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Titanium dioxide/adsorbent hybrid photocatalysts for photodestruction of organic substances of dilute concentrations

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Abstract

Utilities of hybrid photocatalyst consisting of TiO_2 and an adsorbent such as activated carbon in photoinduced mineralization of organic substances of very dilute present concentrations are demonstrated for the photodecomposition of propionaldehyde in air atmosphere, and propyzamide and bromoform dissolved in water. The substrates of target were adsorbed on the adsorbent support, and then a high concentration environments of the substrate was formed around the loaded TiO_2, resulting in an increase in the photodestruction rate. Evidences for the diffusion of propionaldeyde adsorbed on the mordenite support to the loaded TiO_2 are presented. Merits of the use of the adsorbents as the support for TiO_2 loading is discussed.

Keywords: Absorbents; Hybrid phtotocatalysts; Environmental remediation; Photodecomposition

1. Introduction

TiO_2 has a high oxidizing power that is capable of oxidizing almost all organic substances finally to CO_2 in the presence of water and oxygen which serves as an acceptor for photogenerated electrons. Using this ability, research works on the abatements of harmful organic substances dissolved in water and of bad smell organic vapor are currently going on in many laboratories [1–37]. The allowance limit of these substances is very low such as less than 0.1 mg dm^{-3} for substances dissolved in water and such as less than 0.1 ppm for vapor of bad smell substances, though the absolute values of the allowance limit are different depending on the kind of the substances. Therefore, the photodegradation of these harmful and/or bad smell substances should be achieved to a level far below the allowance limit.

However, there is one serious problem to achieve this. According to chemical reaction kinetics, the rate of chemical reactions is determined by the concentration of substances of target. The lower the concentration, therefore, the lower the chemical reaction rate. This means that it will take a very long time for organic substances of target to be photodestructed to desired low levels. We attempted to solve this serious problem by making composites of TiO_2 with adsorbents. Referring to the present technology, activated carbon is widely used to remove organic substances of dilute concentration from water and air atmosphere. If TiO_2 is loaded on adsorbents such as activated carbon, therefore, the adsorbent makes a high concentration environment of substances of target around the loaded TiO_2 by its adsorption, and then the rate of photodestruction will be enhanced, as compared to the rate obtained at unloaded TiO_2.

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With such idea, we have been investigating the effect of adsorbents on the enhancement of the rate of photodestruction of organic substances in very dilute concentrations [38–45]. In this paper, the utilities of TiO_2-loaded adsorbent photocatalysts for purification of water and air atmosphere are described.

2. Effect of the amount of adsorption on the rate of photodegradation [40]

Quantitative discussion was made on photodegradation of gaseous propionaldehyde over TiO_2-loaded mordenite of various amounts. Experiments were carried out in a closed cell of 15 cm^3 capacity into which 1.22×10^{-6} mol of gaseous propionaldehyde and 4.6 ppm water vapor were introduced. The photodecomposition of propionaldehyde gave CO_2 as a final oxidation product.

$$CH_3CH_2CHO + 4O_2 \rightarrow 3CO_2 + 3H_2O \qquad (1)$$

It was found that water vapor was needed to induce photodecomposition of organic substances [39]. The time course of CO_2 evolution is shown in Fig. 1 for three different loadings of TiO_2 on a mordenite support. The rate constant of photodestruction was evaluated by applying the time course of CO_2 evolution to the pseudo first-order rate equation and was plotted as a function of the TiO_2 content. The results are shown in Fig. 2a. Figure 2b shows the amount of adsorption of propionaldehyde (S_{ads}) as a function of the TiO_2 content. By comparing these two figures, it is noticed that the highest decomposition rate was achieved at 50 wt.% TiO_2 loading beyond which the amount of adsorbed propionaldehyde decreased. It is obvious that a decrease of the amount of adsorbed substrate caused a decrease in the decomposition rate.

