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Electrochemical reduction of CO_2 in methanol with aid of CuO and Cu_2O

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ABSTRACT

The electrochemical reduction of CO_2 in methanol-based electrolyte was investigated with zinc particle-pressed electrodes. In order to evaluate the characteristic of copper oxide catalysts for the electrochemical reduction of CO_2, zinc particles mixed with CuO and Cu_2O powders were pressed for fabricating a disk plate of electrode. Without copper oxide particles, only formic acid and carbon monoxide were formed in the electrochemical reduction of CO_2, and the formation of hydrocarbons could scarcely be observed. On the other hand, hydrocarbons were obtained for the zinc particle-pressed electrodes containing copper oxide particles. At CuO/Zn particle-pressed electrode, the Faradic efficiency of ethylene was better relative to that of methane at all conditions tested. With Cu_2O/Zn powder-pressed electrode, the current efficiency of methane was larger compared with that of ethylene in the low content range of Cu_2O (1–2.5%). The maximum formation efficiencies of methane and ethylene were of 7.5% and 6.8% with the electrode consisted of Cu_2O/Zn, respectively. It was found that copper oxide catalysts (CuO and Cu_2O) were effective for the formation of hydrocarbons, especially ethylene, in the electrochemical reduction of CO_2 in methanol-based electrolyte.

1. Introduction

Carbon dioxide (CO_2) is the ultimate by-product of all processes involving oxidation of carbon compounds and its increasing presence in the atmosphere. In view of the vastness of its supply, CO_2 represents a potential source of C1 feedstock for the production of chemicals and fuels. The thermodynamic stability and the relative kinetic inertness of CO_2 require its preliminary activation or, alternatively, the activation or modification of the substrates. Therefore, the electrochemical method appears to become one of the very suitable methods for the conversion and reduction of CO_2 [1–3].

A number of researchers have actively investigated the electrochemical reduction of CO_2 using various metallic electrodes in organic solvents, because organic nonaqueous solvents dissolve much more CO_2 than water does [4–7]. It has been described that two-electron reduced products were produced by the electrochemical CO_2 reduction in dimethyl sulfoxide (DMF), *N*,*N*-dimethyl formamide (DMSO), acetonitrile (MeCN), and propylene carbonate (PC). However, even at a copper electrode, few hydrocarbons such as methane and ethylene have been obtained in these organic solvents [7].

Methanol (MeOH) is a better medium of CO_2 than water, particularly at low temperature. The solubility of CO_2 in MeOH is about four times that in water, at ambient temperature, and more than seven times that in water, at temperatures below 273 K [8–10]. Therefore, MeOH has been industrially used as a physical absorbent of CO_2 in the Rectisol method, at 243–263 K [10]. Currently, over 70 large-scale plants apply the Rectisol process. Therefore, the direct electrochemical reduction of CO_2 in MeOH is an advantageous choice, especially when the process is performed under energetically efficient conditions. Many research groups (our group [11–24], Fujishima and co-workers [25], Koleli et al. [26], Schrebler et al. [27], Eggins et al. [28]) have brought focus into the electrochemical reduction of CO_2 in methanol-based electrolyte.

On the other hand, Frese [29] have studied the electrochemical reduction of CO_2 at intentionally oxidized Cu electrodes in water. Methanol, CO and methane were detected as the reduction products. Terunum et al. have evaluated the relationship between hydrocarbon production in the electrochemical reduction of CO_2 in water and the characterization of Cu electrode [30]. Chang et al. [31] have investigated the electrochemical reduction of CO_2 with Cu_2O-catalyzed carbon clothes. In the study, only methanol was formed as the product, and its Faradaic efficiency was not clarified. Thus far, in the electrochemical reduction of CO_2 in methanol-based catholyte, little information on the electrolysis with the copper oxide electrocatalyst has been reported. This study deals mainly with the electrochemical reduction of CO_2 in methanol with aid of CuO and Cu_2O.

