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Preparation of porous sheet composite impregnated with TiO_2 photocatalyst by a papermaking technique

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Abstract Titanium dioxide (TiO_2) powder-containing sheet composites, called TiO_2 sheet, were prepared by a papermaking technique, and their photocatalytic efficiency was investigated. The TiO_2 powders were homogeneously scattered over the fiber-mix networks tailored within the catalyst sheet. Under UV irradiation, the TiO_2 paper could decompose *p*-hydroxyacetophenone (*p*-HAP), although the degradation efficiency by the TiO_2 sheet was lower than that by the TiO_2 powder. Scanning electron microscopy revealed that coverage of the TiO_2 particles inside the sheet by alumina binder which was used to improve the sheet strength caused the deterioration of the photocatalytic performance. Internal addition of alumina binder made the TiO_2 sheet porous and such a TiO_2 sheet exhibited high photocatalytic performance equivalent to that of TiO_2 powder. The porous structure of TiO_2 sheet might contribute to effective transport of *p*-HAP to the surface of TiO_2 particles inside the sheet, resulting in high degradation performance. In addition, TiO_2 sheet prepared using TiO_2 sol showed higher photocatalytic efficiency than TiO_2 powder and it was indicated that the porous sheet structure might provide suitable conditions for TiO_2 catalysis for photodecomposition.

Introduction

The entry of various hazardous chemical compounds into natural water environments and their deleterious effects on the earth's ecosystems is a cause for serious concern. In particular, some man-made chemical compounds, such as dioxins, azo dyes, herbicides and pesticides, are not assimilated or degraded by organisms because they are not natural compounds, thus methods for the decomposition or detoxification of such recalcitrant compounds are needed [1, 2].

Over the past two decades, photocatalytic degradation of organic pollutants by titanium dioxide (TiO_2) has attracted much attention as a promising chemical treatment for water remediation [3–7]. Under near-UV irradiation, hydroxyl radicals and other active oxygen species that possess a high oxidizing power are formed on the surface of TiO_2 crystal and almost all organic compounds can be decomposed to CO_2 and H_2O by the attack of these radicals [8, 9]. Thus, many studies on the use of TiO_2 photo-oxidation for the decomposition of environmental pollutants have been carried out. Pollutants that have been investigated include dioxin [10], trichloroethylene [11], endocrine disrupting chemicals [12, 13] and other volatile organic compounds [14]. Photocatalysis is also a novel treatment method for recalcitrant organic contaminants in water, however, its practical application in aqueous media is limited because of the difficulty of recovering small TiO_2 particles. Therefore, molded photocatalysts such as pellets and beads are practical alternatives [15]. In this case, although molded solid photocatalyst is easy to handle, it is generally inferior to the original powdery catalyst in respect to catalytic performance. The efficiency of photodegradation by TiO_2 depends on its contact with the target compounds around the surfaces of the TiO_2 crystal [16, 17]. The poor performance

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of molded catalyst is presumed to be due to the reduced accessibility of the target molecules to the catalyst surfaces caused by either the aggregation of particles or intra-particle diffusion limitations [18]. Hence, related research and development on effective fabrication methods is now being actively pursued.

We have previously reported the preparation of TiO_2 powder-filled paper-like composites for treatment of environmental pollution [12–14, 19–21]. In the present study, we focused on the porous paper structure and prepared porous paper-like composites impregnated with TiO_2 photocatalyst from ceramic fibers by a papermaking technique. The TiO_2 sheets prepared were used for the decomposition of *p*-hydroxyacetophenone (*p*-HAP) under UV irradiation and their photocatalytic performance was compared to that of TiO_2 powder.

Experimental

Materials

TiO_2 powder (ST-01, 275 $m^2 g^{-1}$, anatase, Ishihara Sangyo Kaisha, Ltd.) and ceramic fibers (ISOWOOL 1260 BULK; Al_2O_3 (ca. 47%) and SiO_2 (ca. 52%), ISOLITE Industry, Ltd.) used as sheet matrix were obtained commercially. The ceramic fibers were cut into lengths ca. 0.5 mm on average before use. Pulp fibers supporting the wet web during the dewatering stage of the papermaking process were bleached hardwood kraft pulp that had been beaten to 265 mL of Canadian Standard Freeness according to Technical Association of the Pulp and Paper Industry (TAPPI) Test Methods T200 and 227 with a standard beater for paper sheet making. Poly(diallyldimethylammonium chloride) (PDADMAC, molecular weight (M_w): ca. 3×10^5; charge density (CD): 5.5 meq. g^{-1}; Aldrich, Ltd.) and anionic polyacrylamide (A-PAM, HH-351; M_w: ca. 4×10^6; CD: 0.83 meq. g^{-1}; Kurita, Ltd.) were used as flocculants for handsheet-making with a dual polymer retention system [12–14, 19–21]. *p*-HAP was reagent grade and purchased from Wako Pure Chemical Industries, Ltd. An alumina sol (snowtex 520, Nissan Chemicals, Ltd.) and TiO_2 sol (STS-01, Ishihara Sangyo Kaisha, Ltd.) were kindly provided and used as binders for enhancing the strength of the sheets.

