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Photocatalytic Degradation of Gaseous Pyridine over Zeolite-Supported Titanium Dioxide

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The photocatalyzed degradation of pyridine in the gas phase was investigated using titanium dioxide semiconductor supported on mordenite. The complete mineralization was found to occur over a catalyst containing 75 wt% TiO_2 and 25 wt% mordenite in about 180 min in the presence of saturated water vapor at 0°C (4.6 Torr). Low water vapor pressure of 0.096 Torr was found to be sufficient to achieve a reasonably high percentage and rate of degradation. Diffusion of pyridine within the catalyst adversely affects the activity when the thickness of the catalyst coating exceeds the penetration depth of illumination. The activity of the zeolite-supported catalysts was higher than that of TiO_2. The photonic efficiency for the complete mineralization of pyridine to CO_2 was determined to be 0.48. © 1994 Academic Press, Inc.

INTRODUCTION

The TiO_2-mediated heterogeneous photocatalysis for the oxidation and reduction of organic and inorganic compounds, respectively, has been extensively studied for environmental decontamination purposes (1–10). The quantitative oxidation of compounds containing phosphorous, sulfur, halogens, and nitrogen has been demonstrated in the literature (11–15). While most of the studies were concerned with the photodegradation in the solution phase, the degradation of gaseous compounds has gained importance only recently (8,16–22). The photodegradation of organic compounds in the gaseous phase is of significance from the point of view of removing the foul-smelling compounds. The degradation of trichloroethylene in the gas phase over TiO_2 in a packed bed reactor has been reported and the quantum yield was estimated to be 0.4–0.9 (16).

The present paper describes the photodegradation of pyridine in the gaseous phase over a TiO_2 semiconductor loaded on zeolite. The investigations focused on the effect of adsorbent on the degradation of pyridine. Nitrogen-containing organic compounds are of special interest since toxic pesticides and herbicides contain nitrogen atoms in their structure. Pyridine is a toxic, flammable organic compound widely used in the synthesis of vitamins, drugs, and rubber chemicals, as a denaturant for alcohol, in antifreeze mixtures, and also in fungicides. It has a bad odor. The tolerance limit in air is 5 ppm (23). The role of inert supports (silica and alumina) on the TiO_2-mediated photodegradation of a few organic compounds in aqueous solutions was reported by Minero *et al.* (24). It was concluded that the rates of photodegradation were not much affected by the initial adsorption of the organics on the supports and the organics were involved in the degradation reaction after being diffused onto the surface of the photocatalyst. No detailed study has been published for the use of adsorbents for gaseous photodegradation reactions. We have chosen a zeolite as the support material in the present study after screening several adsorbents.

EXPERIMENTAL

Screening Test of Adsorbents

The capacity of various solid supports to adsorb pyridine (Wako, Japan) was determined by allowing the adsorbents to equilibrate with gaseous pyridine for 1 h and subsequently extracting the adsorbed pyridine into ethanol. The amount of pyridine was determined by absorbance measurements at 258 nm.

Preparation of the TiO_2–Zeolite Catalyst

In the present study, TiO_2-loaded mordenite (Tosoh, Japan) samples with different loadings of TiO_2 were prepared. Here, the preparation of the catalyst with a target of 80 wt% TiO_2 loading is described. A calculated amount of titanium tetraisopropoxide (Walko, Japan) was added slowly to a well-stirred 1 *M* HCl solution to yield a final volume ratio of alkoxide to HCl of 1 : 4, resulting in about 0.68 *M* TiO_2 microcrystals. The above slurry was stirred continuously for a further 2 h to get a clear sol. Before mordenite was added, the pH of the sol was changed from

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about 0.4 to 3 to avoid acid leaching of the zeolite by adding aqueous sodium hydroxide under vigorous stirring. Then, a known amount of mordenite was added so as to give 13.6 g/liter and the stirring was continued for one more hour. The pH of the aqueous suspension was finally made 7 and the resulting solid was washed several times with distilled water. The solid was then filtered off and vacuum dried. The final product was calcined at 300°C for about 1 h. The TiO_2–zeolite prepared in this way contained 75 wt% TiO_2. This catalyst will be referred to as TiO_2(75%)-zeolite. The TiO_2 content in the catalyst was determined by dissolving a known quantity in hot H_2SO_4 and finally by applying absorbance measurements to the resulting solution (25). A TiO_2 powder without zeolite was also prepared using the same procedure. Furthermore, commercially available TiO_2 powder (Degussa P-25) containing mainly anatase was used as received.