3. Effects of adsorption strength of adsorbent supports on the rate of photodegradation rate [40]

If similar experiments were carried out using various kinds of adsorbent supports at a fixed amount of TiO_2 loading of 53 wt.%, results as shown in Fig. 3 were obtained, where the amount of adsorption and the decomposition rate are plotted as a function of

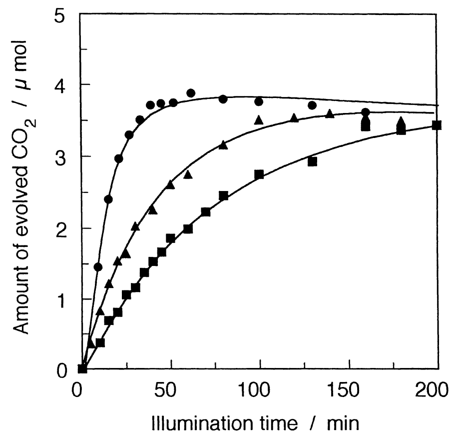

Fig. 1. Time course of the amount of CO_2 produced by photodecomposition of propionaldehyde over TiO_2-loaded mordenite. 1.22×10^{-6} mol of propionaldehyde and 4.6 torr water vapor were contained in a cell of 15 cm^3 capacity. The amount of catalyst film prepared on a glass plate (1.0 cm width and 4.0 cm length) was 1.0 mg cm^{-2} including the support. The TiO_2 content in the catalyst was 5 (■), 11 (▲), and 53 (●) wt.%. Illumination was carried out using a 10 W fluorescent black lamp. The hybrid photocatalyst film was prepared by coating the glass plate with TiO_2 colloid containing suspended mordenite. The TiO_2 colloid was prepared by hydrolysis of titanium tetraisopropoxide.

adsorption constant (K_{ad}) which was obtained by applying adsorption isotherms obtained at the TiO_2-loaded adsorbent photocatalysts to the Langmuir adsorption equation given by the following equation.

$$\frac{C_s}{S_{ad}} = \frac{C_s}{S_{ad}^{max}} + \frac{1}{K_{ad} S_{ad}^{max}} \qquad (2)$$

where C_s is the concentration of propionaldehyde in the gas phase, S_{ad} the amount of adsorbed propionaldehyde, S_{ad}^{max} the maximum amount of adsorption. It is recognized from the results shown in Fig. 3 that the highest decomposition rate was obtained with the use of mordenite as a support for TiO_2. Mordenite gives a high amount of adsorption, yet the adsorption strength is moderate enough to allow diffusion of adsorbed propionaldehyde to the loaded TiO_2. Adsorbents having a too high adsorption constant such as activated carbon gave a lowered decomposition rate presumably due to retardation of easy diffusion of the adsorbed propionaldehyde.

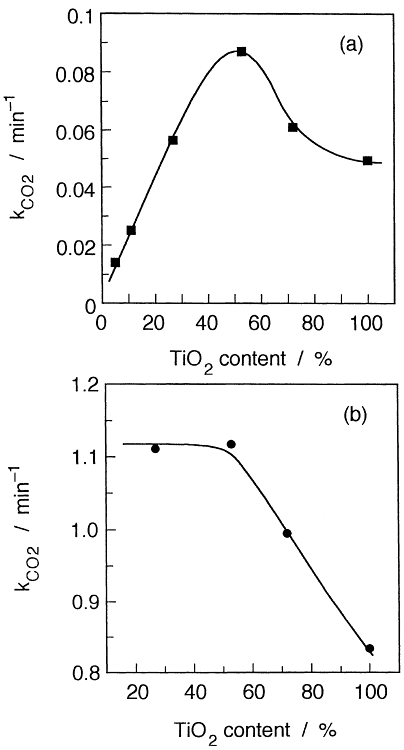

Fig. 2. Rate constant of CO_2 evolution in the photodecomposition of propionaldehyde (a) and the amount of adsorbed propionaldehyde on the photocatalyst films (b) as a function of TiO_2-loadings on mordenite. The amount of photocatalyst film was 1.0 mg cm^{-2} including the mordenite support.

