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Effect of activated carbon content in TiO_2-loaded activated carbon on photodegradation behaviors of dichloromethane

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Abstract

The effect of the amount of TiO_2 loading on activated carbon support on the photodecomposition of dichloromethane was studied. The apparent adsorption constant of the TiO_2-loaded activated carbon for dichloromethane was found to decrease with increase of the fraction of the loaded TiO_2. It was found that the apparent rate constant of CO_2 evolution became small with increase of the activated carbon content, suggesting that the adsorbed substrate on the activated carbon support was not easily involved in the photodecomposition reaction. However, the use of mixed suspensions of TiO_2 and activated carbon showed lower activities than the TiO_2-loaded activated carbon for photodegradation of dichloromethane. The role of the activated carbon support in the photodecomposition of dichloromethane is discussed. © 1997 Elsevier Science S.A. All rights reserved.

Keywords: Activated carbon; Photodegradation; Dichloromethane; TiO_2; Photocatalyst

1. Introduction

Recently, fairly intensive studies have been done on light-induced mineralization of organic pollutants with use of TiO_2 photocatalysts [1–9]. The photodecomposition of halogenated organic compounds is of particular importance [10a–10f,11a–11b–21], because they are formed from various sources in the course of water treatments using chlorine and chlorite. Photodegradation processes in general occur with attack of organic substrates by activated oxygen species, such as $OH^{\bullet}$, $O_2^{\bullet -}$, and HOOH, generated on TiO_2 particle surfaces by reduction of dissolved oxygen in solution and/or oxidation of surface hydroxyl of TiO_2 [1–9,22–26]. For target substances to be photodecomposed, it is essential for them in the bulk solution to be supplied to TiO_2 particles to make adsorption. Unfortunately the TiO_2 particles usually have low adsorption abilities for organic pollutants, and furthermore target substances are in such low concentrations as in a ppm level or below. Accordingly, the rate of photodecomposition of pollutants to be expected is usually very low.

One strategy to enhance the rate of photodegradation has been proposed recently: use of adsorbents as the support for TiO_2 provides high concentration environments of target substances around TiO_2 photocatalyst [27–30a–30d–34]. We demonstrated previously that the use of zeolites, silica and activated carbon as supports for TiO_2 loading was effective in concentrating propyzamide of a ppm level onto the supports and thereby the rate of its photodecomposition was greatly enhanced as compared to the case of using naked TiO_2 [30d]. In order to obtain high decomposition rates of target substances of very dilute concentration, the target substances must be exclusively adsorbed on the absorbent supports, and the adsorbed substances must be quickly oxidized at the loaded TiO_2. However, such situations are not necessarily guaranteed with the use of adsorbent supports. If adsorbed substances are tightly bound to adsorbent supports, they may not be involved in photodecomposition reactions.

In the present study, photodecomposition of dichloromethane on TiO_2-loaded activated carbon photocatalysts was investigated focusing to the effect of adsorbed of dichloromethane on its decomposition rate.

2. Experimental

Activated carbon powder (Wako Pure Chemicals) was used as a support for TiO_2 loading. Other chemicals used in this study were of reagent grade and purchased from Wako Pure Chemical Industry. Aqueous solutions were prepared using doubly distilled water.

The TiO_2-loaded activated carbon (TiO_2/AC) was prepared using the same procedures as those described in our

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previous paper [30a–30d]. 3.7 cm^3 of titanium tetraisopropoxide was added drop by drop to 15 cm^3 of 1 M HNO_3 aqueous solution, followed by agitation for 2 h to give a transparent TiO_2 sol in which 1.0 g TiO_2 was contained. The pH of the colloidal solution was adjusted to pH 3 with addition of 1 M NaOH solution after dilution of the colloid with 50 cm^3 water, resulting in a turbid TiO_2 colloid. After adding an adequate amount of activated carbon to the TiO_2 colloids, the resulting mixed suspension was agitated for 1 h at room temperature, followed by centrifugation and then washing with distilled water. The centrifugation–washing procedures were repeated several times until the pH of the supernatant became neutral. Then the isolated TiO_2/AC was dried under vacuum and subjected to heat treatments at 300°C for 1 h. The amount of the loaded TiO_2 on the adsorbents was determined by colorimetric analysis using sodium 1,2-dihydroxybenzene-3,5-disulfate (Tiron) as a complex agent [35]. Naked TiO_2 powder was prepared using the same procedures as described above except for addition of the adsorbent. The BET specific surface area of the prepared TiO_2/AC was determined by argon adsorption at liquid nitrogen temperature using a model 2205 Shimadzu-Micromeritics surface area analyzer. We use the term "photocatalysts" below in cases where there is no need to discriminate between TiO_2/AC and the naked TiO_2.

