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Cu Modified TiO₂ Catalyst for Electrochemical Reduction of Carbon Dioxide to Methane

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Abstract: Electrochemical reduction of CO₂ (ECO₂R) is gaining attention as a promising approach to store excess or intermittent electricity generated from renewable energies in the form of valuable chemicals such as CO, HCOOH, CH₄, and so on. Selective ECO₂R to CH₄ is a demanding task but has not been achieved to the desired level in ECO₂R employing active Cu catalysts.

Keywords: electrochemical reduction of CO₂; Cu; TiO₂

1. Introduction

Electrochemical reduction of CO₂ (ECO₂R), which uses renewable electricity to produce fuels and chemical feedstocks from CO₂, has attracted attention not only as an eco-friendly material synthesis process but also as a novel method to store intermittent renewable electricity which is generated from renewable energies such as solar, wind power, and so on [1]. Among metal catalysts, Cu is known to exhibit the highest activity in ECO₂R [2] and also produces multi-carbon products such as hydrocarbons and alcohols. Meanwhile, the selective production of CH₄, which is widely used as a fuel, is a demanding task but has not been achieved to the desired level in ECO₂R employing active Cu catalysts.

CH₄ formation proceeds through the addition of 8 electrons and 8 protons to CO₂ (Equation (1)).

\[
CO₂ + 8H^+ + 8e^- \rightarrow CH₄ + 2H₂O
\] (1)

In this process, CH₄ formation is thought to occur via *CHO formation by protonation of *CO [3]. The *CHO formation competes with both the C–C coupling of two *CO and hydrogen evolution reaction (HER), which significantly lowers selectivity for the production...
of CH$_4$. Recently, the formation of isolated Cu sites has been found to effectively improve the selectivity for the CH$_4$ production by suppressing the unfavorable C–C coupling [4,5]. However, the selectivity for the production of CH$_4$ from CO$_2$ (CO$_2$ to CH$_4$ selectivity) should be improved. The increase of surface area is found to efficiently suppresses the Cu agglomeration on a support material such as carbons [6] and oxides [4,7,8]. However, the formation relatively large Cu portions where C–C couplings preferentially progress cannot be suppressed in conventional impregnation synthesis.

Titanium dioxide (TiO$_2$) is a multifunctional material with many advantages, being ubiquitous, low-cost, and environmentally friendly. TiO$_2$ is a widely used catalyst material for various application [9] due to its high activity and adequate stability. Recently, we have uncovered relatively high overpotentials for electrochemical H$_2$ evolution and the favorable interactions of oxygen species included in organic acids, oximes, and imines with the surface of TiO$_2$-based catalysts for electrochemical hydrogenation [10–18], which could enhance the selectivity for the production of CO$_2$-derived chemicals in ECO$_2$R. Highly dispersed and isolated Cu sites on TiO$_2$ are expected to suppress the generation of multi-carbon products and show high selectivity for CH$_4$ synthesis. Thus, we develop Cu-TiO$_2$ catalysts presenting isolated Cu sites with high dispersion for the selective CH$_4$ production by the electrochemical reduction of CO$_2$.

