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Photoelectrochemical reduction of CO_2 at p-InP electrode in copper particle-suspended methanol

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ABSTRACT

The photoelectrochemical reduction of CO_2 in copper particle-suspended methanol was studied by using a p-type InP photoelectrode. In the absence of copper particles, only formic acid and carbon monoxide were formed during the photoelectrochemical reduction of CO_2, and the formation of hydrocarbons could not be observed. However, hydrocarbons were formed on the addition of copper particles into the catholyte. The current efficiencies of methane and ethylene were better below 273 K than at ambient temperature (288 K). The maximum Faradaic efficiencies of methane and ethylene were $r_f = 0.56\%$ and 0.80%, respectively. The total current efficiency of hydrocarbons became maximum at 263 K, and the maximum efficiency was $r_f = 1.21\%$. On the basis of these observations, it was realized that it is possible to roughly change and control the reduction product distribution by the addition of metal particles into the catholyte during the photoelectrochemical reduction of CO_2. This research can contribute to the large-scale manufacture of useful organic products from readily available and cheap raw materials, e.g., the manufacture of CO_2-saturated methanol from industrial absorbers (the Rectisol process).

1. Introduction

The reduction in the atmospheric loading of carbon dioxide (CO_2) has been considered on a global level for preventing the reinforcement of the greenhouse effect, which may in turn increase the average temperature of the earth to such an extent that a series of catastrophic events may occur. Therefore, the development of CO_2 sequestration technologies that involve capture and secure storage and conversion methods has been of significant interest from the practical viewpoint [1–3]. Photoelectrochemical and photoelectrocatalytic methods involving p-type semiconductor electrodes seem to be very efficient methods for the conversion and reduction of CO_2. This is because of the solar energy conversion technology involved; therefore, such methods can be regarded as artificial models for photosynthesis occurring in plants [1–3].

Following the first report of the photoelectrochemical reduction of CO_2 by Halmann in 1978 [4], the studies have been performed on the reduction of CO_2 and the production of useful products with a low input energy. Various p-type semiconductors have been used, including p-GaP, p-CdTe, p-GaAs, p-InP, p-SiC, and p-Si and its diamond coats [5–22]. Thus far, the photoelectrochemical CO_2 reduction has been exclusively examined in aqueous solutions. Recently, many investigators have actively studied the photoelectrochemical reduction of CO_2 using various p-type photoelectrodes in organic solvents because CO_2 is more soluble in organic aprotic solvents than in water [6,19,20]. It has been reported that two-electron reduced products containing carbon monoxide, oxalic acid, and formic acid were produced by the electroreduction of CO_2 in dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl formamide (DMF), propylene carbonate, and acetonitrile. However, few hydrocarbons have been obtained in these organic solvents.

Methanol is a better solvent for CO_2 than water, particularly at low temperatures. The solubility of CO_2 in methanol is approximately four times that in water at ambient temperature and more than eight times that in water at temperatures below 273 K [23–25]. Therefore, methanol has been industrially used as a physical absorbent of CO_2 in the Rectisol method at 243–263 K [25]. Currently, over 70 large-scale plants employ the Rectisol process. Therefore, the direct photo/electrochemical reduction of CO_2 in methanol is an advantageous choice, especially when the process is performed under energetically efficient conditions. We have investigated the electrochemical reduction of CO_2 at various metallic electrodes using methanol as the solvent [26–35]. Next, the photoelectrochemical reduction of CO_2 in methanol at p-type semiconductor electrodes such as p-Si, p-GaAs, and p-InP has been reported [36,37]. Furthermore, we have studied the photoelectrochemical reduction of CO_2 in methanol at metal-modified

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p-InP photoelectrode [38]. In the photoelectrochemical reduction, hydrocarbons such as methane and ethylene were formed, and the maximum Faradaic efficiencies of methane and ethylene were $r_f = 0.7\%$ and 0.2%, respectively.

The electrochemical reduction of CO_2 at lead and zinc electrodes in metal particle-suspended methanol has recently been investigated [39]. It is noted that methane and ethylene could be obtained, even though a copper cathode was not used. In the photoelectrochemical reduction of CO_2 in both aqueous and nonaqueous organic solutions, there has been little information on the photoelectrolysis in the suspension [40]. This study deals mainly with the photoelectrochemical reduction of CO_2 at p-InP electrode in copper particle-suspended methanol.

2. Experimental

The instruments and experimental conditions for the photoelectrochemical reduction of CO_2 are listed in Table 1. The photoelectrochemical reduction of CO_2 was performed in a laboratory-made, divided H-type cell. An Aldrich Nafion 117 ion exchange membrane (0.18 mm thickness) was used as the diaphragm. The cathode potential was measured with respect to an Ag/AgCl, sat. KCl electrode that was connected to the catholyte using a Luggin capillary (the agar salt bridge) in order to compensate for the ohmic potential drop due to the solution resistance between the reference and working electrodes.

