

Article

Electrochemical Carbon Dioxide Reduction in Methanol at Cu and Cu₂O-Deposited Carbon Black Electrodes

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Abstract: The electrochemical reduction of carbon dioxide in methanol was investigated with Cu and Cu₂O-supported carbon black (Vulcan XC-72) nanoparticle electrodes. Herein, Cu or a Cu₂O-deposited carbon black catalyst has been synthesized by the reduction method for a Cu ion, and the drop-casting method was applied for the fabrication of a modified carbon black electrode. A catalyst ink solution was fabricated by dispersing the catalyst particles, and the catalyst ink was added onto the carbon plate. The pH of suspension was effective for controlling the Cu species for the metallic copper and the Cu₂O species deposited on the carbon black. Without the deposition of Cu, only CO and methyl formate were produced in the electrochemical CO₂ reduction, and the production of hydrocarbons could be scarcely observed. In contrast, hydrocarbons were formed by using Cu or Cu₂O-deposited carbon black electrodes. The maximum Faraday efficiency of hydrocarbons was 40.3% (26.9% of methane and 13.4% of ethylene) at -1.9 V on the Cu₂O-deposited carbon black catalyst. On the contrary, hydrogen evolution could be depressed to 34.7% under the condition.

Keywords: CO₂ electrochemical reduction; copper; carbon black; methanol; methane

1. Introduction

The increasing carbon dioxide (CO₂) greenhouse gas concentration in the atmosphere has created serious problems associated with the energy supply based on fossil fuel [1,2]. Therefore, it is very significant to decrease the atmospheric CO₂ concentration, and a promising approach is a C-based fuel technique, which is obtained from abundant sources containing CO₂ by applying the renewable energy as energy input. The electrochemical CO₂ reduction appears to be one potential of the most important methods for the CO₂ conversion, because of its simplicity, environmental friendliness, and low cost [3–9].

The reduction products can be roughly controlled by the metallic material type of electrode. Four distinct groups for the metal catalyst have been identified for the electrochemical reduction of CO₂ [8]: (1) metals that mainly produce HCOOH (Pb, Hg, Cd, In, Sn, and Tl), (2) metals that mainly produce CO (Au, Ag, Pd, Ga, and Zn), (3) metals that form hydrocarbons such as CH₄ and C₂H₄ (Cu), and (4) metals that mainly produce hydrogen, H₂ (Pt, Ni, Fe, and Ti).

Methanol (MeOH) is a better medium for CO₂ than water. The solubility of CO₂ in methanol is more than about four times that in water, at ambient temperature [10]. Therefore, in the Rectisol method, methanol has been used as a physical absorbent of CO₂ on an industrial scale [10]. Recently,

over 70 large-scale plants have applied the Rectisol process. Therefore, the electrochemical CO₂ reduction in methanol may become an energetically efficient method.

Recently, the electrochemical reduction of CO₂ at a modified carbon material electrode has been investigated. Carbon blacks have been widely applied into the various fields of electrochemistry due to their good electrical properties, high mesoporous distribution, low cost, and high availability [11]. Various carbon blacks containing acetylene black, Black Pearl, Ketjen black, and Vulcan XC-72 have been applied into the electrodes for supercapacitors or catalyst supports in the electrochemical fields.

