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Effect of solvents on photocatalytic reduction of carbon dioxide using TiO_2 nanocrystal photocatalyst embedded in SiO_2 matrices

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Abstract

Photocatalytic reduction of CO_2 in various kinds of solvents was studied using TiO_2 nanocrystals embedded in SiO_2 matrices (Q-TiO_2/SiO_2) as the photocatalyst. It was found that the major reduction products were formate and carbon monoxide, and their total amount increased on increasing the concentration of CO_2 dissolved. The ratio of formate to carbon monoxide was greatly influenced by the kind of solvent, and increased on increasing the dielectric constant of the solvent. If bulk TiO_2 was used as the photocatalyst, the rate of CO_2 reduction was low compared to that obtained with Q-TiO_2/SiO_2, but the ratio of formate to carbon monoxide obtained was not greatly different from that obtained with the Q-TiO_2/SiO_2. The effect of solvent on the reduction behavior of CO_2 is discussed in terms of stabilization of reaction intermediates.

Keywords: Photocatalytic reduction of CO_2; Effect of solvents; TiO_2/SiO_2 photocatalyst; Q-particles

1. Introduction

Photoinduced reduction of carbon dioxide using semiconductor photocatalysts has been studied intensively [1–29], and it has been shown that size-quantized semiconductor particles (Q-particles) possess high activities for CO_2 reduction, when used as photocatalysts [17–29]. For example, Q-ZnS particles loaded on SiO_2 particles had high activities for reduction to HCOOH [17,18], and Q-TiO_2 particles immobilized in poly(vinyl pyrrolidone) gel film exhibited remarkably high activities for reducing CO_2 to methanol, compared to bulk TiO_2 particles [19].

So far, two-electron reduction products of carbon monoxide and formate [17,18,20–25], a six-electron reduction product of methanol [19,26], and an eight-electron reduction product of methane [27,28] have been reported as the reduction products of CO_2. Which reduction products are obtained may depend on the preparation conditions of the photocatalysts and the environment under which the photocatalytic experiments are carried out, and the importance of the latter factor is suggested from the results obtained by using different charged conditions of stabilizers for Q-CdS particle photocatalysts [21] and by adsorbing In^{3+} on Q-CdS particles in *N,N*-dimethylformamide solution [22]. It was reported that in the electrochemical reduction and the photoassisted electrochemical reduction of CO_2, the kind of product was varied by changing the electrode materials [30,31], the applied potentials [32,33] and the kind of solvent used [34,35]. However, little is known about the role of solvents in the reduction behavior of CO_2. In this paper, we will report that solvents used for photoreduction studies of CO_2 play crucial roles in determining the kind of products. In the present study, Q-TiO_2 nanocrystals embedded in SiO_2 matrices (Q-TiO_2/SiO_2), prepared by using sol–gel techniques [29], were used as the photocatalysts.

2. Experimental

Tetraethyl titanate and tetraethyl orthosilicate of reagent grade were purchased from Nacalai Tesque, Inc. A variety of organic solvents of reagent grade were purchased from Wako Pure Chemicals and distilled prior to use. Water was distilled twice under atmospheric pressure. Commercially available TiO_2 powder (Nippon AEROSIL, P-25) was used as the bulk material, which had an average diameter of 21 nm, a specific surface area of $50\ m^2\ g^{-1}$ and was a mixture of anatase (70%) and rutile (30%) [36].

TiO_2 nanocrystals immobilized in SiO_2 matrices (Q-TiO_2/SiO_2) were prepared using the same procedures as those already reported [29]. An ethanol solution ($25\ cm^3$) con-

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taining 8.0×10^{-2} mol dm^{-3} HCl and 4.4 mol dm^{-3} H_2O was added to an ethanol solution of the same volume which contained 0.10 mol dm^{-3} $Ti(OEt)_4$) and 1.0 mol dm^{-3} $Si(OEt)_4$, resulting in a sol consisting of TiO_2 and SiO_2. The Ti/Si mole ratio used in this study was fixed at 0.10. After stirring for 2 h, 0.14 cm^3 of the sol were cast on a quartz plate (2.0 cm^2). A transparent gel film of Q-TiO_2/SiO_2 containing 7.0 μmol of TiO_2 was formed after drying under nitrogen. The sample for transmission electron microscopy (TEM) and electron diffraction analysis was prepared by dropping the mixed sol of TiO_2 and SiO_2 onto amorphous carbon overlayers on a Cu grid. A Hitachi H-800 transmission electron microscope operating at 200 kV was used for these experiments. FT-IR spectra were measured by a JASCO FT/IR-3 spectrometer using KBr discs with a powder of the Q-TiO_2/SiO_2 film, which was made by stripping the Q-TiO_2/SiO_2 from the glass substrate.

