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Photocatalytic reactivity of transparent titania sols prepared by peptization of titanium tetraisopropoxide

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Abstract

Photocatalysis of a transparent aqueous sol, which was prepared by peptizing titanium tetraisopropoxide in nitric acid for 7 days followed by dialysis was examined for the color-fading of methylene blue (MB) and Orange II and for the degradation of 4-chlorophenol (4-CP). Measurements of XRD patterns of the powders obtained by drying the sol indicated the formation of anatase. Under argon-bubbling, MB was degraded via the formation of colorless leuco form and the color of the sol returned to original by bubbling air in the dark. Reaction rates for oxidative degradation of MB under air-bubbling showed maximum at the 0.013 mol-Ti dm^{-3} in the sol and at pH 4.2. Reaction rates for color-fading of Orange II were higher by a factor of 6.8 than that of MB. The dependence of rates on the concentrations of MB or Orange II in the sol was discussed with the rate law. For the degradation of 4-CP in the sol under the irradiation for 6 h, 92.7% of 4-CP was completely dechlorinated and 69.5% of the initial TOC was decreased.

Keywords: Photocatalyst; Transparent sol; Titania

1. Introduction

Photocatalytic degradation of pollutants on TiO_2 surfaces has been an active field for research [1]. In most research, TiO_2 was used in the form of powder particles, often dispersed in solution. However, for practical applications, a more suitable form of the TiO_2 photocatalyst is a film strongly bound to a substrate such as glasses or ceramics. In fact, TiO_2 films on various substrates have been used commercially in the applications such as self-cleaning, anti-fogging and anti-bacterial. In order to get good appearance of products, developing a transparent sol for coating is required. Ichinose et al. prepared homogeneous and translucent peroxo-modified anatase sols and studied photocatalytic oxidation rates of gaseous isopropanol on the TiO_2 films prepared from the sols [2]. Various methods were used for preparing the transparent sol but only a few studies on photocatalytic activity of the sol itself are found in the literature. Sayilkan et al. synthesized nano-TiO_2 powders by hydrothermal process at 200 °C and prepared transparent sols by dispersing them ultrasonically in water [3]. They described that methylene blue (MB) was not degraded but Reactive Red 120 was degraded in the sol. Ban et al. prepared a transparent titanate sol by mixing titanium tetraisopropoxide and tetramethylammonium hydroxide or triethylamine, followed by diluting with water and mentioned that the photocatalytic reaction mechanism of the titanate sol was different from that of the TiO_2 powder [4].

Andrson et al. synthesized porous TiO_2 pellets by sol–gel techniques including processes of peptization, dialysis, concentration, drying and firing [5]. We used these pellets for photocatalytic degradation of volatile chlorinated organic compounds in the gas phase [6]. We fabricated TiO_2 films on glasses by coating the highly dispersed sol obtained after dialysis and used them for removal of Cu(II) ions from water [7]. In this paper, we describe that even in the sol, photocatalytic action is observed. Features of the prepared sol are transparent, no thermal treatment and purification by dialysis. For the TiO_2 powder suspension, kinetic data were often analyzed by Langmuir–Hinshelwood mechanism, which assumes preadsorption of reactants on the adsorption sites of TiO_2. However, since the prepared sol is transparent, the colloids in the sol might act as a homogeneous photocatalyst. It is interesting to perform kinetic study for the degradation of organic compounds in the transparent sol. Textile dyes and chlorinated organic compounds have become a focus of environmental remediation efforts using

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TiO_2 photocatalysts because of their resistance to biological degradation in wastewater treatment [8–11]. In this paper, we describe photocatalysis of a transparent aqueous sol for color-fading of the dyes such as MB and Orange II and for degradation of 4-chlorophenol (4-CP).

2. Experimental

2.1. Preparation of the transparent sol

A mixture of 3.9 ml HNO_3, 540 ml H_2O and 45 ml $Ti(OC_3H_7)_4$ was peptized at room temperature for 7 days to form a highly dispersed colloidal solution. This sol was then dialyzed in a molecularly porous dialysis tube (molecular weight cut-off: 3500) for 3 days until approximately pH 4 was obtained. The concentration of the sol was estimated to be 0.229 mol-Ti dm^{-3}.