Baturina et al. [12] reported the activities of Cu nanoparticles supported on single-wall carbon nanotubes (SWNTs), carbon black (Vulcan XC-72R), and Ketjen Black (KB) for CO₂ electroreduction using a sealed rotating disk electrode (RDE). Moreover, the same research group [13] investigated the effect of support on the electrocatalytic activity of Cu nanoparticles for the CO₂ electroreduction using three types of nanostructured carbons: onion-like carbon (OLC), single-wall carbon nanotubes (SWNT), and reduced graphene oxide (RGO). Shinagawa et al. [14] studied the CO₂ electrochemical reduction in aqueous media with the size-controlled carbon-supported nanometric CuS catalysts. Furukawa et al. [15] explored the CO₂ electroreduction activities of Pt–Ru sputtered Pt–Ru/C powder electrodes under acidic conditions. Yin et al. [16] showed that Pd–Cu bimetallic alloy nanoparticles on a C support have excellent catalytic activity with high selectivity to CO. Zhang et al. [17] tested nanostructured tin catalysts loaded onto high surface area carbon supports for selective electrochemical CO₂ reduction. Geioushy et al. [18] investigated the efficient electrochemical CO₂ reduction on graphene-supported Cu₂O electrodes. Cao and Wen [19] studied the Cu nanoparticles decorating reduced graphene oxide nanohybrids for the electrocatalytic CO₂ reduction. Qin et al. [20] investigated the chloride-derived copper-modified carbon paper electrode for electrochemical CO₂ reduction. Guo et al. [21] explored the efficient and tunable CO₂ reduction at Co₃O₄–carbon dots–C₃N₄ catalysts. Pérez-Rodríguez et al. [22] tested the electrochemical reduction of CO₂ in water at various non-noble metal (Ni, Cu, Co, and Fe) catalysts deposited on commercially carbon black (Vulcan XC-72R).

Since water is the solvent acting as the medium in the electrochemical CO₂ reduction at modified carbon material electrodes in all of these previous reported works, there is little information on the modified carbon material electrodes in the organic solvents. Therefore, the present work has mainly dealt with the electrochemical reduction of CO₂ in methanol at Cu and Cu₂O-deposited carbon black (Vulcan XC-72R) electrodes.

2. Materials and Methods

2.1. Materials and Instruments

All of the chemicals that were used were of analytical grade. Copper nitrate (>99%), sodium tetrahydroborate (>95%), and sodium hydroxide (>97%) were obtained from FUJIFILM Wako Pure Chemical Corp. and were used as received without further purification. Nafion (5 wt% in propanol) and isopropanol (>99%) were obtained from Sigma-Aldrich Co. Carbon black (Vulcan XC-72) was purchased from Cabot Corp. Carbon plate (thickness of 0.50 mm, 99.5%) was purchased from Nilaco Corp. The pure water was obtained from an ultrapure water system (Advantec MFS Inc.) resulting in a resistivity >18 MΩ cm. For the characterization of Cu species, an X-ray diffractometer (XRD, RIGAKU Ultima IV, sample horizontal type) was used with Cu K_α radiation ($\lambda = 0.15406$ nm) at 40 kV and 50 mA. The deposition of Cu species into carbon black was analyzed by scanning electron microscope (S-4000, Hitachi) and transmission electron microscope (H-700H, Hitachi).

2.2. Catalyst Preparation

Cu and Cu₂O-deposited carbon black catalysts were prepared by a reduction method with a reducing agent. For metallic copper loading, copper nitrate (0.076 g) and carbon black (0.030 g) was added to 20 mL of water; then, the suspension solution was subjected to the ultrasound. The pH of suspension solution was about two. Then, in order to reduce the copper ion and deposit metallic

Cu onto carbon black, 20 mL of NaBH_4 (6 mg/mL) was added into the suspension during vigorous stirring. The copper loading was 40 wt% for carbon black. In the case of Cu_2O loading, the same procedure was performed, except that the solution pH for the suspension was adjusted to five by adding the sodium hydroxide solution. Finally, the reaction was completed for the stirring for 30 min after the addition of the reducing agent. The Cu and Cu_2O -supported carbon black was collected by centrifugation (15,000 rpm) for five minutes, and the catalysts were washed several times with water and ethanol, and then were dried in oven at 60 °C overnight.

2.3. Electrode Fabrication

The drop-casting method was used for the electrode fabrication. First, 10 mg of Cu or Cu_2O -supported carbon black was added with 4.96 mL of isopropanol and 40 μL of Nafion 117 solution (5 wt%), and was dispersed by ultrasonic irradiation. This suspension (25 μL) was dropped on a carbon plate ($10 \times 10 \times 0.5 \text{ mm}^3$), and was dried for two hours. The loading of the catalyst was 0.05 mg/cm².

