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Photocatalytic reduction of CO_2 using TiO_2 powders in liquid CO_2 medium

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Abstract

The photocatalytic reduction of CO_2 was investigated using TiO_2 powders in liquid CO_2 medium. The TiO_2 powders with liquid CO_2 medium were illuminated in a stainless steel vessel. After reducing CO_2 pressure to the ordinary state, purified water was added to the vessel containing the TiO_2 powders without air contamination. No gaseous reduction products were observed and formic acid was exclusively obtained in the aqueous solution. It seems that formic acid is produced through the protonation of the reaction intermediates on the TiO_2 powders with purified water. © 1997 Elsevier Science S.A.

Keywords: Photocatalytic reduction; Carbon dioxide; Titanium dioxide; Liquid CO_2 medium

1. Introduction

Photocatalytic reduction of CO_2 using photosensitive semiconductor powders has been widely studied in aqueous solutions [1–20]. So far, the studies have been performed exclusively at ordinary temperature and pressure. In these conditions, however, the concentration of CO_2 in water is very small because of its low solubility [21,22] and, furthermore, photocatalytic reduction of CO_2 is competitive with H_2 formation via water reduction. Therefore, selective reduction of CO_2 is one of the major problems for the photocatalytic reduction of CO_2 in aqueous solutions. Increase in CO_2 pressure is one of the measures for increasing the concentration of CO_2 and improving the CO_2 reduction selectivity [23,24]. At the ultimate, liquid CO_2 can be used as a medium. Liquid CO_2, however, is non-polar and non-electroconductive, and hence the addition of supporting salts to liquid CO_2 needs for electrochemical or photoelectrochemical reduction [25–27]. On the other hand, these properties should be of no consequence in the photocatalytic reduction of CO_2 using the semiconductor powders. But, little information on the photoreduction of CO_2 using the semiconductor powders in liquid CO_2 medium has been presented.

Recently, in many studies for the photocatalytic reduction of CO_2, TiO_2 has been shown to be one of the effective catalysts for the reduction by illumination with light [5–20]. Therefore, it has been found that the photocatalytic effect of TiO_2 on reduction of CO_2 is of great interest.

In this work, we present a photocatalytic reduction of CO_2 using TiO_2 powders in only liquid CO_2 medium. Moreover, the mechanism of the photoreduction of CO_2 in liquid CO_2 medium is discussed, based on the characterizations of the TiO_2 powders by electron spin resonance (ESR) after the end of illumination.

2. Experimental

2.1. Procedures

The photocatalytic reduction was carried out in a stainless steel vessel (inner volume, 57.5 ml) with a window through which TiO_2 powders in liquid CO_2 medium was illuminated, as shown in Fig. 1. A commercially available pressure glass device with 21 mm diameter aperture (KLINPORT KPT-C1Q, Nihon Klingage CO. Ltd.) was fitted in the window, because the window glass transmitted almost all the light rays of wavelength above 340 nm and energy of 3.6 eV, which is

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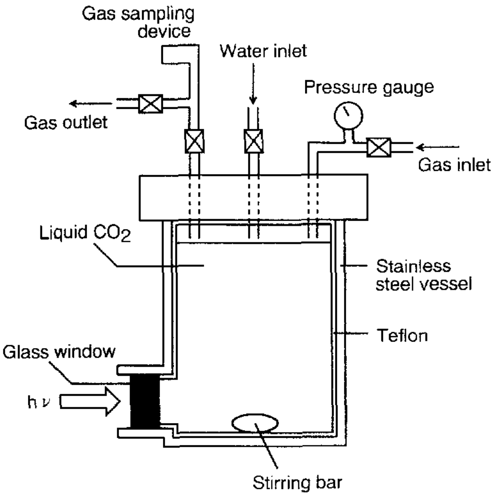

Fig. 1. Stainless steel vessel for photocatalytic reduction of CO_2 under high CO_2 pressure.

higher than the bandgap energy of TiO_2 (3.0 eV). The inner surface was completely covered by Teflon to prevent contamination from the stainless steel and its catalytic effect on CO_2 reduction. The vessel was placed in a water bath at 293 K.