The aqueous solutions of dichloromethane, trichloromethane (chloroform) and tetrachloromethane for photodegradation experiments were prepared with use of air-saturated water. 10 cm^3 of an air-saturated aqueous solution containing 1.0 mmol dm^{-3} of substrate was put in a Pyrex reaction cell (1.5 cm diameter, 11 cm height, 18 cm^2 capacity) and then an adequate amount of the photocatalyst was added to give the concentration of 0.20 g TiO_2 dm^{-3}. After the gas phase in the reaction cell was filled with air, the top of the cell was sealed with a rubber septum through which sampling was made intermittently during the photodecomposition experiments. Prior to the photodecomposition experiments, the suspension was stirred for more than 12 h in the dark to achieve adsorption equilibrium of the substrate to the photocatalyst. The illumination of the suspension was carried out with use of a 10 W fluorescent black lamp at room temperature. The fluorescent black lamp had a nearly symmetrical distribution of the spectrum ranging from 300 nm to 430 nm with 352 nm at its peak. The light intensity was 1.8 mW cm^{-2}, as determined by an Eppley Lab Model E-6 thermopile. The amount of CO_2 produced by the photodecomposition of dichloromethane was determined by means of gas chromatography using a Yanaco G2800 gas chromatograph equipped with a TCD detector and a Porapak T column (Waters) at 100°C. Helium was used as a carrier gas.

Adsorbability of the photocatalysts for the substrates was determined as follows. 10 cm^3 of an aqueous solution containing various concentrations of substrate was put in the Pyrex reaction cell and then an adequate amount of the photocatalyst was added to give the concentration of 0.20 g TiO_2 dm^{-3}. After stirring for a given time, the suspension was subjected to filtration using a 0.2 μm membrane filter. The determination of substrates in the filtrate was performed using a GC-MS (Shimadzu, GC-17A and CLASS-5000) equipped with a fused silica capillary column (DB-1, J & W Scientific, 30 m long, 0.252 mm i.d., 0.25 μm film thickness) with ascending temperature from 60 to 100°C at 0.5°C s^{-1}. The amount of the adsorbed substrates was determined by subtracting the amount of the substrate in solution from its total amount after the adsorption was completed.

3. Results and discussion

3.1. *Characterization of TiO_2-loaded activated carbon photocatalyst*

The specific surface area of the photocatalysts was linearly increased by increasing the content of the activated carbon in TiO_2/AC, because the specific surface area of activated carbon of 950 m^2 g^{-1} was much greater than that of TiO_2 which had the specific surface area of 152 m^2 g^{-1}. Fig. 1 shows the time course of the concentration decrease of dichloromethane caused by adsorption onto the photocatalyst. If the naked TiO_2 was added to 1.0 mmol dm^{-3} dichloromethane solution, only 10% of dichloromethane was adsorbed. On the other hand, if 80 wt.% TiO_2-loaded activated carbon was suspended in the same solution about 60% of dichloromethane was removed. As shown in the figure, the adsorption equilibrium was attained at about 5 h. Fig. 2(a) shows relationships between the amount of adsorbed dichloromethane on the photocatalysts having different amounts of the loaded TiO_2 (S_{ad}) and the concentration of dichloromethane in solution phase (C_S) under equilibrium conditions. The increase of the content of activated carbon in the photocatalysts caused an increase of adsorption of dichloromethane on the photocatalysts depending on the concentration of dichloromethane. The effect was more marked when the TiO_2 content in the photocatalyst become small. If the Langmuir adsorption isotherm given by Eq. (1) is applied to the results given in Fig. 2(a), results given in Fig. 2(b) were obtained.

