



Pergamon

Energy 24 (1999) 21–30

ENERGY

Photocatalytic reduction of CO₂ using TiO₂ powders in supercritical fluid CO₂

Satoshi Kaneco*, Hidekazu Kurimoto, Yasuhiro Shimizu, Kiyohisa Ohta, Takayuki Mizuno

Department of Chemistry for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507, Japan

Received 11 May 1998

Abstract

The photocatalytic reduction of CO₂ was investigated using TiO₂ powders in supercritical fluid CO₂. These were irradiated in a stainless steel vessel at 9.0 MPa and 35°C. After reducing the CO₂ pressure to the ordinary state, pure water was added to the vessel while avoiding air contamination. No gaseous reduction products were observed. Formic acid was obtained only in aqueous solution. The optimal irradiation time for the production of formic acid was 5 h. Addition of acidic solutions rather than pure water was preferable for formic acid formation. Formic acid seems to be produced through the protonation of reaction intermediates on TiO₂ powders in solutions. The CO₂-reduction system described here may be of practical value for efficient CO₂-conversion and fixation, storage of solar energy, and production of raw materials for the photochemical industry. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Photocatalytic reduction of CO₂ using photosensitive semiconductor powders has been widely studied in aqueous solutions [1–19]. These studies were performed at ordinary temperature and pressure. Under these conditions, the concentration of CO₂ in water is extremely small because of its low solubility [20,21]. Furthermore, photocatalytic reduction of CO₂ competes with H₂ formation via water reduction, i.e. selective reduction of CO₂ is a major problem in the photocatalytic reduction of CO₂ in aqueous solutions. An increase in CO₂ pressure is one of the measures

* Corresponding author. Fax: + 81-59-231-9442, 9471 or 9427; e-mail: kaneco@chem.mie-u.ac.jp

for increasing the concentration of CO₂ and improving the CO₂ reduction selectivity [22,23]. At best, supercritical fluid CO₂ may be used as the medium, as is described here.

A fluid is considered to be supercritical if its temperature and pressure both exceed the critical values. Fluids near their critical point exhibit a strong dependence of fluid density in temperature and pressure which causes pronounced changes in their solvent characteristics [24]. Therefore, supercritical fluids have attracted attention as media in which to conduct chemical reactions because the physical and chemical properties may be altered through modest changes in temperature and pressure [25–27]. Since CO₂ has easily accessible critical parameters ($P_c = 7.4$ MPa and $T_c = 31^\circ\text{C}$ [27,28]), it is readily feasible to use supercritical fluid CO₂ as a medium. Because this fluid is non-polar and non-electroconductive, addition of supporting salts to supercritical fluid CO₂ will be needed for electrochemical or photoelectrochemical reduction. On the other hand, these properties should be of no consequence in the photocatalytic reduction of CO₂ using semiconductor powders. However, little information on the photoreduction of CO₂ using semiconductor powders has been presented.

Here we describe photocatalytic reduction of CO₂ using TiO₂ powders in supercritical fluid CO₂. The mechanism of photoreduction of CO₂ is also discussed, based on characterizations of TiO₂ powders by electron spin resonance (ESR) following termination irradiation.

2. Experimental studies

2.1. Procedures

The instruments and stainless steel vessel used for the photocatalytic reduction of CO₂ were described in Ref. [29]. The stainless steel vessel (inside volume = 57.5 ml) was equipped with a window. A commercially available pressure glass device with 21 mm diameter aperture (KLINPORT KPT-C1Q, Nihon Klingage Co. Ltd.) was fitted to the window because window glass transmits almost all of the wavelengths above 340 nm (3.6 eV). The inner surface of the vessel was completely covered by teflon to prevent contamination by stainless steel and a possible effect on catalytic CO₂ reduction. The vessel was placed in a water bath at 35°C.