2.4. Electrochemical Reduction of CO_2

The conditions for the electrochemical CO_2 reduction are given in Table S1 in the Supplemental Material. The electrochemical CO_2 reduction was carried out in a laboratory-made H-type cell. The cathode and the anode compartments were separated by an ion exchange membrane (Aldrich Nafion 117-type, 0.18-mm thickness). A silver rod coated with an insulator, except for the tip, was used as a quasi-reference electrode (Q.R.E.). The Ag Q.R.E. has a potential of about +0.100 V versus Ag/AgCl-saturated KCl that was connected with the catholyte.

Methanol (FUJIFILM Wako Pure Chemical Corp., >99%) was used as received without further purification. Sodium chloride was used as the supporting electrolyte in the methanol. Mechanical treatment of the platinum anode 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 alcohol. The Pt anode was electrochemically polished in phosphoric acid by oxidation. Before the electrochemical CO_2 reduction, the anode was washed with both water and ethanol.

A potentiostatic electroreduction procedure (potential constant mode) was applied. First, CO_2 gas was bubbled for two hours while stirring the methanol catholyte. Next, the CO_2 -saturated solution was electrolytically reduced in the cathode potential range of -1.7 to -2.0 V (versus Ag Q.R.E.). The Faraday efficiencies of the main reduction product formations were calculated from the total charge passed of 50 Coulomb.

The gaseous products, which were collected in a homemade gas collector, and the liquid products, in the catholyte, were analyzed by gas chromatography (GC) and high performance liquid chromatography (HPLC), respectively.

3. Results and Discussion

3.1. Physicochemical Characterization

The crystal structure of the as-synthesized catalysts was analyzed by XRD technique, and their patterns are given in Figure 1. When the Cu^{2+} ion in the suspension at pH 2 was reduced by NaBH_4 , the characteristic peaks appeared at two theta angles— 43.3° , 50.5° , and 74.2° —which can be assigned to reflections (111), (200), and (220) for Cu metal, respectively. When the copper ion in the solution was reduced at pH 5, the peaks at 36.4° , 42.3° , 61.3° , and 73.5° could ascribe to the reflections (111), (200), (220), and (311) of the cubic crystal structure of Cu_2O , respectively. The peak for carbon was observed in the carbon black Vulcan XC-72. According to the XRD patterns, there were no other peaks detected for the impurities, and the sharpness of pure Cu_2O and Cu peaks indicated their crystalline nature. The pH of the suspension was effective for controlling the Cu species for the metallic copper and Cu_2O species deposited on the carbon black. In order to explore the deposition of Cu particles

onto carbon black, the surface of carbon black was checked by SEM and TEM. The TEM images for Cu species on the carbon black surface are illustrated in Figure 2. The large Cu blocks with a diameter of 500 nm were observed in the limited area in the SEM images, and were located onto the coagulation of carbon black. However, the TEM images showed that very fine Cu particles with an average size of 10 nm could be obtained onto the carbon black surface, as illustrated in Figure 2b. Therefore, it was confirmed that nanosized Cu particles could be deposited onto the surface of carbon black.

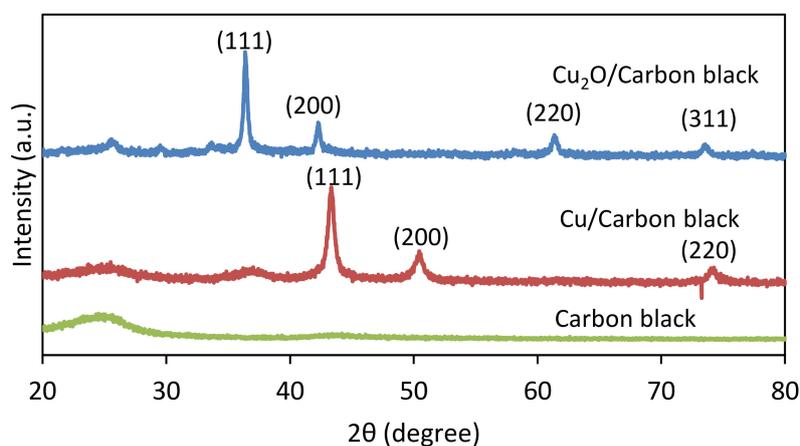


Figure 1. XRD patterns of Cu and Cu_2O /carbon black and carbon black.