For comparison, the commercial sols of STS-03 (Ishihara Sangyo) and MPT-422 (Ishihara Sangyo) and the TiO_2 powder (Degussa P-25 from Nippon Aerosil) were used.

2.2. Photocatalytic experiments

The obtained sol mixed with aqueous solutions containing MB (total volume: 3 ml) was poured into a glass optical cell (1.0 cm × 1.0 cm × 4.0 cm), which was immersed into a plastic water-bath thermostated at 30 °C. The sol was purged with air using air pump (NISSO, Chikara α1500) for 30 min before irradiation. Four 4 W black light were stood parallel near the side of the water-bath. Air-purging and irradiation were conducted through the experiments. At appropriate times, the absorbance of the mixed solution in the cell was measured by UV–vis spectrophotometry. It is noted that no filtration were needed since the sol was transparent. The photon flux entering into the cell for the color-fading of MB was estimated to be 1.52×10^{-8} einstein s^{-1} by potassium tris(oxalato)ferrate(III) chemical actinometer.

Some experiments with MB and all the experiments with Orange II or 4-CP were performed by placing 100 ml of the mixed solution in a 200 ml beaker. Aliquot samples were withdrawn at appropriate times and analyzed by UV–vis spectrophotometry for the color-fading of the dyes or by HPLC for the degradation of 4-CP. Concentrations of MB and Orange II were estimated from the absorbance at 665 and 484 nm, respectively. Total organic carbon (TOC) was measured by TOC analyzer (Shimadzu, 5000A) and the formation of Cl^- from the dechlorination of 4-CP was confirmed by ion-chromatography (Shimadzu, PIA-1000). For the experiments without oxygen, nitrogen (99.999%) or argon (99.95%) was used instead of air pump. The photon flux entering into the beaker used for the reaction was estimated to be 1.23×10^{-7} einstein s^{-1} by potassium tris(oxalato)ferrate(III) chemical actinometer.

3. Results and discussion

3.1. Properties of the sol

Fig. 1 shows an absorption spectrum of the prepared sol (length of light pass: 1 cm, concentration: 0.229 mol-Ti dm^{-3}) and an XRD pattern of the powder obtained by drying the sol at room temperature. The obtained sol was transparent and the absorbance increased drastically below 400 nm. The peaks in the XRD were attributable to anatase crystals and the particle diameter was calculated to be 3.9 nm by using Scherrer equation. This fact suggests that the anatase is formed during the preparation of the sol. TEM images of the sol showed the presence of tiny particles of size ca 4 nm forming agglomerates (Fig. 2).

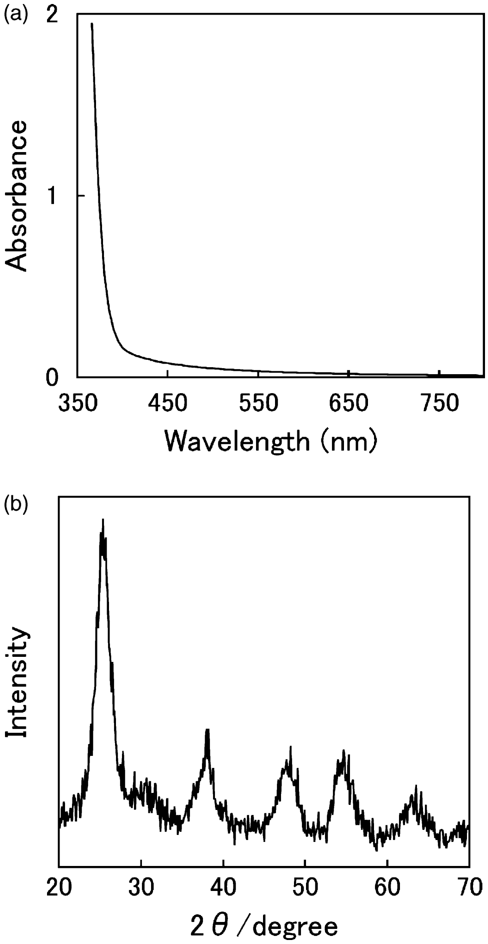

Fig. 1. Properties of the prepared sol. (a) Absorption spectrum, (b) XRD patterns of the powder obtained by drying the sol.

