

Synthesis and properties of a microtube photocatalyst with photoactive inner surface and inert outer surface

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Abstract

Synthesis of a photocatalyst with a novel particle form, its photoactivity, and the degradation of polyvinyl alcohol containing the photocatalyst were studied in detail. A microtube photocatalyst with titanium dioxide particles supported on the inner surface of the microtube was synthesized by adding fine titanium dioxide particles in the formation process of basic magnesium carbonate microtube. The photoactivity of the microtube photocatalyst was confirmed from the decomposition of 2-propanol under blacklight irradiation. Moreover, the microtube photocatalyst was found to cause no degradation of polyvinyl alcohol, whereas, it decomposed 2-propanol with its photoactivity when impregnated in a polyvinyl alcohol foam. This fact was considered to be derived from the unique structure of the microtube photocatalyst, which has a photoactive inner surface with titanium dioxide and an inert outer surface of basic magnesium carbonate.

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1. Introduction

The photocatalysis of titanium dioxide has intensively been studied since the “Honda–Fujishima effect [1]” was reported. In recent years, titanium dioxide photocatalyst is used for diverse applications, such as agents for the decomposition of various pollutants [2–7]. However, titanium dioxide decomposes almost all of organic compounds with its photoactivity, so that, it is not allowed to be mixed with organic products [8]. Hence, commercially applied products containing photocatalyst are restricted to inorganic materials, such as tiles [9], glasses [10–13], ceramics [14–16], and so on.

Some photocatalyst particles miscible with organic compounds were reported as a muskmelon-type photocatalyst [17] having a porous silica layer on the surface of titanium dioxide particle and an apatite-coated titanium dioxide photocata-

lyst [18]. However, the photocatalytic activity is considered to decrease by the presence of inactive substances on the surface of titanium dioxide. Hence, there is a strong demand for the development of novel photocatalysts that have both high photocatalytic activity and wide utilizability with organic compounds to expand the application field of photocatalyst. If this demand is met, the immobilization of photocatalyst powder by organic binders and the endowment of photocatalytic activity to organic materials will be possible.

We have so far studied how to control the particle form of basic magnesium carbonate ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, hydro-magnesite), and found that microtubes with a surface of “house of cards [19,20]” structure composed of leaflike fine crystals of the carbonate can be synthesized by adjusting the temperature and pH of reaction system [21]. In the present study, we attempted to synthesize a photocatalyst with a novel particle form using the combination of basic magnesium carbonate microtube and fine titanium dioxide particles. Moreover, photoactivity of the photocatalyst obtained and degradation of organic compound containing the photocatalyst under blacklight irradiation were examined.

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2. Experimental

2.1. Materials

Magnesium hydroxide (reagent grade, Kanto Chemical) and carbon dioxide (liquefied carbon dioxide for industrial use) as starting materials, and sodium hydroxide (extra reagent grade, Kanto Chemical) for the additive to control pH were used for the synthesis of basic magnesium carbonate microtube. A 40 wt% aqueous dispersion of anatase-type titanium dioxide having a diameter of 20 nm (STS-21, Ishihara Sangyo Kaisha) was used as photocatalytic particles to be combined with the microtube.

2-Propanol (extra reagent grade, Kanto Chemical) was used for the evaluation of photocatalytic activity. The alcohol undergoes no auto-oxidation by ultraviolet irradiation and heating, and is selectively oxidized to form acetone through the photocatalytic reaction on the surface of titanium dioxide [22–25].

Also, a partially formalized polyvinyl alcohol (PVAf) foam with three-dimensional continuous open pores (PVA sponge sheet-D, Aion) was used as the organic compound in which the photocatalyst was impregnated. Polyvinyl alcohol is comparatively stable against ultraviolet irradiation [26] and degraded by the photocatalytic oxidation reaction of titanium dioxide [27].