4. Diffusion of adsorbed propionaldehyde to the loaded TiO_2 [41]

TiO_2-loaded adsorbent films which was consisted of 0.5 mg cm^{-2} TiO_2 and 0.5 mg cm^{-2} adsorbent was prepared on a glass plate of 1.0 cm width and 4.0 cm length, and exposed to the humid propionaldehyde to attain the adsorption equilibrium. Then irradiation of the photocatalyst film was performed from the back side through the glass plate whose surface was covered with a Teflon tape of its 1.0 cm width and 3.6 cm length. Since the Teflon tape did not allow the light penetration, photodecomposition of propionaldehyde took place on one tenth of the photocatalyst film. Fig. 4 shows the time course of CO_2 evolution. The rate of CO_2 evolution was much lower in that case than the total area irradiation, but the amount of evolved CO_2 increased with time till a constant amount of CO_2 was obtained which was equal to that expected from the amount of adsorption in the whole body of the hybrid photocatalyst films. Also shown in this figure are simulation curves of CO_2 evolution obtained by one-dimensional diffusion equation with several different diffusion constants (D_{app}). In the case of using mordenite as the support, D_{app}=2.5×10^{-4} cm^2 s^{-1} was found to fit in the experimentally obtained curves. These results suggest strongly that adsorbed propionaldehyde in the dark part of the photocatalyst films were involved in the photodecomposition by being supplied to the TiO_2 particles in the irradiated area by the diffusion. The values of the diffusion constant obtained are 3–4 orders of magnitude smaller than the diffusion coefficients reported for gaseous

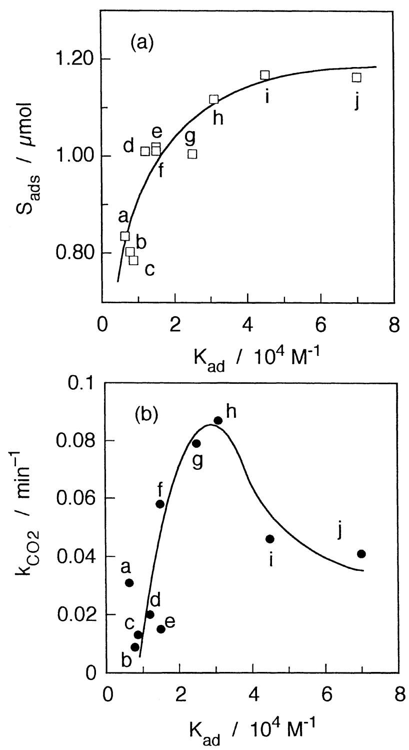

Fig. 3. Amount of adsorbed propionaldehyde (S_{ads}) on the photocatalyst films containing 47 wt.% adsorbent support (a) under the condition of photodecomposition experiments and the rate constant of CO_2 evolution (b) as a function of the adsorption constant (K_{ad}). The photocatalyst film contained 0.5 mg cm^{-2} TiO_2. a: Naked TiO_2, and the adsorbents used were: b: zeolum A-5, c: zeolum A-3, d: zeolum F-9, e: zeolum A-4, f: alumina, g: silica, h: mordenite, i: ferrierite, and j: activated carbon.

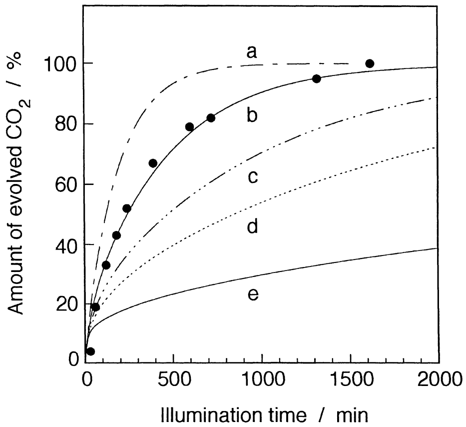

Fig. 4. Time course of CO_2 evolution obtained by irradiation of 1 cm width and 0.4 cm length of a photocatalyst film of 1.0 cm width and 4.0 cm length which consisted of 50 wt.% TiO_2 and 50 wt.% mordenite. The amount of propionaldehyde was 1.22 μmol in a cell of 15 cm^3. (●): Experimentally obtained values, and curves were theoretically predicted time courses obtained by simulations with use of D_{app} values of 1.0×10^{-3} (a), 2.5×10^{-4} (b), 1.0×10^{-4} (c), 5.0×10^{-5} (d), and 1.0×10^{-5} $cm^2\ s^{-1}$ (e). $k_{app}=1.5\times10^{-3}\ s^{-1}$, which was obtained by irradiation of the whole surface, was used.