For the photocatalytic degradation experiments, catalysts were coated on a glass plate of 4 × 1 cm area. The coating of the catalyst was achieved by spreading a slurry of the catalyst in acetone on a glass plate using a syringe. The solvent was allowed to evaporate and the plates were then heated at 300°C for half an hour and subsequently at 400°C for half an hour in a furnace, and then the furnace was slowly cooled. The BET specific surface area of the catalysts was determined by argon adsorption at liquid nitrogen temperature using a Shimadzu-Micromeritics Model 2205 surface area analyzer.

Photodegradation Experiments

The photodegradation of pyridine was carried out by the following method except where noted otherwise. The reaction cell was 1.5 cm in diameter and 10 cm in height and equipped with an air-tight glass stopcock. The outer mouth of the stopcock was sealed with a rubber septum through which the sampling was made intermittently during the course of the photodegradation experiments. The catalyst-coated glass plate was placed vertically inside the reaction vessel. Prior to photodegradation experiments, the catalysts were preirradiated with a 10-W black fluorescent UV lamp for about 10 h in air to remove adsorbed impurities. The UV lamp used has a nearly symmetrical distribution of the spectrum ranging from 300 to 430 nm with 352 nm as its peak. A humid air prepared by passing dry air through distilled water kept at desired temperatures (0, 5, and 10°C for 4.6, 6.5, and 9.2 Torr, respectively; 1 Torr = 133.3 $N\ m^{-2}$) was then passed for 10 min. The lower water vapor pressures of 1.95, 0.78, and 0.096 Torr were attained by passing humid air of 4.6 Torr through traps kept at −10, −20, and −40°C, respectively, and the resulting humid air was introduced into the reaction cell. The traps had sufficient cooling effect; the low temperatures were achieved by cooling a bath containing acetone. The excess water vapor was found to be condensed inside the traps. After filling the reaction cell with the humid air, 1 ml of air containing 10 Torr of pyridine (vapor pressure of pyridine at 13°C is equal to 10 Torr) was injected into the cell and the photodegradation experiments were carried out by illuminating the photocatalyst through the wall of the cell with the 10-W UV lamp. The intensity of the light used was measured using a thermopile and was ca. 8 mW/cm^2. The amount of CO_2 evolved was determined by a gas chromatograph (Yanaco G-2800) using a Porapak T column.

RESULTS AND DISCUSSION

Characterization of the Catalyst

First, various adsorbents were tested for the adsorption of pyridine. The amounts of pyridine adsorbed per unit weight of the adsorbent in 1 h equilibration were as follows: (a) zeolite (mordenite), 5.93 mg/g, (b) activated charcoal (Wako, Japan), 4.15 mg/g; (c) clay (montmorillonite, Kunimine Industrial Co., Japan), 3.85 mg/g; and (d) activated alumina (Woelm, Germany), 2.37 mg/g. The TiO_2 prepared in this study adsorbed to the extent of 1.49 mg/g, while the P-25 Degussa TiO_2 adsorbed 2.96 mg/g. Since the highest adsorption was attained with zeolite, it was chosen as the support material in the present study. The amount of pyridine adsorbed by TiO_2(75%)-zeolite was determined to be 2.70 mg/g. The rate of adsorption of pyridine was also found to be higher at zeolite than TiO_2 as shown in Fig. 1. The results given in Fig. 1 were obtained by injecting 1 ml of 10-Torr pyridine into the reaction cell containing the glass plate coated with 6 mg