2.2. Synthesis of basic magnesium carbonate microtube combined with titanium dioxide

Basic magnesium carbonate microtube was synthesized according to the flow chart given in Scheme 1. First, an aqueous magnesium hydrogen carbonate solution was prepared by

bubbling carbon dioxide gas into 2.0 L of an aqueous dispersion of magnesium hydroxide (30 g/L) at a rate of 2.0 L/min for 45 min (reaction 1). Then amorphous $x\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2$ particles were prepared by adding 5 M aqueous sodium hydroxide solution to the magnesium hydrogen carbonate solution obtained above (reaction 2). Subsequently, the temperature of the reaction system was raised to 45 °C and maintained at this temperature for 30 min to permit the formation of metastable magnesium carbonate trihydrate (reaction 3). Finally, basic magnesium carbonate was formed while maintaining the reaction system at 55 °C for 60 min after 10 mL of 5 M aqueous sodium hydroxide solution was added (reaction 4). All reactions were carried out under stirring. Basic magnesium carbonate microtube with an inner diameter of 1–2 μm and outer diameter of 2–3 μm was obtained under the reaction conditions mentioned above.

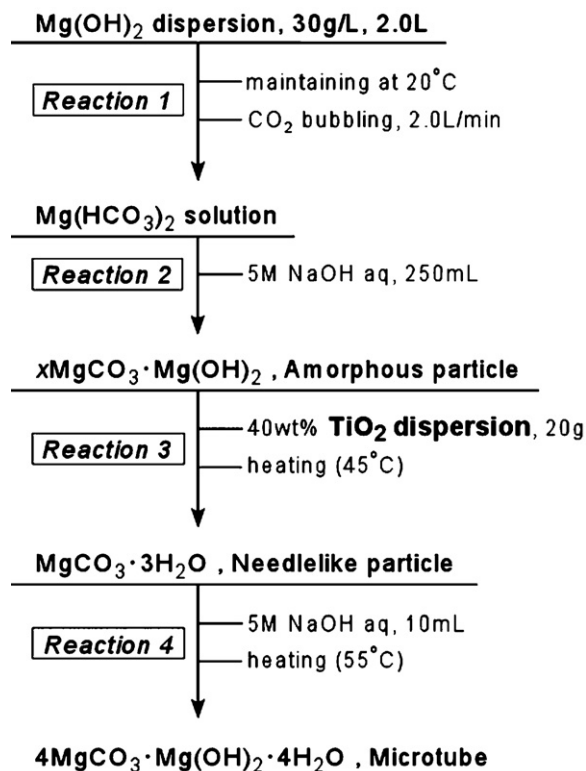
Basic magnesium carbonate microtube combined with titanium dioxide particles was synthesized by adding 20 g of the titanium dioxide dispersion at 40 wt% to the reaction system after the formation of $x\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2$ particles with the addition of sodium hydroxide solution in reaction 3. The combined microtube obtained was dewatered with a suction filter, washed with ethanol, and dried at 50 °C in a vacuum oven to obtain the sample powder.

The sample powder was analyzed with an X-ray diffractometer (XRD; MPD1880, Philips) and X-ray fluorescence spectrometer (XRF; ZSX-100E, Rigaku) to determine the crystal phase and content of titanium dioxide. Observations of particle form were conducted using a scanning electron microscope (SEM; S-4800, Hitachi) and the distribution of titanium dioxide particles combined with the microtube was examined with an X-ray microanalyzer (XMA; Genesis 2000, EDAX).

2.3. Evaluation of photocatalytic activity

Ultraviolet–visible absorption of the sample was measured by a solid state diffuse reflectance method using an ultraviolet–visible spectrometer (V-570, JASCO).

Photocatalytic activity was evaluated by measuring decreases in the concentration of 2-propanol under blacklight irradiation using the apparatus shown in Fig. 1. First, the powder sam-



Scheme 1. Flow chart for preparing basic magnesium carbonate microtube.

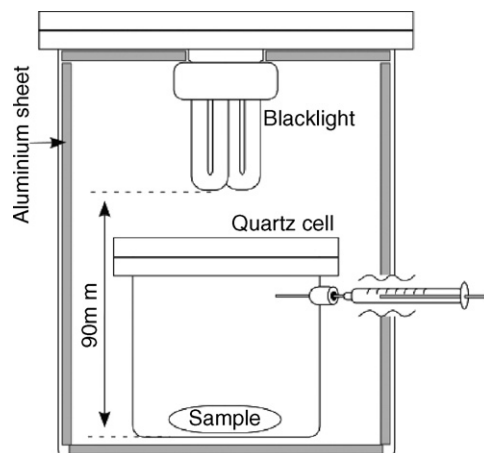


Fig. 1. Apparatus for the evaluation of photoactivity.