2. Results

To enhance their dispersity, Cu-TiO$_2$ catalysts were prepared via a one-pot solvothermal method (See Section 4). The crystal structures of the prepared TiO$_2$, Cu-TiO$_2$, and Cu-TiO$_2$ treated with H$_2$ (Cu-TiO$_2$-H) were examined by X-ray diffraction (XRD) (Figure 1 and Figure S1). All samples showed a diffraction pattern mostly attributable to an anatase phase of TiO$_2$, but a very small peak from a brookite phase was also observed at 14.7°. The intensity of the brookite peak of Cu-TiO$_2$ seemed slightly large compared to that in the XRD pattern of TiO$_2$. It has been reported that the formation of brookite phase preferentially occurs in alkaline conditions. The usage of DMF as an alkalescent organic solvent probably induces the formation of brookite phase [19–21]. No diffraction peaks from copper oxides such as Cu$_2$O or CuO were observed in the Cu-TiO$_2$, despite the introduction of Cu. In contrast, Cu-TiO$_2$-H showed a diffraction peak from Cu. It is notable that no shift in the diffraction peak position of the anatase phase was observed in either Cu-TiO$_2$ or Cu-TiO$_2$-H, although the ionic radii of the 6-coordinated Ti$^{4+}$ ions (0.605 Å) and Cu$^{2+}$ ions (0.73 Å) are different and a Cu$^{2+}$ ion is larger than that of a Ti$^{4+}$ ion [22], which suggests that most of the Cu species are precipitated over the TiO$_2$ surface as CuO$_x$ clusters on Cu-TiO$_2$, where the clusters are too small to be detected by XRD, and as Cu nanoparticles (NPs) on Cu-TiO$_2$-H, rather than being enclosed in the TiO$_2$ lattice. To obtain detailed structural parameters for the catalysts, we conducted Rietveld profile fitting of these XRD patterns (Figure S1). Structural parameters are summarized in Table S1. The lattice constants of anatase phase constituting Cu-TiO$_2$ and Cu-TiO$_2$-H showed a slight increase in the a-axis but a slight decrease in the c-axis compared to those of pure TiO$_2$, suggesting the possibility of incorporation of Cu species into the TiO$_2$ lattice. The weight fraction of Cu species deposited on TiO$_2$ was estimated by the Rietveld analysis to be low (1.9%), even though the initial starting amount was 10%. Considering the slight change in the structure of Cu-TiO$_2$ and Cu-TiO$_2$-H, a relatively large percentage of Cu species (more than 5%) possibly exists as amorphous on the surface of TiO$_2$. 

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Figure 1. XRD patterns of (a) TiO2, (b) Cu-TiO2, and (c) Cu-TiO2-H. The simulated XRD patterns of anatase, brookite, and Cu are also presented.

To confirm the oxidation state of Cu on Cu/TiO2, the diffuse reflectance UV-Vis spectra of the catalyst were measured (Figure 2). The inset represents the Tauc plots [23,24] where the \((F(R) h\nu)^{1/2}\) is plotted as a function of photon energy. The indirect band gap was estimated from an X-intercept of a linear fit of the Tauc plot, and the determined band gap values are also given in the inset. The band gap energy of TiO2 was estimated to be 3.10 eV, which is slightly small compared to the reported value of anatase TiO2 [25]. Cu-TiO2 showed a large red-shift in optical absorption edge compared to that of TiO2, with an estimated band gap of 1.46 eV, which occurs probably by interaction between CuO and TiO2. Furthermore, absorption bands appeared in the region of 400–600 nm and 600–1200 nm. The former absorption band is assignable to the interfacial charge transfer from a TiO2 O 2p valence band to a Cu(II) ions connected to TiO2 [26], whereas the latter comes from a d–d transition of Cu (II) species [27]. These Cu(II) states may exist either as Cu(II) clusters or amorphous oxide grains of CuO. Cu-TiO2-H exhibited a remarkably larger red-shift of the absorption edge in optical absorption than Cu-TiO2 and with 1.16 eV of band gap, revealing good contact between Cu and TiO2 grains. Additional absorption bands appeared in the region of 400–600 nm and 550–1200 nm. The former absorption band was assigned to the interfacial charge transfer from the TiO2 O 2p valence band to the Cu(II) ions attached to TiO2 [26], whereas the latter band was attributable to the Cu surface plasmon resonance of Cu NPs [28–30]. Therefore, we confirmed the formation of Cu NPs in these catalysts from the XRD and DRS results.