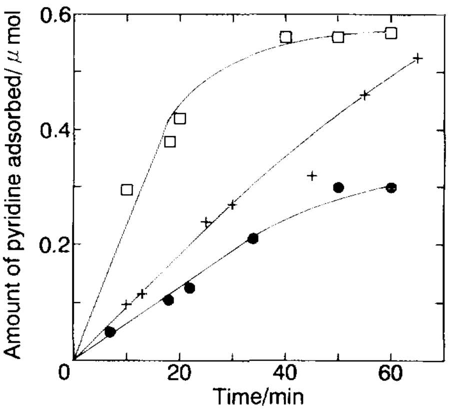

FIG. 1. Variation of the amount of pyridine adsorbed in the dark with time. One milliliter of air containing 10 Torr of pyridine was injected into the reaction cell containing (□) zeolite, (●) naked TiO_2, and, (+) TiO_2(75%)-zeolite catalysts coated on a glass plate. The amount of catalysts used was 6 mg. Water vapor pressure used was 4.6 Torr.

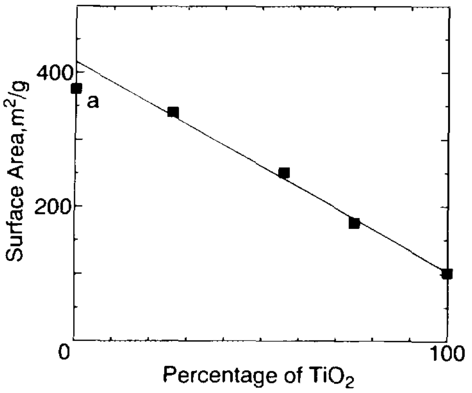

FIG. 2. Variation of surface area with the composition (wt%) of the TiO_2-zeolite catalyst: (a) Mordenite.

of zeolite or TiO_2 or TiO_2(75%)-zeolite and by extracting the amount of pyridine adsorbed at various time intervals. The rate of adsorption of pyridine at zeolite was higher by 3.7 times than that of TiO_2, while that of TiO_2 (75%)-zeolite was 1.5 times higher than that of TiO_2. In a separate experiment, it was found that the amount of pyridine adsorbed onto the TiO_2-free zeolite coating was not changed even after 3 h of illumination and no CO_2 evolved. Hence, it was concluded that the support material itself was inactive for the degradation of pyridine.

The TiO_2-zeolite catalyst prepared with a target of 80 wt% TiO_2 yielded a catalyst with 75 wt% TiO_2. Most of the experiments were carried out with this catalyst. We have also prepared catalysts containing 18 and 56% TiO_2. The X-ray diffraction pattern of the TiO_2 without zeolite showed fairly sharp peaks which corresponded to the anatase form as the only crystalline phase. Figure 2 shows the variation of the surface area with the composition of the catalyst. The surface area decreased with increase in the TiO_2 content, but the TiO_2(75%)-zeolite, which was most often used as the photocatalyst in the present study, had a surface area (175 m^2/g), much higher than the P-25 Degussa TiO_2 (surface area 50 m^2/g), which has been widely used as a photocatalyst for a variety of reactions.

The thickness of the coated catalyst layer on a 4 × 1-cm glass plate was 4.4 μm in dry state for the coating of 4 mg of TiO_2(75%)-zeolite as determined by SEM, and the thickness was in proportion to the coated amount. The TiO_2 prepared by the hydrolysis method yielded a thickness of 4 μm for a coating of 5 mg over 4 cm^2 area. The penetration depth of the coatings, for the light of 352 nm wavelength which was the maximum intensity line for the lamp used in the present study, was calculated based on the optical absorption coefficient (α) values determined by transmittance measurements using a thin catalyst coating on a quartz plate. The α values at 352 nm were 0.43×10^4/cm for TiO_2 and 1.32×10^4/cm for TiO_2(75%)-zeolite.

Effect of Water Vapor Pressure on the Photodegradation Behavior of Pyridine

Initial experiments to confirm the gaseous photodegradation process were carried out using the Degussa P-25 TiO_2 photocatalyst. The photodegradation curves for pyridine decomposition at various water vapor pressures are given in Fig. 3. The initial concentration of pyridine in the cell was 866 ppm. Experiments were carried out over a wide range of water vapor pressures, from 0.096 to 9.2 Torr. The results are given with normalization to the amount of carbon dioxide that is theoretically expected if all the carbons contained in the injected pyridine are degraded completely to CO_2. It was found that water vapor pressure as low as 0.096 Torr was sufficient to achieve a reasonably high photodegradation yield of pyridine. The results obtained in the presence of 1.95 Torr water vapor was quite similar to that obtained at 4.6 Torr, leading to a complete degradation in about 180 min of illumination. The total degradation of pyridine in aqueous solutions was reported to yield ammonium and nitrate ions apart from CO_2 over P-25 TiO_2 with a 20-W fluorescent lamp (12). In that case the reactions can be written as