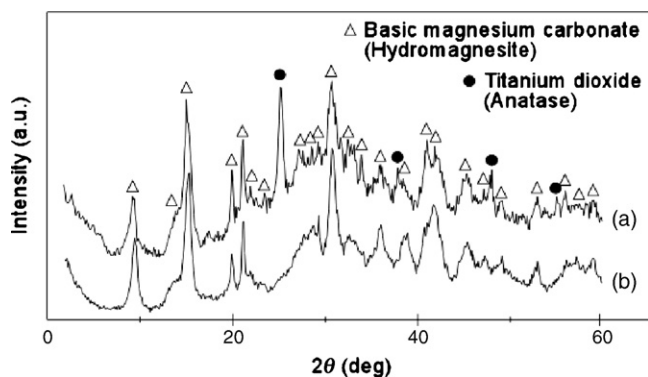


Fig. 2. XRD patterns of the combined microtube (a) and basic magnesium carbonate microtube (b).

ple was placed in a quartz cell with a volume of 300 mL and 0.5 μL of 2-propanol was then injected into the cell. After being allowed to stand at 30 $^{\circ}\text{C}$ for 90 min, the cell was set in the apparatus. Subsequently, blacklight (ELD15BLB, Toshiba Lightec) irradiation was started. The intensity of ultraviolet-ray was about 0.8 mW/cm^2 at the bottom of the cell. Gas samples in the cell were extracted using a microsyringe at specified time periods after blacklight irradiation started, and analyzed with a gas chromatograph–mass spectrometer (GC–MS; HP6890/5973, Hewlett Packard) to determine the concentrations of 2-propanol and acetone formed in the photocatalytic oxidation of the alcohol.

2.4. Evaluation of photoactivity and degradation of PVAf foams containing photocatalyst

PVAf foam with 50 mm length, 50 mm width, and 5 mm thickness was cut off, dipped into a toluenic dispersion of the

photocatalyst, and dried in a vacuum chamber to prepare a PVAf foam containing the photocatalyst.

The photoactivity of the foam was evaluated by measuring decreases in the concentration of 2-propanol under blacklight irradiation with the apparatus shown in Fig. 1. Also, a gas sample in the quartz cell after blacklight irradiation was extracted and measured with the GC–MS to analyze the gas composition.

In addition, L value (brightness), a value (the axis red–green), and b value (the axis yellow–blue) in the Hunter color system [28] of the foam were measured with a tristimulus filter-type colorimeter (TC-8600A, Tokyo Denshoku) to estimate the degree of degradation of PVAf from the changes in the color of the foam.

3. Results and discussion

3.1. Synthesis of microtube combined with titanium dioxide

Basic magnesium carbonate microtube combined with titanium dioxide was synthesized by adding 20.0 g of the titanium dioxide dispersion at 40 wt% to the reaction system in reaction 3.

Fig. 2 shows the XRD pattern of the combined microtube obtained. The diffraction peaks assigned to basic magnesium carbonate (hydromagnesite) and titanium dioxide (anatase) were detected for the combined microtube. The content of titanium dioxide was found to be 9.1 wt% by XRF analysis.

The results of SEM observations on the combined microtube are shown in Fig. 3. The formation was confirmed of basic magnesium carbonate microtube with a surface of house of cards structure. Titanium dioxide fine particles added to the reaction system were observed only on the inner surface of the microtube. Fig. 4 shows elemental mappings of the combined microtube

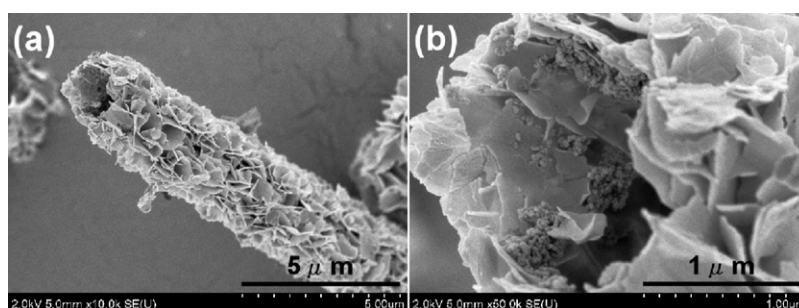


Fig. 3. SEM images of the combined microtube.