The carbon dioxide photoreduction experiments were carried out using a quartz cell (9.0 cm^3 capacity) whose top was sealed with a rubber septum. The transparent Q-TiO_2/SiO_2 film coated on a quartz plate (1.0×2.0 cm^2) was immersed vertically in 5.0 cm^3 of various solutions containing 1.0 mol dm^{-3} 2-propanol as a hole scavenger. After CO_2 was bubbled into the solutions for 30 min, the photocatalyst film was irradiated with light of wavelength longer than 300 nm obtained by passing light from a 500 W high-pressure mercury arc lamp through a colored glass filter. In the case of using bulk TiO_2, 7.0 μmol of TiO_2 powder were put on the bottom of the reaction cell so as to make a uniform layer for irradiation from the bottom. To compare the results obtained for the Q-TiO_2/SiO_2 film and the bulk TiO_2, experiments were carried out without magnetically stirring the solution. The irradiation intensity was 1.0 W cm^{-2} for all cases.

Carbon monoxide produced in the gas phase was determined using a gas chromatograph (Yanaco, G-2800) equipped with a molecular sieve 5A column (GL Sciences) and a thermal conductivity detector. Helium was used as a carrier gas. Acetone produced in the liquid phase was determined using a gas chromatograph (Yanaco G-180) equipped with a BX-10 column (GL Sciences) and a flame ionization detector. A high-pressure liquid chromatograph (Tosoh CCPD) equipped with an organic acid column (waters) and a UV detector (Tosoh UV-800) was used to determine the formate. The eluent used was 0.3% H_3PO_4 solution, and its flow rate was 0.80 cm^3 min^{-1}. The amounts of samples taken from the reactor for GC and HPLC analysis were 0.20 and 0.020 cm^3, respectively. The concentration of carbon dioxide dissolved in various solutions under the conditions of the photoreduction experiments was determined by a Yanaco G2800 gas chromatograph equipped with a TCD detector and a Porapak T column (GL Sciences). While all the values of CO_2 solubility in the solvents used were not available in the literature, it was found that the amount of CO_2 dissolved in water, acetonitrile and CCl_4 was in good agreement with that predicted from the solubility of CO_2 reported in the literature [37–39].

The labeling experiments were performed using $^{13}CO_2$ gas prepared by adding aqueous sulfuric acid solution to $Ba^{13}CO_3$ (Aldrich, 98% ^{13}C). The identification of ^{13}CO was made using GC/MS consisting of a Shimadzu GC-17A gas chromatograph and a CLASS-5000 quadrupole mass spectrometer. The amount of sample taken from the gas phase in the reactor GC/MS analysis was 0.20 cm^3. ^{13}C NMR spectra of the solution were recorded on a BRUKER AM-600 spectrometer and the chemical shifts were referenced to tetramethylsilane.

A TiO_2 single crystal (rutile) (0.46 cm^{-2}) was reduced by a stream of hydrogen at 600 °C and then polished with 0.05 μm alumina, washed with deionized water, and finally dipped in a mixture of H_2SO_4–$(NH_4)SO_4$ (1:1) at 200 °C for 30 min. An In–Ga (3:1) alloy was pasted onto one end-face of the TiO_2 crystal and a copper wire was attached there with silver epoxy. Then a TiO_2 electrode was fabricated by coating the TiO_2 crystal with silicone resin so as to expose one naked end-face to solution. The capacitance of the electrode was measured at 1 kHz as a function of the applied potential using the lock-in technique. A lock-in-amplifier (NF circuit, LI-574A), a potentiostat (Hokuto Denko, HA 301) and a function generator (NF circuit, FB-121B) were used in these measurements. A Pt flag was used as the counter-electrode. The electrode potentials are referred to SCE. The photoreduction experiments were carried out using CO_2-saturated solutions containing 1 M $LiClO_4$ as the supporting electrolyte, except for the use of dichloromethane as solvent, when 1 M tetrabutylammonium perchlorate was used as the supporting electrolyte.