Methanol (99%, Nacalai Tesque, Inc., Japan) was used as received without further purification. The water content in pure methanol was less than 0.1% (confirmed by the Karl Fischer test). Sodium hydroxide (96%, Nacalai Tesque, Inc.) was used as the ionophore in the methanol-based electrolyte. Copper particles (diameter: 1 μm, purity: 99.99%, CUE08PB, Kojundo Chemical Laboratory Co., Ltd.) were added to the catholyte for preparing a metal particle suspension. It has been reported in a previous paper [35] that the pH of methanol in the presence of a supporting salt (80 mmol dm^{-3} NaOH) at 243 K was approximately 14 and the pH decreased to approximately 5.3 after saturation of the catholyte with CO_2. The p-Type InP wafer was cut into chips (area: approximately $1.0 \times 1.0\,cm^2$), washed with a mixture of conc. HCl and HNO_3, etched in CP-4A (a mixture of 47% HF, 60% HNO_3, 99.7% CH_3COOH, and H_2O with a volume ratio of 3:5:3:22) and finally etched again with the mixture of concentrated acids to remove any organic contaminants on the surface. Ohmic contact was made on the rear side of the p-InP piece by using an In alloy. A Pt foil was used as the counter electrode. The Pt anode was electrochemically activated at 500 mA for 100 s in 14.7 mol dm^{-3} phosphoric acid.

Table 1
Apparatus and experimental conditions for the photoelectrochemical reduction of CO_2

Photoelectrochemical reduction	
Cell	H-type cell
Potentiostat/galvanostat	Hokuto HA-501
Coulometer	Integrator 1109 (Fusou Seisakujyo, Inc., Japan)
Potential sweep	Hokuto HB-111 function generator
XY recorder	Graphtec WX1100
Working electrode	p-InP [(100), Zn-doped, $5 \times 10^{17}\,cm^{-3}$, SHOWA DENKO K.K.]
Counter electrode	Pt foil (30 mm × 20 mm, Thickness: 0.1 mm, 99.98% purity)
Reference electrode	Ag/AgCl sat. KCl (Horiba, 2060A-10T)
Electrolyte	
Catholyte	100 mmol dm^{-3} NaOH in methanol (70 cm^3) (Cu particles added: ϕ1 μm, 99.99% purity, 0.1–1 g)
Anolyte	300 mmol-dm^{-3} KOH in methanol (70 cm^3)
Carbon dioxide	99.9999% purity
Potential	−2.4 to −2.8 V vs. Ag/AgCl (sat. KCl)
Temperature	258, 263, 273, 288 K (±0.5 K)

Table 2
Analytical instruments used for examining the products obtained from the reduction of CO_2

Product analysis	
Gaseous products	Gas chromatography TCD (GL Sciences GC-320, Molecular Sieve 5A; 13X-S, Ar and He carrier gas) FID (GL Sciences GC-353B, Porapak Q, N_2 carrier gas)
Liquid products	HPLC with UV detector (Hitachi L4000) TCD and FID gas chromatography

A 5000-W xenon lamp (Ushio, UXL-5000DK-B-O, Tokyo, Japan) was used to illuminate the semiconductor photocathode. Wavelengths shorter than 300 nm were filtered out by the cell wall. A discontinuous photoelectrochemical reduction procedure was used. First, CO_2 gas was bubbled into the methanol catholyte for 1 h at the rate of 30 ml min^{-1}. The CO_2-saturated solution was then photoelectrolytically reduced at cathodic polarizations in the range of −2.4 to −2.8 V vs. Ag/AgCl, sat. KCl. The catholyte was magnetically stirred in order to maintain the suspension conditions. The temperatures of the electrolytes were controlled by using a cooling device (ESC-50, EYELA, Tokyo, Japan). The Faradic efficiencies of the formation of the major products were calculated from the total charge passed during the batch electrolyses, which was set to 30 C. The gaseous products obtained during the photoelectroreduction were collected in a gas collector and analyzed by gas chromatography (GC). The products soluble in the catholyte were analyzed by high performance liquid chromatography (HPLC) and GC. A conventional column (length: 4 mm; i.d.: 2.2 mm) was used for GC. The detailed information is given in Table 2. In the control experiment, nitrogen gas was used. The surface morphology of the p-type InP electrode was examined by scanning electron microscopy (SEM, Hitachi S-4000, Japan).

3. Results and discussion

Literature values [8–10] for the solubilities of CO_2 in pure methanol at 288, 263 and 243 K and in water at 288 K were 4.6, 8, 15 and 1.07 cm^3 cm^{-3}, respectively. It has been presented in a previous study [35] that the solubility of CO_2 in a solution of 80 mmol dm^3 methanolic NaOH at 243 K was approximately 15 cm^3 cm^{-3} (approximately 670 μmol CO_2/cm^3 methanol). Although $NaHCO_3$ may be formed in the methanol while bubbling CO_2 through the solution for several minutes, the amount of $NaHCO_3$ in the catholyte is assumed to be very small since no precipitate can be observed. Therefore, CO_2 can be considered to be physically dissolved, i.e., under intact form in the methanol catholyte. The solubility of CO_2 in our system is greater than that of CO_2 in water, which is very advantageous.