$$C_5H_5N \xrightarrow{11/2\,O_2} 5CO_2 + NH_4^+ + OH^- \qquad [1]$$

$$C_5H_5N \xrightarrow{15/2\,O_2} 5CO_2 + NO_3^- + H^+ + 2H_2O. \qquad [2]$$

The same reactions are likely to occur in the photodegradation of gaseous pyridine because water vapor was required to enhance the decomposition rates, as shown in Fig. 3. Photogenerated positive holes oxidize hydroxyls

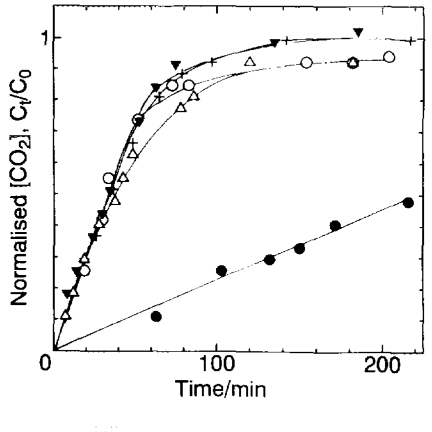

FIG. 3. Photodegradation curves for pyridine decomposition over P-25 Degussa TiO_2 at various humidity levels. One milliliter of air containing 10 Torr of pyridine was injected into the reaction cell containing humid air of various water vapor pressures and immediately illuminated. The amount of catalyst used was 3.7 mg. (△) 0.096 Torr, (▼) 0.78 Torr, (+) 4.6 Torr, (○) 9.2 Torr, and (●) dry air.

on the TiO_2 surface to result in hydroxyl radicals, which are then involved in the oxidation of adsorbed pyridine (26, 27). In the present study, identification of products has been made by gas chromatography for the only gas phase in the cell, but no nitrogen-containing species was obtained, although the time course of the CO_2 production gave definite evidence on photodecomposition of pyridine. Presumably, the nitrogen species were absorbed on the photocatalyst.

Effect of the Use of Adsorbent on the Photodegradation Behavior

To demonstrate the effect of the use of zeolite as a support material for TiO_2 photocatalyst, the experiments were carried out with TiO_2 and the TiO_2–zeolite catalysts with various TiO_2 loadings. The results obtained at TiO_2 (56%)-zeolite and TiO_2(75%)-zeolite are shown in Fig. 4. The amount of TiO_2–zeolite catalysts was used 1.5 mg. Similar photodegradation profiles were obtained at TiO_2 (18%)-zeolite and naked TiO_2 of different thicknesses. As shown in Fig. 4, the decomposition increased linearly with illumination time for about 100 min and the apparent rates were determined in this region. Figure 5 shows the variation of the apparent reaction rate with the amount of TiO_2. The change in apparent rate for the various zeolite-supported catalysts is also included for comparison. The increase in the apparent rates of the different catalysts is due to an increase in the amount of dispersed TiO_2 on the catalyst surface. However, the rate per unit weight of TiO_2 was evaluated to be 0.007 ± 0.0005 μmol/min/mg for the different naked TiO_2 coatings. The rate per unit weight for the three zeolite-supported catalysts containing 18, 56, and 75% TiO_2 worked out to be 0.021 ± 0.001 μmol/min/mg. It is obvious from these values that TiO_2–zeolite possessed higher activity than the naked TiO_2.

