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Photocatalytic reduction of carbon dioxide in the presence of nitrate using TiO_2 nanocrystal photocatalyst embedded in SiO_2 matrices

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Abstract

Photocatalytic reduction of CO_2 in the presence of nitrate ions in various solvents was studied using TiO_2 nanocrystals embedded in SiO_2 matrices as photocatalysts. Both formate and carbon monoxide were produced as the reduction products of CO_2, ammonia as the reduction product of nitrate, and in addition to these products, urea was formed as a major reduction product of both CO_2 and NO_3^-. The selectivity of these reactions was greatly influenced by the kind of solvents used, and with increasing the dielectric constant of solvents, the amount of formate and carbon monoxide produced decreased, while those of urea and ammonia increased. These results suggest that the reduction reaction of nitrate ions was the rate-determining step of the formation of urea. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Urea; Photocatalytic reduction; Nitrate; Carbon dioxide; Solvent effect

1. Introduction

The photocatalytic reduction of carbon dioxide with the use of semiconductor particles have attracted much attentions to the point of utilization of solar energy [1–15]. So far various kinds of reduction products of CO_2, such as formate [9], carbon monoxide [10], methanol [12] and methane [14,15] were reported. What reduction products obtained seems to be influenced by preparation conditions of photocatalysts and environments under which the photocatalytic experiments are carried out. In our previous studies using TiO_2 nanocrystal photocatalysts [16] and surface-modified CdS photocatalysts [17], it was revealed that the ratio of formate to carbon monoxide obtained as reduction products of CO_2 increased with the increase of the dielectric constant of solvents used.

Furuya et al. [18] have reported electrochemical synthesis of urea having C–N bonds at Cu-loaded gas-diffusing electrode by reduction of carbon dioxide in the presence of nitrate ions. Recently, we found that the irradiation of TiO_2 nanocrystal photocatalysts immobilized in polyvinylpyrrolidinone (PVPD) film in CO_2-saturated propylene carbonate containing nitrate ion caused the formation of urea [19]. Referring to the above mentioned results obtained on photoreduction of CO_2, the selectivity of urea formation will be also influenced by the environments under which the photocatalytic reaction is performed. In order to confirm this idea, we have investigated the effect of solvents on the selectivity of products in photocatalytic reductions of CO_2 in the presence of NO_3^- using TiO_2 nanocrystals embedded in SiO_2 matrices as photocatalysts

2. Experimental section

Tetraethyl titanate and tetraethyl orthosilicate of reagent grade were purchased from Nacalai Tesque. 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. TiO_2 nanocrystals immobilized in SiO_2 matrices (Q-TiO_2/SiO_2) were prepared using the same procedures as already reported [11]. The Ti/Si mole ratio used in this study was fixed to 0.10. An ethanol solution (25 cm^3) containing both 80 mmol 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. After stirring for 2 h, 0.14 cm^3 of the sol was cast on a quartz plate (2.0 cm^2). A transparent gel film of Q-TiO_2/SiO_2 which contained 7.0 μmol of TiO_2 was formed after being dried under nitrogen. As already reported in our previous papers [11,16], the Q-TiO_2 particles embedded in the SiO_2 matrices were spherical in shape and had the anatase

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structure as determined by electron diffraction analyses using a Hitachi H-800 transmission electron microscope at operation voltage 200 kV for these experiments. The average diameter was 5.3 nm and its standard deviation was 1.2 nm. The obtained TiO_2 nanocrystals had the absorption onset at 320 nm which was greatly blue-shifted from that of bulk TiO_2, due to size quantization effects.

The photoreduction experiments of carbon dioxide 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 vertically immersed in 5.0 cm^3 of various kinds of solutions containing 20 mmol dm^{-3} lithium nitrate and 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 at 1.0 W cm^{-2} with light of wavelengths longer than 300 nm obtained by passing lights from a 500 W high pressure mercury arc lamp through a colored glass filter. The quantum efficiencies for photocatalytic reaction TiO_2 surface were determined on the basis of the amount produced by irradiation at 280 nm for 40 h and the number of incident photons on the Q-TiO_2/SiO_2 film which was determined by ferrioxalate actinometry. Monochromatic light of wavelength at 280 nm was obtained using an interference filter.