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2. Experimental

2.1. Fabrication of powder-pressed cathode

The powders of zinc ($\phi \sim 7$ μm) and Cu_2O ($\phi \sim 100$ nm) were provided by Nacalai Tesque Inc., Kyoto, Japan. The CuO powders ($\phi \sim 33$ nm) were obtained from Sigma–Aldrich, Japan. First, zinc particles were mixed with CuO or Cu_2O powders. A mixture of 500 mg was pressed with an FTIR disk creator at 200 kg/cm^2. A diameter and a thickness of the disk were 10 and 1.0 mm, respectively. The fabricated electrode was used for the electrolysis without further purification.

2.2. Electrochemical CO_2 reduction

The apparatus and experimental conditions for the electrochemical reduction of CO_2 are shown in Table 1. Electrochemical reduction of CO_2 was performed in a laboratory-made, divided H-type cell. An Aldrich Nafion 117-type ion exchange membrane (0.18 mm thickness) was used as the diaphragm. A silver rod covered with epoxy, with only the end exposed, was used as a quasi-reference electrode (Q.R.E.). The Ag Q.R.E. has a potential of approximately +100 mV vs. Ag/AgCl-saturated KCl that was connected with the catholyte through the Luggin capillary (the agar salt bridge), which was used in the previous work [17,19]. In order to lower the ohmic potential drop due to solution resistance between the reference and working electrodes, the top of Ag Q.R.E. was closely placed on the surface of cathode. However, in this reduction system, the IR drop between the end of Ag Q.R.E. and the working electrode could not be completely compensated owing to the large solution resistance of catholyte.

Methanol (99%, Nacalai Tesque, Inc., Japan) was used as received without further purification. Water content in the pure methanol was less than 0.1% (confirmed by the Karl Fischer test). Potassium hydroxide (85%, Nacalai Tesque, Inc.) was used as the ionophore in the methanol-based electrolyte. The pH of methanol with 300 mmol dm^{-3} KOH supporting salt at 243 K were approximately 14 and the pH after the saturation of the catholyte with CO_2 were about 7.5. Mechanical processing of the Pt electrode required polishing each surface with successively finer grades of alumina powder (Baikalox emulsion, manufactured by Baikowski International Co.) down to 0.05 μm, followed by the removal of grease with acetone. The Pt anode was activated electrochemically at 500 mA for 100 s in 14.7 mol dm^{-3} phosphoric acid. Before the electroreduction, the cathode and anode were rinsed with both water and ethanol.

A discontinuous electroreduction procedure was used. First, CO_2 gas was bubbled into the methanol catholyte for 1 h at a rate of 30 mL min^{-1}. Then, the CO_2-saturated solution was reduced electrolytically at cathodic polarizations in the range from −2.5 to −3.2 V vs. Ag/AgCl, sat. KCl. The catholyte was magnetically stirred. The Faradic efficiencies of formation for the main products were calculated from the total charge passed during batch electrolyses, which was set to 50 C. Gaseous products obtained during the electroreduction were collected in a gas collector and were analyzed by GC. Products soluble in the catholyte were analyzed by using HPLC and GC. In control experiment, nitrogen gas was used.

Table 1
Apparatus and experimental conditions.

Electrochemical reduction	
Cell	H-type cell
Potentiostat/galvanostat	Hokuto HA-3001A
Coulometer	Integrator 1109 (Fusou Seisakujyo, Inc., Japan)
Potential sweep	Hokuto HB-111 function generator
XY recorder	Graphtec WX1100
Working electrode	CuO/Zn disk (ϕ10 mm, 1 mm thickness) Cu_2O/Zn disk (ϕ10 mm, 1 mm thickness)
Counter electrode	Pt foil (30 mm × 20 mm, 0.1 mm thickness, 99.98% purity)
Reference electrode	Ag rod quasi-reference electrode (ϕ2.0 mm × 100 mm, 99.98% purity)
Electrolyte	
Catholyte	300 mmol dm^{-3} KOH in methanol
Anolyte	300 mmol dm^{-3} KOH in methanol
Carbon dioxide	99.9999% purity
Potential	−2.5 to −3.2 V vs. Ag Q.R.E.
Temperature	243 ± 0.5 K
Product analysis	
Gas 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