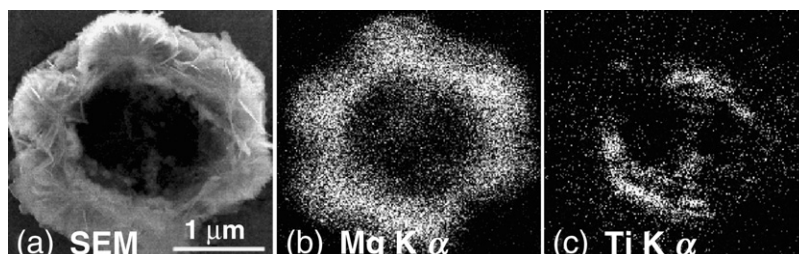


Fig. 4. X-ray microanalysis of the combined microtube. (a) SEM image, (b) elemental mapping of Mg, and (c) elemental mapping of Ti.

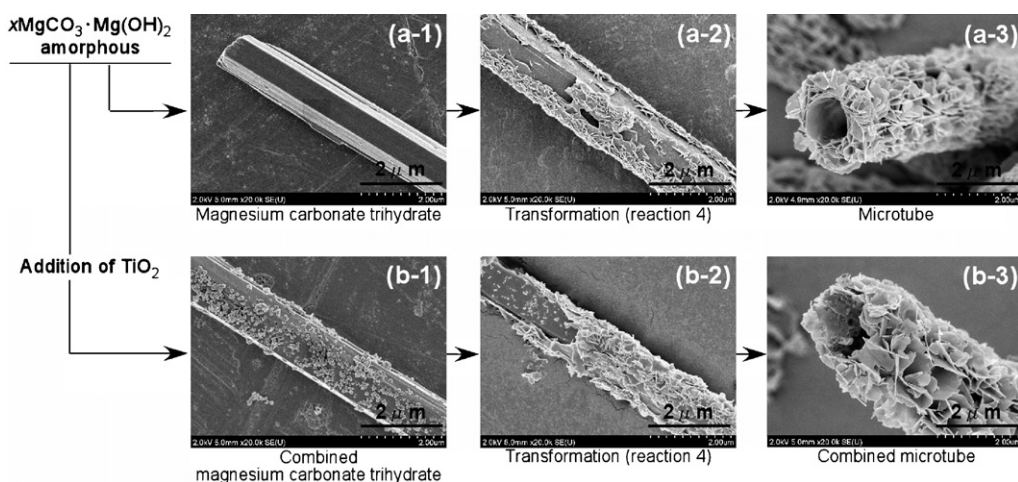


Fig. 5. Formation process of basic magnesium carbonate microtube (a-1–3) and the combined microtube (b-1–3).

measured with XMA. The elemental mapping of Ti (Fig. 4(c)) indicated that titanium dioxide particles were distributed selectively on the inner surface of the microtube. As a result, the present method was found to be able to synthesize the combined microtube with a novel and unique structure in which titanium dioxide particles are localized in the inner surface layer.

This unique structure of the combined microtube is likely to be formed by the following mechanism. We can observe that needlelike particles of metastable magnesium carbonate trihydrate deposited in reaction 3 act as a template of the microtube (Fig. 5(a-1)), and that the redeposition of basic magnesium carbonate onto the template and the dissolution of the trihydrate occur simultaneously to form the microtube in reaction 4 (Fig. 5(a-2,3)). In this process, titanium dioxide particles added in reaction 3 are supported on the surface of the needlelike particles to form the combined magnesium carbonate trihydrate (Fig. 5(b-1)). Subsequently, reaction 4 occurs to transform the combined trihydrate to the basic carbonate (Fig. 5(b-2)). Then, titanium dioxide particles on the surface of the trihydrate are left behind on the inner surface of the microtube (Fig. 5(b-3)). The combined microtube would thus be formed through the mechanism mentioned above.

3.2. Photoactivity of combined microtube

Fig. 6 shows the results of measurements of ultraviolet–visible absorption. Absorption under 390 nm was detected for the combined microtube, whereas virtually only little absorption was observed with basic magnesium carbonate microtube without titanium dioxide. Hence, it was confirmed that ultraviolet–ray necessary for photocatalysis could reach titanium dioxide particles combined on the inner surface of the microtube.