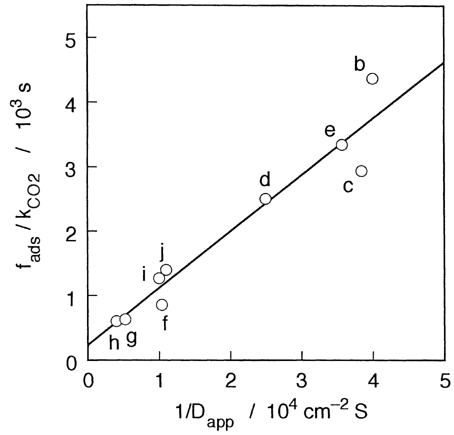

Fig. 5. Plots of f_{ads}/k_{obs} vs $1/D_{app}$ for a variety of TiO_2-loaded adsorbent photocatalyst films. The symbols are the same as those given in Fig. 3.

molecules. The same techniques were applied to the photoevolution of CO_2 at hybrid photocatalyst films of a variety of adsorbents. The D_{app} values obtained ranged between 2.4×10^{-4} and 2.5×10^{-5} $cm^2\ s^{-1}$. If it is assumed that the loaded TiO_2 particles were embedded in adsorbent supports and that the adsorbed propionaldehyde diffused to the loaded TiO_2 particles in a homogeneous medium of the adsorbent support, then the following equation seems to be valid:

$$\frac{f_{ads}}{k_{obs}} = \frac{1}{k_{max}} + \frac{V_{film}}{4\pi RND} \tag{3}$$

where k_{max} is the maximum apparent rate constant obtained when all of substrates are adsorbed on the adsorbent ($f_{ads}=1$), V_{film} the volume of the photocatalyst film, N the number of TiO_2 particles in the photocatalyst film, and R is the radius of the loaded TiO_2 particles. Plots on the left-hand side of Eq. (3) as a function of $1/D_{app}$ gave a straight line, as shown in Fig. 5, evidencing that the higher the diffusion constant the greater the decomposition rate. Experimentally f_{ads} values were not greatly different among the kind of adsorbent used and ranged between 0.98 and 0.65.

5. Photodestruction of propyzamide dissolved in aqueous solution [38,42]

Hybrid photocatalyst films consisting of TiO_2 and activated carbon was found to enhance the rate of photodestruction of propyzamide (3,5-dichloro-N-(1,1-dimethyl-2-propynyl)benzamide) dissolved in water. Propyzamide is a herbicide widely used in golf links. Preliminary experiments showed that the destruction rate was enhanced with increasing the amount of loaded TiO_2 up to 80 wt.%. Fig. 6 shows the time course of the concentration decrease of propyzamide and that of CO_2 evolution obtained for 70 wt.% TiO_2-loaded adsorbents of three kinds (mordenite, silica, alumina) and the naked TiO_2. CO_2 was obtained as one of the final destruction products of propyzamide.

$$C_{12}H_{11}ONC_{12}+15O_2 \rightarrow 12CO_2+4H_2O + 2HCl + HNO_3 \tag{4}$$

The amount of propyzamide given in the figure was the sum of that collected both from the solution phase and from the photocatalysts. As clearly shown in this figure, the rate of decrease of propyzamide was the highest at the naked TiO_2, suggesting that the use of adsorbent supports retarded the apparent rate of photodecomposition of propyzamide. However, the CO_2 evolution did not appreciably occur at the naked