To investigate the dispersion of Cu NPs on TiO2, we conducted scanning transmission electron micrography (STEM) for Cu-TiO2-H. A high-angle annular dark-field STEM (HAADF-STEM) image of the Cu-TiO2-H (Figure 3) suggested that Cu NPs with a diameter of 2–3 nm, which appear as white dot-like objects, were well dispersed over a TiO2 grain, indicating that isolated Cu clusters are formed in Cu-TiO2-H. On the other hand, Cu-TiO2 (Figure S2) suggested that Cu NPs with a diameter of 2–5 nm, which appear as white aggregated objects, existed in a TiO2 grain, indicating that larger Cu NPs are formed in Cu-TiO2 compared to Cu-TiO2-H.
Figure 2. Diffuse reflectance spectra of (a) TiO$_2$, (b) Cu-TiO$_2$, and (c) Cu-TiO$_2$-H samples. The inset is the Tauc plots for the determination of the bandgap of the samples.

To investigate the dispersion of Cu NPs on TiO$_2$, we conducted scanning transmission electron micrography (STEM) for Cu-TiO$_2$-H. A high-angle annular dark-field STEM (HAADF-STEM) image of the Cu-TiO$_2$-H (Figure 3) suggested that Cu NPs with a diameter of 2–3 nm, which appear as white dot-like objects, were well dispersed over a TiO$_2$ grain, indicating that isolated Cu clusters are formed in Cu-TiO$_2$-H. On the other hand, Cu-TiO$_2$ (Figure S2) suggested that Cu NPs with a diameter of 2–5 nm, which appear as white aggregated objects, existed in a TiO$_2$ grain, indicating that larger Cu NPs are formed in Cu-TiO$_2$ compared to Cu-TiO$_2$-H.

Figure 3. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and EDS mapping images of Cu-TiO$_2$-H.

Figure 4 provides Cu 2p$_{3/2}$ XPS spectra of Cu-TiO$_2$ and Cu-TiO$_2$-H. A relatively broad Cu 2p$_{3/2}$ XPS peak centered at 932.5 eV and the shoulder peak near 934.3 eV in the high binding energy side were observed on Cu-TiO$_2$. The main and the shoulder peaks could be attributed to Copper oxide containing Cu(I) and Cu(II), and Cu(OH)$_2$ species, respectively, which implies that Cu clusters in Cu-TiO$_2$ are composed of Cu(I) and Cu(II). Furthermore, the presence of a well known shake-up satellite at higher binding energies than that for the main peak strongly indicates the presence of Cu(II) species in Cu-TiO$_2$[32]. Therefore, Cu clusters in Cu-TiO$_2$ may exist mainly as CuO-like and Cu(OH)$_2$-like species. Cu-TiO$_2$-H showed the sharp Cu 2p$_{3/2}$ peak centered at 932.6 eV, which is attributed to the formation of Cu(0). The absence of the shake-up satellite, as observed in Cu-TiO$_2$, suggests that Cu NPs on Cu-TiO$_2$-H are mainly composed of Cu(0) species, which is consistent with the observation in the XRD measurement for Cu-TiO$_2$-H. Figure S3A shows Ti 2p XPS spectra of TiO$_2$, Cu-TiO$_2$, and Cu-TiO$_2$-H. All catalysts exhibited a symmetrical peak centered around 458.6 eV, which is a typical peak with characteristic binding energy value for Ti 4+ ions contained in anatase TiO$_2$[33], although the spectrum of TiO$_2$ had a slightly extended tail which possibly comes from the formation of Ti$^{3+}$. There was also no obvious peak shift in these catalysts. Therefore, Ti ions near the surface of all catalysts would have an analogous chemical environment. Figure S3B represents O$_{1s}$ peaks at around 529.7 eV in XPS spectra of TiO$_2$, Cu-TiO$_2$, and Cu-TiO$_2$-H, which are assigned to lattice oxygen of TiO$_2$[33]. In addition, each spectrum contained two other weak
Figure 4 provides Cu 2p3/2 XPS spectra of Cu-TiO2 and Cu-TiO2-H. A relatively broad Cu 2p3/2 XPS peak centered at 932.5 eV and the shoulder peak near 934.3 eV in the high binding energy side were observed on Cu-TiO2. The main and the shoulder peaks could be attributed to Copper oxide containing Cu(I) and Cu(II), and Cu(OH)2 [31] species, respectively, which implies that Cu clusters in Cu-TiO2 are composed of Cu(I) and Cu(II). Furthermore, the presence of a well known shake-up satellite at higher binding energies than that for the main peak strongly indicates the presence of Cu(II) species in Cu-TiO2 [32]. Therefore, Cu clusters in Cu-TiO2 may exist mainly as CuO-like and Cu(OH)2-like species. Cu-TiO2-H showed the sharp Cu 2p3/2 peak centered at 932.6 eV, which is attributed to the formation of Cu(0). The absence of the shake-up satellite, as observed in Cu-TiO2, suggests that Cu NPs on Cu-TiO2-H are mainly composed of Cu(0) species, which is consistent with the observation in the XRD measurement for Cu-TiO2-H. Figure S3A shows Ti 2p XPS spectra of TiO2, Cu-TiO2, and Cu-TiO2-H. All catalysts exhibited a symmetrical peak centered around 458.6 eV, which is a typical peak with characteristic binding energy value for Ti4+ ions contained in anatase TiO2 [33], although the spectrum of TiO2 had a slightly extended tail which possibly comes from the formation of Ti3+. There was also no obvious peak shift in these catalysts. Therefore, Ti ions near the surface of all catalysts would have an analogous chemical environment. Figure S3B represents O1s peaks at around 529.7 eV in XPS spectra of TiO2, Cu-TiO2, and Cu-TiO2-H, which are assigned to lattice oxygen of TiO2 [33]. In addition, each spectrum contained two other weak shoulder peaks on the higher binding energy side of the main O 1s peak. The former peak observed at 530.8 eV can be attributed to the hydroxide group or water molecules that are present at the surface [34], and the other peak at 531.9 eV is originated from organic contaminants containing oxygen species [35]. Cu-TiO2-H showed a relatively large peak at 530.8 eV, which is attributed to the existence of hydroxide groups or water molecules. Chalastara et al. reported that a brookite-rich sample has a larger amount of surface-bound OH/H2O groups than anatase-rich samples [36]. The increase of intensity at 530.8 eV indicates the increase of a brookite phase in Cu-TiO2-H. The number of defects such as Ti3+ and oxygen vacancy on the surface of these catalysts did not change so much by the introduction of Cu or by the change of the atmosphere during heating. The all-measured core level positions for the samples are summarized in Table S2.