3.1. *Effect of addition of copper particles*

In the photoelectrochemical reduction of CO_2 at p-type InP electrodes in a methanol-based electrolyte [37], formic acid and carbon monoxide were the principal products obtained from CO_2, and no hydrocarbons such as methane and ethylene were formed. However, hydrocarbons are formed during the electrochemical reduction of CO_2 in copper particle-suspended methanol [39]. Hence, we can consider the usage of a solution suspended with metal particles for photoelectrochemical reduction. Therefore, the influence of the addition of copper particles on the photoelectrochemical reduction of CO_2 at a p-InP cathode in methanol was evaluated at 288 K, as illustrated in Fig. 1. In the photoelectro-

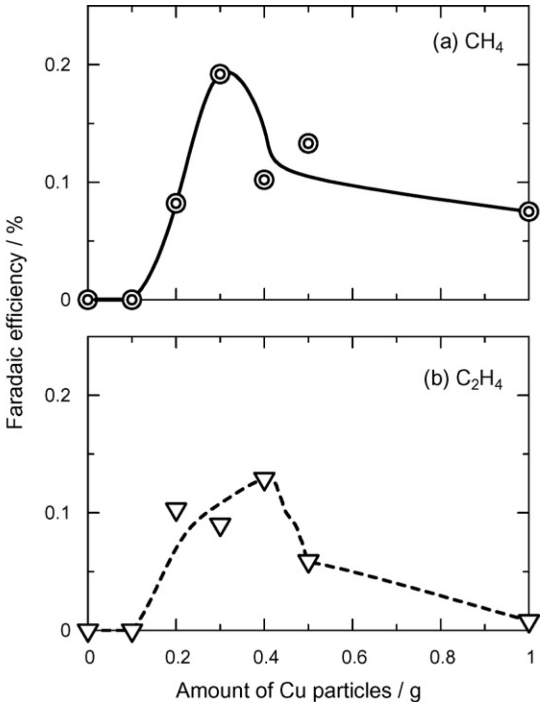

Fig. 1. Effect of amount of metal particles on Faradaic efficiencies of hydrocarbons formed by the photoelectrochemical reduction of CO_2 at the p-InP photocathode in copper particle-suspended methanol. (◎) CH_4; (▽) C_2H_4; potential: −2.5 V; temperature: 288 K.

chemical reduction of CO_2 at the p-InP electrode without copper particles, the hydrocarbons were not formed, which is the same as the previously obtained results [37]. However, in the presence copper particles, the methane and ethylene were formed, and their Faradaic efficiencies increased with the amount of copper particles in the methanol catholyte. The maximum efficiencies of methane and ethylene were $r_f = 0.19\%$ and 0.13% with 300 mg and 400 mg of copper particles, respectively. Ethane formation ($r_f = 0.01\%$) was observed only in the suspension containing 300 mg of copper particles. The total hydrocarbon efficiency was maximum (0.28%) with 300 mg of Cu particles. When the amount of copper particles was increased to more than 400 mg, a decrease in the formation efficiencies of hydrocarbons was observed. The morphology of the p-type InP cathode surface before and after the electrolysis was evaluated by SEM. No electrodeposited copper particles could be observed on the p-InP surface. Consequently, hydrocarbons such as methane and ethylene could be formed during the photoelectrochemical reduction of CO_2 at the p-InP photoelectrode in copper particle-suspended methanol. For the subsequent experiments, 300 mg of copper particles was added to the methanol-based catholyte.

3.2. Current–potential curves

The current–potential (*I–V*) curves of the p-InP electrode in copper particle-suspended methanol were recorded at 288 K. The potential was scanned at a sweep rate of 50 mV s^{-1}. The typical *I–V* curves are shown in Fig. 2. Under illumination, relatively large photocurrent densities were observed both in the presence and absence of copper particles, although the dark current in the absence of illumination was very small. At a potential of −2.5 V, the photocurrent density after the addition of 300 mg copper particles had reduced by only 30% relative to those obtained without the copper particles. The decrease in the photocurrent density with the amount of copper particles may be due to the decreased light penetration and increased light scattering. The onset (starting) potential of the cathodic current, i.e., the potential value at which a current density of 0.1 mA cm^{-2} is observed, in copper particle-suspended methanol was approximately −0.7 V. The onset potential obtained after the addition of copper particles was found to be shifted to a more positive value than that (ca. −0.8 V) obtained in the absence of copper particles. No voltammetric peak was observed in the potential range up to −2.8 V because further CO_2 reduction may proceed with increasingly negative potentials. Once the onset potentials were determined from the polarization experiments, we attempted to investigate the effect of potential on the photoelectrochemical reduction of CO_2 at the p-InP cathode in copper particle-suspended methanol.

