts determined from the analysis of the products in the photoirradiated solution. Table 3 shows the values thus obtained, which were calculated on the assumption that superoxide ion produces the same molar amount of hydrogen peroxide, and a half-molar amount of acetone by Reaction (1).

4. Discussion

As shown in Table 3, the rate for the production of acetone agreed with the sum of the rate for the production of hydrogen peroxide and the half-rate for the production of superoxide ion, within the error limits. This result indicated that the reduction of molecular oxygen, as the counter reaction of the oxidation of 2-propanol, leads to the production of both hydrogen peroxide and superoxide ions, and that the production of water is negligibly small.

The results shown in Table 3 also indicate that the products obtained from molecular oxygen depend on the TiO₂ powder used for the reaction. The chief reaction paths on photoirradiated rutile and anatase TiO₂ particles are illustrated in Figs. 6a and 6b, respectively. The difference between rutile and anatase particles is that the main product from molecular oxygen on rutile particles was superoxide ion, and that on anatase particles was hydrogen peroxide. However, the production of superoxide ion on the anatase particles could not be neglected; the amount reached 20% of hydrogen peroxide in some cases, depending on the type of powder used. Although the origin of the effect of the crystal structures on the reaction paths remains to be clarified, we consider that the surface atomic arrangements or the surface defects, i.e., the kinks and steps, are responsible for the reaction paths. The standard electrode potential of the reduction of oxygen to hydrogen peroxide is 0.682 V vs NHE (at pH = 0), and that to superoxide ion is -0.563 V. Thus, the path to hydrogen peroxide is thermodynamically more favorable than that to superoxide ion. However, the path to hydro-

Table 3

Estimated	production	rates (of acetone,	hydrogen	peroxide,	and	superoxide
ion using	different Ti	O ₂ pov	vders*				

TiO ₂ powder	Acetone (10 ⁻⁷ mol/min)	H_2O_2 (10 ⁻⁷ mol/min)	O_2^- (10 ⁻⁷ mol/min)
NS-90	0.5	0.0^{**}	1.0
CR-EL	0.75	0.1	0.9
TIO-3	0.8	0.0	1.6
TIO-2	3.3	2.9	0.4
ST-21	5.4	5.3	0.2
ST-11	2.75	2.7	0.5

 * The error range of the data for acetone and hydrogen peroxide is approximately ± 0.2 .

** The calculated value is -0.1.



Fig. 6. Models for the photocatalytic reaction on a rutile particle (a) and on an anatase particle (b).

gen peroxide is assumed to require catalytic activity because it is a two-electron process. Since the anatase powders are produced at lower temperatures than the rutile powders, the presence of a higher density of surface defects is expected in the case of the anatase powders. This may be the reason for the high catalytic activity observed for the production of hydrogen peroxide on anatase powders.

It is known that fine anatase particles are active in many kinds of photocatalytic reaction in which molecular oxygen is utilized as the electron acceptor. The wider band gap of the anatase particles than that of the rutile particles has often been considered as the reason for the higher activity of anatase particles. However, our results indicated that the difference in the activity in terms of the reduction of molecular oxygen also contributes to the high activity of anatase particles. When the reduction of oxygen is the rate-determining step of the whole reaction process on TiO₂ particles, the ease of oxygen reduction on the anatase surface leads to a highly efficient reaction. As regards the activity of rutile powders, although the reaction of superoxide ion with 2-propanol increases the efficiency in terms of the production of acetone, the activity was still lower than that associated with the anatase powders, as shown in Table 2. This finding was probably due to the low activity of rutile powders in terms of the reduction of oxygen. However, rutile powders may be of interest from the viewpoint of the syntheses of certain organic compounds produced using superoxide ion as the oxidant [34]. Rutile powders are also important for some photocatalytic reactions in which strong electron acceptors are used in place of molecular oxygen. For example, when Fe^{3+} ion is added to the reaction solution, rutile particles show very high photocatalytic activity and oxidize some compounds, which cannot be photocatalytically oxidized on anatase particles [30].

5. Conclusions

We have quantitatively studied the reduction products obtained from molecular oxygen in TiO_2 -photocatalyzed reactions carried out in aqueous solutions containing 2-propanol. It was concluded that the main product is superoxide ion when rutile particles are used, whereas the main product is hydrogen peroxide when anatase particles are used. This difference is important because it is related to the fact that the photocatalytic activity of anatase powders is higher than that of rutile powders in many photocatalytic reactions when molecular oxygen is used as the electron acceptor.

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