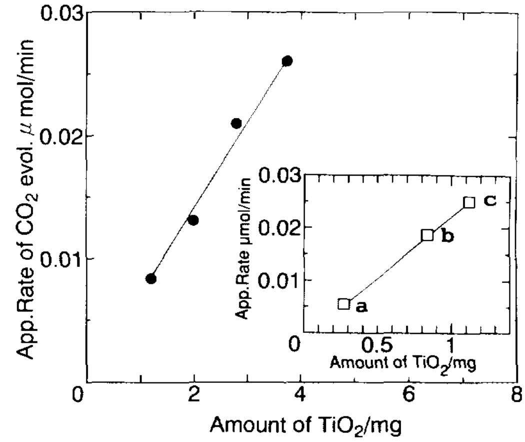

FIG. 5. Comparison of variation of apparent rate of CO_2 evolution determined for the first 100 min of illumination with the amount of TiO_2. (●) Naked hydrolyzed TiO_2. (Inset) TiO_2–zeolite. Percentage of TiO_2 in the TiO_2–zeolite catalysts was (a) 18, (b) 56, and (c) 75. The amount of TiO_2–zeolite catalysts used was 1.5 mg. One milliliter of air containing 10 Torr of pyridine was injected and immediately illuminated. Water vapor pressure in the reaction cell was 4.6 Torr.

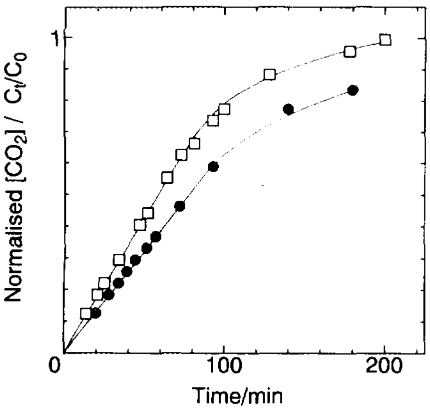

FIG. 4. Photodegradation curves for pyridine over zeolite supported TiO_2. TiO_2 content in the TiO_2–zeolite catalysts: (●) 56%, (□) 75%. The amount of catalyst used was 1.5 mg. One milliliter of air containing 10 Torr of pyridine was introduced into the cell and immediately illuminated. Water vapor pressure in the reaction cell was 4.6 Torr.

It was already described in the first section that zeolite adsorbed more pyridine than the TiO_2 if comparison was made on a unit weight basis. Hence, all the pyridine injected in the decomposition experiments would get adsorbed by the TiO_2–zeolite catalysts in a relatively shorter time when compared to TiO_2. To account for the higher decomposition rates at the TiO_2–zeolite, it seems reasonable to assume that pyridine migrated from zeolite support to TiO_2. Pyridine adsorbed on zeolite as well as on the TiO_2 particles must be involved in the decomposition reaction.

Effect of Quantity of Catalysts on the Decomposition Behavior

Figure 6 shows the photodegradation curves for different weights of TiO_2(75%)-zeolite catalyst. Only the TiO_2 amounts are given in the legend to Fig. 6 for comparison purposes. It is obvious from Fig. 6 that the apparent rate decreased with increase in the coating thickness. Also, the rate per unit weight of TiO_2 showed the same trend. A plausible explanation for the observed dependence of the rate on the thickness of the catalyst layer is that the higher weight coatings of 3.75 and 4.7 mg of TiO_2 would yield thicknesses of 5.5 and 6.93 μm, respectively. The light penetration depth calculated for the TiO_2(75%)-zeolite catalyst was only 3.5 μm. Hence, pyridine adsorbed by the inner layers of the catalyst (beyond 3.5 μm) would have to diffuse to the active sites before degradation.

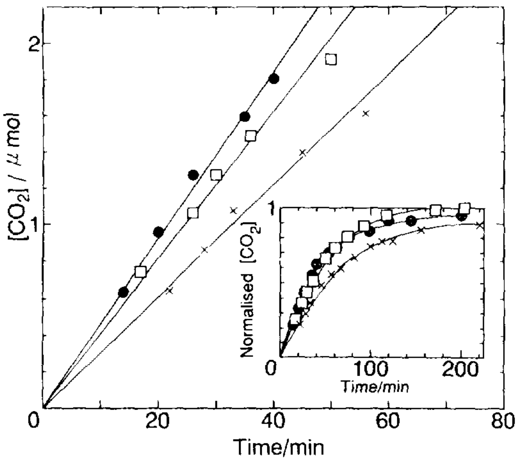

FIG. 6. Initial rate of photodegradation for pyridine over TiO_2 (75%)-zeolite catalyst. One milliliter of air containing pyridine at 10 Torr vapor pressure was injected into the cell and immediately illuminated. Pyridine concentration, 866 ppm. The amount of TiO_2 in the catalysts was (●) 2 mg, (□) 3.75 mg, and (×) 4.7 mg. Water vapor pressure used was 4.6 Torr. (Inset) Time course of complete photodegradation—conditions as given above.