TiO_2 (Wako Junyaku, anatase; specific surface, 8.7 m^2 g^{-1}; diameter, 230 nm; purity, 99.9%) was pretreated by boiling in 1 M nitric acid and then thoroughly rinsed with distilled-deionized water prior to use. The TiO_2 powders (50 mg) were placed in the stainless steel vessel. After deoxygenation by flowing highly purity CO_2 (99.9999%) through the vessel for 30 min, the vessel was closed tightly and then the CO_2 pressure was increased to 6.5 MPa. The TiO_2 powders were continuously dispersed in liquid CO_2 medium by a magnetic stirrer during illumination with a Xe lamp (990 W, Ushio Electronics Co.) through the window. The light intensity was 0.96 kW m^{-2}. After the end of illumination (30 h), CO_2 pressure was reduced to the ordinary state. To the vessel containing the TiO_2 powders was added degassed-purified water (5 ml) without air contamination to protonate the reaction intermediates on the TiO_2 powders. Gaseous reduction products were sampled through a sampling valve and analyzed by FID and TCD gas chromatography. The analysis of gaseous products was performed immediately after illumination and the addition of purified water, respectively. The liquid sample was analyzed by high performance liquid chromatography with a UV detector.

2.2. *ESR analysis*

After illumination, CO_2 pressure was reduced to ambient state and the TiO_2 powders were transferred to an ESR quartz glass tube in an atmosphere of CO_2 without air contamination. Then, ESR spectra of the TiO_2 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 the beginning, we tried to photocatalytically reduce CO_2 on TiO_2 powders in liquid CO_2 medium without any proton source, because little water can be dissolved into liquid CO_2 [28]. After illumination, no reduction products were identified in vaporized CO_2. However, since any reduced products could be adsorbed on the TiO_2 powders illuminated, the TiO_2 powders were washed with a small amount of purified 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 TiO_2 might react with the water to form formic acid. Hence, we made it our procedures to reduce photocatalytically CO_2 in liquid CO_2 medium through two steps, i.e. illumination of the TiO_2 powders and then the addition of purified water. When the same procedures were performed in highly purity nitrogen medium without CO_2 as a reference, no reduction products were detected. Also, when the dark reduction of CO_2 was performed in liquid CO_2 medium, CO_2 was not reduced. From the results, it was concluded that formic acid was produced by the photocatalytic reduction of CO_2.

The influence of temperature and pressure on the yield of formic acid was studied for 30 h illuminations. Accordingly, illumination of the TiO_2 powders (50 mg) was carried out at various temperatures (273, 278, 283, 288, 293 and 298 K) and pressures (5.0, 6.0, 6.5, 7.0 and 8.0 MPa). However, the yield of formic acid was almost constant and was not affected by temperature and pressure. The density of liquid CO_2 can not almost change in these conditions [29]. Thus, the results may indicate that the interaction of CO_2 with the surface species of the TiO_2 powders or the catalytic activity of TiO_2 can not be effected by temperature and pressure. Consequently, all subsequent illuminations were made with liquid CO_2 medium of 293 K and 6.5 MPa, because of the reproducibility for the production of formic acid.