TiO₂ (Wako Junyaku, anatase, specific surface = 8.7 m²·g⁻¹ diameter = 230 nm, purity = 99.9%) was pretreated by boiling in 1 M nitric acid and then thoroughly rinsed with distilled and deionized water prior to use. The TiO₂ powders (50 mg) were placed in the stainless steel vessel. After deoxygenation by flowing high-purity CO₂ (99.9999%) through the vessel for 30 min, the vessel was closed tightly and the CO₂ pressure increased to 9.0 MPa. The TiO₂ powders were continuously dispersed in supercritical CO₂ by using a magnetic stirrer during irradiation with an Xe lamp (990 W, Ushio Electronics Co.) through the window. The light intensity was 0.96 kW·m⁻². After completion of illumination (5 h), the CO₂ pressure was reduced to ambient. We then added to the vessel containing the TiO₂ powders a degassed aqueous solution (5 ml) without air contamination to protonate the reaction intermediates on the TiO₂ powders. The gaseous reduction products were sampled through a sampling valve and analyzed by using FID and TCD gas chromatography. Analyses of gaseous products were performed immediately after irradiation and addition of water or the aqueous solution. The liquid sample was analyzed by using high-performance liquid chromatography with a UV detector.

2.2. ESR analysis

After irradiation, CO₂ pressure was reduced to ambient state and the TiO₂ powders were transferred to an ESR quartz glass tube in an atmosphere of CO₂ without air contamination. Then, ESR spectra of the TiO₂ powders were measured at 77 K with a JES-TE200 (JEOL, X-band) spectrometer with 100 kHz field modulation and a low temperature accessory. The *g* values were measured relative to a DPPH sample (2.0036).

3. Results and discussion

In many studies for the photocatalytic reduction of CO₂, TiO₂ has been shown to be one of the effective catalysts for the reduction by irradiation with light [4–19]. Therefore, TiO₂ was selected as the photocatalyst for the reduction of CO₂ in this study.

In the beginning we tried to photocatalytically reduce CO₂ on TiO₂ powders in supercritical fluid CO₂ without any proton source, because little water can be dissolved into supercritical fluid CO₂ near the critical point [30]. After irradiation, no gaseous reduction products were identified. However, since any reduced products could be adsorbed on the TiO₂ powders irradiated, the TiO₂ powders were washed with a small amount of pure water without air contamination after pressure reduction to the ordinary state. Consequently, it was found that gaseous reduction products were not obtained and formic acid was exclusively produced in the water. This suggested that reaction intermediates on the surface of TiO₂ might react with the water to form formic acid. Hence, we made it our procedure to reduce photocatalytically CO₂ in supercritical fluid CO₂ through two steps, that is, irradiation of the TiO₂ powders and then the addition of aqueous solution such as pure water. When the same procedure was performed in highly purity nitrogen medium without CO₂ as a reference, no reduction products were detected. Also, when the dark reduction of CO₂ was performed in supercritical fluid CO₂, CO₂ was not reduced. From the results, it was concluded that formic acid was produced by the photocatalytic reduction of CO₂.

3.1. Effects of temperature and pressure

The influences of temperature and pressure on the production of formic acid were studied. Accordingly, irradiation of the TiO₂ powders (50 mg) was carried out at various temperatures (35, 40, 45 and 50°C) and pressures (8.0, 9.0 and 10.0 MPa) for 5 h irradiations. The effects were evaluated by adding pure water. The yield of formic acid almost become constant and was not affected by temperature and pressure. The physical and chemical properties of the supercritical fluid near the critical point can be altered through the changes in temperature and pressure [25–27]. However, the results were different from expected. Thus, it may indicate that the interaction of CO₂ with the surface species of the TiO₂ powders or the catalytic activity of TiO₂ can not be effected by temperature and pressure. Consequently, all subsequent irradiations were made with supercritical fluid CO₂ of 35°C and 9.0 MPa, because of the reproducibility for the production of formic acid.

3.2. Effect of irradiation time

In order to select optimal irradiation time, the effect of irradiation time on the formic acid formation was investigated. The results are illustrated as shown in Fig. 1. The yield of formic acid increased sharply and linearly with irradiation time until 5 h. After that time, the production yield decreased gradually until 20 h. During this period, it was observed that the dispersed TiO_2 particles began to coagulate and the state of dispersion became worse. The yield of formic acid reached a maximum value of $8.8 \mu\text{mol/g-cat}$ for 5 h irradiations. This value was several times larger than those obtained by Ishitani et al. [13] and Hirano et al. [14].