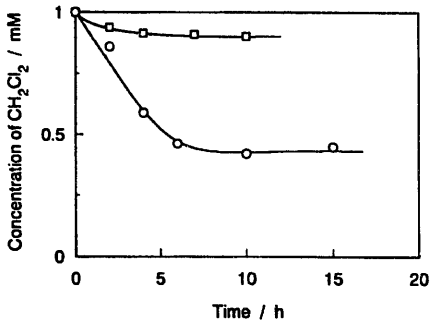

Fig. 1. Changes in the concentration of dichloromethane in solution caused by adsorption onto the photocatalyst in the dark: (□) naked TiO_2 and (○) the 80 wt.% TiO_2-loaded activated carbon. Photocatalyst was suspended in 10 cm^3 of 1.0 mmol dm^{-3} dichloromethane aqueous solution so as to give 0.20 g TiO_2 dm^{-3}.

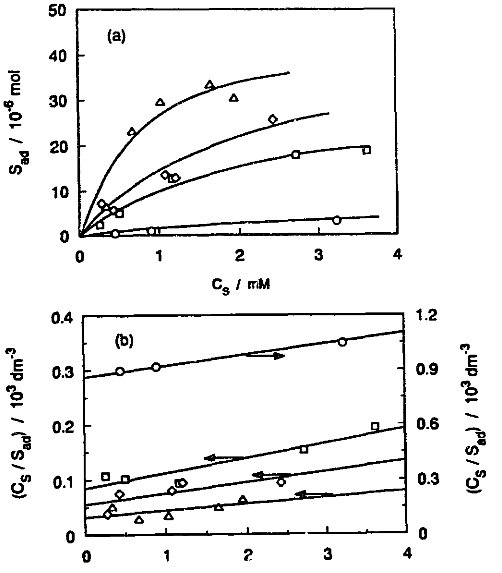

Fig. 2. Relationship between the amount of adsorption of dichloromethane (S_{ad}) and its concentration in solution (C_S) obtained by suspending TiO_2/AC (a), and plots of the left-hand side of Eq. (1) as a function of C_S (b). The photocatalyst was suspended in 10 cm^3 of dichloromethane solution with various concentration to give 0.20 g TiO_2 dm^{-3}. The loaded TiO_2 content was 65 (△), 80 (◇), 90 (□) and 100 (○) wt.%.

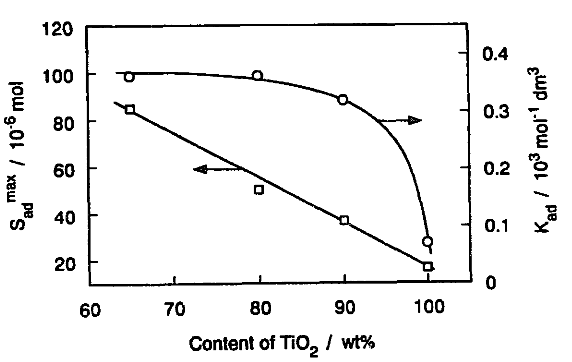

Fig. 3. Influence of the loaded TiO_2 content on the adsorption constant of dichloromethane (K_{ad}) and the maximum amount of adsorbed dichloromethane (S_{ad}^{max}). The photocatalyst was suspended in 10 cm^3 of dichloromethane solution with various concentration to give 0.20 g TiO_2 dm^{-3}.

$$\frac{C_s}{S_{ad}}=\frac{C_s}{S_{ad}^{max}}+\frac{1}{K_{ad}S_{ad}^{max}} \tag{1}$$

where K_{ad} is the adsorption constant and S_{ad}^{max} is the maximum value of S_{ad}. Values of C_S/S_{ad} depended linearly on C_S, and from the relations obtained, K_{ad} and S_{ad}^{max} were determined.

Fig. 3 shows the dependence of K_{ad} and S_{ad}^{max} on the content of TiO_2 of the photocatalyst. With increase of the TiO_2 content, the S_{ad}^{max} decreased linearly, indicating that the amount of adsorption sites of the photocatalysts was controlled by the content of activated carbon. On the other hand, the K_{ad} values were almost constant for TiO_2 contents lower than 90 wt.% and beyond that they decreased steeply. Considering that K_{ad} of the naked TiO_2 is small but K_{ad} of the photocatalyst greatly increased with increase of a little amount of activated carbon, it is concluded that the activated carbon has a great adsorption strength and dichloromethane is mainly adsorbed on the surface of the activated carbon rather than on the surface of the loaded TiO_2 particles.

