JOURNAL OF MATERIALS SCIENCE **37** (2002) 2937–2941

Preparation of composite TiO_2-zeolite sheets using a papermaking technique and their application to environmental improvement

Part I *Removal of acetaldehyde with and without UV irradiation*

H. ICHIURA*, T. KITAOKA, H. TANAKA
Department of Forest and Forest Products Sciences, Kyushu University,
Fukuoka 812-8581, Japan
E-mail: h_ichi@agr.kyushu-u.ac.jp
E-mail: tkitaoka@agr.kyushu-u.ac.jp

Composite titanium dioxide (TiO_2)-zeolite sheets were prepared using a papermaking technique and were tested with regard to their ability to remove acetaldehyde, which is often used as a typical volatile organic compound. It was demonstrated that the composite TiO_2-zeolite sheet could remove acetaldehyde much more effectively under UV irradiation than a sheet of TiO_2 alone. Acetaldehyde removal by a composite TiO_2-zeolite sheet with a TiO_2/zeolite ratio of 1 : 4 was particularly effective under the conditions adopted in this work although the composite sheet contained only one fifth of the amount of TiO_2 in the TiO_2 sheet. Additionally, the combination of TiO_2 and zeolite was a useful method to solve the disadvantage of adsorbents, which were the decrease of the performance when the material was saturated or equilibrated with the adsorbates. Consequently, a composite TiO_2-zeolite sheet can be utilized as a high functional material to prevent environmental pollution.

1. Introduction

These days, there are many kinds of environmental pollution all over the world. Volatile organic compounds (VOC), dealt with in this study, have caused various environmental problems. It is well known that VOCs bring about global warming and induce photochemical smog. Also, VOCs are carcinogenic and smell bad, and degrade a housing environment. Studies to solve these problems have been actively undertaken [1–4].

Adsorbents have usually been applied for the removal of environmental pollutants. Especially, zeolite, which has a high adsorption capability, has generally been used as a material which removes NO_X, CO_2, and VOC [5–7]. Zeolite, which is a hydrated alkali-aluminum silicate, has a characteristic three-dimensional structure [8]. A number of artificial zeolites are presently commercially available. They have been used in various applications such as desiccants, molecular sieves, ion exchangers and catalysts [9–14]. Zeolite sheets have been prepared using a papermaking technique in our study [15, 16], and it was reported that the adsorptivity of the sheet was very high [15]. However, the performance of the zeolite was virtually abolished when it was saturated or when the adsorption equilibrium was reached. Furthermore, a toxic substance adsorbed by the adsorbent may be desorbed again by a change in the surrounding conditions such as temperature and humidity.

In this study, to solve these problems, composite sheets of titanium dioxide (TiO_2) and zeolite having the characteristics of adsorptivity and light catalyst were prepared by a papermaking technique. As the harmful materials adsorbed by zeolite can be decomposed by TiO_2 photocatalysis, the zeolite will be expected to have a durable performance. It is well known that most organic compounds involving environmental pollutants can be oxidized to CO_2 by the hydroxyl radicals produced on the TiO_2 surfaces when TiO_2 adsorbs photons with greater energies than the band gap [17, 18]. Therefore, there have been many studies on TiO_2 photocatalysis for the removal of toxic materials from the environment. For example, the decomposition of dioxin, trichloroethylene [19–21] and VOC [22–24] has attracted a great deal of attention. The adsorbability of toxic substances on TiO_2 is thus an important factor determining its decomposition ability [22, 23]. In the cases of dilute pollutants at ppm levels, it is very difficult to decompose them completely by TiO_2 photocatalysis alone. An effective way of achieving a rapid and efficient decomposition under such dilute conditions should be to prepare a composite sheet with

---

*Author to whom all correspondence should be addressed.

zeolite to concentrate the toxic substances around the TiO_2.

In this report, the adsorption and photocatalytic decomposition of acetaldehyde gas with sheets prepared under various conditions using a papermaking technique [15] were studied. The synergistic effect of irradiating the composite TiO_2-zeolite sheets with UV irradiation ($\lambda = 365$ nm) on the photocatalytic decomposition of VOC was investigated in detail. And the potential application of the composite TiO_2-zeolite sheet to VOC removal was studied.