3. Results and discussion

3.1. Characterization of Q-TiO_2/SiO_2 film

The Q-TiO_2/SiO_2 film prepared with Ti/Si = 0.10 had the absorption onset at 310 nm which was strongly blue-shifted from that of bulk TiO_2 (400 nm), as already reported in our previous paper [29], indicating that the TiO_2 particles embedded in the SiO_2 matrices exhibited large size quantization effects. The size distribution of TiO_2 particles in the Q-TiO_2/SiO_2 film was determined by TEM observations as shown in Fig. 1. The average diameter was 5.3 nm and the standard deviation was 1.2 nm. The Q-TiO_2 particles were spherical in shape and had the anatase structure as determined by electron diffraction analyses. Fig. 2 shows FTIR spectra of the Q-TiO_2/SiO_2 film and an SiO_2 film prepared by using the same sol–gel technique with $Si(OEt)_4$ only as the starting material. Absorption signals assigned to Si–O–Si vibrations were observed at 1080 and 800 cm^{-1} in both cases, while another absorption peak due to Ti–O–Si vibration was observed at 950 cm^{-1} for the Q-TiO_2/SiO_2 film [40], evidencing that the TiO_2 particles were chemically bound to the SiO_2 matrices. Furthermore, small signals due to surface OH groups were observed at around 3400 cm^{-1} both for the SiO_2

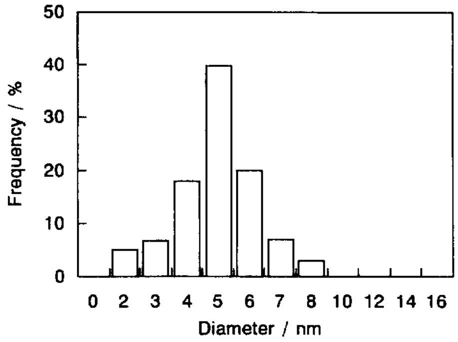


Fig. 1. Size distribution of Q-TiO_2/SiO_2 (Ti/Si = 0.10) determined by transmission electron microscopy. The total number of particles counted was 200. The average diameter is 5.3 nm with standard deviation of 1.2 nm.

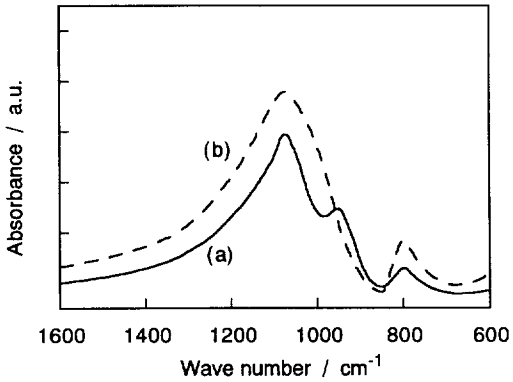


Fig. 2. FTIR spectra of (a) Q-TiO_2/SiO_2 films and (b) SiO_2 films.

matrix and Q-TiO_2/SiO_2, suggesting the presence of a hydroxylated surface. However, the degree of surface hydroxylation was not determined, because it was not easy to determine the amount of OH on Q-TiO_2 separated from that on the SiO_2 matrix.

3.2. Photocatalytic reduction of CO_2 in various kinds of solvents

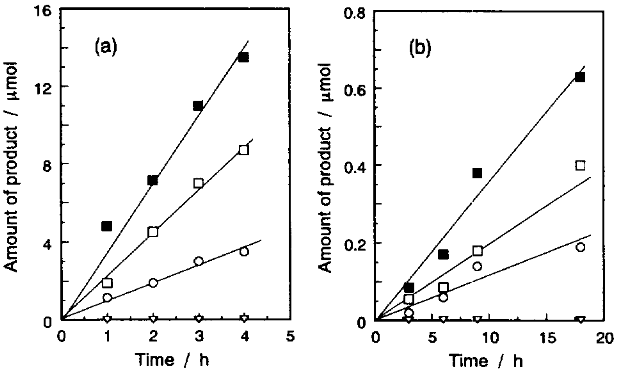


Fig. 3. Time course of the production of formate (□), carbon monoxide (○), hydrogen (▿) and acetone (■) using photocatalysts (a) Q-TiO_2/SiO_2 and (b) P-25 TiO_2 powder. The solution used was CO_2-saturated acetonitrile containing 1.0 M 2-propanol.