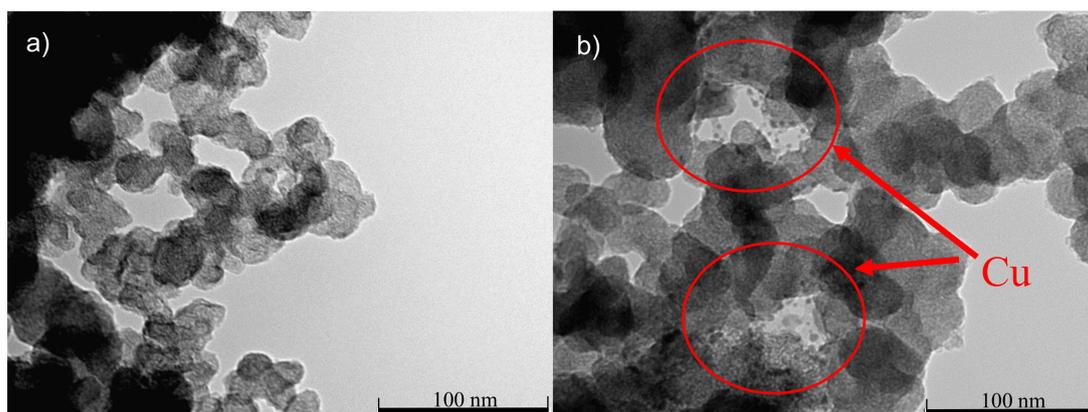


Figure 2. TEM images for (a) bare carbon black and (b) Cu-deposited carbon black.

3.2. Effect of Potential

First, the current-potential curves were measured in CO_2 and N_2 -saturated methanol. The scan sweep rate for the potential was 50 mV s^{-1} . The typical current-potential curve for the Cu-deposited carbon black electrode is shown in Figure S1 in the Supplemental Material. The onset (starting) potentials of the cathodic current—that is, those potential values at which a current density of 0.1 mA cm^{-2} is observed in CO_2 -saturated methanol—was about -0.7 V . Since further CO_2 reduction may proceed with increasing the negative potentials, any voltammetric peak could not be observed in the potential range down to -2.0 V . After the onset, potentials could be estimated from the current-potential curve experiment, the influence of potential on the electrochemical CO_2 reduction at Cu or Cu_2O deposited carbon black cathodes was investigated.

Figures 3–5 shows the effect of applied voltages toward the electrochemical CO_2 reduction with prepared electrodes. Figure 3 displays that an increase in current density with increasing the applied voltage showed the rate of reaction on the electrode surface. Methane, ethylene, carbon monoxide, and methyl formate were the principal products identified by the analytical system used in the present work. First, formic acid was produced on the cathode surface by the electrochemical reduction of

CO₂. Then, formic acid can be partially converted to methyl formate in methanol, and it should be considered that methyl formate may be under the dissociation equilibrium of methanol and formic acid. The electrochemical activity of Cu or Cu₂O-deposited carbon black to reduce CO₂ was investigated under a series of potentials. As shown in Figure 4, hydrocarbons (methane and ethylene) were observed at all of the tested voltages. The Faradaic efficiencies of carbon monoxide and methyl formate roughly increased as the potential decreased. On the other hand, the Faradaic efficiency of hydrogen increased. Ethylene was almost constant at all of the potentials (approximately 13%). The current efficiency curve for CH₄ was convex, and the maximum Faraday efficiency for methane was obtained at −1.9 V (26.9%). Figure 5 shows a similar trend to those obtained with Cu₂O-deposited carbon black. At −1.9 V, the Faradaic efficiency of methane was maximum, and the efficiency was 30.6%. The amount of ethylene produced was constant (about 5%). Table S2 in the Supplemental Material shows the results for the electrochemical CO₂ reduction using the Cu plate electrode and the bare carbon black electrode under the same conditions. Only carbon black loading electrodes could not produce any hydrocarbons. In the electrochemical reduction of CO₂ in methanol at the Cu plate electrode, the total Faraday efficiencies of hydrocarbons were 23.0%. It was found in the present study that the hydrocarbon generation efficiencies at the Cu₂O-deposited carbon black electrode were better than those obtained with the Cu plate electrode. The results mean that the electrocatalytic performance for hydrocarbon formation per Cu amount in this work was much better relative to that obtained conventionally with the Cu plate electrode.