Carbon monoxide and ammonia produced were determined using a gas chromatograph (Yanaco, G-2800) having a thermal conductivity detector, equipped with a molecular sieve 5A column (GL Sciences) and amipack 141 column (GL Sciences), respectively. Helium was used as a carrier gas. Acetone produced 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 formate. The eluent used was 0.3% H_3PO_4 solution, and its flow rate was 0.80 cm^3 min^{-1}. A high-pressure liquid chromatograph (Jasco CO-965) equipped with a Tsk-Gel (ODS-80 Tm) and a UV multiwavelength detector (Jasco MD-910) was used to determine urea. The eluent used was a mixed solution of acetonitrile (60%) and water (40%), and its flow rate was 0.50 cm^3 min^{-1}. The amount of samples taken for GC and HPLC analysis was 0.20 and 0.020 cm^3, respectively.

3. Results and discussion

Fig. 1 shows the time course of the production of several substances obtained by irradiation of Q-TiO_2/SiO_2 films in CO_2-saturated acetonitrile containing $LiNO_3$ and 2-propanol. As shown in the figure, formate and carbon monoxide were obtained as the reduction products of CO_2, and ammonia as the reduction production of nitrate after irradiation for ca. 2 h with simultaneous production of very small amount of H_2. Furthermore, urea which has C–N bonds was produced. As an oxidation product of 2-propanol, acetone alone was produced. The reactions giving these products are given by Eqs. (1)–(7).

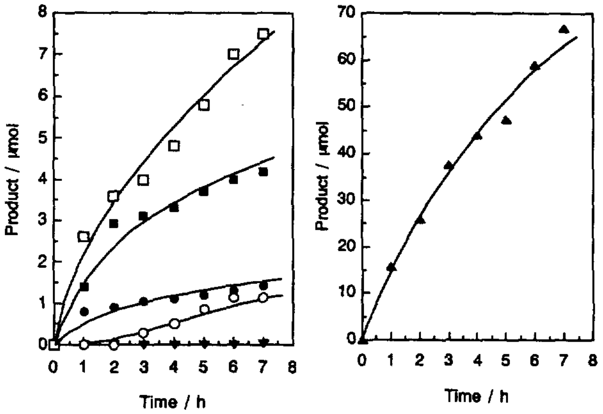

Fig. 1. Time course of the photo-production of formate (■), carbon monoxide (●), urea (□), hydrogen (▼), ammonia (○), and acetone (▲) over Q-TiO_2/SiO_2 film immersed in CO_2 saturated acetonitrile containing 20 mmol dm^{-3} $LiNO_3$ and 1.0 mol dm^{-3} 2-propanol.

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

Oxidation reaction

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

Reduction reaction

$$CO_2 + H^+ + 2e^- \rightarrow HCOO^- \quad (3)$$

$$CO_2 + H^+ + 2e^- \rightarrow CO + OH^- \quad (4)$$

$$NO_3^- + 10H^+ + 8_e^- \rightarrow NH_4^- + 3H_2O \quad (5)$$

$$2NO_3^- + CO_2 + 18H^+ + 16e^- \rightarrow (NH_2)_2CO + 7H_2O \quad (6)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (7)$$

If the amount of electrons and holes involved in the production of these substance was evaluated with use of these equations, the results shown in Fig. 2 were obtained. It is seen that chemical stoichiometry was satisfied during the irradiation time.

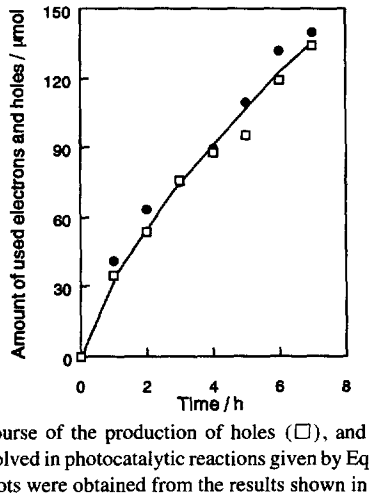

Fig. 2. Time course of the production of holes (□), and electrons (●), which were involved in photocatalytic reactions given by Eqs. (2)–(7). The data used for plots were obtained from the results shown in Fig. 1.