Photocatalytic activity was evaluated for powder samples of the combined microtube and titanium dioxide for reference, respectively, using the apparatus shown in Fig. 1. Each of 300 mg portions of the combined microtube or 27 mg of titanium dioxide was placed in the quartz cell. The amount of titanium dioxide placed in the cell was the same. 2-Propanol ($0.5 \mu\text{L}$) was

then injected into the cell, the initial concentration of which was $487 \mu\text{L/L}$. After being injected into the cell, the alcohol vaporized and adsorbed onto the powder. An adsorption equilibrium was attained within 90 min. Then, blacklight irradiation was started to evaluate the photoactivity.

Fig. 7 shows changes in the concentrations of 2-propanol and acetone with time under blacklight irradiation. A decrease in the concentration of 2-propanol under blacklight irradiation was detected with the combined microtube. Then, the formation and increase in the concentration of acetone along with the decomposition of the alcohol were observed. Subsequently, a decrease with time in the concentration of acetone was confirmed. Hence, the combined microtube was found to be able to decompose 2-propanol and acetone under blacklight irradiation, which indicated that the combined microtube could be used as a novel photocatalyst, named “microtube photocatalyst”.

Meanwhile, when compared with the microtube photocatalyst, titanium dioxide photocatalyst decomposed 2-propanol and acetone quickly. The result indicates that the photoactivity of titanium dioxide photocatalyst is higher than that of the microtube photocatalyst, if the evaluation of photocatalytic activity was conducted for powder samples. The photoactivity of the microtube photocatalyst is feared to be deteriorated by decrease

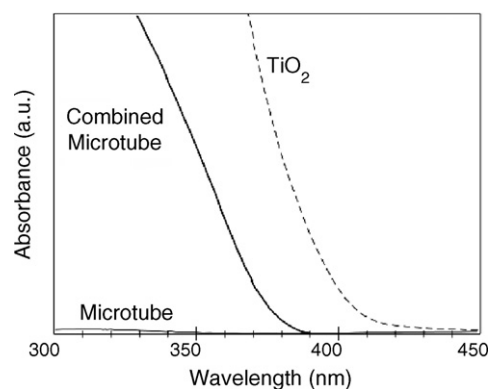


Fig. 6. Ultraviolet–visible absorption spectrum of the combined microtube.

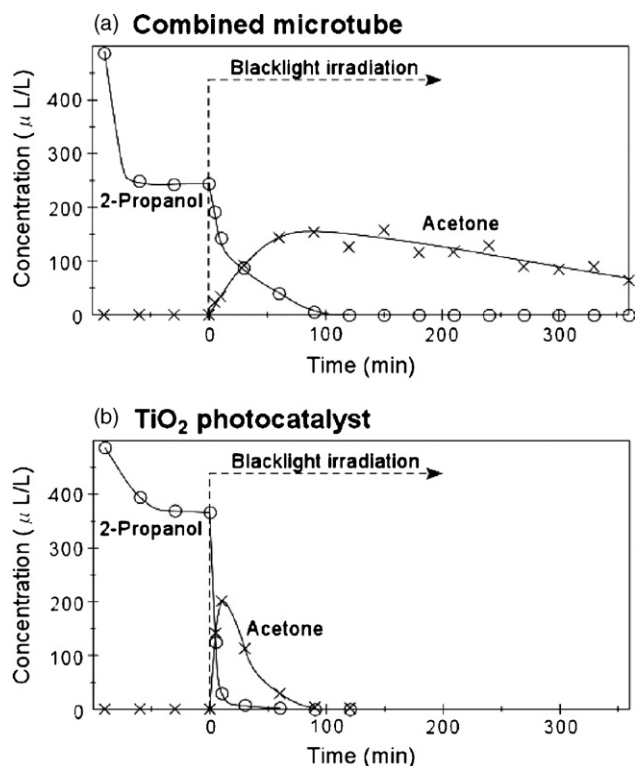


Fig. 7. Changes with time in the concentrations of 2-propanol and acetone under blacklight irradiation for the combined microtube powder (a) and titanium dioxide photocatalyst powder (b).

in the absorption efficiency of ultraviolet-ray for titanium dioxide, because titanium dioxide particles are present in the microtube surrounded by basic magnesium carbonate wall. Decrease in the adsorption rate of 2-propanol onto photoactive titanium dioxide is also likely to cause a lowering in the photoactivity of the microtube photocatalyst, because the alcohol adsorbs onto the inert surface of basic magnesium carbonate.