The difference in Cu state between Cu-TiO2 and Cu-TiO2-H was further examined by the measurement of Cu-K edge X-ray absorption near edge structure (XANES) spectra using a conversion electron yield (CEY) method, which reflects information on the species near surface region due to the shallow escape depth of Auger electrons from an atom irradiated by X-rays within a sample [37]. Figure 5 shows XANES spectra of Cu-TiO2 and Cu-TiO2-H, and standard samples such as Cu foil, Cu2O, and CuO. Small pre-edge bumps at 8978 eV were observed on Cu-TiO2 and CuO, which is attributed to dipole-forbidden 1s → 3d transition and is indicative of existence of Cu2+ ions, implying that the surface of Cu-TiO2 contains Cu(II) ions. Cu-TiO2-H showed an XANES spectrum similar to that of Cu foil, suggesting that the Cu species on the surface of Cu-TiO2-H are Cu(0) species. XANES spectra were further analyzed in detail. The first derivatives of the XANES spectrum of CuO gave a small pre-edge bump at 8978 eV for the 1s → 3d transition [38], peak for the 1s → 4p transition [39,40] (Figure 5). The spectrum also showed a small pre-edge bump at 8978 eV attributed to the 1s → 3d transition, but the spectral features in the region related to the 1s → 4p transition were significantly different from those of CuO, meaning that the oxidation state of Cu on Cu-TiO2 is different from that of CuO, although it includes Cu(II) species. The red shift and increase in intensity of the 1s → 4p peak was interpreted as an increase of covalency in the ligand–copper bond [40]. Cu(II) states on Cu-TiO2 may emerge as Cu(OH)2-like species, which is consistent with the observation in the XPS measurement for Cu-TiO2. The first derivative spectra of Cu-TiO2-H and Cu foil look similar, indicating that Cu(OH)2 is the main oxidation state of Cu species in Cu-TiO2-H, which is consistent with all observations discussed above.
100%, which has been explained by the experimental errors introduced by GC detection or we further calculated the ratios of FE for CH\textsubscript{4} and CH\textsubscript{3}OH. The calculated percentages of CH\textsubscript{4} for the Cu-TiO\textsubscript{2} and Cu-TiO\textsubscript{2}-H catalysts are summarized in Table S3. On the other hand, Cu-TiO\textsubscript{2} showed lower FE for CH\textsubscript{4} than Cu-TiO\textsubscript{2}-H, meaning that the formation of Cu NPs on TiO\textsubscript{2} increases ECO\textsubscript{2}R activity. All catalysts produced H\textsubscript{2}, CO, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{4} as gaseous products, which were detected by online gas chromatography. We could not observe other gaseous product such as HCOOH.