3. Results and discussion

Literature data [8,9] for the solubilities of CO_2 in pure methanol and water, at 288 K, were of 4.6 and 1.07 $cm^3\ cm^{-3}$, respectively. It has been presented in a previous study [21] that the solubility of CO_2 in a solution of 80 mmol dm^{-3} KOH/methanol, at 243 K, was about 16 $cm^3\ cm^{-3}$ (about 710 μmol CO_2/cm^3 methanol). Although $KHCO_3$ may be formed in the methanol while bubbling CO_2 through the solution for several minutes, the amount is assumed to be very small or negligible, since one cannot observe any precipitate. Therefore, a large proportion of CO_2 can be considered to be physically dissolved, i.e., under intact form in the methanol catholyte. The increased solubility of carbon dioxide in our system relative to water appears to be very advantageous. In the electrochemical reduction of CO_2 at zinc wire electrodes in methanol-based electrolyte, the predominant formations of carbon monoxide and formic acid were observed, respectively [22], and the current efficiency of methane was less than 0.4%. On the other hand, it has been pointed out in the previous work [29–31] that copper oxides seem to give the effective electrode conditions for the formation of hydrocarbon in the electrochemical CO_2 reduction in methanol-based catholyte. Hence, zinc cathodes in combination with copper oxides were evaluated in the present work. The electrolysis was performed at 243 K because temperature in the Rectisol process is customarily in the range of 243–263 K [10].

3.1. Effect of copper oxide content

The influence of the copper oxide content on the electrochemical reduction of CO_2 at Zn particle-pressed electrodes in methanol is illustrated in Figs. 1 and 2. The current densities decreased gradually as the copper oxide contents increased in the disk electrode. In the normal electrochemical reduction of CO_2 at Zn particle-pressed electrodes (without copper oxides), the distributions of the reduction products were almost the same as those obtained with the wire electrodes [22], except for much higher Faradaic efficiency of carbon monoxide and hydrogen. The reason for higher formation efficiency of CO and hydrogen compared to that at the wire electrodes may be due to the difference of the electrode type. Hydrocarbons such as methane, ethylene and ethane were produced with both CuO/Zn and Cu_2O/Zn electrodes. The Faradaic efficiency of ethane was less than 0.1%. The current efficiencies for hydrocarbons at Cu_2O/Zn electrode were better relative to those obtained with CuO/Zn electrode. The