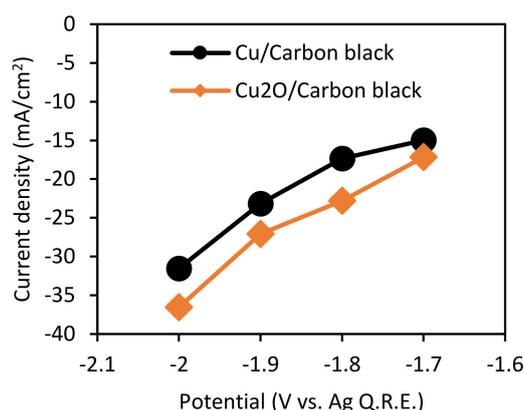


Figure 3. Potential versus current density for CO₂ reduction.

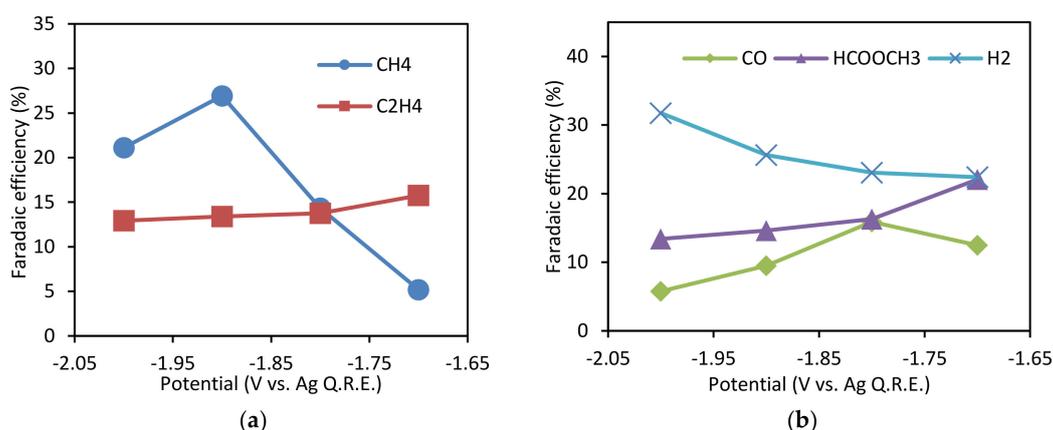


Figure 4. Influence of potential on the Faradaic efficiencies of products during the electrochemical reduction of CO₂ at Cu/carbon black electrode in NaCl/methanol. (a) hydrocarbons; (b) CO, HCOOCH₃, and H₂.