The difference in Cu state between Cu-TiO\textsubscript{2} and Cu-TiO\textsubscript{2}-H was further examined by XPS measurements. Figure 4 shows XPS spectra of Cu-TiO\textsubscript{2} and Cu-TiO\textsubscript{2}-H, and standard samples such as Cu foil, Cu\textsubscript{2}O, and CuO. Small pre-edge bumps were observed at 8978 eV for the Cu(0) species in Cu foil, suggesting that the Cu species on the surface of Cu-TiO\textsubscript{2}-H are Cu(0) species. Cu-TiO\textsubscript{2} contains Cu(II) ions. Cu-TiO\textsubscript{2}-H showed an XANES spectrum similar to that of CuO, giving a small pre-edge bump at 8978 eV for the Cu(II) species in Cu NPs under the potential and enhances ECO\textsubscript{2}R activity. The measured total Faradaic efficiencies on the TiO\textsubscript{2} and Cu-TiO\textsubscript{2} catalysts sometimes became slightly higher than 100%, which has been explained by the experimental errors introduced by GC detection or inconsistencies in the flow rate, as shown in some reports [41–43]. Cu-TiO\textsubscript{2}-H exhibited higher ECO\textsubscript{2}R activity than TiO\textsubscript{2} and Cu-TiO\textsubscript{2}, as shown in the LSV results. Faradaic efficiency for the production of CH\textsubscript{4} reached 18% with 36 mA cm\textsuperscript{-2} of partial current density at −1.8 V vs. RHE (Figure 6F), where CH\textsubscript{4} partial current density was defined as a product of the average total current density and the Faradaic efficiency for the production of CH\textsubscript{4} in ECO\textsubscript{2}R at each potential. Notably, Faradaic efficiency for CH\textsubscript{4} production was significantly lower than the selectivity for CH\textsubscript{4}, and the selectivity for CH\textsubscript{4} reached 70% at −1.8 V vs. RHE, which compares with prior reports related to highly dispersed or single-site copper catalysts (Table S3). On the other hand, Cu-TiO\textsubscript{2} and Cu-TiO\textsubscript{2}-H showed different CH\textsubscript{4} partial current densities (Figure 6F (b) and (c)), although the selectivity for CH\textsubscript{4} in the products from CO\textsubscript{2} is lower than Cu-TiO\textsubscript{2}-H. Cu-TiO\textsubscript{2}-H showed larger FE\textsubscript{CH4}/FE\textsubscript{C1+C2} values than TiO\textsubscript{2}. This result is probably attributable to Cu sites homogeneously dispersed on these catalysts. DRS results represented that the band gap of Cu-TiO\textsubscript{2}-H is narrower.
than that of Cu-TiO$_2$ (Figure 2), which implies that Cu species on Cu-TiO$_2$-H have better contact with the TiO$_2$ support than those on Cu-TiO$_2$. Such favorable interactions between Cu catalysts and the TiO$_2$ support in Cu-TiO$_2$-H may enhance the electrical conductivity, resulting in its high CH$_4$ partial current density on Cu-TiO$_2$-H. These results indicate that Cu(0) loading on TiO$_2$ is indispensable and effective to enhance activity in the ECO$_2$R to CH$_4$. However, the state of catalysts under operating conditions are not well clarified and need to be further studied.