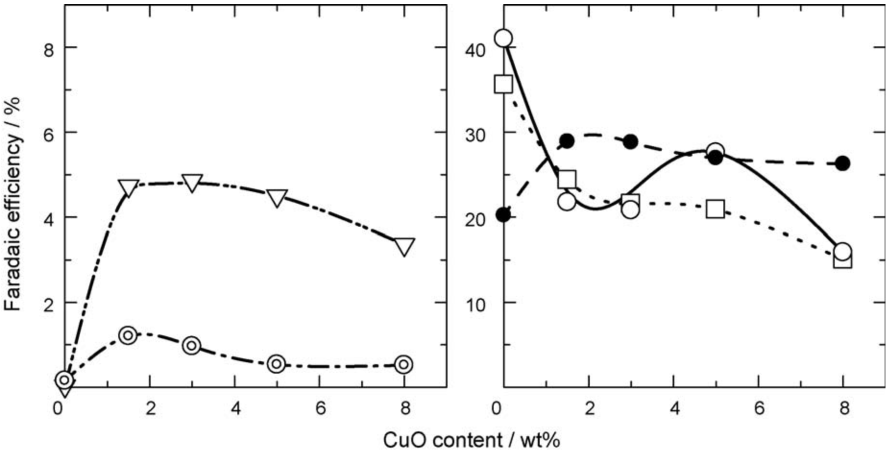

Fig. 1. Effect of CuO content on Faradaic efficiencies for the products by electrochemical reduction of CO_2 at CuO/Zn powder-pressed electrode in KOH/methanol. ◎, CH_4; ▽, C_2H_4; ○, CO; □, HCOOH; ●, H_2; potential, −3.0 V; temperature, 243 K.

formation efficiency curve of methane was concave, and the maximum efficiency was 7.5% at the Cu_2O content 2.5 wt%. The current efficiency of ethylene increased sharply with an increase in the Cu_2O content up to 2.5 wt%, and then the efficiency was almost constant. The maximal Faradaic efficiency of ethylene (6.8%) was obtained at the Cu_2O content 7.0 wt%. With increasing the copper oxide content in the electrode, the formation efficiencies of formic acid and carbon monoxide tended to decrease gradually. On the other hand, the current efficiency of hydrogen increased slightly. In the electrochemical CO_2 reduction at Cu electrode in LiOH/methanol-based electrolyte, the Faradaic efficiency of methane was extremely high (for example, 63.0% at −4.0 V [17]). Although the formation efficiency for hydrocarbons in this work was worse relative to that obtained with Cu electrode, it could be experimentally confirmed that copper oxides (CuO and Cu_2O) had an electrocatalytic power to reduce CO_2 to hydrocarbons. For the subsequent experiments, 1.5 wt% CuO/Zn and 2.5 wt% Cu_2O/Zn particle-pressed electrodes were used for the evaluation of potential effect.

3.2. Current–potential curves

The current–potential curves at zinc powder-pressed electrodes containing CuO and Cu_2O in KOH/methanol were recorded at 243 K. The potential was scanned at a sweep rate of 50 mV s^{-1}. The typical current–potential curve for the electrode containing Cu_2O is illustrated in Fig. 3. The onset (starting) potentials of the cathodic current, i.e. those potential values at which a current density of 0.1 mA cm^{-2} is observed, in CO_2-saturated methanol were approximately −0.5 and −1.2 V on CuO/Zn and Cu_2O/Zn cathodes, respectively. No voltammetric peak was observed in the potential range down to −2.5 V because further CO_2 reduction may proceed with increasingly negative potentials. Once the onset potentials were determined from polarization experiments, we attempted to investigate the effect of potential on the electrochemical reduction of CO_2 at CuO/Zn and Cu_2O/Zn cathodes in methanol-based catholyte.

3.3. Effect of potential on the product Faradaic efficiency

The results dealing with the effect of the potential on the formation efficiencies for the products by the electrochemical reduction of CO_2 on zinc powder-pressed electrodes in KOH/methanol are shown in Figs. 4 and 5. With CuO/Zn electrode, the current efficiencies for formic acid, carbon monoxide and hydrogen were nearly independent on the potential. The maximum formation efficiencies of methane and ethylene were of 2.7% and 4.7% at −3.1 and −3.0 V, respectively. Though the current efficiency curve of formic acid was concave with Cu_2O/Zn electrode, the efficiencies for carbon monoxide and hydrogen