3.1. *Effect of illumination time*

In order to select optimal illumination time, the effect of illumination time on the yield of formic acid was investigated. The results are shown in Fig. 2. The yield of formic acid increased sharply with illumination time until 5 h. After the time, the production yield was suppressed gradually until 30 h. During this period, it was observed that the dispersed TiO_2 particles began to coagulate and the state of dispersion became worse. Therefore, the suppression of the production yield after 5 h might be attributed to deterioration of photocatalytic activity due to coagulation of the TiO_2 particles. The yield of formic acid reached a maximum value of 8.4 μmol $(g\text{-cat})^{-1}$ for 30 h illuminations. This value was several times larger than those obtained by Ishitani et al. [14] and Hirano et al. [15]. Over 30 h, the yield of formic acid turned from an increase into a decrease. The reason for this turn is not

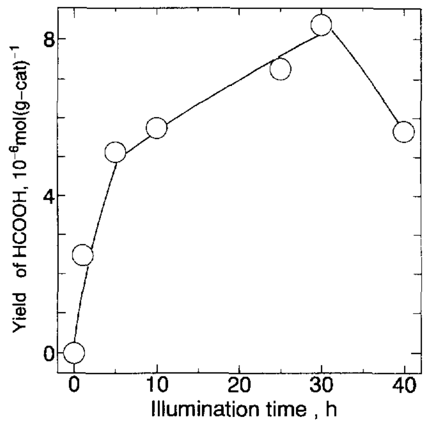

Fig. 2. Effect of illumination time on the yield of formic acid. TiO_2, 50 mg; temperature, 293 K; pressure, 6.5 MPa.

clear. It may be attributable to deterioration of photocatalytic activity due to coagulation, diminishment of the adsorption power 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.

3.2. Effect of the surface area of TiO_2

If the reaction intermediates from CO_2 are accumulated on the surface of TiO_2, the yield of formic acid should increase linearly with the total surface area 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. 3. 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. In excess of the area, the production of formic acid plateaued. These phenomena may be due that the amount of TiO_2 in liquid CO_2 medium was too large for the light to reach every particle.

From the data in the present study, we tried to estimate the density of the intermediate products on the surface of TiO_2, assuming that all of the intermediate products were situated on the surface of TiO_2 and protonated to formic acid with purified water. The density was approximately 5.8×10^{12} molecules of the intermediate products per 1 mm^2. The value was about a few tenths smaller than the density of the CO_2 monolayer [21]. Therefore, the density was sparse and the intermediate products were considered to be situated on the specific surface sites of TiO_2.

3.3. ESR characterization

In order to clarify a reaction scheme for the photoreduction of CO_2 on the TiO_2 powders in liquid CO_2 medium, we studied the ESR characterizations of the TiO_2 powders. Fig. 4 shows the ESR signals measured at 77 K with the TiO_2 catalyst after the end of illumination. The ESR signals consisted two different radical species. From the literature reported [16,18–20,30–33], the signal with a $g_\perp$ value of 1.981 can be attributed to the characteristic photogenerated Ti^{3+} ions. Henglein et al. have recently proposed that in the two-electron reduction $\cdot CO_2^-$ radicals formed in the uptake of the first electron were strongly adsorbed by ZnS particles [4]. Yamanaka and coworkers described that $\cdot CO_2^-$ radicals were detected near a g value of 2.00 by ESR measurements [34,35]. Therefore, another signal with a $g_\perp$ value of 2.015 may probably consist of $\cdot CO_2^-$ radicals. When illumination of the TiO_2 powders was performed in high-purity nitrogen medium without CO_2 as a blank, this signal could not be observed.

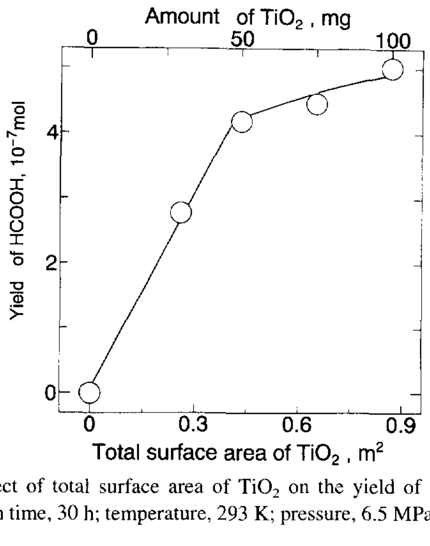

Fig. 3. Effect of total surface area of TiO_2 on the yield of formic acid. Illumination time, 30 h; temperature, 293 K; pressure, 6.5 MPa.