![Cu K-edge spectra (A) and first derivative of Cu K-edge XANES spectra (B) of reference compounds. (a) Cu-TiO$_2$, (b) Cu-TiO$_2$-H. The inset figure shows overlay of the spectra of CuO and (a) Cu-TiO$_2$.](image)
It has been reported that composite materials of Cu and CeO$_2$ exhibit high CH$_4$ selectivity [4,7,44,45], where abundant oxygen vacancy (V$_O$) sites on CeO$_2$ play an important role in both CO$_2$ adsorption and activation. Wang et al. suggested that Cu site surrounded by 3V$_O$ effectively promoted CH$_4$ formation, where the 2V$_O$ neighboring Cu are filled with the two oxygen atoms of CO$_2$ and should enhance the CO$_2$ adsorption and activation [4].

In this study, the surface of the prepared TiO$_2$ samples may consist of low concentration of V$_O$. CO$_2$ dissociation unfavorably occur on stoichiometric anatase surface compared to Vo-rich surface due to its large CO$_2$ dissociation energy [46]. HER mainly proceeded on the TiO$_2$ catalyst, although small amounts of C1 products, such as CO, HCOO$^-$, and CH$_4$, were generated (Figure 6B). In contrast, Cu-TiO$_2$ and Cu-TiO$_2$-H, where Cu(0) species were well dispersed over a TiO$_2$ grain, showed high selectively for the production of CH$_4$. Hence, well dispersed Cu species on TiO$_2$ would play a key role in the formation of CH$_4$. Therefore, it is reasonable that homogeneity of Cu NPs in their size and dispersity on TiO$_2$ can be a key for the high CO$_2$-to-CH$_4$ selectivity.
3. Materials and Methods

3.1. Materials

Titanium tetrabutoxide monomer (95.0%), anhydrous copper (II) acetate (97%), N,N-dimethylformamide (99.5%), 2-propanol (99.7%), ethanol (99.5%), acetone (95.5%), hexane (96.0%), and potassium hydroxide were purchased from FUJIFILM Wako Pure Chemical Corporation. Nafion® perfluorinated resin solution (5 wt% in mixture of lower aliphatic alcohols with a water content of 45%) was purchased from Sigma-Aldrich Corporation. All chemicals were used without further purification. All the solutions were prepared with deionized water.

3.2. Preparation of Cu-TiO₂ Composite Catalysts

For the preparation of Cu-TiO₂ composite catalyst, including 10 wt% of Cu species, titanium tetrabutoxide (2.8 mmol, 1 mL) was quickly added to a mixture of 30 mL of N,N-dimethylformamide (99.5%), 0.215 mL of 2-propanol, and 73 mg of anhydrous copper(II) acetate in a 50 mL Teflon-lined stainless-steel autoclave to avoid exposing the sample to the air, and the mixture was sonicated for 2 h at room temperature. The container was sealed, heated from room temperature to 200 °C over 30 min in an electrical oven, and maintained for 20 h. The product was separated by centrifugation 7500 rpm for 10 min and washed several times with ethanol, acetone, and hexane. After that, it was dried under vacuum at room temperature. Finally, the precursor was calcined at 450 °C for 30 min under air or flowing H₂ (60 mL min⁻¹) to obtain TiO₂ and Cu-TiO₂-x samples, where X is the calcination atmosphere, air or H₂; heating rate of 15 °C min⁻¹.