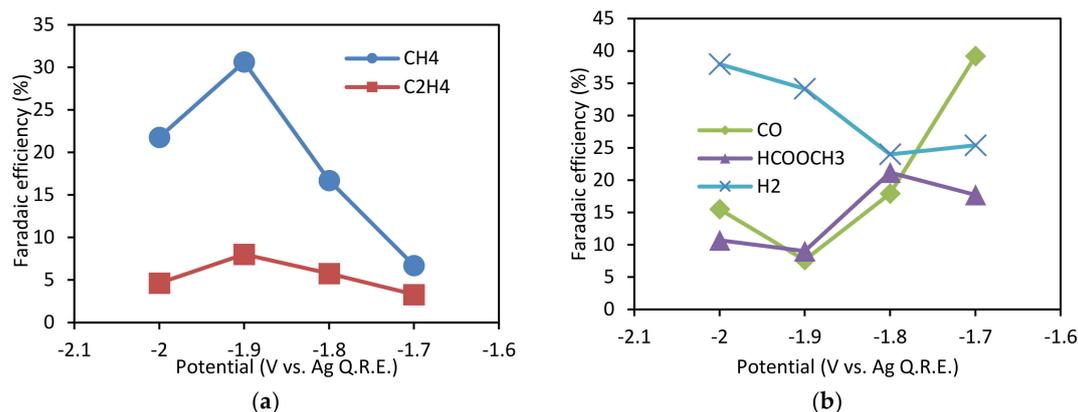


Figure 5. Influence of potential on the Faradaic efficiencies of products during the electrochemical reduction of CO₂ at Cu₂O/carbon black electrode in NaCl/methanol. (a) hydrocarbons; (b) CO, HCOOCH₃, and H₂.

3.3. Effect of Loading Amount

The influence of copper and copper oxide content on the electrochemical reduction of CO₂ at the modified carbon black electrode is shown in Figures 6 and 7. Both the Cu and Cu₂O contents scarcely affected the current densities. For the metallic copper-deposited carbon black electrode, the total formation efficiencies for hydrocarbons increased with the content of Cu up to 40 wt%, and the efficiencies was 40%. Then, the efficiencies for hydrocarbons decreased at 50 wt%. On the Cu₂O-deposited carbon black electrode, the maximum Faradaic efficiencies for total hydrocarbons were 40% at 40 wt% Cu₂O. Consequently, 40 wt% Cu and 40 wt% Cu₂O were optimum loading amounts for the formation of hydrocarbons in the electrochemical reduction of CO₂ in methanol at the modified carbon black electrode.

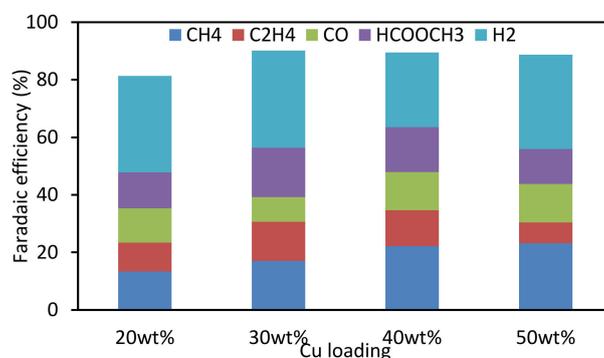


Figure 6. Influence of Cu loading on the Faradaic efficiencies of products during the electrochemical reduction of CO₂. Potential: -1.9 V, catholyte: 0.15 M of NaCl in methanol.

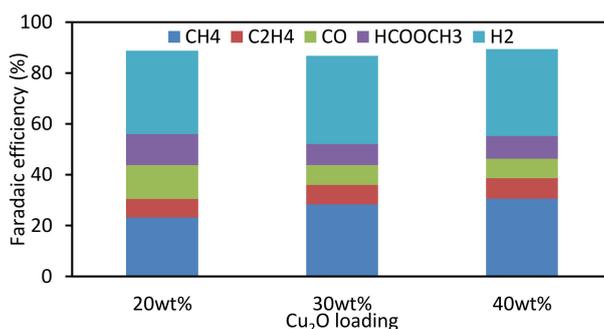


Figure 7. Influence of Cu₂O loading on the Faradaic efficiencies of products during the electrochemical reduction of CO₂. Potential: -1.9 V, catholyte: 0.15 M of NaCl in methanol.

3.4. Effect of Catalyst Preparation Temperature

Figures 8 and 9 show the influence of the catalyst preparation temperature on the electrochemical reduction of CO₂ in the methanol at modified carbon black electrodes. The catalyst preparation temperature scarcely affected the current densities. In the case of the Cu-deposited carbon black electrode, a low temperature for catalyst preparation improved the formation of hydrocarbons in the electrochemical CO₂ reduction in the methanol. The results may be due to the finer Cu particles produced in the low temperature. In the case of Cu₂O-deposited carbon black, the Faradaic efficiencies for the products by the electrochemical reduction of CO₂ had similar trends to the electrode fabricated under various catalyst preparation temperatures.