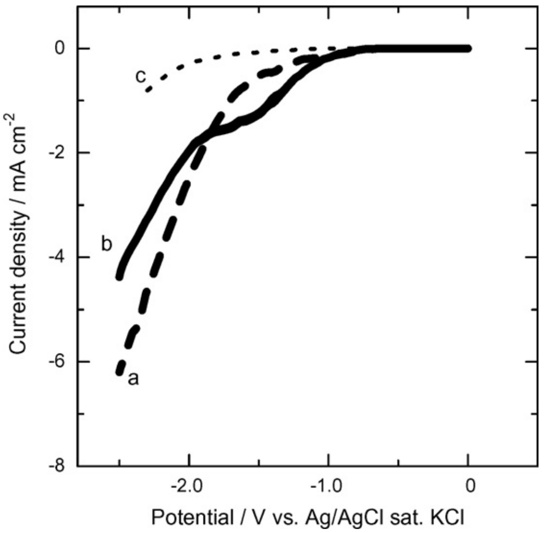

Fig. 2. *I–V* curves for the p-InP photocathode in CO_2-saturated methanol at 288 K. (a) Without copper particles. (b) With copper particles (300 mg). (c) Dark experiment (without illumination).

3.3. Effect of potential on the product Faradaic efficiency

The results dealing with the effect of the potential on the current efficiencies for the products by the photoelectrochemical reduction of CO_2 at the p-InP photocathode in copper particle-suspended methanol at 288 K are shown in Fig. 3. The total current density increased from 4.3 to 9.4 mA cm^{-2} as the potential became more negative. The current efficiency curves for methane and ethylene exhibited a convex pattern, and the maximum efficiencies were obtained at −2.5 and −2.6 V, respectively. In the photoelectrochemical reduction of CO_2 at the p-InP electrode in the methanol-based electrolyte, formic acid was predominantly formed [37]. However, in copper particle-suspended methanol, the formation of carbon monoxide was predominant at all the potentials studied. The Faradaic efficiency curves of CO and formic acid became maximum at −2.7 and −2.6 V, and their efficiencies were $r_f = 45.2\%$ and 21.1%, respectively. The curve of hydrogen formation efficiency was concave, and the minimum ($r_f = 19.7\%$) was obtained at −2.5 V. The total current yield of the electroreduction products did not add up to 100%; the reason for this has not been clarified as yet. The residual current might be attributed to the formation of methanol from CO_2. Methanol production by the electroreduction of CO_2 in aqueous electrolytes has been previously reported by Frese [41] and reviewed by Jitaru et al. [42]. From the viewpoint of hydrocarbon formation and the decrease in hydrogen evolution, −2.5 V was selected as the optimum potential for the photoelectrochemical reduc-

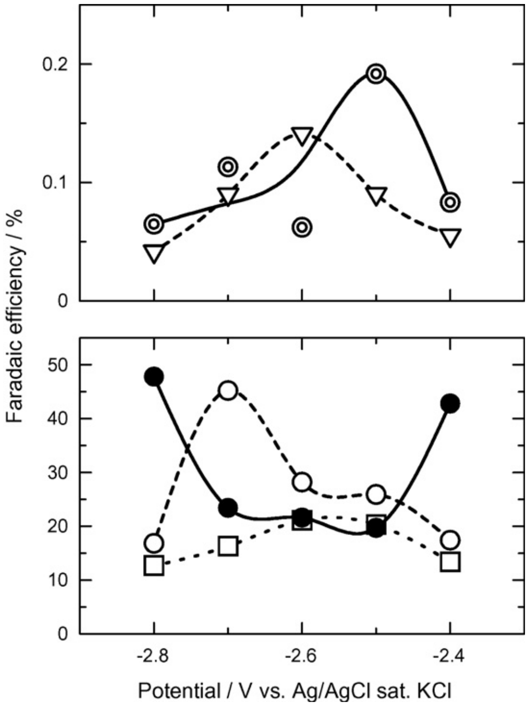

Fig. 3. Effect of potential on Faradaic efficiencies of the products formed by the electrochemical reduction of CO_2 at p-InP photocathode in copper particle-suspended methanol. (◎) CH_4; (▽) C_2H_4; (○) CO; (□) HCOOH; (●) H_2; temperature: 288 K; copper particles: 300 mg.