3.3. Photoactivity and degradation of PVAF foams containing photocatalyst

PVAF foams containing the microtube photocatalyst (a), titanium dioxide photocatalyst (b), and no photocatalyst (c) were prepared as shown in Table 1, and evaluated for their photoactivities under blacklight irradiation using the apparatus shown in Fig. 1.

Fig. 8 shows changes in the concentrations of 2-propanol and acetone with time under blacklight irradiation for the PVAF

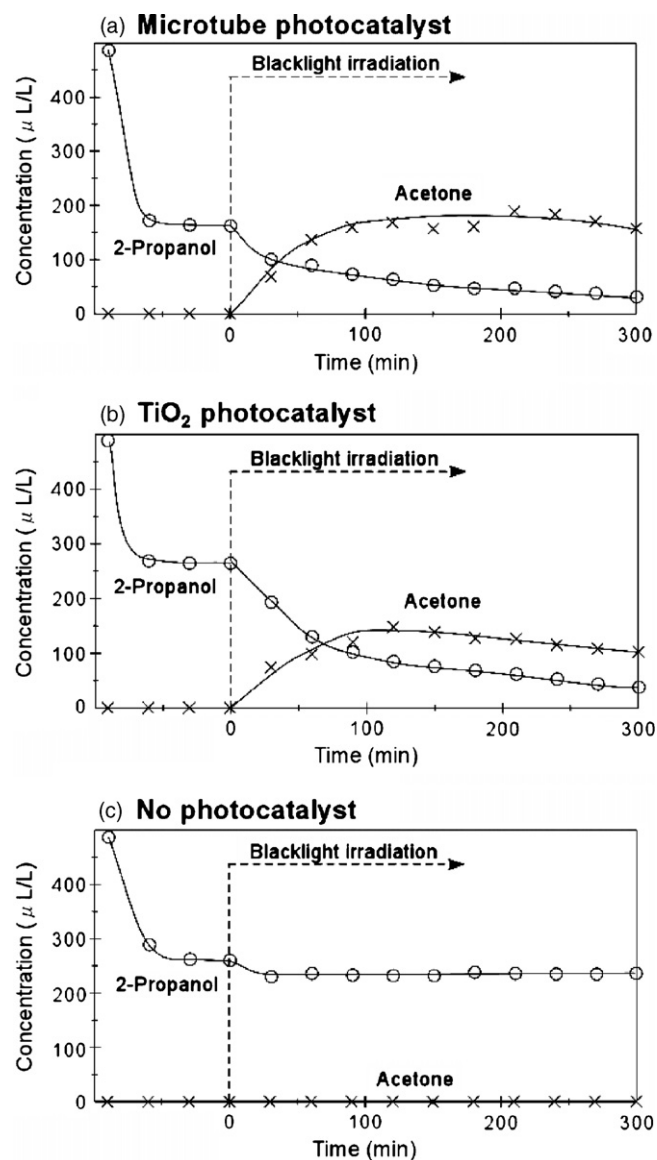


Fig. 8. Changes with time in the concentrations of 2-propanol and acetone under blacklight irradiation for the PVAF foams containing microtube photocatalyst (a), titanium dioxide photocatalyst (b), and no photocatalyst (c).

foams (a)–(c). As in the evaluation of photoactivity for powder samples mentioned in Section 3.2, the decomposition of 2-propanol and formation of acetone were found with the PVAF foams (a) and (b). Though the photoactivity of titanium dioxide photocatalyst was higher than that of the microtube photocatalyst when the evaluation was made for the powder samples, almost no difference was found between the PVAF foams (a) and (b).