Over 5 h, the yield of formic acid turned from an increase into a decrease. The reason for this turn may be attributable to deterioration of photocatalytic activity due to coagulation, diminishment of the adsorption powder of the particles, saturation of the adsorption sites on the surface of TiO_2 with intermediate products, and an increase in the recombination of the intermediate products with positive holes on the surface of TiO_2 . From the data in the literature, however, it could not explain which factor is predominant in these phenomena.

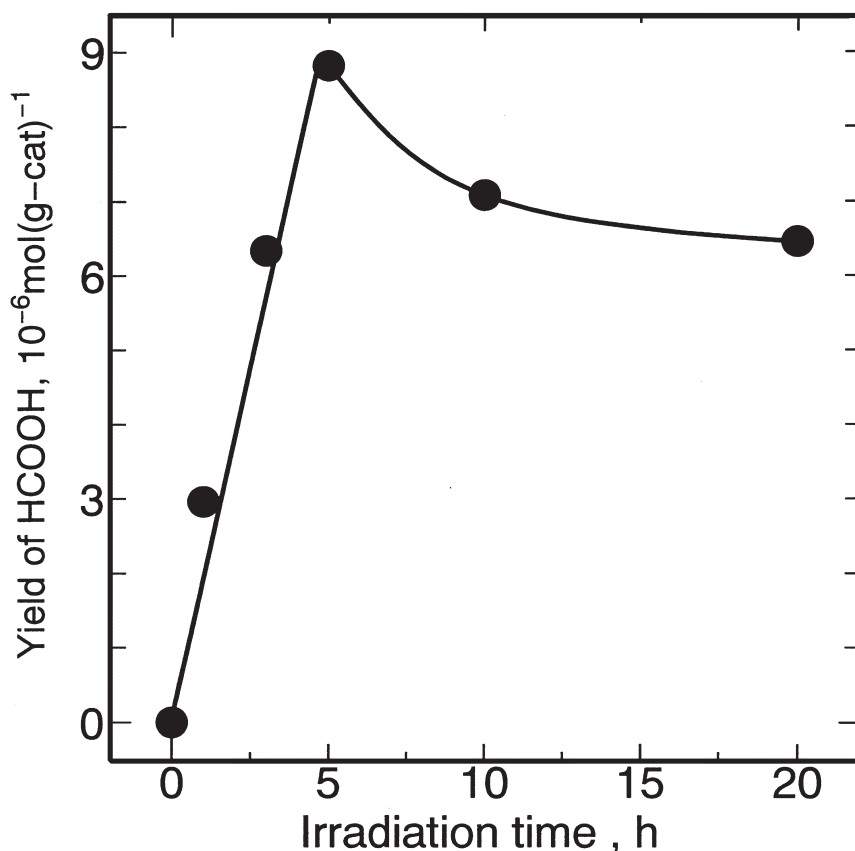


Fig. 1. Effect of irradiation time on the yield of formic acid; 50 mg of TiO_2 , $T = 35^\circ\text{C}$, $p = 9.0 \text{ MPa}$, protonation by pure water.

3.3. Effect of the surface area of TiO_2

The yield of formic acid should increase linearly with the total surface area of TiO_2 , provided the reaction intermediates from CO_2 are accumulated on the surface of TiO_2 . In order to demonstrate the speculation, the effect of the total surface area of TiO_2 on the yield of formic acid was evaluated. The results are shown in Fig. 2. Before measurements, it was confirmed by the BET method that the total surface area of TiO_2 used was almost directly proportional to the amount of TiO_2 up to about 1.0 m^2 . The production of formic acid almost linearly increased with increasing the total surface area of TiO_2 up to approximately 0.4 m^2 . Above that area, the production of formic acid decreased. These phenomena might be due to the fact that the amount of TiO_2 in supercritical fluid CO_2 was too large for the light to reach every particle. Therefore, from these results, it was considered that reaction intermediates were situated and remained on the surface of the TiO_2 particles.