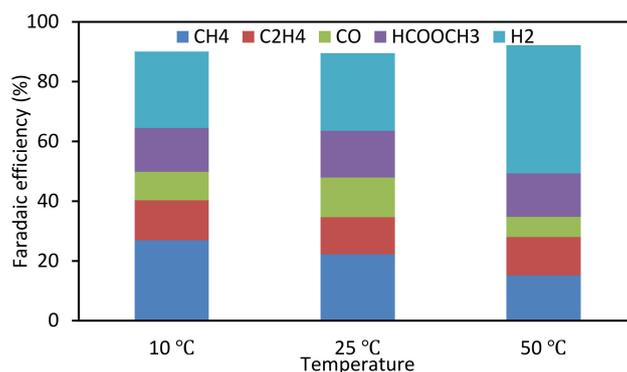


Figure 8. Influence of catalyst preparation temperature on the Faradaic efficiencies of products during the electrochemical reduction of CO₂ at Cu/carbon black electrode. Potential: −1.9 V, catholyte: 0.15 M of NaCl in methanol.

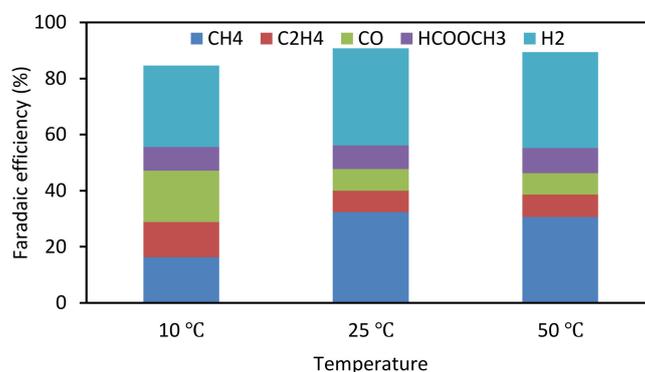


Figure 9. Influence of catalyst preparation temperature on the Faradaic efficiencies of products during the electrochemical reduction of CO₂ at Cu₂O/carbon black electrode. Potential: −1.9 V, catholyte: 0.15 M of NaCl in methanol.

3.5. Reaction Mechanism

According to the results in Table S2, the electrochemical reduction of CO₂ with bare carbon black particles could not produce any hydrocarbons. In the systems, methyl formate and CO were formed by the reduction of carbon dioxide. Furthermore, it was confirmed that the hydrocarbons were produced under all of the conditions by loading copper on the carbon black.

Hence, it should be considered that Cu or Cu oxide particles play a significant role in the conversion of CO₂ to hydrocarbons. Therefore, it is reasonable to speculate the same mechanism as the conventional copper plate, and the reaction mechanism of the main products in the present work can be presumed as shown in Figure S2 of the Supplemental Material [3–9,11–22].

The Faradaic efficiencies for methane and ethylene at Cu₂O/carbon black electrode were better relative to the results obtained with the copper plate, indicating that the charge transfer by carbon particles is very effective. The role of Cu species is illustrated in Figure 10. Although the electrochemical

reduction of CO₂ in water and organic solvent at copper-based electrodes has been actively investigated, the catalytic mechanism could not be clarified, and is under the investigation. The adsorbed CO species are the first intermediate formed during the electrochemical reduction of CO₂, and these CO species are very important for the formation of hydrocarbons. Montoya et al. [23] reported it that in a recent electrokinetic study, *CH_xO intermediate is favored in the C–C coupling reaction rather than the *CO intermediate. However, the evidence for the direct observation of *CH_xO could not be reported thus far.