2. Experimental section

2.1. Materials

The pulp used was a bleached hardwood kraft pulp beaten to a Canadian Standard Freeness (CSF) of 265 ml in a Technical Association of Pulp and Paper Industry (TAPPI) standard beater. Inorganic materials used were zeolite Y type and ceramic fiber, and TiO_2 kindly provided by Mitsubishi Heavy Industry Ltd. and Ishihara Techno Co., respectively. Poly (diallyldimethylammonium) chloride (PDADMAC) and anionic polyacrylamide (A-PAM) were used as retention aids. An alumina sol provided by Nissan Chemicals Inc. was used as binder to provide sheet strength after ignition at 700°C [15].

2.2. Preparation of the composite sheets [16]

Pulp slurry was mixed with PDADMAC, followed by the addition of inorganic suspensions containing zeolite, ceramic fiber and TiO_2, and A-PAM in that order. The levels of addition of PDADMAC and A-PAM were 0.1% and 1.0% on solids, respectively. Handsheets with a grammage of 250 g/m^2 were prepared according to TAPPI method-205. The wet sheets were pressed under 350 kPa for 5 minutes and dried in a convection oven at 105°C for 30 minutes. The composition of the sheet-making stock was pulp 10%, ceramic fiber 24.5%, zeolite 65.5-0% and TiO_2 0-65.5%.

After being soaked in the alumina sol, the composite sheets were pressed under 350 kPa for 5 minutes and were kept in an air-conditioned chamber (20°C, 65% RH) for 24 hours. The sheets were then ignited in an electric furnace at 700°C for 20 minutes to remove the wood pulps used in preparation of the sheets and to give strength to the inorganic sheets by calcination of the binder.

Table I gives the data for the sheet samples used in the experiments. The table shows the proportions of zeolite and TiO_2 in the inorganic material in the sheet, excluding the ceramic fiber.

2.3. Retention of inorganic materials

The retention of inorganic materials including zeolite, ceramic fiber and TiO_2 was estimated from the ash residues of sheets ignited in an electric furnace at 700°C for 20 minutes. These values were corrected for the weight losses of the inorganic materials themselves determined by heating them at 700°C.

TABLE I Retention of inorganic materials and proportion of TiO_2 and zeolite in the sheets

		Composition of sheets (%)	
Sheet	Retention (%)	TiO_2	Zeolite
Zeolite sheet	95.0	0	100
TiO_2 sheet	90.1	100	0
Composite sheet/Ti : ZE = 2 : 1	95.0	67	33
Composite sheet/Ti : ZE = 1 : 1	87.2	50	50
Composite sheet/Ti : ZE = 1 : 2	90.8	33	67
Composite sheet/Ti : ZE = 1 : 4	91.6	20	80
Composite sheet/Ti : ZE = 1 : 8	86.4	11.1	88.9
Composite sheet/Ti : ZE = 1 : 12	90.8	7.7	92.3

(Ti : TiO_2, ZE : Zeolite).

2.4. Adsorption and photocatalytic decomposition of acetaldehyde

The adsorption and photocatalytic decomposition of gaseous acetaldehyde were studied at room temperature. Sheets 25 mm × 25 mm in size were placed in a 200 ml reaction vessel equipped with a quartz cover and different amounts of acetaldehyde (5 vol% in He) were injected into the vessel using a microsyringe. The sheet was irradiated through the quartz window with a UV lamp (Ultra Violet Products, Inc., UVGL-25; 4W, 365 nm,) from a distance of 10 cm for a fixed time. After irradiation, gas samples were withdrawn from a sampling port on the side of the vessel and injected into the gas chromatograph (GC) using a microsyringe. The acetaldehyde concentration was determined using GC (Shimadzu model GC-17A Ver. 3) equipped with a 30 m × 0.53 mm Supel-Q PLOT column (SUPELCO) and a thermal conductivity detector, using He as the carrier gas.