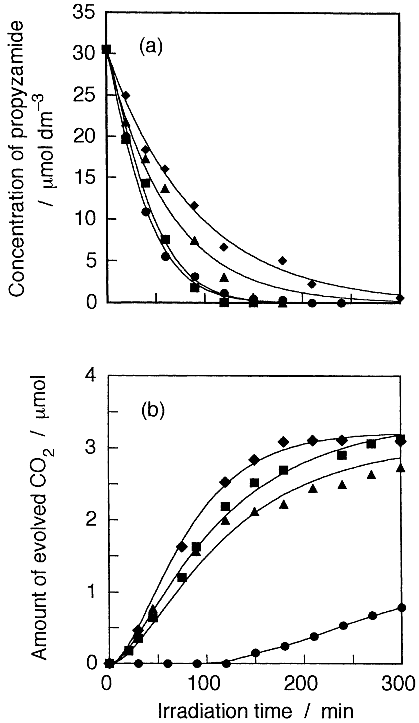

Fig. 6. Time course of changes in the concentration of propyzamide dissolved in water (a) and of changes in the amount of CO_2 evolution (b), caused by irradiation with a 400 W xenon lamp of air-sarated 10 cm^3 suspension containing 30.5 μmol dm^{-3} of propyzamide and 1.0 g dm^{-3} of TiO_2 of hybrid photocatalysts. Adsorbent support: (●) none, (◆) 30 wt.% activated carbon, (■) 30 wt.% silica, and (▲) 30 wt.% mordenite.

TiO_2 even when propyzamide mostly disappeared. In contrast, CO_2 evolution commenced to occur from the beginning of irradiation if the adsorbents were used as the support. Furthermore, the photodecomposition of propyzamide completed at earlier irradiation time at the TiO_2-loaded adsorbents, as recognized from the appearance of saturation in the amount of evolved CO_2 for irradiation for longer than 200 min. The time course of the CO_2 evolution accorded qualitatively with the amount of adsorption of propyzamide obtained in the beginning of the photodestruction experiments; naked TiO_2 adsorbed 1.4%, TiO_2-loaded mordenite 14.5%, TiO_2-loaded silica 24.7%, and TiO_2-loaded activated carbon 91.5% of the total amount used in the photodestruction experiments. It is then concluded that even in the photodestruction of organic substances dissolved in solution, the hybrid photocatalysts having the greater adsorbability for the substrate show the higher activities for its photodestruction.

When naked TiO_2 was used, the decrease in the concentration of propyzamide occurred without evolving CO_2. The concentration decrease in that time period was brought about by the formation of various kinds of intermediates. If the intermediates were collected at the irradiation time of 15 min, substances having the molecular weight as given in Fig. 7 were obtained. This figure shows how much the intermediates were collected from the solution phase and how much from the photocatalyst. It was suggested from the time course taken for those intermediates (not shown) that the intermediates were easily oxidized to another intermediates. By repeating such oxidation reactions, the substrate was finally oxidized to CO_2.

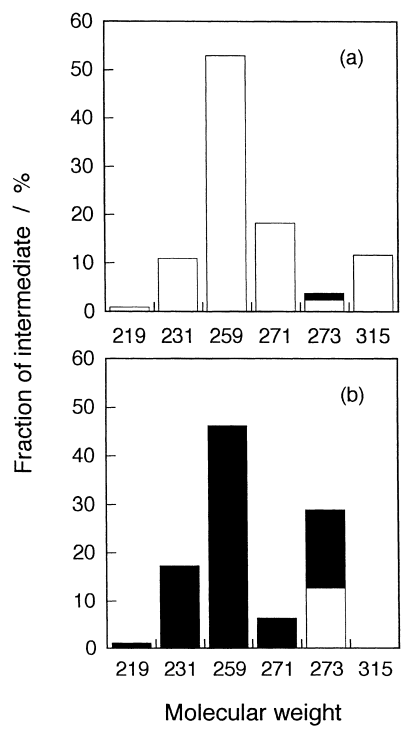

Fig. 7. Distribution of the intermediates obtained after irradiation for 15 min for the use of naked TiO_2 (a) and 70 wt.% TiO_2-loaded activated carbon (b). The open and filled parts represent the fraction of the intermediates dissolved in solution and adsorbed on the photocatalyst, respectively.