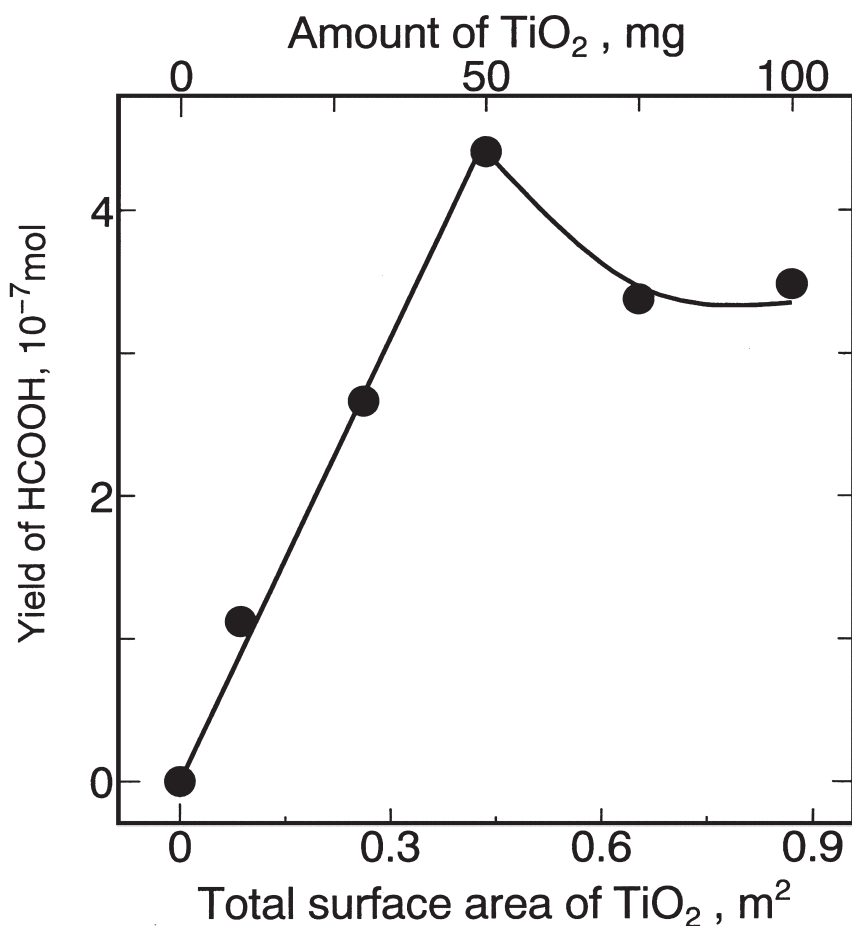


Fig. 2. Effect of the total surface area of TiO_2 on the yield of formic acid; irradiation time = 5 h, $T = 35^\circ\text{C}$, $p = 9.0 \text{ MPa}$, protonation in pure water.

3.4. Effect of aqueous solution for protonation

It is important to select the appropriate solution for protonation in order to achieve larger production of formic acid. Therefore, the effect of the aqueous solution for protonation on the formation of formic acid was studied. First, 50% alcohol solutions (in pure water), such as methanol, ethanol and 2-propanol, were tested for protonation. However, by the addition of these alcohol solutions, the formic acid formation were approximately the same as that with pure water. Next, nitric, hydrochloric and phosphoric acid solutions were used for protonation. The results are illustrated in Fig. 3. The amount of formic acid increased with pH for all acid solutions. It may be due that the acid solutions contain a lot of H^+ and are advantageous for desorption of reaction intermediates from the surface of the TiO_2 particles [31]. Therefore, the acid solutions were effective for the protonation of intermediate products after the end of irradiation.