Thus, the rate attained a limit as the thickness of the coating was increased.

The experiments were also carried out using a different procedure. Catalyst-coated glass plates were equilibrated with pyridine for 1 h as described under Experimental and the plates were then immediately put into the reaction cells. Humid air of 4.6 Torr vapor pressure was passed over the cell for 10 min. After filling the cell with the humid air, the photodegradation experiments were carried out by illuminating the catalyst through the wall of the cell. The amount of pyridine adsorbed at the beginning of illumination of the photocatalyst was evaluated using a reference catalyst sample which had the coating of the same weight and was kept in the reaction cell without illumination.

The amounts of pyridine adsorbed and the apparent rates are given in Table 1 for the various coatings used. As the initial amount of pyridine adsorbed was different for different coatings, only the apparent rates (and not the rate per unit weight) are compared. The increase in the rate with the thickness of the coating for naked TiO_2 parallels the observation made by the injection of pyridine into the reaction cell and immediately illuminating the catalyst. The maximum thickness used, ca. 9.6 μm, was well within the light penetration depth of 10.5 μm calculated for TiO_2. This led to a higher amount of the catalyst being exposed to illumination, in addition to a higher adsorption of pyridine, resulting in an increase in the rate with the thickness. However, for the TiO_2(75%)-zeolite, the thickness of the catalyst coatings (4.4, 8.8, and 13.2 μm) as compared to the light penetration depth (3.5 μm) limits the decomposition rate as discussed above. An almost comparable initial decomposition rate was obtained at all three coatings. Also, it was found that the total conversion of pyridine at 200 min of illumination was 93% for a 4-mg coating, while the values were 65 and 61% for 8- and 12-mg coatings, respectively. The results strongly suggest that the diffusion rate of pyridine controlled the rate of its decomposition when the catalyst coating thickness was large.

A coating of 2.66 mg of TiO_2(75%)-zeolite which contained 2 mg of TiO_2 was used for the determination of photonic efficiency (28, 29). The light source used was a 500-W mercury lamp at a monochromatic wavelength of 365 nm. One milliliter of air containing 10 Torr of pyridine was injected and the photodegradation was followed. The number of irradiated photons was determined to be 0.107×10^{-6} einstein/min by ferrioxalate actinometry. The CO_2 evolution rate was 0.012×10^{-6} mol/min. As mentioned above, the reactions given by Eqs. [1] and [2] must have taken place in the photodegradation of gaseous pyridine. In those cases, 22 and 30 electrons are involved in the formation of an ammonium ion and a nitrate ion, respectively, and 1 mol of pyridine would yield 5 mol of CO_2 in both reactions. If it is assumed that only reaction [1] took place, the photonic efficiency for this reaction is given by

$$\text{Photonic efficiency} = \frac{CO_2 \text{ evolution rate}}{\text{Photon flow rate}} \times \frac{22}{5}$$
$$= 0.112 \times 4.4 = 0.49.$$

A similar calculation gives a photonic efficiency of 0.67 if only reaction [2] took place. Since it is likely that both

TABLE 1

Amount of Pyridine Adsorbed, Surface Area, and Initial Rate Obtained on Various Catalyst Coatings

Catalyst	Surface area (m^2/g)	Pyridine[a] adsorbed (μmol)	Initial[b] (apparent) rate (μmol/min)
(a) TiO_2(75%)-zeolite	175.50		
1. 4 mg		0.33	0.034
2. 8 mg		0.76	0.039
3. 12 mg		0.93	0.040
(b) Naked TiO_2	101.75		
1. 4 mg		0.20	0.017
2. 8 mg		0.43	0.034
3. 12 mg		0.68	0.048

[a] Pyridine gas was equilibrated with the catalyst plates for 1 h.