3.2. Photodecomposition of dichloromethane

Fig. 4(a) shows the time course of CO_2 evolution with illumination of the naked TiO_2 and TiO_2/AC having 80, 90 and 100 wt.% of the TiO_2 content. The complete decomposition of dichloromethane to CO_2 is given by

$$CH_2Cl_2+O_2 \rightarrow CO_2+2HCl \tag{2}$$

Since 10 μmol of dichloromethane was contained in the reaction cell, the evolution of the same amount of CO_2 is theoretically expected, and the results given in Fig. 4(a) show that the theoretically predicted amount of CO_2 evolved with irradiation for more than 50 h. It is evident that the rate of CO_2 evolution increased with increase of the TiO_2 content. If it is assumed that the photodecomposition of CH_2Cl_2 to CO_2 proceeded with the pseudo-first-order kinetics with respect to its concentration [11a,36], the rate of CO_2 production at a given illumination time is given by

$$\frac{d(CO_2)}{dt}=k_{CO_2}\{(CO_2)_{max}-(CO_2)\} \tag{3}$$

where k_{CO_2} is the apparent rate constant for CO_2 evolution, $(CO_2)_{max}$ is the amount expected from complete decomposition of CH_2Cl_2, 10 μmol, and (CO_2) is that obtained at a given illumination time. Integration of Eq. (3) gives

$$\ln[(CO_2)_{max}/\{(CO_2)_{max}-(CO_2)\}]=k_{CO_2}t \tag{4}$$

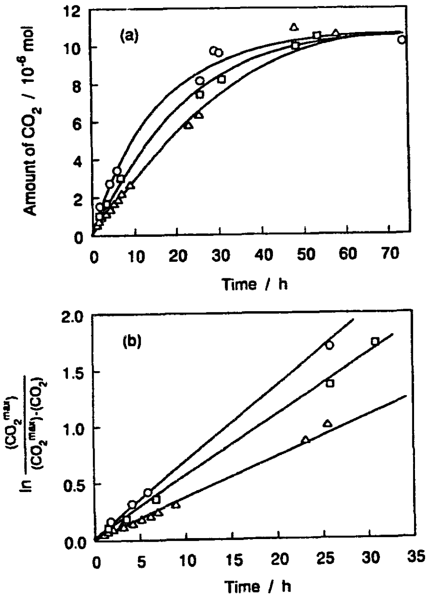

Fig. 4. Time course of CO_2 evolution in photodecomposition of dichloromethane over various photocatalysts (a) and plots of the left-hand side of Eq. (4) as a function of the illumination time (b). (○) naked TiO_2, 90 (□) and 80 (△) wt.% TiO_2-loaded activated carbon. Photocatalyst was suspended in 10 cm^3 of 1.0 mmol dm^{-3} dichloromethane aqueous solution to give 0.20 g TiO_2 dm^{-3}. The illumination was performed with a 10 W fluorescent black lamp.

When the left-hand side of Eq. (4) was plotted as a function of the illumination time for the results given in Fig. 4(a), fairly good linear relations were obtained as shown in Fig. 4(b), from which k_{CO_2} was determined.

Fig. 5 shows k_{CO_2} determined in this way as a function of the TiO_2 content. With an increase of the amount of the loaded TiO_2, k_{CO_2} increased, while the amount of adsorbed CH_2Cl_2 under the present experimental condition (S_{ad}^{photo}) decreased with increase of the TiO_2 content. About 80% of dichloromethane was adsorbed for 30 wt.% TiO_2-loaded activated carbon, while as small as 10% for the naked TiO_2. When the photodecomposition occurs, dichloromethane must be supplied from the bulk solution to the loaded TiO_2 by diffusion. If the adsorbed dichloromethane is involved in the photodecomposition, it must be supplied to the loaded TiO_2 mainly by the surface diffusion. Considering that k_{CO_2} increased with increase in TiO_2 content of TiO_2/AC whereas S_{ad} decreased, the non-adsorbed dichloromethane seems to be more predominantly involved in the decomposition reaction. The diffusion constant of dichloromethane adsorbed on activated carbon must be much lower than that in the bulk solution. The results obtained here make a marked contrast to those obtained for photodecomposition of propyzamide, where adsorbed propyzamide is more readily photodecomposed [30a,30].