The main difference for the electrochemical reduction of CO₂ in methanol electrolyte between the copper metal foil electrode and Cu₂O (or Cu)-deposited carbon black electrode was the current efficiencies for methane and ethylene formation. The difference may be owing to contributions of the hydrogen molecule on the carbon support. Roughly, the excess hydrogen may introduce the electrochemical reduction of CO₂ toward methane and ethylene generation. Furthermore, carbon black may enhance the electron transfer mobility with metallic copper and Cu₂O. As a consequence, the combination of metallic copper and Cu₂O was effective for the improvement of hydrocarbon formation in the electrochemical reduction of CO₂ in the methanol-based electrolyte.

The comparison of the present work with previous studies for the electrochemical reduction is displayed in Table S3 in the Supplemental Material. The Faradaic efficiencies for methane and ethylene were similar or better than those obtained with previous works. The reason could not be clarified, and it maybe seems due to the enhancement of the electron transfer mobility [3–9,11–22].

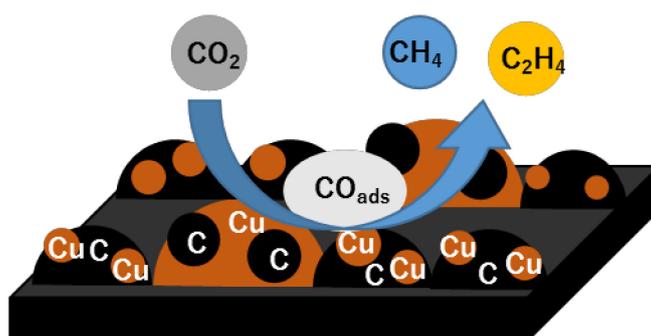


Figure 10. Reaction mechanism of the electrochemical reduction of CO₂ at Cu and Cu₂O-deposited carbon black electrode.

4. Conclusions

Cu and Cu₂O-supported carbon black (Vulcan XC-72) nanoparticles were prepared by using the chemical reduction method for the deposition of Cu ion into carbon black, and the drop-casting method was applied for the fabrication of a modified carbon black electrode. The Cu or Cu₂O loading amount and the electrode preparation temperature could be optimized for the electrochemical reduction of CO₂ in the methanol. The maximum Faradaic efficiency of hydrocarbons was observed at -1.9 V with 40.3% (26.9% of methane and 13.4% of ethylene) on the Cu₂O-deposited carbon black catalyst. On the other hand, hydrogen formation could be depressed to 34.7%. Since the copper content was very trace (20 μg Cu/cathode), the effective efficiency of Cu will become very high. For instance, although the production rates for methane and ethylene were about $0.65 \text{ mmol min}^{-1} \text{ kg}^{-1}\text{-Cu}$ and $0.19 \text{ mmol min}^{-1} \text{ kg}^{-1}\text{-Cu}$ at the Cu plate electrode, for the Cu₂O/carbon black electrode, they were approximately $24,000 \text{ mmol min}^{-1} \text{ kg}^{-1}\text{-Cu}$ and $8000 \text{ mmol min}^{-1} \text{ kg}^{-1}\text{-Cu}$, respectively. The developed electrode will provide a clear framework for the future advancement of electrochemical conversion of CO₂. Furthermore, carbon-supported copper oxide nanoparticles may be applied into the hybrid materials for carbon dioxide adsorption [24].

Supplementary Materials: The following are available online at <http://www.mdpi.com/2305-7084/3/1/15/s1>, Figure S1: Current–potential curves in CO₂-saturated and N₂-purged methanol, Figure S2: Reaction mechanism of the electrochemical reduction of CO₂ at the Cu and Cu₂O-deposited carbon black electrodes in methanol, Table S1:

Apparatus and experimental conditions, Table S2: Effect of electrode on the Faradaic efficiencies of products by the electrochemical reduction of CO₂, Table S3: Comparison of the present electrode with other electrodes that were reported previously.

Author Contributions: N.U. and S.K. conceived and designed the experiments. N.U. performed the experiments and wrote the paper. I.T., M.F. and H.K. analyzed the results and advised the project.

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Conflicts of Interest: The authors declare no conflict of interest.

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