3. Results and discussion

3.1. Adsorption of acetaldehyde onto zeolite sheet

Fig. 1 shows the adsorption of the acetaldehyde on a zeolite sheet, powdered zeolite, spherical zeolite and paper.

Clearly the adsorption of acetaldehyde was more extensive and took place much more rapidly onto the zeolite sheet and powdered zeolite than onto paper. The initial rate of adsorption on the zeolite sheet was superior to that on the commercial spherical zeolite (Wako Pure Chemical Industries, Ltd.). This result implied that the entrances to pores in the spherical zeolite were partly choked with binder and that the specific surface area was much smaller than that of the zeolite sheet. The adsorptivity of the zeolite sheet was similar to that of powdered zeolite, which indicates that the function of the zeolite is substantially maintained when it is made into sheets by a papermaking technique.

However, the adsorption equilibrium of acetaldehyde on zeolite sheets was readily reached about 25 ppm and the adsorptivity of the zeolite sheet then decreased. The

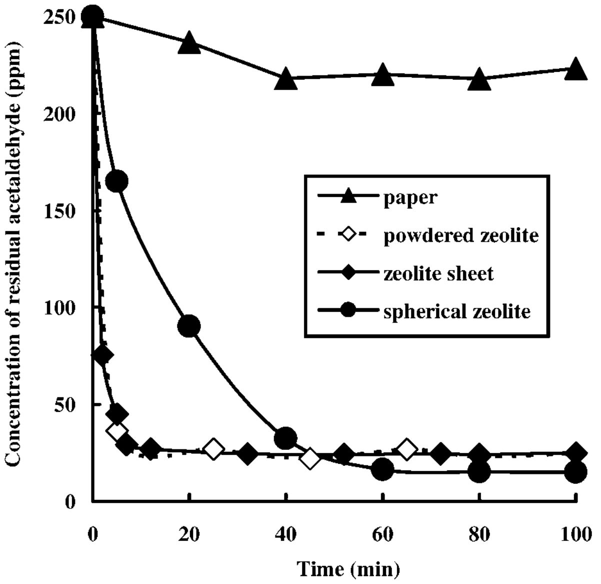

Figure 1 The adsorption of acetaldehyde onto various samples: (▲), paper; (●), spherical zeolite; (◇), powdered zeolite; (♦), zeolite sheet.

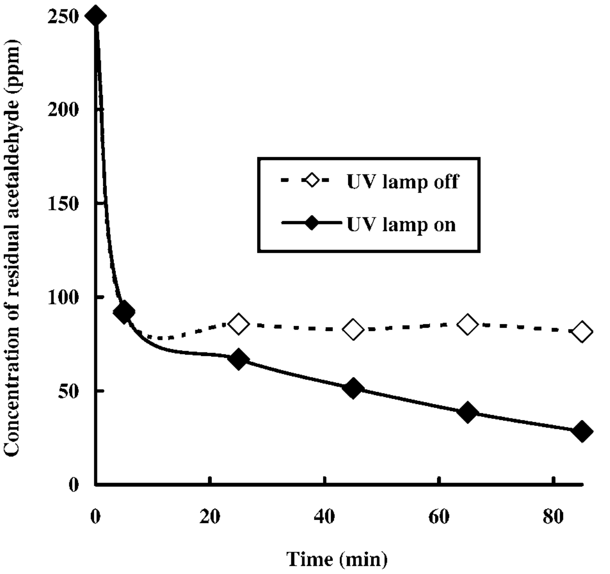

Figure 2 The effect of UV-irradiation on acetaldehyde removal by composite TiO_2-zeolite sheets: (◇), UV lamp off; (♦), UV lamp on.

sheet made of zeolite alone could not therefore remove acetaldehyde completely.