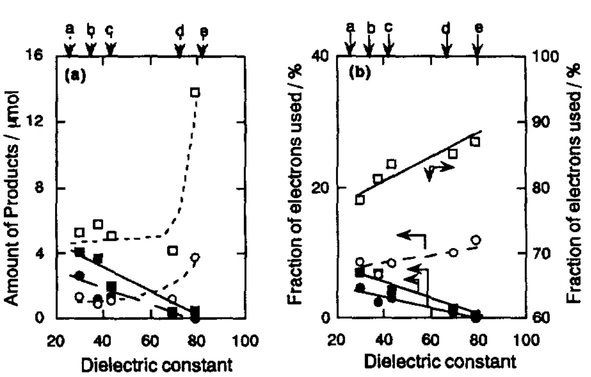

Fig. 3. (a) Relationship between the dielectric constant of solvent used and amount of products, and (b) fraction of photogenerated electrons in production of formate (■), carbon monoxide (●), ammonia (○), and urea (□). The results were obtained by irradiation of Q-TiO_2/SiO_2 for 5 h. Solvents used were: (a) Ethylene glycol monoethyl ether, (b) acetonitrile, (c) sulfolane, (d) propylene carbonate, (e) water.

It was found that the urea production was influenced by the kind of solvents used in the experiments, as shown in Fig. 3. The experiments were carried out using CO_2-saturated solvents containing 20 mmol dm^{-3} $LiNO_3$ and 1.0 mol dm^{-3} 2-propanol. The results shown in Fig. 3a were obtained for 5 h-irradiation of the Q-TiO_2/SiO_2 film, and showed that with increase of dielectric constant [20–23] of solvent, the amount of urea and ammonia increased and those of formate and carbon monoxide decreased. If the fraction of photogenerated electrons used in reduction reaction was calculated, results shown in Fig. 3b were obtained. It is clearly seen that carbon dioxide became predominantly reduced to urea with increase of the dielectric constant of solvents used. The ammonia production also took place more easily with increase of dielectric constant of the solvents. Accordingly, it may be said that the formation of urea was preferred in solvents in which reduction of nitrate ions to ammonia occurred easily. These results may have resulted from different degrees of dissociation of $LiNO_3$ in the solvents. With decrease of polarity of the solvents used, the dissociation of $LiNO_3$ occurs to a less extent and then the amount of NO_3^- available for the reduction reaction on TiO_2 is decreased. The details about the reaction mechanism of NO_3^- reduction are under investigations. If water, which had the highest dielectric constant among the solvents used in the present study, was used, near 90% of the photogenerated electrons were involved in the urea production, and the quantum efficiency obtained in the presence of 20 mmol dm^{-3} $LiNO_3$ were 15.5% for urea, 3.17% for ammonia, 0.16% for formate and 17.5% for acetone. In contrast, the production of urea could not observed if bulk TiO_2 particles (P-25) immobilized in PVPD film was used as photocatalyst [19] and aqueous solutions containing nitrate ions were used as the medium in which photocatalytic reduction of CO_2 was investigated. The observed discrepancy may arise from the fact that the Q-TiO_2/SiO_2 film had much higher photocatalytic activities than bulk TiO_2 particles due to a negative shift of the conduction band edge caused by the size quantization effect and the large specific surface area, as reported in our previous paper [16]. Unfortunately the specific surface area of TiO_2 nanoparticles could not directly be measured because of being immobilized in SiO_2 matrices, but the specific surface area of 290 m^2 g^{-1} deduced by using the average diameter of the obtained TiO_2 nanoparticles (5.3 nm) and the density of anatase TiO_2 of 3.89 g cm^{-3} [24], whereas bulk TiO_2 particles (P-25), was 50 m^2 g^{-1} [25].

The production of ammonia and urea showed a tendency to increase with an increase in the concentration of nitrate ions, as shown in Fig. 4 which was obtained in aqueous solutions. On the other hand, the formate production was not changed by changing the concentration of nitrate ions. It is concluded from those results that the reduction of nitrate was the rate-determining step in the photoformation of urea in the presence of saturated CO_2 whose concentration was ca. 20 mmol dm^{-3} in the case of aqueous solutions.

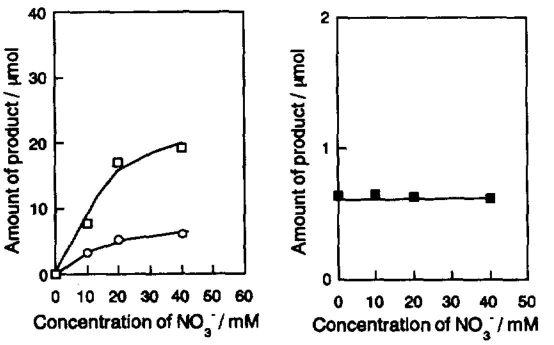

Fig. 4. The relationship between the amount of produced formate (■), urea (□), ammonia (○) and the concentration of nitrate. The solvent used was CO_2-saturated water containing 1.0 mol dm^{-3} 2-propanol.

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