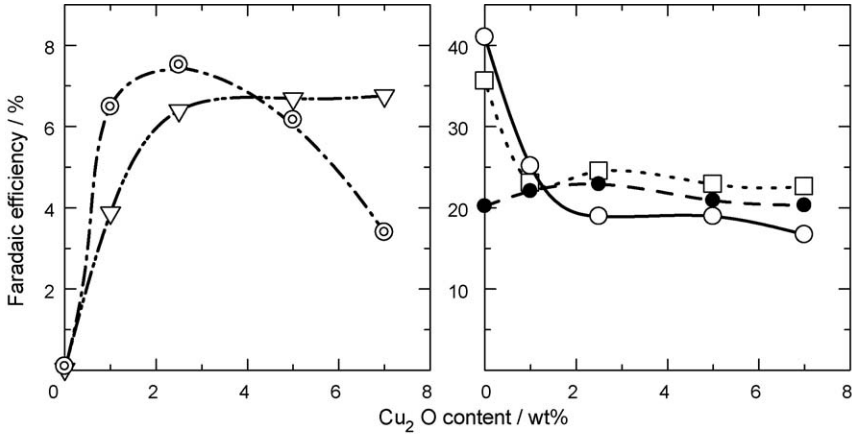

Fig. 2. Effect of Cu_2O content on Faradaic efficiencies for the products by electrochemical reduction of CO_2 at Cu_2O/Zn powder-pressed electrode in KOH/methanol. ◎, CH_4; ▽, C_2H_4; ○, CO; □, HCOOH; ●, H_2; potential, −3.0 V; temperature, 243 K.

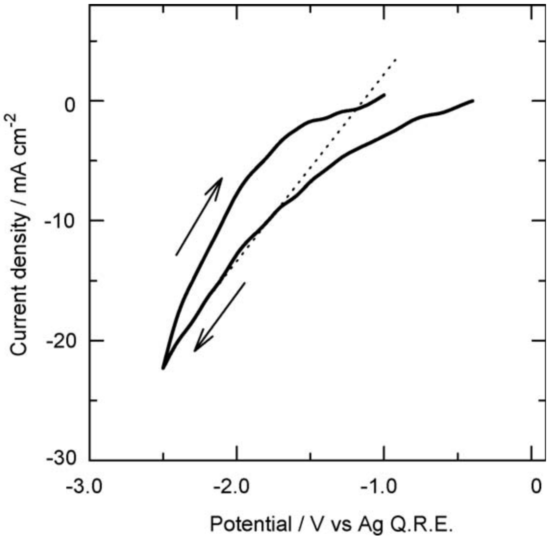

Fig. 3. Current–potential curves for Cu_2O/Zn powder-pressed electrode in CO_2-saturated methanol. Cu_2O content, 2.5 wt%; temperature, 243 K.

were almost constant. The best Faradaic efficiency of methane was obtained at −3.0 V. Also, the maximal total efficiency for hydrocarbons was observed at the same potential (13.9%).

Generally, in the electrochemical reduction of CO_2 in water, hydrogen formation is simultaneous to 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 electrochemical reduction of CO_2 at 2.5 wt% Cu_2O/Zn particle-pressed electrode in KOH/methanol, the Faradaic efficiency for hydrogen formation, at 243 K, was less than 25%. In the electrochemical reduction of CO_2 at Zn electrode in aqueous solution, the current efficiency of hydrogen was 68.1% [31]. It has been reported that low temperature was effective for the depression of hydrogen formation in the methanol electrolyte [11–24]. Therefore, we were able to confirm that methanol-based catholyte, at low temperature, was suitable to suppress hydrogen formation.

3.4. Reaction mechanism

The mechanism of the electrochemical reduction of CO_2 in KOH/methanol was investigated for CuO and Cu_2O-supported Zn electrodes. When the electrolysis with the electrode was conducted under a nitrogen atmosphere as the control experiment, the electrolysis yielded exclusively hydrogen. The previous GC–MS study with deuterated methanol catholyte demonstrated that no reduction product was produced from the decomposition of methanol [12]. Many investigators [25–28] stated that the reduction products were produced from CO_2 in the CO_2 electrochemical reduction in methanol. Consequently, the needed products were produced by the electrochemical reduction of CO_2. The experimental data in this work and literature reports [1–7,11–31,32] suggest that the pathways, by which carbon monoxide and formic acid on Zn powder-pressed electrodes containing copper oxide were formed, seems to be the same as those in the electrochemical reduction of CO_2 in methanol-based electrolyte at Zn electrode.