3.2. Photocatalytic decoloration of methylene blue

The UV–vis spectra of the sol containing MB was not changed in the dark but decreased under illumination as shown in Fig. 3. Fig. 4 illustrated the change in the absorbance of 665 nm in the case of air-bubbling and argon-bubbling. As shown in Fig. 4(b), even if the argon-bubbling, the color of MB was faded by illumination but recovered by bubbling air in the dark. Mills and Wang described that MB was reduced by photocatalysis of TiO_2 to its colorless leuco form, LMB, in the absence of oxygen and MB was regenerated by introducing oxygen in the dark [12]. Thus, in the case of argon-bubbling, the color-fading was occurred via the formation of LMB. On the other hand, when air-bubbling was conducted under illumination, the absorbance did not increase at all after the light was turned off. In the case of

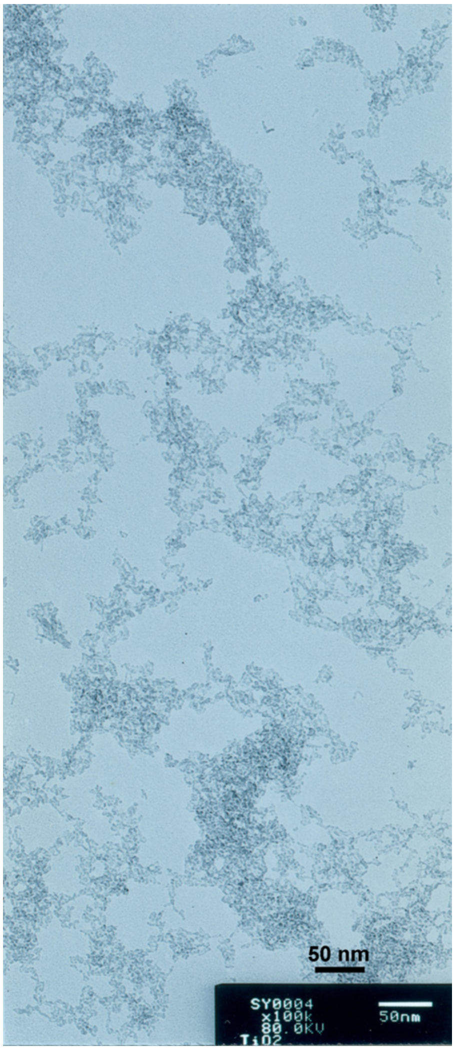

Fig. 2. TEM images of the prepared sol.

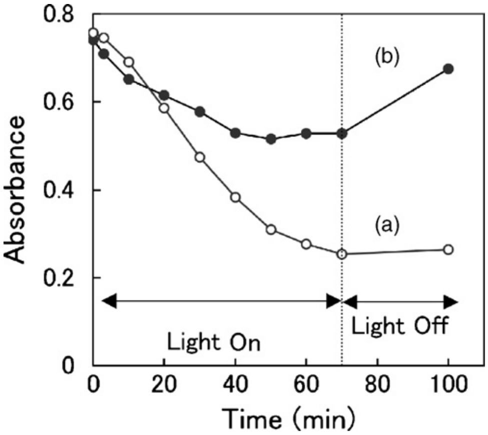

Fig. 4. Variation in the absorbance at 665 nm. The solution (100 ml) containing 0.013 mol-Ti dm^{-3} and 1×10^{-5} mol dm^{-3} MB was air-purged (a) or Ar-purged under illumination followed by air-purging in the dark (b).

air-bubbling, the MB was photodegraded by oxidation. Thereafter, the experiments were performed under air-bubbling.