Preparation of TiO_2-ceramic fiber composite

Figure 1 illustrates the preparation conditions for TiO_2-containing sheets. The suspension of ceramic fibers was mixed with PDADMAC (1.0% total solids), followed by the sequential addition of TiO_2 powder, and A-PAM (1.0% total solids), in that order at 3-min intervals. Subsequently, the mixture was poured into a pulp suspension, and handsheets with a grammage of 155 g m^{-2} were prepared according to the TAPPI Test Methods T205. Following pressing at 350 kPa for 5 min, the wet sheets were dried in an oven at 105 °C for 30 min. After being soaked in an alumina sol, the composite sheets were pressed at 350 kPa for 5 min, and then ignited at 700 °C for 20 min to remove organic pulp and to improve physical strength by calcination of the alumina binder [12, 13]. Hereafter, we call this sheet Al-soaked sheet (Fig. 1-a). Two types of TiO_2 sheet were prepared in a similar manner, and we call these Al-mixed sheet (Fig. 1-b) and TiO_2 sol sheet (Fig. 1-c).

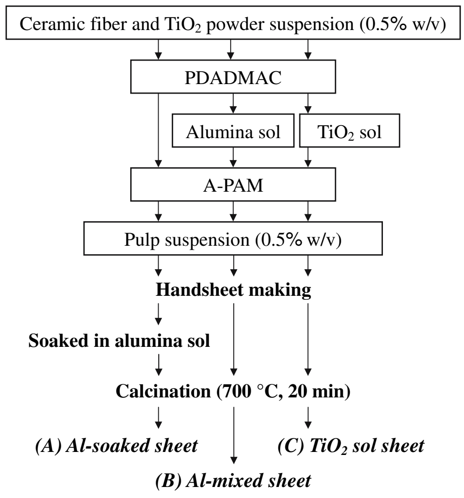

Fig. 1 Preparation conditions of porous TiO_2 sheets

Photocatalytic decomposition of *p*-HAP

The *p*-HAP solution (50 µM, 25 mL) prepared using Millipore water was poured into a glass vessel. Either TiO_2 powder (100 mg) or TiO_2 sheet with a TiO_2 content of 100 mg was put into the reaction vessel, and irradiated with a Hg–Xe lamp with a 365-nm band-pass filter (0.2 mW mm^{-2}). After UV irradiation for 1, 3, 6 or 12 h, a designated aliquot filtered through a membrane filter (Chromatodisk, pore size: 0.45 µm; GL Sciences, Ltd.) was subjected to high-performance liquid chromatography (HPLC). The HPLC analysis was carried out using a Shimadzu STR ODS-II column and a UV detector at 278 nm with a mobile phase of 20% acetonitrile in 0.05% phosphoric acid at a constant flow rate of 1.0 mL min^{-1}. The coefficient of variance for the HPLC was less than 5% based on three measurements.

Other analyses

Scanning electron microscopy (SEM) observation and energy dispersive X-ray spectroscopy (EDS) analysis of the surface of the TiO_2 sheet were performed using a JSM-5600 apparatus and a JED-2140 analyzer from JEOL, Ltd., respectively, after carbon coating. The electron accelerating voltage was set at 10 kV. The TiO_2 content of the porous sheet was determined by atomic absorption analysis through the elution of Ti^{4+} from the sheet with 98% sulfuric acid. Other inorganic matters were gravimetrically measured after calcination at 700 °C for 20 min. Mercury intrusion analysis was conducted by using a Poremaster 33P-KUK (YUASA IONICS, Ltd.) to evaluate the average pore diameter and porosity of catalyst sheets.