In order to get positive evidence of the TiO_2-loading on activated carbon for enhancing the photomineralization of dichloromethane, comparative studies were carried out using mixed suspensions of 80 wt.% TiO_2 and 20 wt.% activated carbon. The results obtained are also plotted in Fig. 5. The k_{CO_2} obtained at the mixed suspension was much lower than that obtained from the TiO_2/AC used, evidencing that the loaded TiO_2 onto activated carbon is certainly involved in the photodecomposition of adsorbed dichloromethane. In the case of using the mixed suspension, the photodecomposition occurs at the time when the irradiated TiO_2 particles strike on the dichloromethane-adsorbed activated carbon. The probability of colliding the irradiated TiO_2 with activated carbon is said not to be high even with use of 80 wt.% TiO_2.

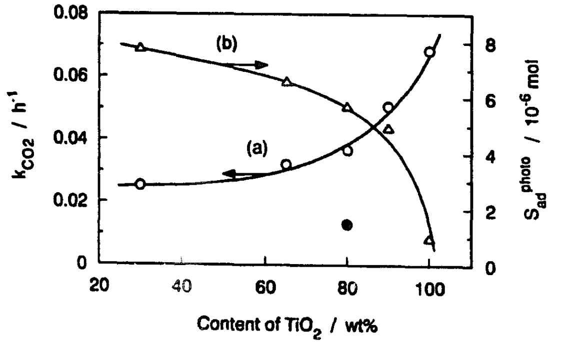

Fig. 5. (a) Relationship between the rate constant of CO_2 evolution and the TiO_2 content inthe photocatalysts. (○) TiO_2/AC and (●) a mixture of 80 wt.% TiO_2 particles and activated carbon. (b) The amount of adsorbed dichloromethane on the photocatalysts under the experimental condition as a function of the TiO_2 content (△).

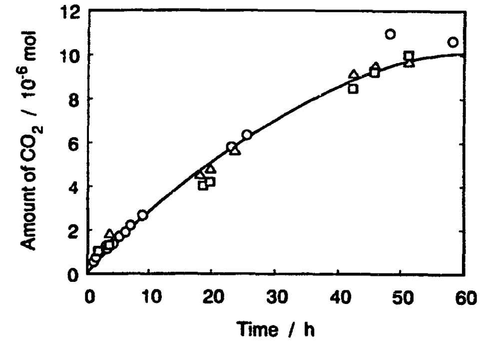

Fig. 6. Time course of CO_2 evolution in photodecomposition of CH_2Cl_2 (○), $CHCl_3$ (△), and CCl_4 (□) over 80 wt.% TiO_2-loaded activated carbon. The photocatalyst was suspended in 10 cm^3 of 1.0 mmol dm^{-3} solution to give 0.20 g TiO_2 dm^{-3}. The illumination was performed with a 10 W fluorescent black lamp.

The photodecomposition of trichloromethane and tetrachloromethane was also investigated using TiO_2/AC. Fig. 6 shows the time course of CO_2 evolution caused by their photodecompositions together with the results on photodecomposition of dichloromethane with use of the 80 wt.% TiO_2-loaded activated carbon as a photocatalyst. This figure shows the rates of photodecomposition obtained were almost same. Ollis et al. reported that the rate constant of photodecomposition of chlorinated methane on naked TiO_2 photocatalysts decreased with order of $CHCl_3 > CH_2Cl_2 > CCl_4$ [10a]. They obtained the rate constant for adsorbed species in which the influence of the diffusion of the substrate from the solution bulk was not included. In the present study the amount of tetrachloromethane, trichloromethane and dichloromethane adsorbed on the TiO_2/AC was found to be almost the same with each other. Considering that not the adsorbed species but the species in solution was mostly involved in the photodecomposition reaction, the finding that the same photodecomposition rate obtained between the three kinds of chlorinated methanes then suggest that the rate of supply of these substances were not greatly different.