It is widely believed in most studies that the first steps in the reduction of CO_2 at high hydrogen overpotential cathodes are as follows [4,32]:

$$CO_2\,(ads) + e^- \rightarrow {}^{\bullet}CO_2^{-}$$

Hydrocarbons are yielded by a series of simultaneous or consecutive electronation/protonation steps. The adsorbed ${}^{\bullet}CO_2^{-}$ radical anion formed in the first electronation step undergoes a second electronation/protonation to yield adsorbed CO as the key intermediate. From a succession of four electronation/protonation steps, an adsorbed reactive methylene group forms, and this may either stabilize as a methane molecule by a subsequent double electronation/protonation sequence or dimerize to form ethylene and ethane. Therefore, copper oxides (CuO and Cu_2O) seem to be relatively easier to produce and chemically adsorb the reaction intermediate CO for the formation of hydrocarbons. Hydrocarbons are formed by the interaction between adsorbed CO and atomic hydrogen at the reaction site, where copper oxide and zinc metal are present side by side or close enough to suppress the evolution of CO and H_2. Such reaction sites may give a large amount of atomic hydrogen. Since the copper oxide sites may be favorable to CO, hydrocarbons might be able to be produced on Cu oxide sites. If the donating of atomic hydrogen to adsorbed CO is less effective, CO is produced without the further reduction to hydrocarbon. Thus, there is a possibility that copper oxides electrochemically produce hydrocarbons. Terunum et al. [30] have suggested that the surface with metal copper, Cu oxide and much adsorbed oxygen had an enhanced activity for the hydrocarbon formation.

Since the electrochemical decomposition of Cu_2O follows the reaction:

$$Cu_2O + 2e^- + 2H^+ = 2Cu + H_2O$$

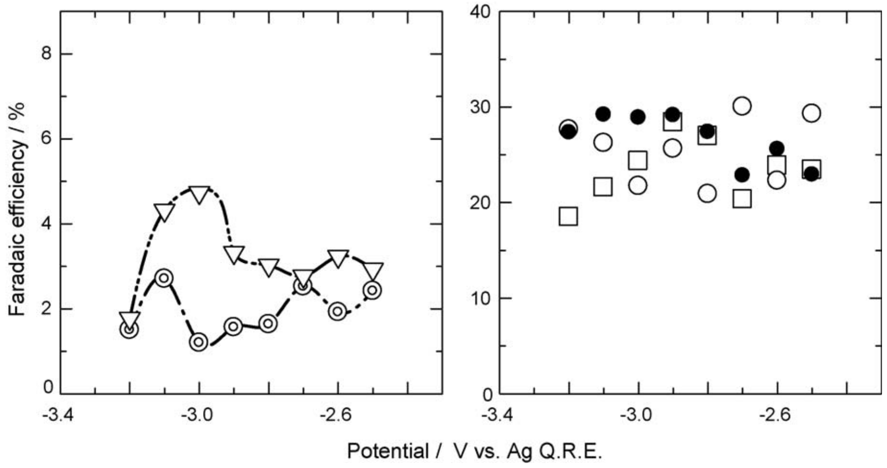

Fig. 4. Effect of potential on Faradaic efficiencies for the products by electrochemical reduction of CO_2 at CuO/Zn powder-pressed electrode in KOH/methanol. ◎, CH_4; ▽, C_2H_4; ○, CO; □, HCOOH; ●, H_2; CuO content, 1.5 wt%; temperature, 243 K.