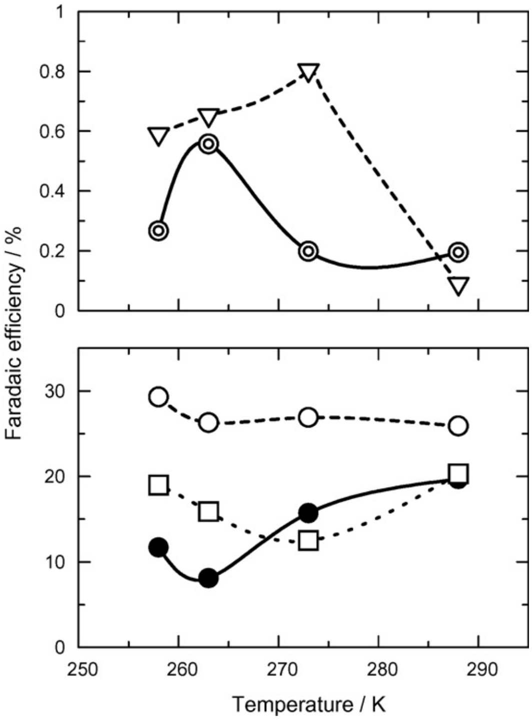

Fig. 4. Effect of temperature on Faradaic efficiencies of the products formed by the electrochemical reduction of CO_2 at p-InP photocathode in copper particle-suspended methanol. (◎) CH_4; (▽) C_2H_4; (○) CO; (□) HCOOH; (●) H_2; potential: −2.5 V; copper particles: 300 mg.

tion of CO_2 at the p-InP electrode in copper particle-suspended methanol.

3.4. Effect of temperature on hydrocarbon formation

In the photoelectrochemical reduction of CO_2 at p-type semiconductor electrodes in a methanol-based electrolyte [37], it has been reported that methanol catholyte at a low temperature was suitable for the improvement in the CO_2 reduction. Therefore, the influence of temperature on the Faradaic efficiencies of the products of the photoelectrochemical reduction of CO_2 at a p-InP photocathode in copper particle-suspended methanol was investigated. The results are illustrated in Fig. 4. At a temperature of less than 273 K, the formation efficiency for ethylene was larger than that for methane. Below 273 K, the current efficiencies of methane and ethylene were relatively better than those obtained at an ambient temperature (288 K). The maximum Faradaic efficiencies of methane and ethylene were $r_f = 0.56\%$ and 0.80%, respectively. The total current efficiency for hydrocarbons reached the maximum at 263 K, and the maximum efficiency was $r_f = 1.21\%$. These values were better than those obtained in the photoelectrochemical reduction of CO_2 in methanol at the metal-modified p-InP photocathode [38]. The formation efficiency of carbon monoxide increased slightly on decreasing the temperature. The current efficiency of formic acid at 288 K was better than that at low temperatures of less than 273 K.

Generally, in the electrochemical reduction of CO_2 in water, hydrogen formation competes with CO_2 reduction. Therefore, the suppression of hydrogen formation is very important because the applied energy is wasted on hydrogen evolution instead of being used for the reduction of CO_2. In the normal photoelectrochemical reduction of CO_2 at the p-InP photocathode in a methanol-based catholyte, the efficiency of hydrogen formation was found in the range of 23–29% [37]. In the copper particle-suspended reduction system, hydrogen formation efficiency tended to decrease with a decrease in the temperature. At a temperature of 263 K, the Faradaic efficiency of hydrogen formation could be decreased to 8%.

3.5. Reaction mechanism

The mechanism for the photoelectrochemical reduction of CO_2 in copper particle-suspended methanol at p-InP photoelectrodes was investigated. GC-mass spectrometric analysis with deuterated methanol catholyte demonstrated that no reduction product was obtained from methanol [34]. Hydrogen was formed exclusively when the electrolysis in the suspension was conducted under a nitrogen atmosphere. Hirota et al. [43] stated that the reduction products were produced from CO_2 during its photoelectrochemical reduction in methanol. Consequently, the desired products were produced by the electrochemical reduction of CO_2.

The experimental data in this study and literature reports [1–22,26–41] suggest the mechanism of formation of methane, ethylene, carbon monoxide, and formic acid at the p-InP photoelectrode, as shown in Fig. 5. Furthermore, the schematic cross sections of the chemical reaction site on the photoelectrode surface are shown in Fig. 6. In the photoelectrochemical reduction of CO_2 in copper particle-suspended methanol, three adsorption/reaction sites can be speculated on the photocathode surface for the photoelectrochemical reduction reaction; (A) the photocathode surface, (B) the area between the photocathode surface and the copper particles, and (C) the surface of the copper particles. At site (B), the chemical species CO_2 can undergo a number of electronation processes from both the photoelectrode surface and the copper particle. As shown on the right side of the reaction pathways in Fig. 5, formic acid and carbon monoxide may be produced at the adsorption site (A). On the other hand, hydrocarbons such as methane and ethylene are probably formed at the adsorption sites (B) and (C),