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References

[1] D.F. Ollis, E. Pelizzetti and N. Serpone, *Photocatalysis; Fundamentals and Applications*. N. Serpone and E. Pelizzetti, Eds.; Wiley: New York, 1989, Chapter 18.
[2] D.F. Ollis, E. Pelizzetti and N. Serpone, *Environ. Sci. Technol.*, *25* (1991) 1522.
[3] M.A. Fox and M.T. Dulay, *Chem. Rev.*, *93* (1993) 341.
[4] A Mills, R.H. Davies and D. Worsley, *Chem. Soc. Rev.*, *22* (1993) 417.
[5] E. Pelizzetti and C. Minero, *Electrochimica Acta*, *38* (1993) 47.
[6] M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev.*, *95* (1995) 69.
[7] A.L. Linsebigler, G. Lu and J.T. Yates Jr., *Chem. Rev.*, *95* (1995) 735.

[8] A. Heller, *Acc. Chem. Res.*, *28* (1995) 503.

[9] (a) P.V. Kamat, *CHEMTECH.*, *26* (1996) 18. (b) U. Strafford, K.A. Gray and P.V. Kamat, *Heterogeneous Chem. Rev.*, *3* (1996) 77.

[10a] C.Y. Hsiao, C.L. Lee and D.F. Ollis, *J. Catal.*, *82* (1983) 418.

[10b] A.L. Pruden and D.F. Ollis, *Environ. Sci. Technol.*, *17* (1983) 628.

[10c] A.L. Pruden and D.F. Ollis, *J. Catal.*, *82* (1983) 404.

[10d] C.S. Turchi and D.F. Ollis, *J. Catal.*, *119* (1989) 483.

[10e] C.S. Turchi and D.F. Ollis, *J. Catal.*, *122* (1990) 178.

[10f] M.L. Sauer, M.A. Hale and D.F. Ollis, *J. Photochem. Photobiol. A: Chem.*, *88* (1995) 169.10

[11a] R.W. Matthews, *J. Phys. Chem.*, *91* (1987) 3328.

[11b] R.W. Matthews, *J. Catal.*, *111* (1988) 264.

[12] (a) H. Al-Ekabi and N. Serpone, *J. Phys. Chem.*, *92* (1988) 5726. (b) H. Al-Ekabi, N. Serpone, E. Pelizzetti, C. Minero, M.A. Fox and R.B. Draper, *Langmuir*, *5* (1989) 250. (c) C. Minero, E. Pelizzetti, P. Pichat, M. Sega and M. Vincenti, *Environ. Sci. Technol.*, *29* (1995) 2226.

[13] (a) T. Hisanaga, K. Harada and K. Tanaka, *J. Photochem. Photobiol. A: Chem.*, *54* (1990) 113. (b) B. Sangchakr, T. Hisanaga and K. Tanaka, *J. Photochem. Photobiol. A: Chem.*, *85* (1995) 187.

[14] (a) C. Kormann, D.W. Bahnemann and M.R. Hoffmann, *Environ. Sci. Technol.*, *25* (1991) 494. (b) J.M. Kesselman, G.A. Shreve, M.R. Hoffmann and N.S. Lewis, *J. Phys. Chem.*, *98* (1994) 13385. (c) W. Choi, A. Termin and M.R. Hoffmann, *J. Phys. Chem.*, *98* (1994) 13669. (d) S.T. Martin, C.L. Morrison and M.R. Hoffmann, *J. Phys. Chem.*, *98* (1994) 13695. (e) W. Choi and M.R. Hoffmann, *Environ. Sci. Technol.*, *29* (1995) 1646. (f) S.T. Martin, A.T. Lee and M.R. Hoffmann, *Environ. Sci. Technol.*, *29* (1995) 2567. (g) N.J. Peill and M.R. Hoffmann, *Environ. Sci. Technol.*, *29* (1995) 2974. (h) W. Choi and M.R. Hoffmann, *J. Phys. Chem.*, *100* (1996) 2161.

[15] (a) S. Kutsuna, K. Takeuchi and T. Ibusuki, *J. Atomos. Chem.*, *14* (1992) 1. (b) S. Kutsuna, Y. Ebihara, K. Nakamura and T. Ibusuki, *Atomos. Environ.*, *27A* (1993) 599. (c) S. Kutsuna, M. Kasuda and T. Ibusuki, *Atomos. Environ.*, *28* (1994) 1627.

[16] L.A. Dibbie and G.B. Raupp, *Environ. Sci. Technol.*, *26* (1992) 492.