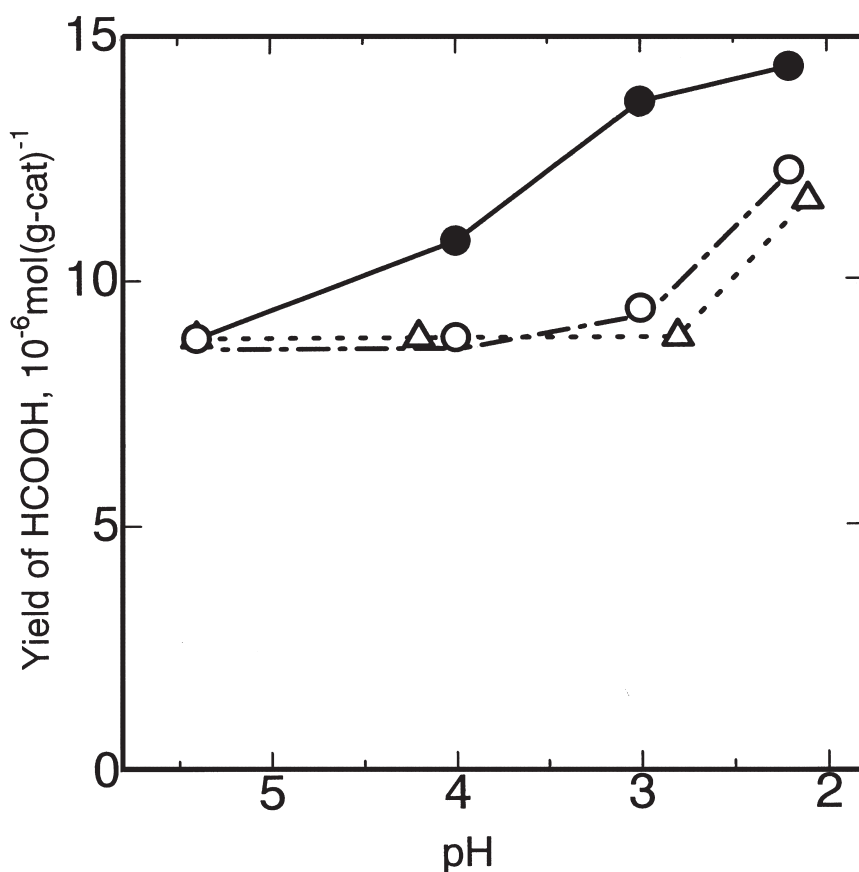


Fig. 3. Effect of acid solutions on the yield of formic acid; irradiation time = 5 h, $T = 35^\circ\text{C}$, $p = 9.0$ MPa, protonation by phosphoric acid (●), nitric acid (○) and hydrochloric acid (Δ).

3.5. ESR characterization

In order to clarify a reaction mechanism for the photoreduction of CO₂ on the TiO₂ powders in supercritical fluid CO₂, the ESR characterizations of the TiO₂ powders were investigated. Fig. 4 shows the ESR signals measured at 77 K with the TiO₂ catalyst after the end of irradiation. The signals were composed of two different radical species. From the literature reported [15,17–19,32–35], the signal with g_{\perp} value of 1.980 can be attributed to the characteristic photogenerated Ti³⁺ ions. Recently, Henglein et al. have proposed that •CO₂[−] radicals formed in the uptake of the first electron were strongly adsorbed by ZnS particles in the two-electron reduction of CO₂ [3]. Yamanaka et al. have reported that •CO₂[−] radicals were detected near g value of 2.00 by ESR measurements [36,37]. Therefore, another signal with g_{\perp} value of 2.014 might probably consist of •CO₂[−] radicals. When irradiation of the TiO₂ powders was performed in highly purity nitrogen medium without CO₂ as a blank, this signal was not be observed.

In view of results of the present study and literature data [15–19,31–34,38–43], the formation of formic acid by irradiation of TiO₂ powders in supercritical CO₂ and protonation in aqueous solution may be estimated as follows. Irradiation is described

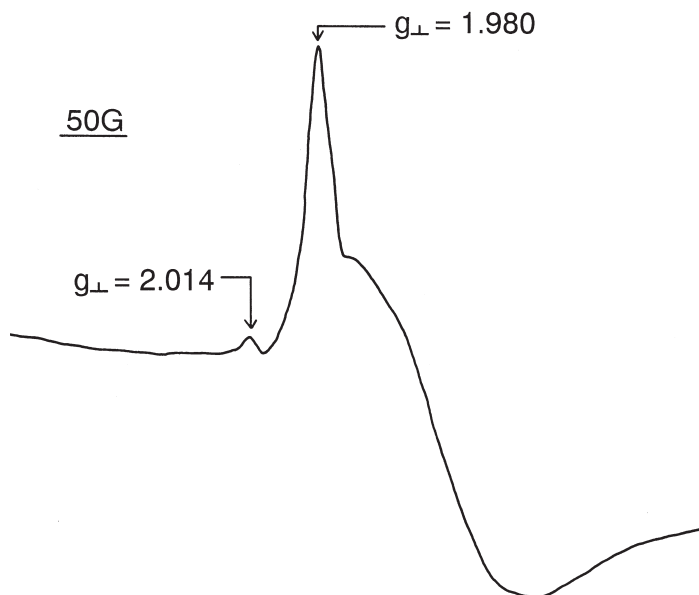
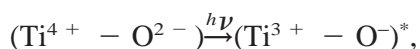
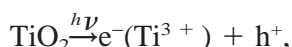
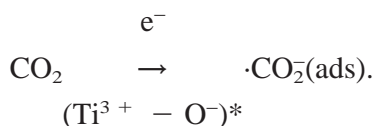