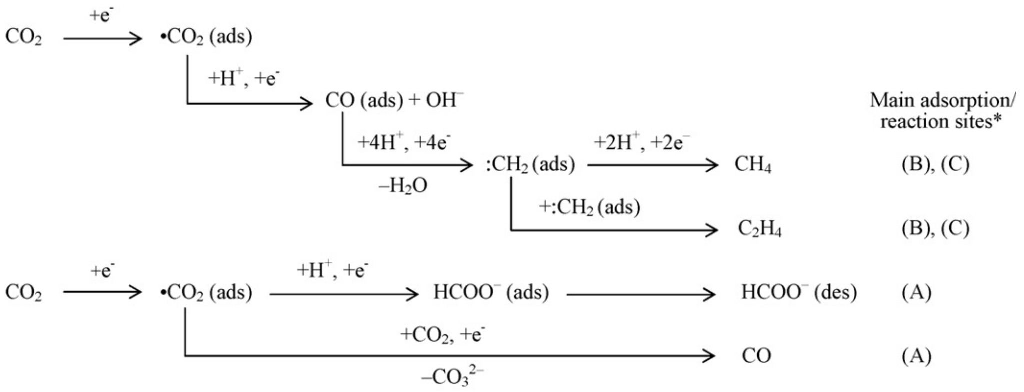

Fig. 5. Reaction mechanism of the photoelectrochemical reduction of CO_2 at p-InP photocathode in copper particle-suspended methanol. (*) Adsorption sites (A), (B), and (C) correspond to those shown in Fig. 6.

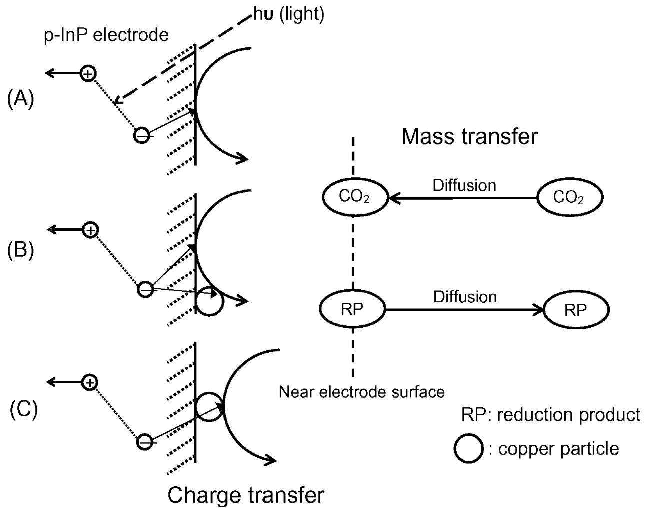

Fig. 6. Schematic cross sections of the adsorption/reaction sites on the cathode.

owing to the catalytic property of copper metal. In the normal photoelectrochemical reduction of CO_2 in a methanol-based electrolyte [38], methane and ethylene were produced at a nickel-modified p-InP photoelectrode, although no hydrocarbon could be formed on Cu-deposited p-InP. The reason for the difference between the photochemical reduction of CO_2 in the present study and that at a copper-modified p-InP electrode is not clear. This difference might be attributed to the poor catalytic activity of copper caused by its low crystallinity when it was coated on the p-InP electrode surface by using vacuum splluttering devices. Thus far, in order to control the distribution of the reduction products in the photoelectrochemical reduction of CO_2, the effect of various factors such as the type of photocathode, supporting salts, temperature, and pressure have been reported [1–3]. In the present study, it is found that the reduction product distribution can be fairly controlled by the addition of metal particles into the catholyte during the photoelectrochemical reduction of CO_2.

4. Conclusion

The photoelectrochemical reduction of CO_2 in copper particle-suspended methanol was studied by using a p-InP photocathode. In the absence of copper particles, formic acid and carbon monoxide were the only reduction products, while methane and ethylene were not obtained at the p-type InP photoelectrode. After the addition of copper particles, hydrocarbons were formed in the photoelectrochemical reduction of CO_2. At <273 K, the current efficiencies of methane and ethylene were better than those obtained at ambient temperature (288 K). In the photoelectrochemical reduction of CO_2, it may be possible to roughly change and control the distribution of reduction products by the addition of metal particles. With the development of nanotechnology that involves the preparation of nanosized metal particles, the present CO_2 photoelectrochemical techniques may become one of the most promising methods for the conversion and reduction of CO_2. Thus, the synthesis of hydrocarbons through the photoelectrochemical reduction of CO_2 might be of practical interest in fuel production, storage of solar energy, and production of intermediates for the petrochemical industry.