3.2. Adsorption and decomposition of acetaldehyde by a composite TiO_2-zeolite sheet

The synergistic effect of the adsorption and photocatalytic decomposition by the composite TiO_2-zeolite sheet was expected to provide a solution to the above problem. Fig. 2 shows the removal of gaseous acetaldehyde by the composite TiO_2-zeolite sheet/Ti : ZE = 1 : 1 (Table I) both on its own and when irradiated with a UV lamp (UV intensity; 0.3 mW/cm^2). When the UV lamp was turned off, the concentration of acetaldehyde was decreased by the adsorption of zeolite mainly in the TiO_2-zeolite composite sheet, but the composite TiO_2-zeolite sheet could not remove the acetaldehyde completely. This result was similar to those shown in Fig. 1.

In the case of the composite sheet irradiated with a UV lamp, however, the acetaldehyde concentration in the reaction vessel continued to decrease further, in contrast to the situation without irradiation. These results suggested that the photocatalytic decomposition by TiO_2 was progressing through a process of continuously repeated adsorption and migration of acetaldehyde in the composite sheets. It is thought that the combination of zeolite and TiO_2 is a useful way of promoting the efficiency of the adsorbent.

3.3. Permanency of TiO_2-zolite composite sheet

In order to assess whether the composite sheet could repeatedly remove the environmental pollutants, a test was carried out in which 50 ppm of acetaldehyde was injected every 60 minutes. The results are shown in Fig. 3.

In the case of TiO_2 sheet alone, the acetaldehyde concentration in the reaction vessel increased as a result of the sequential addition, the main reason being that TiO_2 could not photocatalytically decompose acetaldehyde if it was not in contact with the TiO_2 surface. In other words, it takes a very long time for a sheet consisting only of TiO_2 to remove acetaldehyde because of the limited adsorption of this pollutant on the TiO_2 surface. The behavior of a composite sheet without UV irradiation was similar, because the adsorption attains equilibrium as in shown Fig. 1.

In the case of the composite sheet irradiated with an UV lamp, however, the acetaldehyde decomposed completely after about 40 minutes. Acetaldehyde could be effectively removed by the combined effect of zeolite adsorptivity and TiO_2 photocatalysis. These results indicate that the composite sheet can continuously remove environmental pollutants and can be utilized semi-permanently.

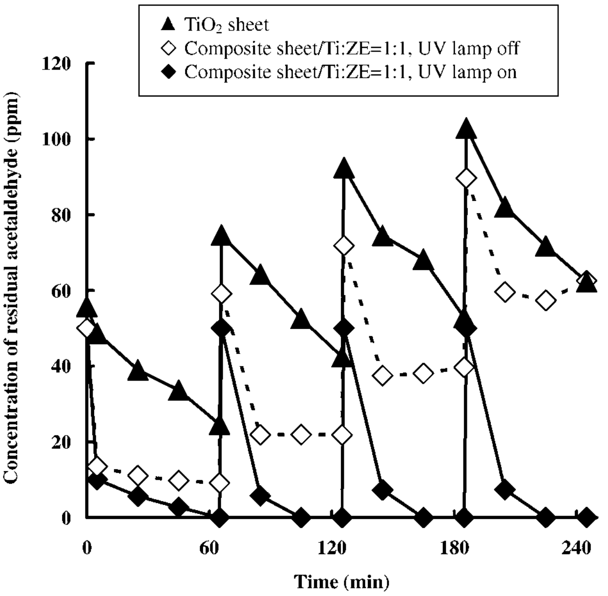

Figure 3 Successive acetaldehyde removal by sheets under various conditions: (▲), TiO_2 sheet; (◇), composite sheet not irradiated with UV; (♦), composite sheet irradiated with UV.