Fig. 4. ESR signals measured at 77 K with TiO₂ powders after irradiation in supercritical CO₂; 50 mg of TiO₂, irradiation time = 5 h: $T = 35^{\circ}\text{C}$, $p = 9.0 \text{ MPa}$.



Protonation θ is described by



When light of energy greater than the TiO_2 band gap is absorbed by TiO_2 , an electron (e^-) and positive hole (h^+) are formed in the catalyst [15,17–19] by charge transfer to the excited state of $\text{Ti}^{3+} - \text{O}^-)^*$. Next, the electron and holes in the lattice are separated and trapped by appropriate sites of TiO_2 to avoid the recombination. CO_2 molecules in supercritical fluid interact with the excited state of $(\text{Ti}^{3+} - \text{O}^-)^*$ [19]. The interactions may result in the formation of $\cdot\text{CO}_2^-$ radicals. The holes may continue to reside on the appropriate sites since the positive hole scavengers are absent during irradiation. Therefore, the radicals and the positive holes might stay trapped by the surface of TiO_2 because of charge neutralization. At the end of irradiation, the catalyst can be considered to have the high reactivity of the excited state of $(\text{Ti}^{3+} - \text{O}^-)^*$, i.e. a number of electron and hole pairs, because Ti^{3+} ions were detected by ESR measurements. During the protonation with the solution such as acids, it seems that the $\cdot\text{CO}_2^-$ radicals react with protons (H^+) in the solution and an electron to form formic acid.

We tried to estimate the density of the reaction intermediates on the surface of TiO_2 using the data in the present study. Provided that all of the intermediate products were situated on the surface of TiO_2 and protonated to formic acid, the density was estimated to be about 9.9×10^{14} molecules of the intermediate products per 1 cm^2 . The value was about a few tenths smaller than the density of CO_2 monolayer [20]. The density was sparse and the reaction intermediates were considered to be situated on the specific surface sites of TiO_2 . Therefore, since no dimerization of reaction intermediates take place during the protonation, it seems that oxalic acid was not formed. The process (1) may be predominant in the protonation, by considering the density.

4. Conclusions

In conclusion, the photocatalytic reduction of CO_2 was carried out using the TiO_2 powders in supercritical fluid CO_2 . The protonation reaction was performed after the end of irradiation. The main reduction product was exclusively formic acid. The protonation with acidic solutions was

preferred rather than pure water for formic acid formation. Formic acid appears to be produced through the protonation of $\bullet\text{CO}_2^-$ radicals which are intermediate species. Since supercritical fluid CO_2 is widely used industrially as reaction medium [25–27], the CO_2 -reduction method by use of supercritical fluid may find applications in the large scale plant for photochemical fuel production.

Acknowledgements

This work was supported by the Ministry of Education of Japan and the Chubu Electric Power Research Foundation. The authors thank Prof. H. Tomioka and Dr. S. Murata of Mie University for the use ESR instruments.