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References

[1] M.M. Halmann, M. Steinberg, Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology, Lewis Publishers, Boca Raton, FL, 1999.
[2] A.M. Scibioh, B. Viswanathan, in: S. Kaneco (Ed.), Photo/electrochemistry and photobiology in the environment, energy and fuel, Research Signpost, Kerala, 2002, pp. 1–46 (Chapter 1).
[3] G.R. Dey, K. Kishore, in: S. Kaneco (Ed.), Photo/electrochemistry and photobiology in the environment, energy and fuel, Research Signpost, Kerala, 2005, pp. 357–388 (Chapter 10).
[4] M. Halmann, Photoelectrochemical reduction of aqueous carbon dioxide on p-type gallium phosphide in liquid junction solar cells, Nature 275 (1978) 115–116.
[5] K. Ito, S. Ikeda, M. Yoshida, S. Ohta, T. Iida, On the reduction products of carbon dioxide at a p-type gallium phosphide photocathode in aqueous electrolytes, Bull. Chem. Soc. Jpn. 57 (1984) 583–584.
[6] I. Taniguchi, B. Aurian-Blajeni, J.O'M. Bockris, The reduction of carbon dioxide at illuminated p-type semiconductor electrodes in nonaqueous media, Electrochim. Acta 29 (1984) 923–932.
[7] I. Taniguchi, B. Aurian-Blajeni, J.O'M. Bockris, The mediation of the photoelectrochemical reduction of carbon dioxide by ammonium ions, J. Electroanal. Chem. 161 (1984) 385–388.
[8] H. Yoneyama, K. Sugimura, S. Kuwabata, Effects of electrolytes on the photoelectrochemical reduction of carbon dioxide at illuminated p-type cadmium telluride and p-type indium phosphide electrodes in aqueous solutions, J. Electroanal. Chem. 249 (1988) 143–153.
[9] J.O'M. Bockris, J.C. Wass, The photoelectrocatalytic reduction of carbon dioxide, J. Electrochem. Soc. 136 (1989) 2521–2528.

[10] J. Ueda, S. Nakabayashi, J. Ushizaki, K. Uosaki, A photoelectrochemical fixation of carbon dioxide. Spontaneous up quality conversion of organic compound, Chem. Lett. 22 (1993) 1747–1750.

[11] H. Flaisher, R. Tenne, M. Halmann, Photoelectrochemical reduction of carbon dioxide in aqueous solutions on p-GaP electrodes: an a.c. impedance study with phase-sensitive detection, J. Electroanal. Chem. 402 (1996) 97–105.

[12] M.G. Bradley, T. Tysak, D.J. Graves, N.A. Vlachopoulos, Electrocatalytic reduction of carbon dioxide at illuminated p-type silicon semiconducting electrodes, J. Chem. Soc. Chem. Commun. (1983) 349–350.

[13] C.R. Cabrera, H.D. Abruña, Electrocatalysis of CO_2 reduction at surface modified metallic and semiconducting electrodes, J. Electroanal. Chem. 209 (1986) 101–107.

[14] L. Junfu, C.Y. Baozhu, Photoelectrochemical reduction of carbon dioxide on a p^+/p-Si photocathode in aqueous electrolyte, J. Electroanal. Chem. 324 (1992) 191–200.

[15] R. Hinogami, Y. Nakamura, S. Yae, Y. Nakato, An approach to ideal semiconductor electrodes for efficient photoelectrochemical reduction of carbon dioxide by modification with small metal particles, J. Phys. Chem. 102 (1998) 974–980.

[16] B. Aurian-Blajeni, M. Halmann, J. Manassen, Electrochemical measurement on the photoelectrochemical reduction of aqueous carbon dioxide on p-Gallium phosphide and p-Gallium arsenide semiconductor electrodes, Sol. Energy Mater. 8 (1983) 425–440.

[17] W.M. Sears, S.R. Morrison, Carbon dioxide reduction on gallium arsenide electrodes, J. Phys. Chem. 89 (1985) 3295–3298.

[18] B.A. Parkinson, P.F. Weaver, Photoelectrochemical pumping of enzymatic CO_2 reduction, Nature 309 (1984) 148–149.

[19] S. Ikeda, Y. Saito, M. Yoshida, H. Noda, M. Maeda, K. Ito, Photoelectrochemical reduction products of carbon dioxide at metal coated p-GaP photocathodes in non-aqueous electrolytes, J. Electroanal. Chem. 260 (1989) 335–345.

[20] H. Noda, S. Ikeda, Y. Saito, T. Nakamura, M. Maeda, K. Ito, Photoelectrochemical reduction of carbon dioxide at metal-coated p-InP photocathodes, Denki Kagaku 57 (1989) 1117–1120.

[21] K. Hashimoto, A. Fujishima, in: J.P. Pradier, C.M. Pradier (Eds.), Carbon Dioxide Chemistry: Environmental Issues, The Royal Institute of Technology, Stockholm, 1994, pp. 388–395.

[22] H. Ono, A. Yokosuka, T. Tasiro, H. Morisaki, S. Yugo, Characterization of diamond-coated Si electrodes for photoelectrochemical reduction of CO_2, New Diamond Frontier Carbon Technol. 12 (2002) 141–144.

[23] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 85th ed., CRC Press, Boca Raton, FL, 2004, pp. 8–88.