3.3. Catalyst Characterization

The metal composition of prepared oxides was determined using an energy dispersive X-ray spectroscopy (EDS, JED-2300, JEOL) equipped with the SEM instrument. Powder X-ray diffraction (XRD) patterns were obtained using synchrotron radiation (λ = 0.740040 Å) at RIKEN Materials Science beamline BL44B2, SPring-8 [47]. Data were acquired using the high-resolution Debye–Scherrer camera equipped with an imaging plate as an X-ray detector. Rietveld analyses were performed using a Topas software package (Bruker AXS Inc., Billerica, MA, USA, version 5). The diffuse reflectance spectra of samples were recorded using a V-670 spectrometer (JASCO, Japan) equipped with an integrating sphere. The diffuse reflection spectra were converted into reflectance spectra using the Kubelka-Munk function. X-ray photoelectron spectroscopy (XPS) studies were performed on a VersaProbeII (ULVAC-PHI) using nonmonochromatic Al Kα radiation. Binding energies in XPS spectra were corrected by referring a C 1s binding energy of the carbon atoms of the ligand in the specimens at 284.6 eV. Scanning transmission electron microscopy (STEM) image was obtained using a JEM-ARM200F (JEOL Co., Tokyo, Japan) at Kyushu University operated at 200 kV. Sample grids for the STEM observations were prepared by dropping ethanol dispersions of the specimens onto a carbon-supported nickel grid. Cu K-edge X-ray absorption fine structure (XAFS spectra of the samples) was measured at Kyushu University beamline BL06 of Kyushu Synchrotron Light Research Center (SAGA-LS, Japan) with an electron storage ring operating at the energy of 1.4 GeV. The energy range of this light source (bending magnet) is 2.1–23 keV. A silicon (111) double-crystal monochromator was used to obtain the incident X-ray beam. The typical photon flux is 10¹⁰ photons per second. The spectra of standard samples such as Cu foil, Cu₂O, and CuO were recorded in the transmission mode at 20 °C using a Si(111) double-crystal monochromator. The spectra of Cu-TiO₂ samples were measured using the conversion electron yield mode. Data processing was carried out by Athena and Artemis included in the Ifeffit package [48].

3.4. Electrode Preparation

The cathode GDE was prepared by airbrushing catalyst inks onto a gas diffusion carbon paper (Fuel Cell Store Sigracet 22 BB, with a microporous layer) with a carrier gas of air. The catalyst ink was prepared with 200 µL of 2-propanol, 200 µL of water,
10 µL of Nafion® solution, and 1 mg of catalyst powder. The catalyst ink mixtures were sonicated in a 4 mL screw neck glass vial for 15 min, and then sprayed onto the gas diffusion carbon paper.

3.5. Electrochemical Reduction of CO₂

The electrochemical measurements were conducted in an electrochemical flow cell setup configuration with the three-electrode system. The geometric area of the cathode in the flow cell is 1 cm², which is used for all current density calculations. 1 M KOH aqueous solution was introduced into the cathode chamber at the rate of 7 mL min⁻¹ and the anode chamber at the rate of 1 mL min⁻¹ by two pumps, respectively. A Nafion 117 cation exchange membrane (Chemours®) was used to separate the cathode chamber and anode chamber. Pure CO₂ gas (Linde, 99.99%) was continuously supplied to the gas chamber of the flow cell at a flow rate of 15 mL min⁻¹. The CO₂RR performance was tested using constant-current electrolysis, i.e., chronopotentiometry while purging CO₂ into the catholyte during the whole electrochemical test. The potentials vs. Hg/HgO reference electrode were converted to values vs. reversible hydrogen electrode (RHE) using the following equation [49].

\[
E (\text{vs. RHE}) = E (\text{vs. Hg/HgO}) + 0.098 \text{ V} + 0.0591 \text{ V} \times \text{pH} \tag{2}
\]

All voltages reported are without iR compensation.

Gas products were analyzed by on-line gas chromatography (Micro GC Fusion®, Inficon, Bad Ragaz, Switzerland) with a Molsieve 5A column and a Plot Q column coupled with thermal conductivity detector (TCD). Liquid products were analyzed high performance liquid chromatograph (HPLC, LC-20AD, Shimadzu) equipped with a refractive-index detector (RID-10A, Shimadzu). The Faradaic efficiency (FE) of products in the electroreduction experiments is defined by the following equation:

\[
FE_i = \frac{n_i \times z_i \times F}{Q} \times 100 \tag{3}
\]