[17] M.R. Nimios, W.A. Jacoby, D.M. Blake and T.A. Milne, *Environ. Sci. Technol.*, *27* (1993) 732.

[18] (a) U. Stafford, K.A. Gray, P.V. Kamat and A. Varma, *Chem. Phys. Lett.*, *205* (1993) 55. (b) K. Vinodgopal, S. Hotchandani and P.V. Kamat, *J. Phys. Chem.*, *97* (1993) 9040. (c) K. Vinodgopal, U. Stafford, K.A. Gray and P.V. Kamat, *J. Phys. Chem.*, *98* (1994) 6797.

[19] (a) J.C.S. Wong, A. Linsebigler, G. Lu, J. Fan and J.T. Yates, Jr., *J. Phys. Chem.*, *99* (1995) 335. (b) G. Lu, A. Linsebigler and J.T. Yates, Jr., *J. Phys. Chem.*, *99* (1995) 7626. (c) J. Fan and J.T. Yates, Jr., *J. Am. Chem. Soc.*, *118* (1996) 4686.

[20] H.Y. Chen, O. Zahraa, M. Bouchy, F. Thomas and J.Y. Bottero, *J. Photochem. Photobiol. A: Chem.*, *85* (1995) 179.

[21] A. Haarstrick, O.M. Kut and E. Heinzle, *Environ. Sci. Technol.*, *30* (1996) 817.

[22] (a) C.D. Jaegar and A.J. Bard, *J. Phys. Chem.*, *83* (1979) 3146. (b) I. Izumi, F.-R. Fan and A.J. Bard, *J. Phys. Chem.*, *85* (1981) 218.

[23] U. Stafford, K.A. Gray and P.V. Kamat, *J. Phys. Chem.*, *98* (1994) 6343.

[24] S. Goldstein, G. Czapski and J. Rabani, *J. Phys. Chem.*, *98* (1994) 6586.

[25] V. Brezova, A. Stasko, S. Biskupic, A. Blazkova and B. Havlinova, *J. Phys. Chem.*, *98* (1994) 8977.

[26] (a) G. Riegel and J.R. Bolton *J. Phys. Chem.*, *99* (1995) 4215. (b) L. Sun and J.R. Bolton, *J. Phys. Chem.*, *100* (1996) 4127.

[27] L. Palmisano, M. Schiavello, A. Sclafani, S. Coluccia and L. Marchese, *New J. Chem.*, *12* (1988) 847.

[28] C. Minero, F. Catozzo and E. Pelizzetti, *Langmuir*, *8* (1992) 481.

[29] (b) T. Ibusuki, S. Kutsuna, K. Takeuchi, K. Shinkai, T. Sasamoto and M. Miyamoto, in D.F. Ollis and H. Al-Ekabi (eds.), *Trace Met. Environ. 3 (Photocatalytic Purification and Treatment of Water and Air)*, Elsevier, Amsterdam, 1993, pp. 375. (c) T. Ibusuki and K. Takeuchi, *J. Mol. Catal.*, *88* (1994) 93.

[30a] H. Uchida, S. Itoh and H. Yoneyama, *Chem. Lett.*, (1993) 1995.

[30b] S. Sampath, H. Uchida and H. Yoneyama, *J. Catal.*, *149* (1994) 189.

[30c] N. Takeda, T. Torimoto, S. Sampath, S. Kuwabata and H. Yoneyama, *J. Phys. Chem.*, *99* (1995) 9986.

[30d] T. Torimoto, S. Ito, S. Kuwabata and H. Yoneyama *Environ. Sci. Technol.*, *30* (1996) 1275.

[31] M.A. Fox, K.E. Doan and M.T. Dulay, *Res. Chem. Intermed.*, *20* (1994) 711.

[32] G. Dagan, S. Sampath and O. Lev, *Chem. Mater.*, *7* (1995) 446.

[33] Y. Xu and C.H. Langford, *J. Phys. Chem.*, *99* (1995) 11501.

[34] C. Anderson and A.J. Bard, *J. Phys. Chem.*, *99* (1995) 9882.

[35] J.H. Yoe and A.R. Armstrong, *Anal. Chem.*, *19* (1947) 100.

[36] R.W. Matthews, *J. Chem. Soc. Faraday Trans 1*, *85* (1989) 1291.