References

- [1] Ayers WM. Catalytic Activation of Carbon Dioxide. ACS Symposium Series. American Chemical Society, Washington, DC, 1988;363:42–204.
- [2] Halmann MM. Chemical Fixation of Carbon Dioxide: Methods for Recycling CO_2 into Useful Products. CRC Press, Boca Raton, 1993:57–66.
- [3] Henglein A, Gutierrez M, Fischer CH. Ber Bunsenges Phys Chem 1984;88:170.
- [4] Cook RL, MacDuff RC, Sammells AF. J Electrochem Soc 1988;135:3069.
- [5] Ulman M, Tinnemans AHA, Mackor A, Blajeni BA, Halmann M. Int J Solar Energy 1982;1:213.
- [6] Blajeni BA, Halmann M, Manassen J. Solar Energy 1980;25:165.
- [7] Halmann M, Ulman M, Blajeni BA. Solar Energy 1983;31:429.
- [8] Halmann M, Katzir V, Borgarello E, Kiwi J. Solar Energy Materials 1984;10:85.
- [9] Rophael MW, Malati MA. J Chem Soc, Chem Commun, 1987:1418.
- [10] Willner I, Maidan R, Mandler D, Durr H, Dorr G, Zengerle K. J Am Chem Soc 1987;109:6080.
- [11] Goren Z, Willner I, Nelson AJ, Frank AJ. J Phys Chem 1990;94:3784.
- [12] Sayama K, Arakawa H. J Chem Soc Chem Commun, 1992:150.
- [13] Ishitani O, Inoue C, Suzuki Y, Ibusuki T. J Photochem Photobiol A Chem 1993;72:269.
- [14] Hirano K, Inoue K, Yatsu T. J Photochem Photobiol A Chem 1992;64:255.
- [15] Anpo M, Chiba K. J Mol Catal 1992;207:74.
- [16] Yamashita H, Kamada N, He H, Tanaka K, Ehara S, Anpo M. Chem Lett 1994:855.
- [17] Yamanaka H, Nishiguchi H, Kamada N, Anpo M, Teraoka Y, Hatano H, Ehara S, Kikui K, Palmisano L, Sclafani A, Schiavello M, Fox MA. Res Chem Intermed 1994;20:815.
- [18] Anpo M. Solar Energy Mater Solar Cells 1995;38:221.
- [19] Anpo M, Yamashita H, Ichihashi Y, Ehara S. J Electroanal Chem 1995;396:21.
- [20] Lide DR, editor. Handbook of Chemistry and Physics, 72nd edn. Boston: CRC Press, 1991:6–4, 9–8.
- [21] Chihara H, editor. Kagaku Binran-Kiso (Handbook of Chemistry-basic, in Japanese), 3rd edn. Tokyo: Maruzen, 1984:II–165.
- [22] Adachi K, Ohta K, Mizuno T. Solar Energy 1994;55:187.
- [23] Mizuno T, Adachi K, Ohta K, Saji A. J Photochem Photobiol A Chem 1996;98:87.
- [24] Helling RK, Tester JW. Environ Sci Technol 1988;22:1319.
- [25] Jain JK. Environ Sci Technol 1993;27:807.
- [26] Thornton TD, Savage PE. AIChE J 1992;38(3):321.
- [27] Shaw RW, Brill TB, Cliffod AA, Eckert CA, Franck EU. Chem Eng News 1991;23:26.
- [28] Black H. Environ Sci Technol 1996;30:124A.
- [29] Kaneco S, Kurimoto H, Ohta K, Mizuno T, Saji A. J Photochem Photobiol A Chem 1997;109:59.
- [30] Chrastil J. J Phys Chem 1982;86:3016.

- [31] Terada K. *Anal Sci* 1991;7:187.
- [32] Huizinga T, Prins R. *J Phys Chem* 1981;85:2156.
- [33] Conesa JC, Soria J. *J Phys Chem* 1982;86:1392.
- [34] DeCanio SJ, Apple TM, Dybowski CR. *J Rhys Chem* 1983;87:194.
- [35] Anpo M, Shima T, Fujii T, Suzuki S, Che M. *Chem Lett* 1987, 1997.
- [36] Kohno H, Yamanaka C, Ikeya M, Ikeda S, Horino Y. *Nucl Instr Meth Phys Res* 1994;891:366.
- [37] Hirai M, Ikeya M, Tsukamoto Y, Yamanaka C. *Jpn J Appl Phys* 1994;33:1453.
- [38] Anpo M. *Res. Chem Intermed* 1989;11:67.
- [39] Kiwi J. *J Phys Chem* 1986;90:1493.
- [40] Brown GT, Darwent JR. *J Phys Chem* 1984;88:4955.
- [41] Wahl A, Ulmann M, Carroy A, Jermann B, Dolata M, Kedzierzawski P, Chatelain C, Monnier A, Augustynski J. *J Electroanal Chem* 1995;396:41.
- [42] Wahl A, Ulmann M, Carroy A, Augustynski J. *J Chem Soc Chem Commun*, 1994:2277.
- [43] Bamwends GR, Tsubota S, Nakamura T, Harata M. *J Photochem Photobiol A Chem* 1995;89:177.