Effect of the preparation method of the sol on the color-fading of MB was examined. The sol peptized for more than 4 days was apparently clear. However, shorter periods of peptization formed more gels during dialysis. The sol peptized for 5 days yielded small amounts of gel on the bottom in the dialysis tubing. No appreciable difference in reaction rate for the color-fading of MB was observed with the sol peptized for 7 days and 10 days. Dialysis was needed because color-fading was not observed with the sol prepared without dialysis after being peptized for 7 days. This could be due to a low pH or the presence of isopropanol, which was produced by hydrolysis of titanium tetraisopropoxide during peptization. Without dialysis, the sol was a strong acid (pH ≒ 1) and the degradation rate of MB became slower as the pH of the sol decreased, as described later. The presence of isopropanol in the sol retards the oxidation of MB because isopropanol is well known to be oxidized on TiO_2 [13,14].

Fig. 5 indicated an effect of concentration of the sol on the initial reaction rate ($V_i = -d[MB]_i/dt$). The maximum rate was observed at 0.013 mol-Ti dm^{-3}. Fig. 6 showed that the rate increased with pH and reached at the maximum value at pH 4.2. Lakshmi described that the degradation rate of MB in aqueous suspensions with commercial TiO_2 powders increased with pH with a maximum at pH 6.9 [15]. The difference in the optimal

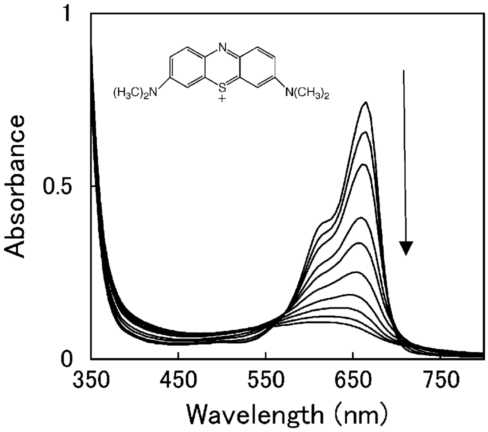

Fig. 3. Variation in the UV–vis absorption spectra of the reaction solution (3 ml) containing 1×10^{-5} mol dm^{-3} MB and 0.013 mol-Ti dm^{-3}. Measurements were performed every 3 min after irradiation.

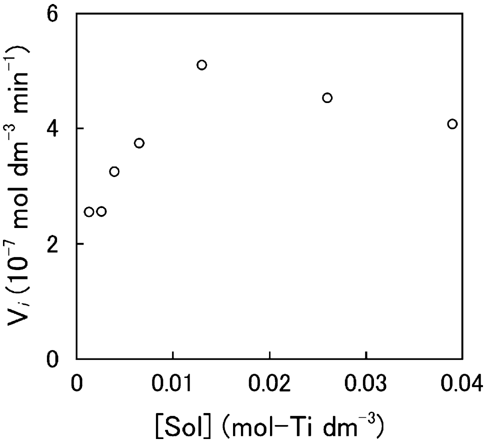

Fig. 5. Effect of the concentration of sol on the initial reaction rate. The solution (3 ml) contained 1.0×10^{-5} mol dm^{-3} MB.

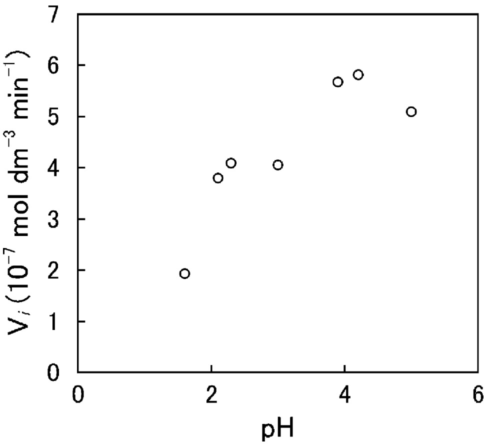

Fig. 6. Effect of pH on the initial reaction rate. Reaction conditions were the same as in Fig. 5 except for 0.013 mol-Ti dm^{-3}.

pH value was ascribed to deterioration in dispersion of the sol since the prepared sol was precipitated at pH above 6.