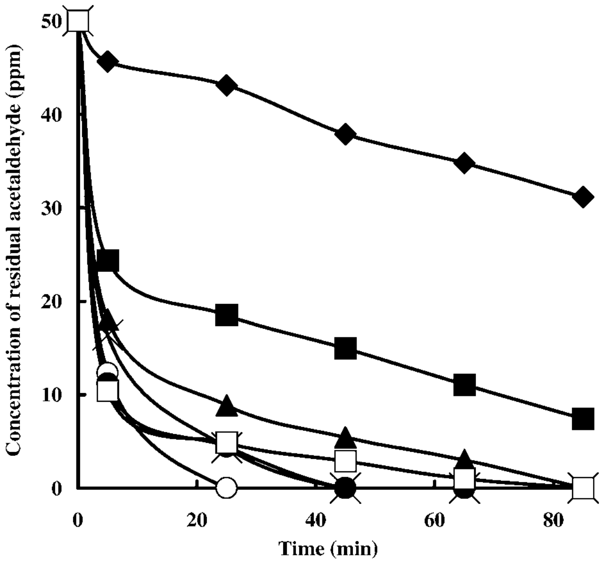

Figure 4 Concentration changes of gaseous acetaldehyde in contrast with composite TiO_2-zeolite sheets irradiated with UV: (♦), TiO_2 sheet; (■), composite sheet/Ti : ZE = 2 : 1; (▲), composite sheet/Ti : ZE = 1 : 1; (×), composite sheet/Ti : ZE = 1 : 2; (○), composite sheet/ Ti : ZE = 1 : 4; (●), composite sheet/Ti : ZE = 1 : 8; (□), composite sheet/Ti : ZE = 1 : 12.

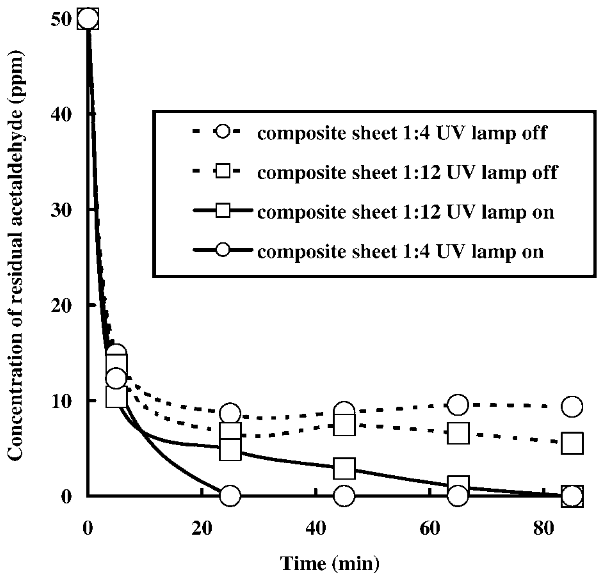

Figure 5 Removal of acetaldehyde by composite sheets: (○), composite sheet/Ti : ZE = 1 : 4; (□), composite sheet/Ti : ZE = 1 : 12; (broken line), UV lamp off; (thick line), UV lamp on.

3.4. Effect of TiO_2/zeolite ratio on the degradation of acetaldehyde

Fig. 4 indicates the effect of the TiO_2/zeolite ratio in the composite sheets on the decrease in acetaldehyde concentration under UV irradiation in order to research the optimum ratios of TiO_2/zeolite in the composite sheets with the high function for effective removal of acetaldehyde. The initial rate ($-dc/dt$, where c is the concentration of acetaldehyde and t is the reaction time) of gaseous acetaldehyde decomposition by the composite TiO_2-zeolite sheet showed a tendency to increase with decreasing TiO_2/zeolite ratio in the sheet. In other words, the decomposition of acetaldehyde occurred more effectively on the sheets with larger amounts of zeolite. This is demonstrated by the value of $-dc/dt$ when t was 5 minutes (see Table II). The removal efficiency after 25 minutes of a TiO_2-zeolite composite sheet with a Ti/ZE ratio of 1 : 8 or 1 : 12 was not, however, greater than that of the composite sheet with a ratio of 1 : 4. Fig. 5 shows the acetaldehyde removal behavior of the composite sheets with the Ti/ZE ratio of 1 : 4 and 1 : 12 alone and irradiated with UV. The acetaldehyde adsorption by the 1 : 12 composite sheet was greater than that of the 1 : 4 composite sheet in the absence of UV irradiation. When the composite sheets were irradiated with UV, on the contrary, the removal efficiency of the 1 : 4 composite sheet was progressively greater than that of the 1 : 12 composite sheet. However, the optimum composition of TiO_2/zeolite may depend upon the experimental conditions such as the pollutant concentration and light intensity.