Results and discussion

Preparation of TiO_2 sheet by papermaking technique

Figure 2 shows an optical image of the TiO_2 sheets. TiO_2 powders were successfully fabricated into a sheet structure by a papermaking technique employing a dual polymer retention system [12–14, 19–21]. The TiO_2 sheet made from ceramic fiber is easy to handle, uniform and flexible. The retention of TiO_2 particles as calculated by atomic absorption analysis reached 90%. The strength of the sheet soaked in alumina sol was markedly improved by the binder calcination, as reported in our previous studies [12, 13]. Inorganic ceramic fibers have no interfiber bonds, like hydrogen bonds between pulp fibers, and the binder treatment is required to provide physical strength. During soaking of the sheet in alumina sol, small alumina particles physically adsorbed onto the ceramic fibers and network are reinforced by binder thermowelding. The sheet strength was high enough that it could be handled in water, and thus the TiO_2 sheet has advantages over the original TiO_2 powders; it is easy to handle, and its recovery from water is easy.

Photocatalytic decomposition of *p*-HAP by TiO_2 sheets

Figure 3 displays the time courses of the *p*-HAP concentrations in water treated by TiO_2 powders and TiO_2 sheets after calcination with or without alumina sol. It was confirmed that neither appreciable adsorption of *p*-HAP onto TiO_2 powders, ceramic fibers, pulp fibers or the TiO_2 sheet nor photolysis of *p*-HAP by the near-UV light without any TiO_2 photocatalyst occurred. The mechanism of the photocatalytic reaction using TiO_2 has been studied in detail [8, 9]. Most organic compounds can be decomposed to CO_2 and H_2O by the attack of hydroxyl radicals that possess a high oxidizing power, indicating the possibility of the formation of intermediates through the radical reaction that occurs randomly. During the photocatalytic decomposition of *p*-HAP using TiO_2, almost no aromatic intermediates were observed in the HPLC analysis [13].

Fig. 2 Optical image of TiO_2 sheets

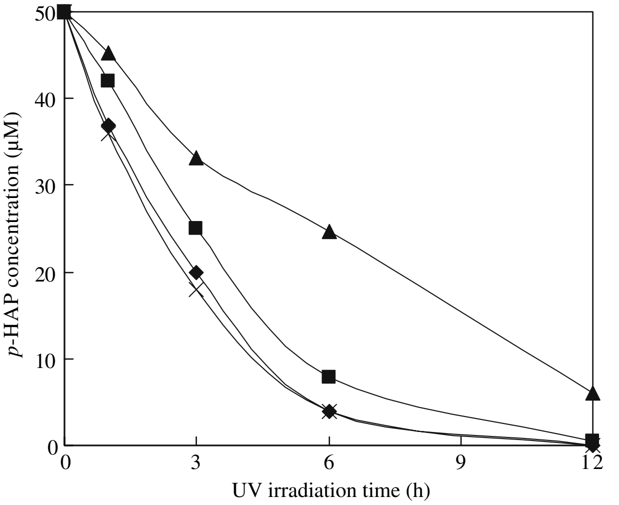

Fig. 3 Time courses of *p*-HAP concentrations; treatment with TiO_2 sheet calcined with 20% alumina sol (closed triangles), 4% alumina sol (closed squares), without using sol (closed diamonds) and TiO_2 powder (crosses)

The TiO_2 sheet could decompose *p*-HAP in water under UV irradiation, however, the performance of the TiO_2 sheet deteriorated with an increased alumina dosage. The degradation efficiency of the sheets calcined with 20% alumina sol was quite low compared to that of TiO_2 powder and *p*-HAP remained in water after 12 h treatment. The SEM images of TiO_2 paper sheets calcined with 4% or 20% alumina sol are shown in Fig. 4 and it was confirmed that the voids of the catalyst sheet were filled. As a positive control, the TiO_2 sheet calcined without using alumina sol exhibited a high degradation efficiency, equivalent to that of TiO_2 powder, indicating that the lower degradation efficiency of the catalyst sheet calcined with alumina sol is not attributable to the state of the TiO_2 particles impregnated in the sheet. From these results, a part of the TiO_2 particles inside the sheet seemed to be covered by alumina sol and accessibility of *p*-HAP to TiO_2 surface was decreased although it is difficult to differentiate between loss in activity due to coating of the TiO_2 by alumina and filling