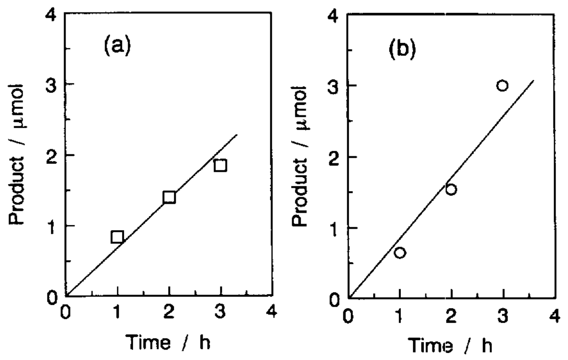


Fig. 4. Time course of the production of formate (□) and carbon monoxide (○) using photocatalyst (a) Q-TiO_2/SiO_2 in water and (b) carbon tetrachloride as solvent.

Photocatalytic reduction of CO_2 on the Q-TiO_2/SiO_2 film in acetonitrile in the presence of 2-propanol resulted in the formation of formate and carbon monoxide as the reduction products (Fig. 3) with simultaneous production of a very small amount H_2. As an oxidation product of 2-propanol, acetone was produced, and no other oxidation and reduction products were obtained. It was found by comparing the sum of the amount of reduction products with that of the oxidation product (acetone) that the chemical stoichiometry of the reduction and oxidation products was maintained in the photoinduced reactions. As shown in Fig. 3, the amount of the products increased linearly with time, indicating that the activities of the TiO_2 photocatalysts did not deteriorate during the photoreduction experiments. According to the results obtained, the rate of photoproduction of formate was greater than that of carbon monoxide. If bulk TiO_2 was used as the photocatalyst, the same products were produced, although their production rates were very low, as shown in Fig. 3. The high activity obtained at the TiO_2/SiO_2 may be due partly to a negative shift of the conduction band edge of TiO_2 due to the size quantization. Labeling experiments confirmed that formate and carbon monoxide were produced from carbon dioxide and not from the solvents. If $^{13}CO_2$ was used instead of $^{12}CO_2$, the mass spectrum of the products in the gas phase gave a signal at $m/z = 29$ which is assigned to ^{13}CO. No signal appeared at $m/z = 44$ which is assigned to $^{12}CO_2$, suggesting that no significant decomposition of the solvent occurred due to the presence of 2-propanol as an effective hole scavenger for photoexcited TiO_2. ^{13}C NMR of the solution gave a signal at 166.3 ppm which is attributed to $H^{13}COOH$ [41], while the signal of $(CH_3)_2^{13}CO$ which should appear at 30.84 ppm was not seen regardless of finding that the amount of acetone was larger than that of formate with GC analysis, evidencing that acetone was produced solely from oxidation of 2-propanol.

Fig. 4 shows the time course of the photoreduction products of CO_2 in water and CCl_4 with Q-TiO_2/SiO_2 as the photocatalyst. In the case of CCl_4, which has a low dielectric constant, CO_2 was selectively photoreduced to carbon monoxide, while formate was exclusively produced in water. If bulk TiO_2 was used as the photocatalyst, the same results were obtained. Fig. 5(a) shows the fraction of photoformed formate and carbon monoxide as a function of the dielectric constant [42–44] of the solvents used. The fraction of for-