In the case of titanium dioxide photocatalyst, oxidant species, such as OH radical generated by ultraviolet-ray absorption are supposed to be consumed not only for the decomposition of 2-propanol and acetone but also for the decomposition of PVAF matrix, because photoactive titanium dioxide particles are in direct contact with the PVAF matrix. In contrast, the oxidant species generated on the surface of titanium dioxide supported

Table 1
Chemical composition of PVAF foams containing photocatalyst

PVAF foam	Photocatalyst		Composition	
	Particle	Content (wt%)	MgO (wt%)	TiO ₂ (wt%)
(a)	Microtube	16.7	6.1	1.5
(b)	Titanium dioxide	1.5	0.0	1.5
(c)	None	0.0	0.0	0.0

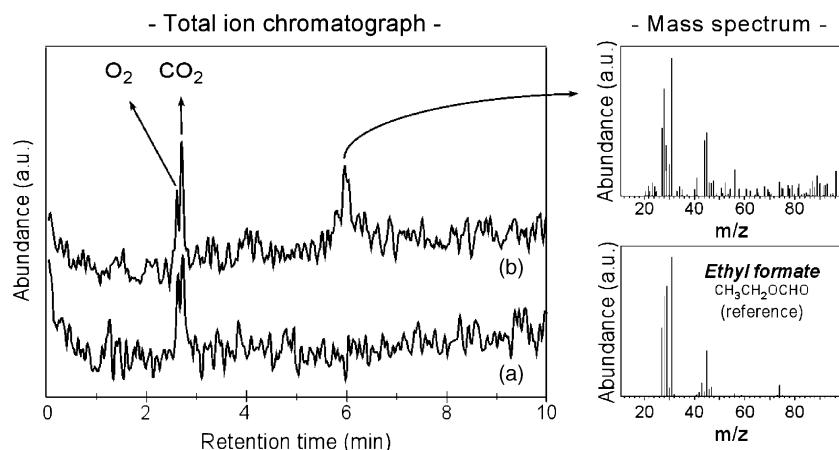


Fig. 9. GC–MS analysis of the gas samples after blacklight irradiation with the PVAF foams containing the microtube photocatalyst (a) and titanium dioxide photocatalyst (b).

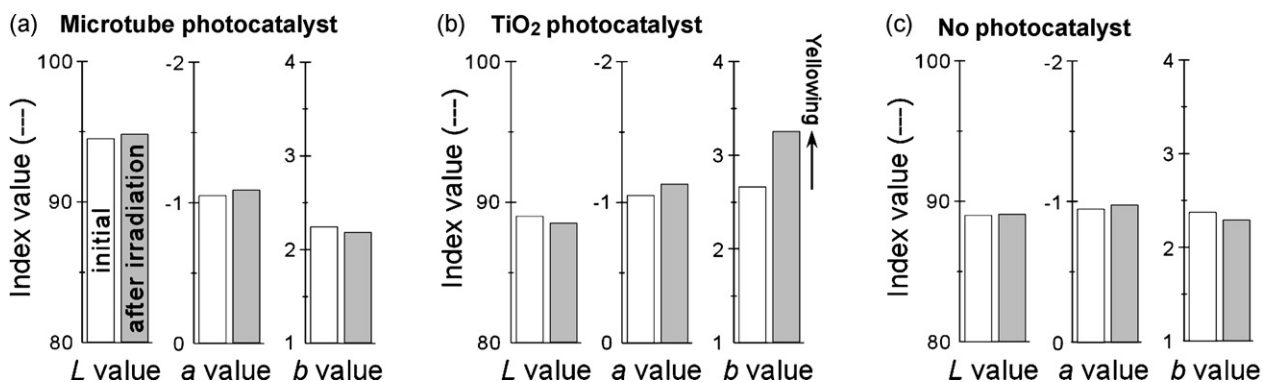


Fig. 10. Hunter color index of initial and blacklight-irradiated PVAF foams containing microtube photocatalyst (a), titanium dioxide photocatalyst (b), and no photocatalyst (c).

on the inner surface of the microtube photocatalyst are quite likely to be utilized selectively for the decomposition of 2-propanol and acetone, because the photoactive inner surface of the microtube photocatalyst with titanium dioxide particles has no contact with the PVAF matrix. Presumably, only little difference in the photoactivity evaluated in terms of decomposition of 2-propanol and acetone was then found between the microtube photocatalyst and titanium dioxide photocatalyst.