Effect of initial concentrations of MB on the reaction rate was investigated. Fig. 7(a) showed that, at the concentration of 0.54×10^{-5} and 1.00×10^{-5} mol dm^{-3}, the MB concentration decreased almost linearly at the irradiation time of 0–15 min and then the reaction rates ($-$d[MB]/d*t*) became smaller as the irradiation time increased. However, at the concentrations more than 1.50×10^{-5} mol dm^{-3}, a decrease in the MB concentration was small at the initial stage of the reaction and accelerated as the irradiation time increased. Thus, two reaction rates were estimated at the irradiation time for 0–9 and 9–15 min as shown in Fig. 7(b). We can see more clearly at higher initial concentration such as 2.36×10^{-5} mol dm^{-3} that the reaction started slowly and then accelerated.

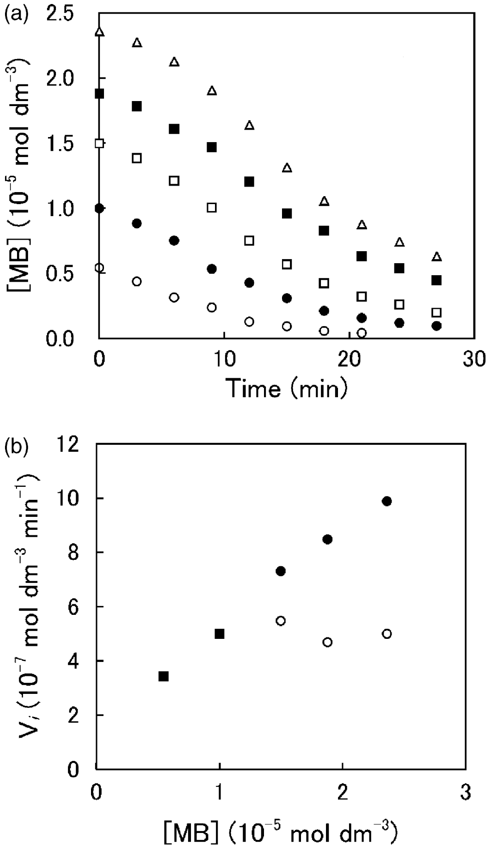

Fig. 7. Effect of the initial MB concentration (2.36 (△), 1.88 (■), 1.50 (□), 1.00 (●) and 0.54 (○) × 10^{-5} mol dm^{-3}) on the decrease in concentration (a) and the initial reaction rate (b). Reaction rates with the MB concentration more than 1.5×10^{-5} mol dm^{-3} were evaluated at the irradiation time of 0–9 min (○) and 9–15 min (●) in (b).

3.3. Photocatalytic decoloration of Orange II

It is well known in the studies on aqueous TiO_2 powder suspension that the surface of TiO_2 has electric charges that are dependent on pH. The surface charge is positive at acidic conditions due to the presence of $TiOH_2^+$ groups, near neutral at pH 5–7, and negative at basic conditions owing to TiO^- groups [16]. This pH-dependent surface charge brings us an expectation that anionic dyes are more easily degradable than cationic MB since the prepared sol is acidic. Fig. 8 depicted variations in the UV–vis absorption spectra of Orange II in the presence of 0.013 mol-Ti dm^{-3} sol under air-bubbling. The concentration of Orange II decreased linearly with the irradiation time and, even at the initial concentrations higher than 1.5×10^{-5} mol dm^{-3}, there was no observation that the reaction rates were accelerated as the irradiation time increased as mentioned in the case of MB. Comparison between the degradation of MB and Orange II under the same experimental condition was shown in Fig. 9. The degradation rate of Orange II ($-$d[Orange II]/d*t*) was estimated to be 2.04×10^{-7} mol dm^{-3} min^{-1} whereas that of MB at the initial stage of the reaction was 3.02×10^{-8} mol dm^{-3} min^{-1}, indicating that the degradation of Orange II was higher by a factor of 6.8 than that of MB. Fig. 10 indicated that the reaction rate increased with the concentration of Orange II and approached a limiting value. This concentration-dependence of the rate has been often observed in TiO_2 powder suspension and explained in terms of Langmuir–Hinshelwood mechanism [17–19]. However, this mechanism assumes preadsorption of the reactants on the adsorption sites of TiO_2, which cannot be adopted for the