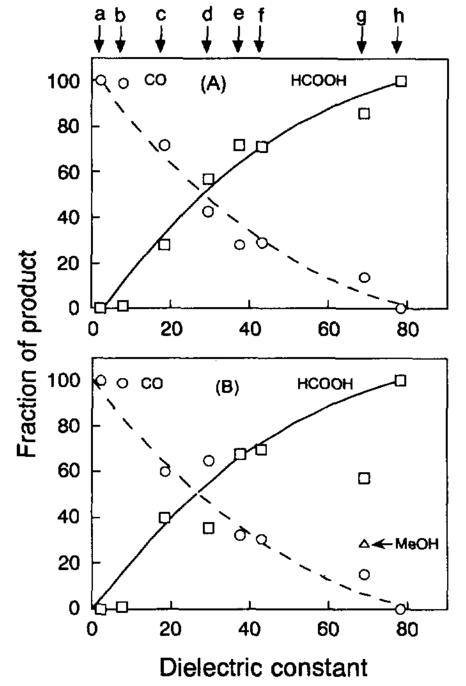


Fig. 5. Fraction of products vs. dielectric constant obtained by irradiation of (A) Q-TiO_2/SiO_2 for 3 h and (B) P-25 TiO_2 for 18 h. The solution contained 1 M 2-propanol in all cases except for the use of 2-propanol as the solvent. Solvents used were: (a) carbon tetrachloride; (b) dichloromethane; (c) 2-propanol; (d) ethylene glycol monoethyl ether; (e) acetonitrile; (f) sulfolane; (g) propylene carbonate; (h) water.

mate increased and that of carbon monoxide decreased with increase of the dielectric constant of the solvent used. In the case of using the bulk TiO_2 photocatalyst, almost the same tendency was obtained as shown in Fig. 5(b). All the solvents used in the present study gave a stoichiometric amount of acetone as an oxidation product. As already reported [19], if propylene carbonate was used as the solvent, methanol was also produced with the bulk TiO_2 photocatalyst. However, the use of Q-TiO_2/SiO_2 did not produce methanol in a detectable amount, though Q-TiO_2 immobilized in poly(vinyl pyrrolidone) film showed a high activity for methanol production. These results suggested that the matrix used for immobilization of Q-TiO_2 has some influence on the reduction behavior of CO_2, although details of the matrix effects are not well known at present.

In order to obtain information on the influence of the concentration of CO_2 on the rate of its photoreduction, the rate of electron capture at CO_2 was determined based on the production rate of the reduction products of CO_2. Fig. 6 shows the rate of electron capture determined for Q-TiO_2/SiO_2 as a function of the concentration of CO_2 in various solvents. It is seen that the electron capture rate was roughly proportional to the concentration of CO_2 in solution. If we used bulk TiO_2 as the photocatalyst, the same tendency of the effect of the concentration of CO_2 was obtained, suggesting that the rate of photogenerated electron capture by CO_2 molecules determined the overall rate of photoreduction of CO_2.

The light-induced reduction of CO_2 to give formate and carbon monoxide in the presence of 2-propanol as the hole scavenger may occur with the reaction mechanisms as given by Eqs. (1)–(4) and 5. Electrons and holes are generated by irradiation of the photocatalysts (Eq. (1)). Acetone is produced by oxidation of 2-propanol by the valence band holes, and simultaneously protons are released (Eq. (2)).

$$TiO_2 \xrightarrow{h\nu} e^- + h^+ \qquad (1)$$

Oxidation reaction

$$(CH_3)_2CHOH + 2h^+ \rightarrow (CH_3)_2CO + 2H^+ \qquad (2)$$

Reduction reaction

$$CO_2 + e^- \rightarrow CO_2^{\bullet -}{}_{(ad)} \qquad (3)$$

$$CO_2^{\bullet -}{}_{(ad)} + H^+ + e^- \rightarrow HCOO^- \qquad (4)$$

$$CO_2^{\bullet -}{}_{(ad)} + H^+ + e^- \rightarrow CO + OH^- \qquad (5a)$$

$$CO_2^{\bullet -} + CO_2 + e^- \rightarrow CO + CO_3^{2-} \qquad (5b)$$

The conduction band electrons reduce CO_2 to the $CO_2^{\bullet -}$ anion radical (Eq. (3)). If the $CO_2^{\bullet -}$ anion radicals are attacked by hydrogen atoms formed by oxidation of 2-propanol (Eq. (2)), formate is produced (Eq. (4)), while cleavage of the C–O bond of the $CO_2^{\bullet -}$ anion radicals results in the formation of carbon monoxide (Eq. (5)).

Reduction of CO_2 to its anion radical occurs at −2.2 V vs. SCE, as obtained in DMF solution [45]. This means that if reduction of CO_2 is initiated by its anion radical formation, the conduction band electrons must have a potential equal to or more negative than −2.2 V vs. SCE. Table 1 shows flat-band potential (E_{fb}) data obtained at a single crystal (rutile) in the electrolyte solutions used in the photoreduction experiments of CO_2. E_{fb} obtained in aqueous solution at pH 4.1 was −0.55 V which accords well with results obtained by other investigators with the assumption that E_{fb} varies at −59 mV per unit increase of pH [46]. According to the results shown in Table 1, E_{fb} values obtained in nonaqueous solutions were more negative than −1.5 V vs. SCE in all cases.