where \(n_i\) is the number of moles of product \(i\), and \(z_i\) represents the number of electrons required for the formation of product \(i\) (\(z_i = 2\) for CO, formic acid, and H₂; \(z_i = 8\) for CH₄; \(z_i = 12\) for C₂H₄; \(z_i = 14\) for C₂H₆). \(F\) is the Faraday constant (96,485 C mol⁻¹ of electrons). \(Q\) is the amount of charge passed during the electrolysis. For the gas products, \(n_i\) was calculated as follows:

\[
n_{i,\text{gas}} = \frac{P_0 \times x_i \times v \times t}{R \times T} \tag{4}
\]

where \(x_i\) is the volume fraction of gas product \(i\); \(P_0\) is atmospheric pressure (1 atm); \(v\) is the CO₂ flow rate (0.015 L min⁻¹); \(t\) is electrolysis time; \(R\) is the ideal gas constant (0.08205 L atm mol⁻¹ K⁻¹); \(T\) is 298 K.

4. Conclusions

We successfully prepared Cu-TiO₂ composite catalysts, where Cu clusters or NPs were well dispersed by a one-pot solvothermal method and subsequent thermal treatment for electrochemical reduction for CO₂. For Cu-TiO₂ sample obtained by calcination of the precursor in air, CuOₓ cluster were dispersed on TiO₂ surface and Cu NPs were formed on Cu-TiO₂-H obtained by hydrogen treatment of the precursor. Cu-TiO₂-H was found to exhibit high selectivity for CH₄ in ECO₂R. Faradaic efficiency for the CH₄ production reached 18% with a CH₄ partial current density of 36 mA cm⁻² at −1.8 V vs. RHE. Furthermore, 70% of FE_{CH₄}/FE_{C₁+C₂} at −1.8 V vs. RHE was achieved. We conclude that homogeneity of the Cu NPs formed on TiO₂ is one of the necessary factors to maximize CH₄ selectivity in the ECO₂R.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12050478/s1, Figure S1: Rietveld analysis results for XRD pattern for (a) TiO$_2$, (b) Cu-TiO$_2$, (c) Cu-TiO$_2$-H. The observed diffraction intensities, calculated patterns, and the difference between the observed and calculated intensity are denoted by red plus signs, a green solid line, and a blue solid line, respectively; Table S1: Structural parameters determined by Rietveld profile fitting for an XRD pattern of TiO$_2$, Cu-TiO$_2$ and Cu-TiO$_2$-H; Figure S2: High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and EDS mapping images of Cu-TiO$_2$; Figure S3: Deconvoluted Ti 2p (A) and O 1s (B) XPS spectra of (a) TiO$_2$, (b) Cu-TiO$_2$, and (c) Cu-TiO$_2$-H. The observed spectra, fitting curves and calculated patterns, and deconvoluted curves are denoted by circle, solid line, and dashed line, respectively; Table S2: XPS peak positions and phase assignment of the TiO$_2$, Cu-TiO$_2$, and Cu-TiO$_2$-H samples; Figure S4: Example of a gas chromatogram (below: enlarged view in the region for CH$_4$ and CO) of H$_2$, CH$_4$, and CO obtained by electrochemical reduction of CO$_2$ using Cu-TiO$_2$-H catalyst on a Molsieve 5A column channel after chronoamperometry operation of 10 min at 1.8 V vs. RHE; Figure S5: Example of a gas chromatogram (below: enlarged view in the region for C$_2$H$_4$) of C$_2$H$_4$ obtained by electrochemical reduction of CO$_2$ using Cu-TiO$_2$-H catalyst on a Plot Q column channel after chronoamperometry operation of 10 min at 1.8 V vs. RHE; Figure S6: Example of a High Performance Liquid Chromatography (HPLC) of liquid products obtained by electrochemical reduction of CO$_2$ using Cu-TiO$_2$-H catalyst after chronoamperometry operation of 10 min at 1.8 V vs. RHE; Table S3: Electrochemical CO$_2$-to-CH$_4$ performance for studies related to highly dispersed or single-site copper catalysts [4,50–53].

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