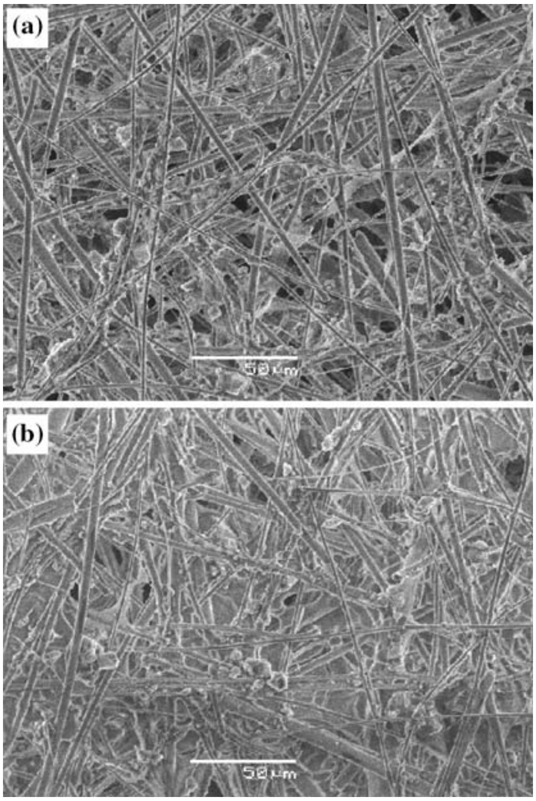

Fig. 4 SEM images of the TiO_2 sheets calcined with (**a**) 4% alumina sol, (**b**) 20% alumina sol

of the void space within the paper preventing access to the TiO_2 surface.

Internal addition of alumina binder and comparison of the degradation efficiency

In the previous section, it was shown that the photocatalytic performance was significantly influenced by the alumina sol. However, the binder treatment is indispensable for improving the sheet strength. The retention behavior of alumina was unable to be controlled by a soaking treatment, resulting in filling of the pores inside the sheet and deterioration of the sheet performance. In this section, another retention method for alumina sol, internal addition, was attempted; the alumina sol binder was added during the sheet formation process with the intent of regulating its retention behavior (Al-mixed sheet, Figure 1-b). The alumina binder used in this study had a cationic charge and it was expected that it might be immobilized by a dual polymer retention system as well as by TiO_2 particles. The internal addition of alumina sol also resulted in a sufficient sheet strength to enable handling in water.

Figure 5 displays the SEM and EDS images of Al-mixed sheet. As compared to the Al-soaked sheet shown in Fig. 4, Al-mixed sheet sustained a porous structure in which TiO_2 particles were uniformly dispersed and immobilized. The average pore size of the TiO_2 sheet associated with the inorganic fiber network was ca. 20 µm (data not shown), as determined by mercury intrusion analysis. The porosities of Al-soaked sheet and Al-mixed sheet were 45% and 77%, respectively, indicating that Al-mixed sheet was more porous than Al-soaked sheet. Such high porosity for the Al-mixed sheet was obtained through the controllable retention of alumina sol.

The time course of the *p*-HAP concentration for the treatment by Al-mixed sheet under UV irradiation is shown in Fig. 6. The photocatalytic performance of Al-mixed sheet was superior to that of Al-soaked sheet, and a high degradation efficiency comparable to that of powdery TiO_2 was achieved. Almost no omission of TiO_2 particles from the catalyst sheet was observed after treatment, as determined by atomic absorption analysis (data not shown). In general, molded catalysts having only nanometer-sized pores exhibit lower performance due to intra-particle diffusion limitations [18]. On the other hand, the Al-mixed TiO_2 sheet has characteristic micrometer scale pores derived from the layered fiber network in which TiO_2 particles are scattered. Recently, such micrometer-scale pores in solid catalysts have attracted much attention, and the unique pore-dependent effects have been investigated with regard to the mass transfer of reactants onto the active catalyst surface [18, 22, 23]. In the case of Al-mixed TiO_2 sheet, effective transport of *p*-HAP to TiO_2 surfaces through micrometer scale pores seemed to occur, resulting in high photocatalytic performance. Thus, the Al-mixed sheet is a novel catalytic material having both practical convenience and high photocatalytic performance.