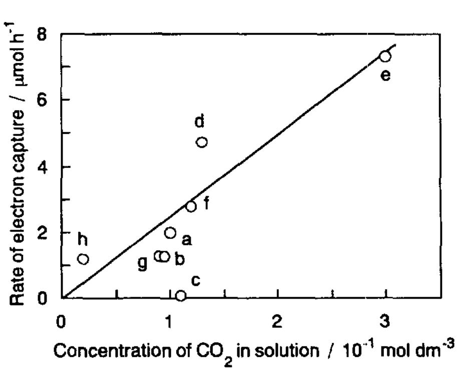


Fig. 6. The rate of electron capture by CO_2 molecules on irradiated Q-TiO_2/SiO_2 photocatalyst in various solutions as a function of the solubility of CO_2: (a) carbon tetrachloride; (b) dichloromethane; (c) 2-propanol; (d) ethylene glycol monoethyl ether; (e) acetonitrile; (f) sulfolane; (g) propylene carbonate; (h) water.

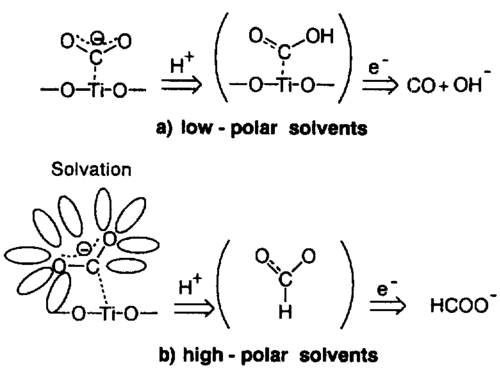
Table 1
The relationship between E_{fb} of TiO_2 single crystal and the type of solution[a]

Solvent	ε	E_{fb}/V vs. SCE
Dichloromethane	9.1	− 1.67
2-Propanol	18.3	− 1.91
Ethylene glycol monoethyl ether	29.6	− 1.83
Acetonitrile	37.5	− 1.75
Sulfolane	43.0	− 1.56
Propylene carbonate	69.0	− 1.58
Water (pH 4.1)	78.5	−0.55

[a] The electrolyte solutions containing 1.0 M 2-propanol were saturated with CO_2. $LiClO_4$ was used as the supporting electrolyte except for the case of dichloromethane when tetrabutylammonium perchlorate was used.

It is well established that the bandgap of anatase TiO_2 is 3.2 eV which is 0.2 eV larger than the bandgap of rutile TiO_2 (3.0 eV). Recent studies of anatase TiO_2 single crystal electrodes revealed that E_{fb} of anatase TiO_2 is 0.20 V more negative than E_{fb} of rutile TiO_2 [47]. Accordingly, it is expected that E_{fb} of the anatase TiO_2 electrode in nonaqueous solutions would be 0.20 V more negative than those shown in Table 1. Furthermore, Q-TiO_2/SiO_2 had an average bandgap of 3.9 eV, being 0.7 eV greater than the bandgap of bulk anatase TiO_2, as reported previously [29]. It seems not unreasonable to assume that one-half the enlargement of the bandgap caused by the size quantization effect contributes to negative shifts of the conduction band potential. Taking these factors into consideration, it is concluded that Q-TiO_2/SiO_2 has a reducing power high enough to reduce CO_2 to its anion radical, whereas p-25 TiO_2 had such an insufficient reducing power as to cause the reduction reaction of CO_2 at a rate of one-hundredth that obtained at Q-TiO_2/SiO_2. According to the results given in Table 1, E_{fb} seems to show a negative shift on decreasing the dielectric constant of the solvent, except for dichloromethane, and in accordance with this tendency, the fraction of CO formation was increased with the decrease of the dielectric constant, as shown in Fig. 6. These results may suggest that the CO formation from CO_2 is kinetically controlled. However, as already described above, the rate of photoreduction of CO_2 was roughly determined by the concentration of CO_2 dissolved in solution, so that the photoreduction of CO_2 is not kinetically controlled.