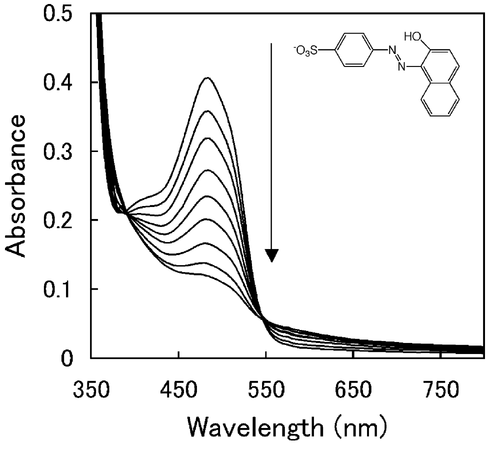

Fig. 8. Variation in the UV–vis absorption spectra of the reaction solution (100 ml) containing 1.9×10^{-5} mol dm^{-3} Orange II and 0.013 mol-Ti dm^{-3}. Measurements were performed every 10 min after irradiation.

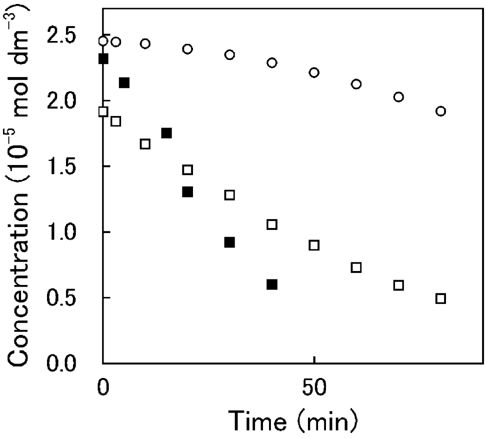

Fig. 9. Comparison between the degradation of MB (○), Orange II (□) and 4-CP (■). The reaction solution contained 0.013 mol-Ti dm^{-3} at pH 4.2.

colloid. A similar type of kinetics can be obtained by considering the following reaction scheme:

$$\mathrm{Ti} + h\nu \xrightarrow{I_a} \mathrm{Ti}^* \tag{1}$$

$$\mathrm{Ti}^* \xrightarrow{k_o} \mathrm{Ti} + \Delta \text{ (thermal deactivation)} \tag{2}$$

$$\mathrm{Ti}^* + \mathrm{Dye} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{Ti}^* \cdots \mathrm{Dye}) \xrightarrow{k_2} \mathrm{Ti}^- + \mathrm{Dye}^+ \tag{3}$$

The titania colloids (Ti) which is photoexcited by absorbing light (I_a) are deactivated to ground-state by thermal process such as recombination of holes and electrons or collision with other colloid particles. Some of the colloids oxidize dyes and the reduced colloids (Ti^-) are oxidized by oxygen. The maximum rate for the degradation of MB was obtained at 0.013 mol dm^{-3}. This may indicate that under higher concentrations, the deactivation process (Eq. (2)) is predominant.

Assuming the steady-state concentrations for Ti^* and encounter complex of ($\mathrm{Ti}^* \cdots \mathrm{Dye}$), the following rate law is obtained:

$$\mathrm{Rate} = \frac{I_a k'[\mathrm{Dye}]}{(k_o + k'[\mathrm{Dye}])} \tag{4}$$

where k' represents $k_1 k_2/(k_{-1} + k_2)$. Eq. (4) suggests that as the concentration of dyes increases, reaction rate increases and approaches the limiting value of I_a when $k_o \ll k'[\mathrm{Dye}]$. This can explain the data as shown in Fig. 10. The value of k_1/k_{-1} for MB must be smaller than that of Orange II because of the electrostatic repulsion between cationic MB and positive surface charge of the colloid. Thus, higher concentrations are necessary for MB to achieve the condition of $k_o \ll k'[\mathrm{Dye}]$ than for Orange II. As a result, as shown in Fig. 7(b), a tendency that the rate increased with an increase in the MB concentration seems to be valid although two rates were obtained by analyzing the experimental data in the different time range. The reason why the rate was slower at early stage of the reaction under the MB concentration more than 1.5×10^{-5} mol dm^{-3} remained unclear.