As shown in Fig. 7, if the naked TiO_2 was used as the photocatalyst, most of intermediates were collected from the solution phase, while most of them from the photocatalyst when TiO_2-loaded activated carbon was used as the photocatalyst. The finding has an important significance in the use of the hybrid photocatalyst for the pollution abatements, because even if some of the intermediates were more toxic than the original substrate, such intermediates are also taken up by the adsorbent support of the hybrid photocatalyst and then further oxidized.

The above-mentioned results were obtained in the experiments in which photocatalysts were suspended in aqueous solution and the suspension was stirred magnetically. In a practical field, photocatalysts in a form of films may be more suited. Attempts were then made to prepare TiO_2 and carbon black hybrid photocatalyst films by spraying a mixed suspension of TiO_2 and carbon black on a glass plate heated on a hot plate [44]. If the decomposition rate of propyzamide was determined as a function of the content of TiO_2 in the hybrid photocatalyst films, the results as shown in Fig. 8a were obtained. Fig. 8b gives the amount of adsorption of propyzamide as a function of the TiO_2 content. It is noticed that Fig. 8a and b have the same feature as Fig. 2a and b obtained for photodecomposition of propionaldehyde in the gas phase. Therefore the same discussion as that given for Fig. 2a and b are valid for the photodecomposition of propyzamide at the hybrid photocatalyst films in solution.

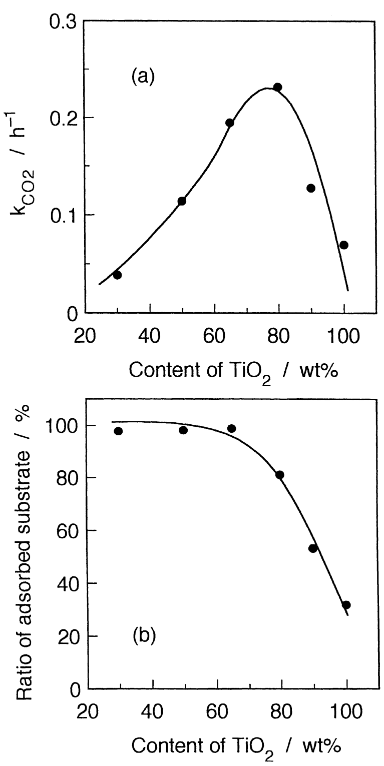

Fig. 8. The rate constant of CO_2 evolution from $10\,cm^3$ solution of $15\,\mu mol\,dm^{-3}$ propyzamide (a) and the percentage of the amount of adsorbed propyzamide on the TiO_2-loaded carbon black film (1.3 cm width and 3.8 cm length) at the beginning of irradiation (b) as a function of the TiO_2 content in the film. The amount of TiO_2 was $0.73\,mg\,cm^2$. Light source used was a 500 W xenon lamp.

6. Photodecomposition of bromoform on TiO_2-loaded carbon black films in aqueous solution [45]

Hybrid photocatalyst films consisting of TiO_2 and adsorbent supports were prepared using the same technique as mentioned above. Photodecomposition of bromoform yielded Br^-

$$CHBr_3+\tfrac{1}{2}O_2+H_2O \rightarrow CO_2+3HBr \tag{5}$$

Fig. 9 shows the rate of photoproduction of Br^- (k_{Br-}) and the amount of adsorbed bromoform as a