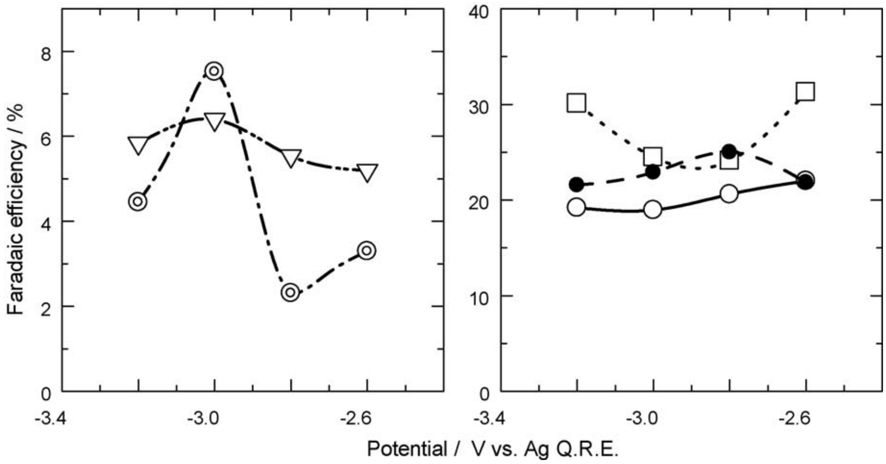

Fig. 5. Effect of potential on Faradaic efficiencies for the products by electrochemical reduction of CO_2 at Cu_2O/Zn powder-pressed electrode in KOH/methanol. ◎, CH_4; ▽, C_2H_4; ○, CO; □, HCOOH; ●, H_2; Cu_2O content, 2.5 wt%; temperature, 243 K.

with standard potential −0.360 V vs. SHE [29], we need to discuss the stability of particle-pressed electrodes. Schoppel and Gerischer [33] have studied the cathodic decomposition of single-crystal p-Cu_2O. They found that between −0.5 and −4.0 V the cathodic dark current increased from zero to about 12 μA cm^{-2}, showing that the rate of cathodic decomposition of relative defect-free crystals in the dark can be very show. Chang et al. [31] have investigated the electrochemical reduction of CO_2 at Cu_2O-catalyzed carbon clothes. In the cyclic voltammetric study, both the Cu_2O and carbon clothes were electrochemically stable between 0 and −1.7 V vs. SCE. Han et al. [34] have reported that the CuO thin film was electrochemically reduced to Cu at the potential of −0.874 V vs. SCE. Therefore, it seems to be appropriate to address the stability of Cu_2O/Zn powder-pressed electrode. Because the total Faradaic efficiencies of the reduction products with CuO/Zn electrode could not reach to 100% when the CuO content was more than 8 wt%, the remaining current might be used for the electrochemical reduction of CuO to copper metal.

4. Conclusion

The electrochemical reduction of CO_2 in methanol-based electrolyte was studied for the evaluation of characteristic of copper oxide catalyst. Zinc particle-pressed electrodes containing CuO and Cu_2O were tested as the cathode. Without the present of copper oxide particles, carbon monoxide and formic acid were formed in the electrochemical reduction of CO_2, and little formation of hydrocarbon could not be observed. On the contrary, the formation of hydrocarbons was obtained with the zinc particle-pressed electrodes containing copper oxide particles. The maximum formation efficiencies of methane and ethylene were of 7.5% and 6.8% with the electrode containing Cu_2O/Zn, respectively. It was found that copper oxide catalysts (CuO and Cu_2O) were effective for the formation of hydrocarbons in the electrochemical reduction of CO_2 in methanol-based electrolyte. In the electrochemical reduction of CO_2, it may become possible to roughly control the distribution of hydrocarbon formations if the electrode can be fabricated precisely. Because methanol is widely used industrially as a CO_2-absorbent at low temperature in the Rectisol process [10], this research may contribute to applications in the conversion of CO_2-saturated methanol into useful products. Thus, the synthesis of hydrocarbons by the electrochemical reduction of CO_2 might be of practical interest in fuel production, storage of solar energy, and production of intermediate materials for the petrochemical industry.

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