Electrochemical Reduction of CO at a Copper Electrode

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CO₂ is electrochemically reduced to CH₄, C₂H₄, and alcohols in aqueous electrolytes at Cu electrode with high current density. CO₂ is initially reduced to adsorbed CO and further to hydrocarbons and alcohols. This paper describes macroscopic electrolytic reduction of CO at a Cu electrode in various electrolyte solutions in order to reveal the unique properties of Cu electrode in comparison with Fe and Ni electrodes. The reaction products from the Cu electrode are CH₄, C₂H₄, C₂H₅OH, *n*-C₃H₇OH, CH₃CHO, and C₂H₅CHO. Neither C₂H₆ nor CH₃OH is produced. CH₄ is favorably produced in aqueous KHCO₃ of high concentrations (*e.g.* 0.3 mol dm⁻³), whereas C₂H₄ and C₂H₅OH are produced in dilute KHCO₃ solutions (0.03 mol dm⁻³). Such product selectivity is derived from the electrogenerated OH⁻ in the cathodic reaction, as is the case in the CO₂ reduction. The partial current densities of CH₄, C₂H₅OH irrespective of pH. The partial current of CH₄ formation is proportional to proton activity and also follows the Tafel relationship. The transfer coefficients are 0.35 for C₂H₄ formation and 1.33 for CH₄ formation. These facts indicate that the reaction paths of CH₄ and C₂H₄ formations are separated at an early stage of CO reduction. Ethanol and *n*-propanol may be reduced from acetaldehyde and propionaldehyde intermediately formed in the reaction. The molecular reaction path is discussed with regard to these experimental results.

1. Introduction

CO₂ is electrochemically reduced to CO, formic acid, and hydrocarbons on metal electrodes.^{1,2} Copper electrode uniquely reduces CO₂ to methane, ethylene, and alcohols at high current densities in aqueous electrolytes,^{1–3} as confirmed by many workers.^{4–6} This reaction is of great interest from the viewpoint of environment, energy, and natural resources, since this reaction may be applied to load-leveling technology as a novel energy storage process in which electrical energy is converted to chemical energy and *vice versa*. Three major problems are pointed out for this process; high overpotential, low product selectivity, and transport problems.⁷ Among them, the transport problems may be basically solved by electrolysis of CO₂ by a gas diffusion electrode,⁸ under high pressure⁹ or by electrolysis of liquid CO₂ in methanol solution under high pressure.¹⁰

The problem involved with the electrode process still remains unsolved at present; the energy conversion efficiency of the copper electrode process is *ca.* 40% mainly due to high cathodic overpotentials.⁷ Development of excellent electrocatalysts with low overpotential is thus necessary for this purpose. Not many metallic electrodes effectively reduce CO₂ to hydrocarbons or alcohols in spite of many attempts to search useful electrocatalysts. Other than the Cu electrode, it has recently been reported that silver can reduce CO₂ to CH₄, C₂H₄, and C₂H₅OH at high current efficiency in pulsed electrolysis accompanied with anodic potential bias.¹¹ It is thus important to understand the fundamental aspects of the Cu electrode process in the electrochemical reduction of CO₂.

CO is also reduced at Cu electrodes, giving similar product distribution.^{3,12} One can thus expect that the electrochemical reduction of CO_2 to hydrocarbons proceeds with intermediate formation of CO. During the electrochemical reduction of CO₂, adsorbed CO is formed at the Cu electrode as demonstrated by

voltammetric, chronopotentiometric,¹³ and infrared spectroscopic measurements.¹⁴ Adsorbed CO markedly prevents hydrogen evolution in aqueous solution as well as other redox reactions and underpotential deposition of metals. *In-situ* infrared absorption spectroscopy revealed that adsorbed CO is present at the Cu electrode surface at potentials more negative than -0.7 V *vs* SHE.

Various metal electrodes reduce CO₂ to CO, *i.e.* Au, Ag, Zn, Pd, and Pt.¹⁵ Among these metals, Cu can effectively reduce CO further to hydrocarbons and alcohols. Thus the electrochemical process of CO reduction at a Cu electrode is of great interest from the scientific viewpoint as well.

Electrochemical reduction of CO₂ at a Cu electrode yields C₂H₄ more favorably with relatively low overpotential than CH₄.³ The selectivity between CH₄ and C₂H₄ in CO reduction depends on the pH of the electrolytes;¹² C₂H₄ formation is favored in relatively high pH solutions as compared with CH₄. Electrolyte cations also affect the selectivity between CH₄ and C₂H₄.¹⁶

This article attempts to reveal comprehensively the electrochemical process of the reduction of CO to CH_4 , C_2H_4 , and alcohols at a Cu electrode as functions of the pH and electrode potential. The reaction mechanism will be discussed on the basis of these experimental results.