Hori et al. [48] postulated a mechanism for the electrochemical reduction of CO_2 at metal electrodes, based on previous studies on CO_2 reduction, that the selectivity of the formation of CO and/or HCOOH is determined by the adsorption strength of $CO_2^{\bullet -}$ relative to the metal substrate. If a metal electrode, such as a transition metal, that allows strong adsorption of $CO_2^{\bullet -}$ is used, the negative charge of the oxygen atom of $CO_2^{\bullet -}$ increased as a result of back-donation from an occupied metal orbital to an unoccupied CO_2 π^* orbital, and then protonation is promoted, breaking the oxygen atom from the anion radical to yield carbon monoxide as the reduction product. In contrast, if $CO_2^{\bullet -}$ does not adsorb strongly onto the electrode substrate, electrons are apt to be localized at the carbon atoms of the anion radical, and then protonation occurs there to give HCOOH. Such an adsorption effect of $CO_2^{\bullet -}$ on the selectivity of reduction of CO_2 may provide an explanation of the solvent effect observed in the present study.



Scheme 1. Hypothetical reduction pathway of CO_2.

When low polar solvents such as CCl_4 and CH_2Cl_2 are used, the $CO_2^{\bullet -}$ anion radicals formed may be adsorbed strongly on Ti sites of the TiO_2 surface as shown by Scheme 1(a), because the anion radicals are not highly solvated in solvents of low polarity. Then the negative charge of one oxygen atom of $CO_2^{\bullet -}$ is increased as mentioned above, and carbon monoxide formation occurs readily with removal of the oxygen atom of the $CO_2^{\bullet -}$ anion radical by a proton. If solvents of high dielectric constant such as water and propylene carbonate are used, the $CO_2^{\bullet -}$ anion radicals formed may be greatly stabilized by the solvents as shown by Scheme 1(b), resulting in weak interaction with the photocatalyst surface. Then the carbon atom of the $CO_2^{\bullet -}$ anion radical tends to react with a proton to give formate. So far various photoreduction studies of CO_2 have been conducted in aqueous solutions, and in most cases formate was obtained even when photocatalysts other than TiO_2, such as ZnS [17,18,23], CdS [21,22] and SiC [14–16], were used. Then it is concluded that the polarity of solvents used in the photoreduction of CO_2 plays the most crucial role in determining the kind of reduction products, either CO or formate.

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References

[1] T. Inoue, A. Fujishima, S. Konishi, K. Honda, Nature 277 (1979) 637.
[2] M. Halmann, V. Katzir, Sol. Energy Mater. 10 (1984) 85.
[3] K. Tennakone, Sol. Energy Mater. 10 (1984) 235.
[4] K.R. Thampi, J. Kiwi, M. Gratzel, Nature 327 (1987) 506.
[5] I. Willner, D. Mandler, J. Am. Chem. Soc. 111 (1989) 1330.

[6] P. Albers, J. Kiwi, New J. Chem. 14 (1990) 135.

[7] Z. Goren, I. Willner, A.J. Nelson, A.J. Frank, J. Phys. Chem. 94 (1990) 3784.

[8] K.R. Thampi, L. Lucarelli, J. Kiwi, Langmuir 7 (1991) 2642.

[9] K. Ogura, M. Kawano, J. Yano, Y. Sakata, J. Photochem. Photobiol., A: Chem. 66 (1992) 91.

[10] I. Taniguchi, B. Aurian-Blajeni, J.O'M. Bockris, Electrochim. Acta 29 (1984) 923.

[11] H. Yoneyama, K. Sugiura, S. Kuwabata, J. Electroanal. Chem. 249 (1988) 143.

[12] H. Noda, A. Yamamoto, S. Ikada, M. Maeda, K. Ito, Chem. Lett. (1990) 1757.

[13] S. Ikada, A. Yamamoto, H. Noda, M. Maeda, K. Ito, Bull. Chem. Soc. Jpn. 66 (1993) 2473.

[14] D.H.M.W. Thewissen, A.H.A. Tinnemans, M. Eeuwhorst-Reinten, K. Timmer, A. Mackor, Nouv. J. Chim. (1983) 73.

[15] S. Yamamura, H. Kojima, J. Iyoda, W. Kawai, J. Electroanal. Chem. 225 (1987) 287.

[16] S. Yamamura, H. Kojima, J. Iyoda, W. Kawai, J. Electroanal. Chem. 247 (1988) 333.