[24] H. Chihara (Ed.), Kagaku binran-kiso, vol. II, 3rd ed., Maruzen, Tokyo, 1984, pp. 158–165 (Handbook of Basic Chemistry, in Japanese).

[25] G. Hochgesand, Rectisol and purisol, Ind. Eng. Chem. 62 (1970) 37–43.

[26] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, in: C. Liu, R.G. Mallinson, M. Aresta (Eds.), Utilization of Greenhouse Gases, ACS Symposium Series 852, American Chemical Society, Washington, DC, 2003, pp. 169–182.

[27] S. Kaneco, K. Iiba, K. Ohta, T. Mizuno, A. Saji, Electrochemical reduction of CO_2 at an Ag electrode in KOH–methanol at low temperature, Electrochim. Acta 44 (1998) 573–578.

[28] S. Kaneco, K. Iiba, K. Ohta, T. Mizuno, A. Saji, Electrochemical reduction of CO_2 on Au in KOH + methanol at low temperature, J. Electroanal. Chem. 441 (1998) 215–220.

[29] S. Kaneco, K. Iiba, S. Suzuki, K. Ohta, T. Mizuno, Electrochemical reduction of carbon dioxide to hydrocarbons with high Faradaic efficiency in LiOH/methanol, J. Phys. Chem. B 103 (1999) 7456–7460.

[30] S. Kaneco, K. Iiba, H. Hiei, K. Ohta, T. Mizuno, T. Suzuki, Electrochemical reduction of carbon dioxide to ethylene with high Faradaic efficiency at a Cu electrode in CsOH/methanol, Electrochim. Acta 44 (1999) 4701–4706.

[31] S. Kaneco, K. Iiba, M. Yabuuchi, N. Nisho, H. Ohnishi, H. Katsumata, T. Suzuki, K. Ohta, High efficiency electrochemical CO_2-to-methane conversion method using methanol with lithium supporting electrolytes, Ind. Eng. Chem. Res. 41 (2002) 5165–5170.

[32] S. Kaneco, R. Iwao, H. Katsumata, T. Suzuki, K. Ohta, Electrochemical carbon dioxide reduction at Sn electrode in KOH/methanol-based electrolyte at ambient temperature and pressure, Photo/Electrochem. Photobiol. Environ. Energy Fuel 1 (2002) 69–75.

[33] S. Kaneco, R. Iwao, H. Katsumata, T. Suzuki, K. Ohta, Carbon dioxide sequestration technology by electrochemical conversion at cadmium electrode in methanol under mild conditions, Photo/Electrochem. Photobiol. Environ. Energy Fuel 2 (2003) 181–189.

[34] A. Naitoh, K. Ohta, T. Mizuno, H. Yoshida, M. Sakai, H. Noda, Electrochemical reduction of carbon dioxide in methanol at low temperature, Electrochim. Acta 38 (1993) 2177–2179.

[35] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, Effect of sodium cation on the electrochemical reduction of CO_2 at a copper electrode in methanol, J. Solid State Electrochem. 11 (2007) 490–495.

[36] S. Kaneco, H. Ohnishi, H. Katsumata, T. Suzuki, K. Ohta, Photoelectrochemical reduction of carbon dioxide on p-Si electrode in methanol at ambient temperature and pressure, ITE Lett. Batt. New Technol. Med. 3 (2002) 196–200.

[37] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, Photoelectrochemical reduction of carbon dioxide at p-type gallium arsenide and p-type indium phosphide electrodes in methanol, Chem. Eng. J. 116 (2006) 227–231.

[38] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, Photoelectrocatalytic reduction of CO_2 in LiOH/methanol at metal-modified p-InP electrodes, Appl. Catal. B: Environ. 64 (2006) 139–145.

[39] S. Kaneco, Y. Ueno, H. Katsumata, T. Suzuki, K. Ohta, Electrochemical reduction of CO_2 in copper particle-suspended methanol, Chem. Eng. J. 119 (2006) 107–112.

[40] K. Ohta, Y. Ohuguchi, S. Kaneco, T. Mizuno, Photoelectrochemical reduction of CO_2 by silicate rock powders, Energy Source 21 (1999) 467–473.

[41] K.W. Frese Jr., in: B.P. Sullivan (Ed.), Electrochemical and Electrocatalytic Reduction of Carbon Dioxide, Elsevier, Amsterdam, 1993, pp. 145–216.

[42] M. Jitaru, D.A. Lowy, M. Toma, B.C. Toma, L. Oniciu, Electrochemical reduction of carbon dioxide on flat metallic cathodes, J. Appl. Electrochem. 27 (1997) 875–889.

[43] K. Hirota, D.A. Tryk, T. Yamamoto, K. Hashimoto, M. Okawa, A. Fujishima, Photoelectrochemical reduction of CO_2 in a high-pressure CO_2 + methanol medium at p-type semiconductor electrodes, J. Phys. Chem. B 102 (1998) 9834–9843.