3.4. Photocatalytic degradation of 4-CP

No degradation of 4-CP was observed under nitrogen-bubbling. When the solution containing 0.013 mol-Ti dm^{-3} sol and 1.0×10^{-4} mol dm^{-3} 4-CP was illuminated under air-bubbling, 4-CP was degraded and Cl^- ion was produced. At the irradiation of 6 h, 92.7% of 4-CP was degraded and the stoichiometric ratio of $[\mathrm{Cl}^-]_{\mathrm{formed}}/[\text{4-CP}]_{\mathrm{degraded}}$ was estimated to be 0.98. These findings suggest that most of 4-CP were dechlorinated. The TOC in the reaction solution decreased from 10.71 to 3.27 mg/L at the irradiation of 6 h, indicating that 69.5% of the initial TOC was decreased. The sol before mixing with 4-CP contained 2.78 mg/L as TOC, which might come from isopropanol that could not be completely removed by dialysis. Although it is necessary to identify the organic compounds in the sol itself, we would like to emphasize that some of 4-CP were mineralized to CO_2 in the sol. As shown in Fig. 9, 4-CP was degraded most effectively among three compounds. The optimal concentration of the sol for the degradation of 4-CP was obtained to be 0.013 mol-Ti dm^{-3}, which was coincident with the results for MB (Fig. 5). Fig. 11 indicated that the reaction rate was not dependent on the initial concentration of 4-CP.

Reaction mechanisms for the degradation of MB, Orange II and 4-CP on TiO_2 powder have been widely investigated. Zhang

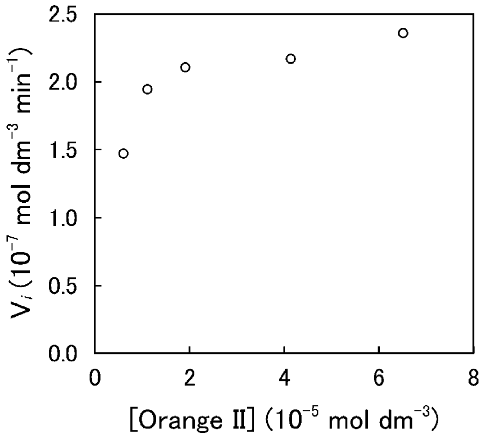

Fig. 10. Effect of the concentration of Orange II on the initial reaction rate. The solution contained 0.013 mol-Ti dm^{-3} at pH 4.2.

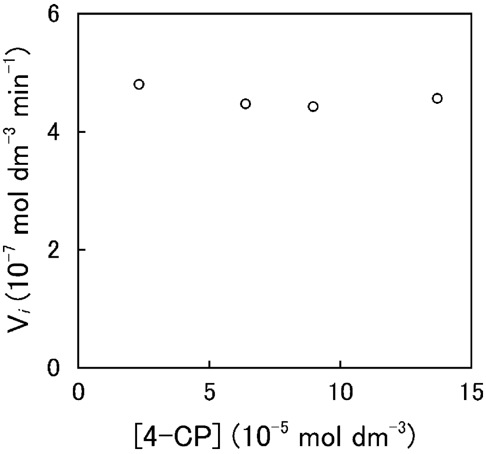

Fig. 11. Effect of the concentration of 4-CP on the initial reaction rate. The solution contained 0.013 mol-Ti dm^{-3} at pH 4.2.

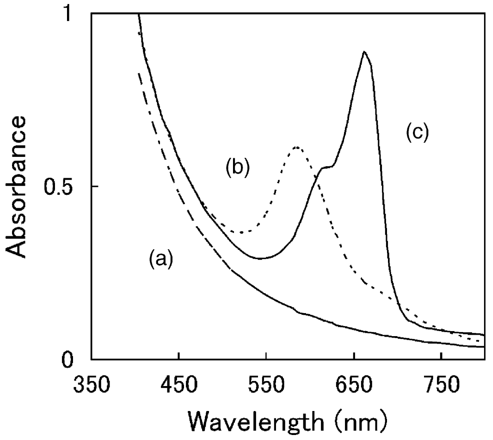

Fig. 12. Absorption spectra of 0.1 wt.% STS-03 (a), 0.1 wt.% MPT-422 with MB (b) and 0.1 wt.% STS-03 with MB (c).