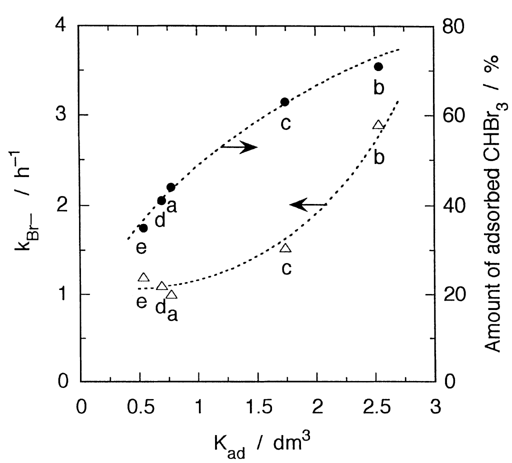

Fig. 9. The rate constant of Br^- production (△) and the amount of adsorbed bromoform (●) on the naked TiO_2 (a), and 80 wt.% TiO_2-loaded carbon black (b), -mordenite (c), -silica (d), and -alumina (e). The photocatalyst films contained $0.73\,mg\,cm^{-2}$ TiO_2 on $10.4\,cm^2$ glass plate. The solution used was $1000\,cm^3$ of $0.80\,\mu mol\,dm^{-3}$ bromoform.

function of adsorption constant (K_{ad}). It is recognized that the rate constant became great with increasing the adsorption constant, indicating that a high condensation of bromoform near TiO_2 particles enhanced its photodecomposition, as already observed for photodecomposition of propionaldehyde in the gas phase and of propyzamide in the solution phase.

7. Conclusion

Our works described in this paper show that the use of adsorbents as a support for TiO_2 is effective in getting high decomposition rates of organic substances both in air atmosphere and in water phase. The merit of the use of the adsorbent supports are summarized as follows: (1) the adsorbent supports make a high concentration environment of organic substances of target around the loaded TiO_2 by adsorption, and then the rate of photooxidation is enhanced; (2) the organic substances are oxidized on the photocatalyst surfaces with adsorbed states, and resulting intermediates are also adsorbed and then further oxidized. Toxic intermediates, if formed, are not released in the air atmosphere and/or in solution phase, and thereby preventing secondary pollution by the intermediates if any; (3) since the adsorbed substances in the adsorbent support are oxidized finally to give CO_2, the high adsorbability of the hybrid photocatalyst for the organic substances is maintained with the use for a long time.

The most important thing in the preparation of hybrid photocatalysts is to select the most suitable adsorbent for TiO_2-loading. The adsorbents should have high adsorbabilities for the substances of target but the diffusion of adsorbed substrates should not be seriously hindered. Activated carbon is widely used as the most efficient adsorbent, but its use as the adsorbent support for TiO_2 does not always give the photocatalyst of the highest activity. It would be true that the kind of adsorbent which gives the highest activity are different depending on the kind of organic substances of target.