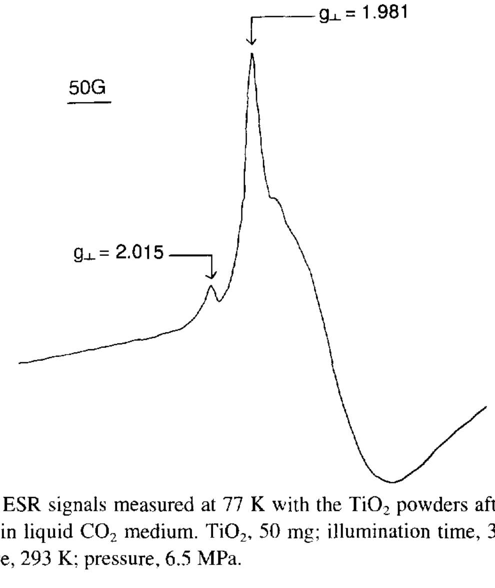

Fig. 4. ESR signals measured at 77 K with the TiO_2 powders after illumination in liquid CO_2 medium. TiO_2, 50 mg; illumination time, 30 h; temperature, 293 K; pressure, 6.5 MPa.

From the results in the present study and the literature [16–20,30–33,36–41], the formation process of formic acid by illumination of the TiO_2 powders in liquid CO_2 medium and the protonation with purified water is suggested to be as follows:
Illumination;

$$\mathrm{TiO_2} \xrightarrow{h\nu} e^-(\mathrm{Ti}^{3+}) + h^+$$

$$[(\mathrm{Ti}^{4+} - \mathrm{O}^{2-}) \xrightarrow{h\nu} (\mathrm{Ti}^{3+} - \mathrm{O}^-)^*]$$

$$\mathrm{CO_2} \xrightarrow[(\mathrm{Ti}^{3+} - \mathrm{O}^-)^*]{h\nu} \cdot\mathrm{CO_2^-}\,(\mathrm{ads})$$

Protonation;

$$\cdot\mathrm{CO_2^-} \xrightarrow[(\mathrm{Ti}^{3+} - \mathrm{O}^-)^*]{2\mathrm{H}^+ + e^-} \mathrm{HCOOH}$$

$$\cdot\mathrm{CO_2^-} + \cdot\mathrm{CO_2^-} \xrightarrow{2\mathrm{H}^+} \mathrm{HCOOH} + \mathrm{CO_2}$$

When light energy larger than the TiO_2 bandgap is absorbed by the TiO_2 powders, an electron (e^-) and positive hole (h^+) pair, namely the charge transfer excited state of $(Ti^{3+} - O^-)^*$, is formed in the catalyst [16,18–20]. 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 interact with the excited state of $(Ti^{3+} - O^-)^*$. The interactions may result in the formation of $\cdot CO_2^-$ radicals. Since the positive hole scavengers are absent during illumination, the holes may continue to reside on the appropriate sites. Therefore, the radicals and the positive holes might keep to be trapped by the surface of TiO_2 because of charge neutralization. At the end of illumination, it can be considered that the catalyst has the high reactivity of the excited state of $(Ti^{3+} - O^-)^*$, i.e. a number of electron and hole pairs because Ti^{3+} ions were detected by ESR measurements. During the protonation with purified water, the $\cdot CO_2^-$ radicals seem to react with protons (H^+) supplied from H_2O and an electron from the excited state of $(Ti^{3+} - O^-)^*$ or another $\cdot CO_2^-$ to produce formic acid.

In conclusion, the photocatalytic reduction of CO_2 was carried out using the TiO_2 powders in only liquid CO_2 medium. The protonation reaction was performed after the end of illumination. The main reduction product was exclusively formic acid. Formic acid seems to be produced through the protonation of $\cdot CO_2^-$ radicals which are intermediate species.

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