TABLE II Apparent velocity of decomposition of acetaldehyde by the sheets with different Ti/ZE ratio

	$-dc/dt$	
Sheet	After 5 minutes	After 25 minutes
TiO_2 sheet	0.87	0.28
Composite sheet/Ti : ZE = 2 : 1	5.13	1.26
Composite sheet/Ti : ZE = 1 : 1	6.39	1.65
Composite sheet/Ti : ZE = 1 : 2	6.60	1.83
Composite sheet/Ti : ZE = 1 : 4	7.54	2.00
Composite sheet/Ti : ZE = 1 : 8	7.76	1.82
Composite sheet/Ti : ZE = 1 : 12	7.92	1.81

(c: Concentration of acetaldehyde, t: reaction time).

TiO_2 and zeolite in the composite sheet were uniformly distributed in the composite sheet and TiO_2 was located in the vicinity of the zeolite. This result confirmed by the mapping procedure of elements (Ti, Si and Al) on the sheet using energy dispersive X-ray spectroscopy (data not shown). Accordingly, it was thought that acetaldehyde adsorbed by zeolite was supplied to TiO_2 photocatalyst by surface diffusion [25, 26]. As a result, the gaseous acetaldehyde adsorbed by the zeolite was continuously decomposed by the coexisted TiO_2 photocatalysts. The TiO_2 photocatalytic decomposition was promoted by the higher concentration of acetaldehyde captured in the zeolite. Thus, a composite TiO_2-zeolite sheet was very effective for the photocatalytic decomposition of acetaldehyde.

It is also suggested that the removal of environmental pollutants by the composite sheet could be effectively achieved when the amount of TiO_2 in the composite sheet was so sufficient to ensure that acetaldehyde adsorbed by the zeolite could easily be decomposed by the TiO_2 photocatalysis.

It was noteworthy that the value of $-dc/dt$ for the composite TiO_2-zeolite sheet with a Ti/ZE ratio of 1 : 4 was over seven times that of the sheet with only TiO_2, as shown in Table II when t was 25 minutes. These results indicate that the photocatalytic decomposition with TiO_2 was greatly promoted by the high adsorptive capability of zeolite, and it is clear that the TiO_2-zeolite composite could effectively decompose and completely remove acetaldehyde even under the lower concentration level.

A composite TiO_2-zeolite sheet is believed to be applicable to the removal of various indoor pollutants if the walls and ceilings of houses are covered with the sheet.

4. Conclusions

A composite TiO_2-zeolite sheet was very effective for the photocatalytic decomposition of acetaldehyde. The gaseous acetaldehyde adsorbed by the zeolite was continuously decomposed by the coexisting TiO_2 photocatalysts. The higher the proportion of zeolite in the composite sheet, the greater was the removal efficiency in the initial stage. However, if the amounts of TiO_2 in the composite sheet were too small, the decomposition of environmental pollutants was retarded. The composite sheet with a Ti/ZE ratio of 1 : 4 was the most effective for the continuous decomposition of acetaldehyde with UV light irradiation under the reaction condition adopted in this work. These results lead to the conclusion that the composite TiO_2-zeolite sheet is potentially applicable as a high functional and new material, which can completely remove toxic substances from the environment and has the characteristics of being easy to handle and flexible in processing. Further details on the application for composite TiO_2-zeolite will be reported in the following articles.

Acknowledgements

This work was supported in part by Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists, the Sumitomo Foundation, the R&D Foundation for Environmental Protection in Steel Industries, and a Grant-in-Aid for Scientific Research (13558075) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors are indebted to Mitsubishi Heavy Industries Ltd. for providing zeolite and ceramic fiber, to Nissan Chemical Co. for the alumina sol and to Ishihara Techno Co., for the TiO_2. Dr. J. Anthony Bristow kindly made a linguistic revision of the manuscript.