GC–MS qualitative analysis was performed on the gas samples in the quartz cell after blacklight irradiation for 300 min. Fig. 9 shows the results. Ethyl formate was detected for the PVAF foam (b) containing titanium dioxide photocatalyst. It is known that the splitting of C–C bond occurs in the decomposition process of polymers by photocatalysis [29,30]. The splitting is supposed to have occurred in the PVAF foam (b) to form ethyl formate that corresponds to a single unit of formalized polyvinyl alcohol. On the other hand, no substance formation through the decomposition of PVAF was detected with the foam (a), which indicated that the microtube photocatalyst caused no degradation of the PVAF matrix by its photoactivity.

In addition, changes in the color of PVAF foams after blacklight irradiation are shown in Fig. 10. Little changes in color were found with the PVAF foams (a) and (c). However, an increase

in b value (the axis yellow–blue) of the Hunter color system was detected with the foam (b), which suggested a yellowing occurred with the foam (b). It is well known that the color of polymers, such as polyvinyl alcohol changes to yellow or brown by oxidation degradation [31]. The PVAF foam (b) was probably degraded and changed its color to yellow by the photoactivity of titanium dioxide, because the dioxide was in direct contact with PVAF matrix. On the other hand, in the case of the microtube photocatalyst, the surface in contact with PVAF matrix is an inert surface of basic magnesium carbonate. Hence, no degradation and change in color would have occurred for the PVAF foam (a).

As mentioned so far, the microtube photocatalyst was found to cause no degradation of organic compounds as matrix, though it decomposed 2-propanol and acetone by its photoactivity when the photocatalyst was impregnated in the organic compounds. The result is considered to be derived from the unique structure of the microtube photocatalyst that has a photoactive inner surface with titanium dioxide particles and an inert outer surface of basic magnesium carbonate (Fig. 11). Therefore, the microtube photocatalyst is expected to solve the problem that photocatalytic particles cannot be mixed with organic compounds, and hence, the microtube will expand the application field of photocatalyst remarkably.

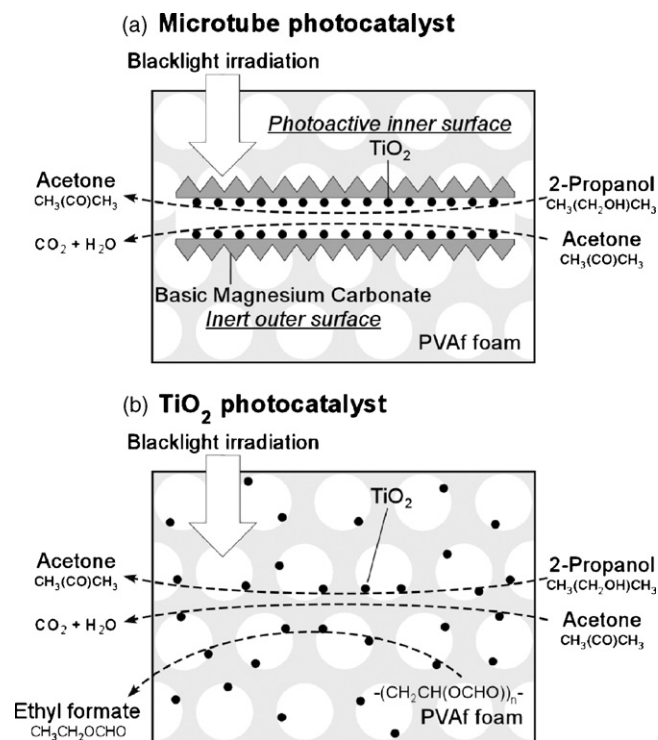


Fig. 11. Photocatalytic reaction models of the microtube photocatalyst (a) and titanium dioxide photocatalyst (b) in PVAf matrix.

4. Conclusions

It was found that the microtube photocatalyst with titanium dioxide particles supported only on the inner surface of basic magnesium carbonate could be synthesized by adding titanium dioxide to the formation process of the microtube. The photoactivity of the microtube photocatalyst was confirmed by decrease in the concentration of 2-propanol under blacklight irradiation. Furthermore, it became appear that, when impregnated in a PVAf foam, the microtube photocatalyst shows no degradation of the PVAf matrix, because of the unique structure with the photoactive inner surface on which titanium dioxide particles are distributed and the inert outer surface of basic magnesium carbonate. Such microtube photocatalyst is considered to be usable as a novel photocatalytic particle miscible with organic compounds.

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