References

[1] D.F. Ollis, E. Pelizzetti, N. Serpone, in: N. Serpone, E. Pelizzetti (Eds.), Photocatalysis: Fundamentals and Applications, Wiley, New York, 1989 (Chapter 18).
[2] D.F. Ollis, E. Pelizzetti, N. Serpone, Environ. Sci. Technol. 25 (1991) 1522.
[3] E. Pelizzetti, C. Minero, Electrochim. Acta 238 (1993) 47.
[4] D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.
[5] A. Mills, R.H. Davies, D. Worsley, Chem. Soc. Rev. 22 (1993) 417.
[6] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[7] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 95 (1995) 735.
[8] A. Heller, Acc. Chem. Res. 28 (1995) 503.
[9] U. Stafford, K.A. Gray, P.V. Kamat, Heterogen. Chem. Rev. 3 (1996) 77.
[10] S. Kutsuna, M. Kasuda, T. Ibusuki, Atomos. Environ. 28 (1994) 1627.
[11] T. Ibusuki, K. Takeuchi, J. Mol. Catal. 88 (1994) 93.
[12] U. Stafford, K.A. Gray, P.V. Kamat, J. Phys. Chem. 98 (1994) 6343.
[13] S. Goldstein, G. Czapski, J. Rabani, J. Phys. Chem. 98 (1994) 6586.
[14] V. Brezova, A. Stasko, S. Biskupic, A. Blazkova, B. Havlinova, J. Phys. Chem. 98 (1994) 8977.
[15] H.Y. Chen, O. Zahraa, M. Bouchy, F. Thomas, J.Y. Bottero, J. Photochem. Photobiol. A 85 (1995) 179.
[16] M.L. Sauer, M.A. Hale, D.F. Ollis, J. Photochem. Photobiol. A 88 (1995) 169.
[17] C. Minero, E. Pelizzetti, P. Pichat, M. Sega, M. Vincenti, Environ. Sci. Technol. 29 (1995) 2226.
[18] B. Sangchakr, T. Hisanaga, K. Tanaka, J. Photochem. Photobiol. A 85 (1995) 187.
[19] G. Dagan, S. Sampath, O. Lev, Chem. Mater. 7 (1995) 446.
[20] N.J. Peill, M.R. Hoffmann, Environ. Sci. Technol. 29 (1995) 2974.
[21] W. Choi, M.R. Hoffmann, J. Phys. Chem. 100 (1996) 2161.
[22] G. Lu, A. Linsebigler, J.T. Yates Jr., J. Phys. Chem. 99 (1995) 7626.
[23] J. Fan, J.T. Yates Jr., J. Am. Chem. Soc. 118 (1996) 4686.
[24] G. Riegel, J.R. Bolton, J. Phys. Chem. 99 (1995) 4215.
[25] L. Sun, J.R. Bolton, J. Phys. Chem. 100 (1996) 4127.
[26] Y. Xu, C.H. Langford, J. Phys. Chem. 99 (1995) 11 501.
[27] Y. Xu, C.H. Langford, J. Phys. Chem. B 101 (1997) 3115.
[28] C. Anderson, A.J. Bard, J. Phys. Chem. 99 (1995) 9882.
[29] C. Anderson, A.J. Bard, J. Phys. Chem. B 101 (1997) 2611.
[30] A. Haarstrick, O.M. Kut, E. Heinzle, Environ. Sci. Technol. 30 (1996) 817.
[31] J. Schwitzgebel, J.G. Ekerdt, F. Sunada, S.-E. Lindquist, A. Heller, J. Phys. Chem. B 101 (1997) 2621.
[32] S. Weaver, G. Mills, J. Phys. Chem. B 101 (1997) 3769.
[33] D.W. Bahnemann, M. Hilgendorff, R. Memming, J. Phys. Chem. B 101 (1997) 4265.
[34] L. Cermenati, P. Pichat, C. Guillard, A. Albini, J. Phys. Chem. B 101 (1997) 2650.
[35] K. Ikeda, H. Sakai, R. Baba, K. Hashimoto, A. Fujishima, J. Phys. Chem. B 101 (1997) 2617.
[36] Y. Ohko, A. Fujishima, K. Hashimoto, J. Phys. Chem. B 102 (1998) 1724.

[37] Y. Ohko, D.A. Tryk, K. Hashimoto, A. Fujishima, J. Phys. Chem. B 102 (1998) 2699.
[38] H. Uchida, S. Itoh, H. Yoneyama, Chem. Lett. (1993) 1995.
[39] S. Sampath, H. Uchida, H. Yoneyama, J. Catal. 149 (1994) 189.
[40] N. Takeda, T. Torimoto, S. Sampath, S. Kuwabata, H. Yoneyama, J. Phys. Chem. 99 (1995) 9986.
[41] N. Takeda, M. Ohtani, T. Torimoto, S. Kuwabata, H. Yoneyama, J. Phys. Chem. B 101 (1997) 2644.
[42] T. Torimoto, S. Ito, S. Kuwabata, H. Yoneyama, Environ. Sci. Technol. 30 (1996) 1275.
[43] T. Torimoto, Y. Okawa, N. Takeda, H. Yoneyama, J. Photohem. Photobiol. A 103 (1997) 153.
[44] N. Takeda, N. Iwata, T. Torimoto, H. Yoneyama, J. Catal. 177 (1998) 240.
[45] H. Yoneyama, H. Kanemoto, N. Takeda, T. Torimoto, Z. Phys. Chem. 213 (1999) 43.