References

1. J. R. DeGORCE-DUMAS, S. KOWAI and P. L. LECROIREC, *Can. J. Microbiol.* **43** (1997) 264.
2. Y. CHUNG, C. HUANG, J. R. PAN and C. TSENG, *J. Envir. Eng.* **124**(4) (1998) 362.
3. R. J. KUDLA, S. SUBRAMANIAN, M. S. CHATTHA and T. E. HOOST, *Ind. Eng. Chem. Res.* **35** (1996) 4394.
4. M. G. SEDIGH, W. J. ONSTOT, L. XU, W. L. PENG, T. T. TSOTSIS and M. SAHIMI, *J. Phys. Chem.* A **102** (1998) 8580.
5. A. DYER, "An Introduction to Zeolite Molecular Sieve" (John Wiley & Sons, New York, 1998).
6. Y. YOKOMICHI, T. NAKAYAMA, O. OKADA, Y. YOKOI, I. TAKAHASHI, H. UCHIDA, H. ISHIKAWA, R. YAMAGUCHI, H. MATSUI and T. YAMABE, *Catal. Today.* **29** (1996) 155.
7. C. L. GARCIA and J. A. LERCHER, *J. Phys. Chem.* **96** (1992) 2230.
8. R. Y. YANAGIDA, A. A. AMARO and K. SEFF, *ibid.* **77**(6) (1973) 805.
9. H. TAKEDA and M. IWAMOTO, *Bull. Chem. Soc. Jpn.* **69** (1996) 2735.
10. T. TABATA, H. OHTSUKA, M. KOKITSU and O. OKADA, *ibid.* **68** (1995) 1905.
11. J. YANG and C. LEE, *AIChE J.* **44**(6) (1998) 1325.
12. J. A. C. SILVA and A. E. RODRIGUES, *ibid.* **43**(10) (1997) 2524.
13. S. U. REGE, J. PADIN and R. T. YANG, *ibid.* **44**(4) (1998) 799.
14. S. M. KUZNICKI, US Patent no. 4,938,939 (1990).
15. H. ICHIURA, N. OKAMURA, T. KITAOKA and H. TANAKA, in Proceedings of Pre-symposium of the 10th ISWPC, Seoul, June 1999, edited by J. Lee (Korea TAPPI, Seoul, Korea) p. 320.
16. H. ICHIURA, Y. KUBOTA, Z. WU and H. TANAKA, *J. Mater. Sci.* **36**(4) (2001) 913.
17. Y. OHKO, K. HASHIMOTO and A. FUJISHIMA, *J. Phys. Chem.* A **101** (1997) 8057.
18. A. L. LINSEBIGLER, G. LU and J. T. YATES, Jr., *Chem. Rev.* **95** (1995) 735.
19. M. D. DRIESSEN, A. L. GOODMAN, T. M. MILLER and G. A. ZAHARIAS and V. H. GRASSIAN, *J. Phys. Chem.* B **102** (1998) 549.
20. J. B. LIU, J. C. CRITTENDEN, D. W. HAND and D. L. PERRAM, *J. Envir. Eng.* **122**(8) (1996) 707.
21. R. A. BURNS, J. C. CRITTENDEN, D. W. HAND and V. H. SELZER, L. L. SUTTER and S. R. SALMAN, *ibid.* **125**(1) (1999) 77.
22. N. TAKEDA, M. OHTANI, T. TORIMOTO, S. KUWABATA and H. YONEYAMA, *J. Phys. Chem.* B **101** (1997) 2644.
23. N. TAKEDA, T. TORIMOTO, S. SAMPATH, S. KUWABATA and H. YONEYAMA, *ibid.* **99** (1995) 9986.
24. Y. OHKO, D. A. TRYK, K. HASHIMOTO and A. FUJISHIMA, *ibid.* B **102** (1998) 2699.
25. C. MINERO, F. CATOZZO and E. PELIZZETTI, *Langumuir* **8** (1992) 481.
26. H. UCHIDA, S. ITOH and H. YONEYAMA, *Chem. Lett.* (1993) 1995.

Received 18 June 2001
and accepted 27 March 2002