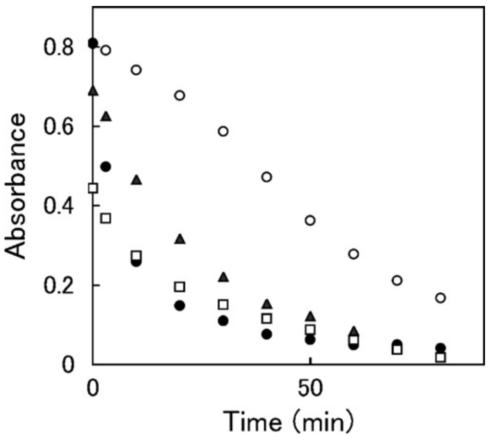

Fig. 13. Changes in absorbance at 665 nm for the prepared sol (○), STS-03 (●), P-25 (▲) and at 584 nm for MPT-422 (□).

et al. proposed *N*-demethylation of MB [9]. Kiwi and coworkers described hydroxylation of the aromatic moiety of Orange II followed by the scission of the azo bond [8,20]. The degradation of 4-CP has been reported to produce aromatic intermediates such as hydroquinone and 4-chlorocatechol, which were further oxidized to carboxylic acids and aldehydes by ring cleavage [21]. Further studies to detect the intermediates formed in the sol are needed in order to determine whether the degradation mechanism in the sol is the same as in TiO_2 powder suspension and discuss the difference in the degradation pathway of these three compounds.

3.5. *Comparison with commercial sols and powders*

The photocatalytic activity of the sol was compared with commercial sols. The optimal concentration of the prepared sol for the degradation of MB and 4-CP was 0.013 mol-Ti dm^{-3} which corresponds to 0.1 wt.% TiO_2 if we assume all Ti atoms exist as TiO_2. Thus, the experiments were conducted by diluting commercial sols to 0.1 wt.% TiO_2 on the basis of the values given by the supplier. The 0.1 wt.% sol of STS-03 or MPT-422 was apparently white and the pH was 3.6 or 6.8, respectively. These sols showed similar absorption spectra in which absorbance increased drastically below 600 nm as shown in Fig. 12(a). Fig. 12(b) and (c) depicted the absorbance of the 0.1 wt.% sol containing 1×10^{-5} mol dm^{-3} MB before irradiation. An absorption peak appeared in MPT-422 sol at 584 nm that was shifted by 81 nm from the peak of MB at 665 nm. By irradiation, the peak at 584 nm decreased with a shift to shorter wavelength and disappeared at the irradiation of 80 min. Since the absorption spectrum of MB at pH 7 was the same as in acidic solution, such a drastic change in the absorption spectrum might be ascribed to SiO_2 that was contained in MPT-422 as an additive. Fig. 13 indicated changes in absorbance at 665 nm except for MPT-422 at 584 nm. For a comparison, experiments for degradation of MB were performed in the suspension with 0.1 wt.% of TiO_2 powder (Degussa P-25) and the absorbance was measured after removing the powder by centrifugation and filtration. The absorbance at $t = 0$ for P-25 was smaller than that for STS-03 or the prepared sol, which is attributable to the adsorption of MB on the TiO_2 powder. Fig. 13 indicated that photocatalytic activity of STS-03 was similar to the TiO_2 powder but that of the prepared sol was much lower. This finding suggests that tiny particles in the prepared sol have a different reactivity from the commercial opaque sols or that the assumption of all Ti in the sol existing as TiO_2 is not valid. In order to clarify these points, we are currently investigating on the reaction mechanism in the sol.

4. Conclusion

The transparent aqueous sol obtained by peptization of $Ti(OC_3H_7)_4$ and the subsequent dialysis has a photocatalytic activity for color-fading of MB and Orange II and for dechlorination of 4-CP.

Acknowledgements

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