[17] A. Henglein, M. Guttieretz, C.H. Fischer, Ber. Bunsenges. Phys. Chem. 88 (1984) 170.

[18] H. Inoue, T. Torimoto, T. Sakata, H. Mori, H. Yoneyama, Chem. Lett. (1990) 1483.

[19] S. Kuwabata, H. Uchida, A. Ogawa, S. Hirao, H. Yoneyama, J. Chem. Soc., Chem. Commun. (1995) 829.

[20] M. Kanemoto, T. Shiragami, C. Pac, S. Yanagida, J. Phys. Chem. 96 (1992) 3521.

[21] H. Inoue, R. Nakamura, H. Yoneyama, Chem. Lett. (1994) 1227.

[22] M. Kanemoto, M. Nomura, Y. Wada, T. Akano, S. Yanagida, Chem. Lett. (1993) 1687.

[23] M. Kanemoto, T. Shiragami, C. Pac, S. Yanagida, Chem. Lett. (1990) 931.

[24] B.R. Eggins, J.T.S. Irvine, P.M. Eileen, J. Grimshaw, J. Chem. Soc., Chem. Commun. (1988) 1123.

[25] S.M. Aliwi, K.F. Al-Jubori, Sol. Energy Mater. 18 (1989) 223.

[26] Y. Matsumoto, M. Obata, J. Honbo, J. Phys. Chem. 98 (1994) 2950.

[27] M. Anpo, K. Chiba, J. Mol. Catal. 74 (1992) 207.

[28] M. Anpo, H. Yamashita, Y. Ichihashi, S. Ehara, J. Electroanal. Chem. 396 (1995) 21.

[29] H. Inoue, T. Matsuyama, B.-J. Liu, T. Sakata, H. Mori, H. Yoneyama, Chem. Lett. (1994) 653.

[30] S. Ikeda, T. Takagi, K. Ito, Bull. Chem. Soc. Jpn. 60 (1987) 2517.

[31] M. Azuma, K. Hashimoto, M. Hiramoto, M. Watanabe, T. Sakata, J. Electrochem. Soc. 137 (1990) 1772.

[32] Y. Hori, A. Murata, R. Takahashi, J. Chem. Soc. Farad. Trans. 1, 85 (1989) 2309.

[33] K. Ohkawa, Y. Noguchi, S. Nakayama, K. Hashimoto, A. Fuijishima, Electroanal. Chem. 369 (1994) 247.

[34] K. Ito, Denki Kagaku 58 (11) (1990) 984.

[35] S. Ikeda, Y. Saito, M. Yoshida, H. Noda, M. Maeda, K. Ito, J. Electroanal. Chem. 260 (1989) 335.

[36] Nippon AEROSIL Report, Technical Bulletin Aerosil, N. 15, (1991) pp. 13.

[37] E. Wilhelm, R. Battino, Chem. Rev. 73 (1973) 1.

[38] A. Gennaro, A.A. Isse, E. Vianello, J. Electroanal. Chem. 289 (1990) 203.

[39] I. Bhugun, D. Lexa, J.-M. Saveant, Anal. Chem. 66, (1994) 3994.

[40] T. Nakayama, J. Electrochem. Soc. 141 (1) (1994) 237.

[41] W. Fresenius, J.F.K. Huber, E. Pungor, G.A. Rechuitzand, W. Simo, Th.S. West, Tables of Spectral Data for Structure Determination of Organic Compounds, 2nd ed., Springer-Verlag, Berlin Heidelberg, New York, 1989, C191.

[42] R.C. Weast, Handbook of Chemistry and Physics, CRC Press Inc., 1969, pp. E-61.

[43] R.C. Weast, Handbook of Chemistry and Physics, CRC Press Inc., 1985, pp. E-50.

[44] The Chemical Society of Japan ed., Kagaku Binran, Kisohen Vol. 1, Maruzen, Inc., 1984, pp. 561.

[45] E. Lamy, L. Nadjo, J.-M. Saveant, J. Electroanal. Chem. 78 (1977) 403.

[46] M.B. Jeffrey, M.S. Wrighton, J. Phys. Chem. 80 (1976) 2641.

[47] L. Kavan, M. Gratzel, S.E. Gilbert, C. Klemenz, H.J. Scheel, J. Am. Chem. Soc. 118 (1996) 6716.

[48] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, Electrochim. Acta 39 (11/12) (1994) 1833.