Sheet preparation using TiO_2 sol

To prepare high performance photocatalyst sheet, application of TiO_2 sol instead of the TiO_2 powder-alumina sol system was investigated. TiO_2 sol is often used to form thin TiO_2 films on various supports, for example glass plate and tile; TiO_2 sol is first coated on the supports and then calcined [24]. In our work, TiO_2 sol was used in order to improve the sheet strength while immobilizing TiO_2 inside the sheet. As shown in Fig. 1-c, TiO_2 sol was added during the sheet formation process, to be immobilized only around the ceramic fibers, in a similar manner to that used for alumina sol retention (TiO_2 sol sheet). Fig. 7 displays an SEM image of TiO_2 sol sheet. TiO_2 was retained around the ceramic fibers and the sheet showed a porous structure. The immobilization of TiO_2 in the sheet was also confirmed through atomic adsorption analysis and its retention reached up to 90%. The sheet strength was also improved through the calcination, to a level equivalent to that of Al-mixed sheet.

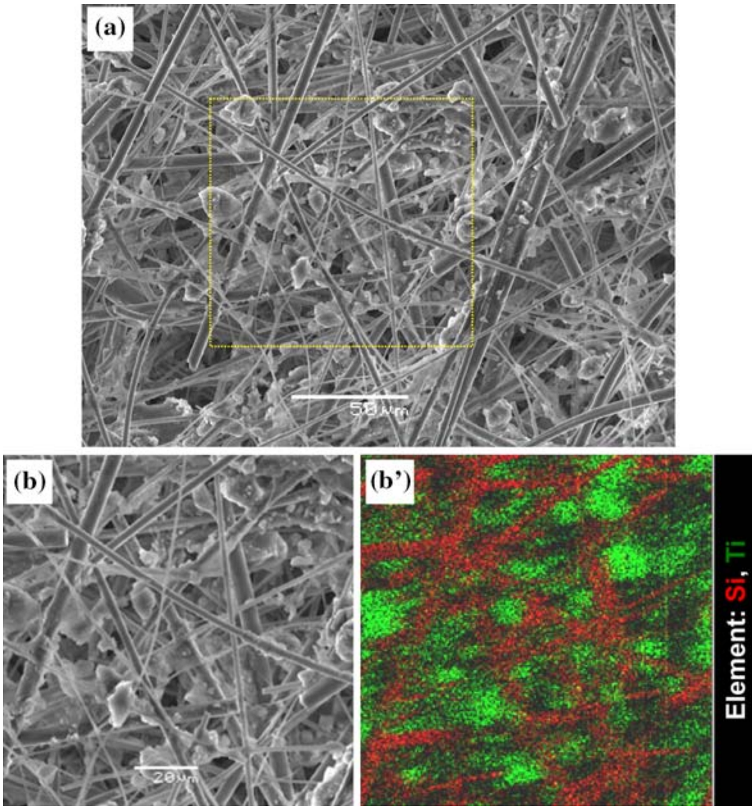

Fig. 5 (**a**) SEM image of the Al-mixed TiO_2 sheet, (**b**) enlarged image of (a). An illustration (**b'**) visualizes the EDS-mapping image of sheet (b)

Figure 8 shows the changes in the concentrations of *p*-HAP when treated by TiO_2 sol sheets with different TiO_2 contents per unit area (2.5, 7.5, 12.5 µg mm^{-2}) under UV irradiation. The total TiO_2 content in the TiO_2 sol sheet was adjusted to 100 mg by controlling the area of the sample specimen. No adsorption of *p*-HAP to the TiO_2 sol sheet was observed. The photocatalytic efficiency was found to

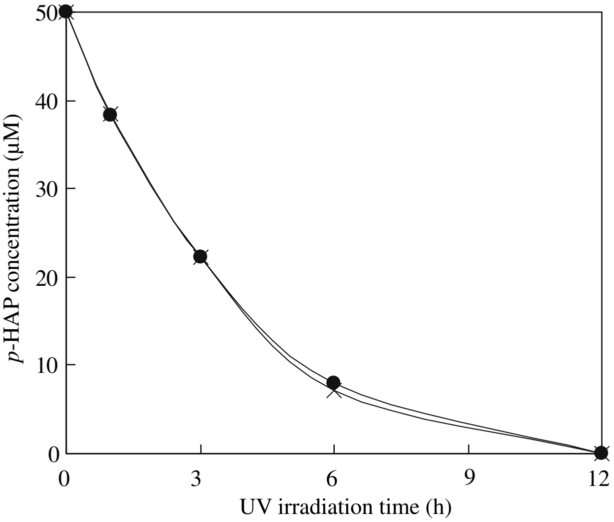

Fig. 6 Time courses of *p*-HAP concentrations; treatment with TiO_2 powder (crosses) and Al-mixed TiO_2 sheet (closed circles)