[b] The initial rate of degradation determined in the linear range of the decomposition curves.

reactions proceeded simultaneously, the actual photonic efficiency would be between 0.49 and 0.67. Regardless the efficiency obtained was fairly large, suggesting that the recombination of photogenerated charge carriers were not high in the photodegradation of gaseous pyridine.

ACKNOWLEDGMENT

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REFERENCES

1. Ollis, D. F., Pelizzetti, E., and Serpone, N., *Environ. Sci. Technol.* **25,** 1522 (1991).
2. Matthews, R. W., *J. Phys. Chem.* **91,** 3328 (1987).
3. Ollis, D. F., Pelizzetti, E., and Serpone, N., *in* "Photocatalysis: Fundamentals and Applications" (N. Serpone and E. Pelizzetti, Eds.), pp. 604–637. Wiley, New York, 1989.
4. Gerischer, H., *Electrochim. Acta* **38,** 3 (1993).
5. Pelizzetti, E., and Minero, C., *Electrochim. Acta* **38,** 47 (1993).
6. Peterson, M. W., Turner, J. A., and Nozik, A. J., *J. Phys. Chem.* **95,** 221 (1991).
7. Al-Ekabi, H., and Serpone, N., *J. Phys. Chem.* **92,** 5726 (1988).
8. Abstracts of the First Int. Conf. on TiO_2 Photocat. Purification and Treatment of Water and Air, London, Ontario, Canada, Nov. 8–13, 1992.
9. Matthews, R. W., *J. Catal.* **111,** 264 (1988).
10. Hashimoto, K., Kawai, T., and Sakata, T., *J. Phys. Chem.* **88,** 4083 (1984).
11. Low, G. K. C., McEvoy, S. R., and Matthews, R. W., *Environ. Sci. Technol.* **25,** 460 (1991).
12. Low, G. K. C., McEvoy, S. R., and Matthews, R. W., *Chemosphere* **19,** 1611 (1989).
13. Harada, K., Hisanaga, T., and Tanaka, K., *New. J. Chem.* **11,** 587 (1987).
14. Bahnemann, D. W., Monig, J., and Chapman, R., *J. Phys. Chem.* **91,** 3782 (1987).
15. Matthews, R. W., *J. Chem. Soc., Faraday Trans. I* **85,** 1291 (1989).
16. Yamazaki-Nishida, S., Nagano, K. J., Phillips, L. A., Cervera-March, S., and Anderson, M. A., *J. Photochem. Photobiol. A:Chem.* **70,** 95 (1993).
17. Dibble, L. A., and Raupp, G. B., *Catal. Lett.* **4,** 345 (1990).
18. Peral, J., and Ollis, D. F., *J. Catal.* **136,** 554 (1992).
19. Suzuki, K., Satoh, S., and Yoshida, T., *Denki Kagaku* **59,** 521 (1991).
20. Bickley, R. I., Munuera, G., and Stone, F. S., *J. Catal.* **31,** 389 (1973).
21. Blake, W. R., and Griffin, G. L., *J. Phys. Chem.* **92,** 5697 (1988).
22. Courbon, H., Formenti, M., Juillet, F., Lisachenko, A. A., Martin, J., and Teichner, S. J., *Kinet. Catal.* **14,** 84 (1973).
23. Hawley, G. G. (ed.), "The Condensed Chemical Dictionary," Van Nostrand, New York, 1977.
24. Minero, C., Catozzo, F., and Pelizzetti, E., *Langmuir* **8,** 481 (1992).
25. Yoe, J. H., and Armstrong, A. R., *Anal. Chem.* **19,** 100 (1947).
26. Turchi, C. S., and Ollis, D. F., *J. Catal.* **122,** 178 (1990).
27. Jaeger, C. D., and Bard, A. J., *J. Phys. Chem.* **83,** 3146 (1979).
28. Serpone, N., Terzian, R., Lawless, D., Kennepohl, P., and Sauve, G., *J. Photochem. Photobiol. A:Chem.* **73,** 11 (1993).
29. As the exact number of photons absorbed by the TiO_2 particles in the coating is not known, the obtained value is referred to as "photonic efficiency" instead of "quantum yield."