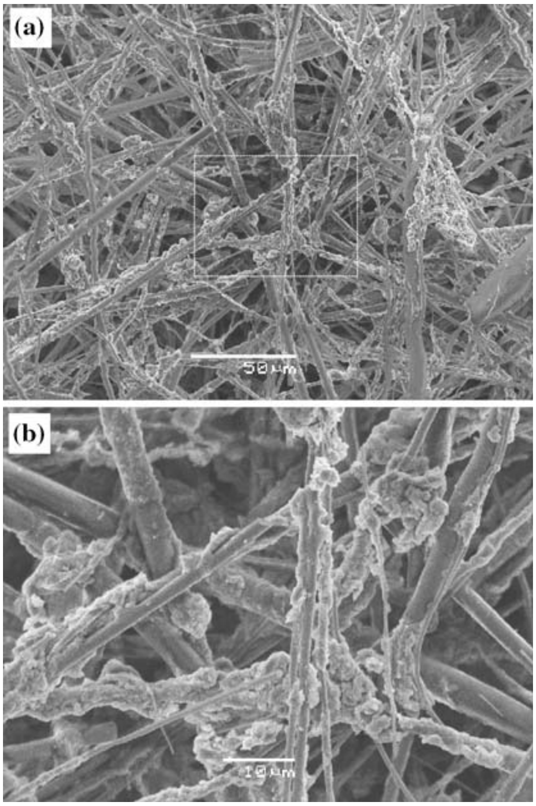

Fig. 7 SEM image of (**a**) the TiO_2-sol sheet and (**b**) enlarged image of (a)

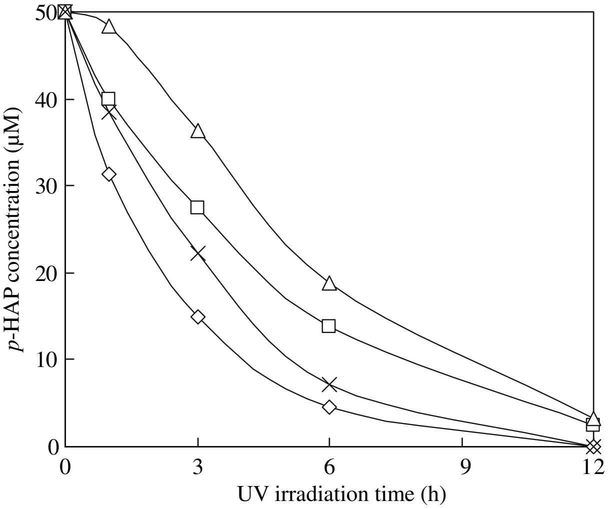

Fig. 8 Time courses of *p*-HAP concentrations; treatment with TiO_2 powder (crosses), TiO_2-sol sheets with different TiO_2 contents per unit area: 2.5 (open diamonds), 7.5 (open squares) and 12.5 μg mm^{-2} (open triangles)

improve with a decreasing TiO_2 content per unit area, as an increased TiO_2 content per unit area seemed to cause aggregation of TiO_2 particles inside the sheet, resulting in a decrease in the accessible TiO_2 surface. The TiO_2 sol sheet with a TiO_2 content of 2.5 μg mm^{-2} exhibited higher degradation performance than that achieved by TiO_2 powder. These results indicate that the accessibility of target molecules to the catalyst surface impacts greatly on the catalytic efficiency, and the TiO_2 sol sheet prepared in this study overcame the deterioration of the catalytic performance which is often observed in immobilized catalysts.

Conclusion

A porous TiO_2 photocatalyst-containing sheet was prepared by using a papermaking technique. The TiO_2 sheet in which TiO_2 particles were homogeneously scattered on the ceramic fiber network exhibited high photocatalytic performance, equivalent to that of powdered TiO_2. In addition, a novel TiO_2 sheet prepared using TiO_2 sol showed higher performance than TiO_2 powder. It was suggested that the characteristic porous structure of the sheet contributed to the mass transfer to the TiO_2 surface inside the sheet, resulting in the high photocatalytic efficiency. The sheet preparation method established in this study is applicable to other powdery materials and almost all of the wide range of solid catalysts used in industrial fields can be impregnated into porous sheet composites. The sheet consisting of inorganic ceramic fiber and alumina binder is thermostable and can be used in thermochemical catalytic processes, such as gas reforming or purification. Thus, catalyst-containing porous sheet composite, which has both practical convenience and high catalytic performance, is a promising candidate for catalyst-based materials.

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