2. Experimental Section

The metal electrodes used in the present study are sheets of Cu (purity, 99.999%) donated by Sumitomo Metals & Mining, Co. Ltd., and Fe (99.9%) and Ni (99.9%) purchased from Furuuchi Kagaku, Co. Ltd. Each metal sheet was cut into a 20 \times 20 mm electrode with a lead strip of the same metal attached. The electrodes were polished with fine emery paper (#1500) and subsequently electrolytically polished in 85% phosphoric acid. Surface oxide film which may be formed after the electropolishing, was cathodically reduced in the electrolytic cell for *ca*. 2 min by 30 \times 10⁻⁶ A cm⁻² prior to the measurements. The electrochemical measurements were con-

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TABLE 1: Faradaic Efficiencies of Various Products Affected by KHCO₃ Concentration^a

		Faradaic efficiencies/%								
KHCO ₃ /mol/L	potential/V vs SHE	$\overline{CH_4}$	C_2H_4	EtOH	n-PrOH	MeCHO	EtCHO	H_2	total	C_2H_4/CH_4
0.03	-1.38	16.2	28.1	13.1	3.1	2.1	2.7	40.1	105.4	1.73
0.05	-1.36	18.5	19.1	7.6	1.9	1.6	1.3	49.4	99.4	1.03
0.1	-1.36	22.3	21.7	7.1	2.2	1.4	0.5	41.7	96.9	0.973
0.2	-1.35	23.2	15.8	7.1	2.2	0.7	0.6	51.5	101.1	0.681
0.3	-1.35	32.4	15.3	6.3	3.5	0.4	0.8	44.8	103.5	0.472

^a Total ionic concentration was kept at 0.3 mol/L by adding KCl. Temperature: 19 °C. Current density: 2.5 mA cm⁻².

 TABLE 2: Faradaic Efficiencies of Various Products from Cu, Fe, and Ni Electrodes^a

		Faradaic efficiencies/%									
electrode	potential/V	CH_4	C_2H_6	C_2H_4	MeOH	EtOH	n-PrOH	MeCHO	EtCHO	H_2	total
Electrolyte: 0.1 M KHCO ₃ ^b											
Cu	-1.36	22.3	0.00	21.7	0.00	7.1	2.2	1.4	0.5	41.7	96.9
Fe	-1.38	1.1	0.4	0.1	0.1	tr. ^c	0.00	tr.	tr.	96.0	97.7
Ni	-1.49	1.1	0.3	0.2	0.5	tr.	tr.	0.1	tr.	100.3	102.5
Electrolyte: 0.1 M KH ₂ PO ₄ + 0.1 M K ₂ HPO ₄ (pH 6.8)											
Cu	-1.24	15.6	0.00	4.1	0.00	0.3	0.00	0.00	0.00	73.0	93.0
Fe	-1.32	2.6	0.8	0.2	0.1	0.2	tr.	tr.	tr.	93.8	97.7
Ni	-1.14	1.5	0.5	0.1	0.2	0.1	tr.	0.1	tr.	89.7	92.1

^{*a*} Potentials *vs* SHE. Temperature: 19 °C. Current density: 2.5 mA cm⁻². ^{*b*} pH is estimated at 9.0 at the electrode surface during the reactions. ^{*c*} tr. indicates a current efficiency between 0.01 and 0.05%.

ducted at 19 °C within \pm 0.5 °C. The electrode potential was measured using an Ag/AgCl reference electrode and is given with respect to SHE in this article. The electrode potential was corrected for the IR drop between the Luggin capillary tip and the electrode by the current interrupter technique.

The catholytes were purified by pre-electrolysis prior to the electrochemical measurements with a Pt black cathode under purified argon atmosphere overnight. The pre-electrolysis is effective and necessary to maintain the activity of Cu electrodes, preventing "deactivation of Cu electrode", which is described in several recent publications.⁶ The effect of pre-electrolysis will be reported in detail elsewhere. CO of high-purity grade (99.9%) was used after passing through KOH solution.

Electrolytic measurements at constant currents or constant potentials were conducted for more than 30 min with K₂HPO₄-KOH, phosphate, or borate buffer solution with the total electrolyte concentration 0.2 mol dm⁻³. CO was continuously sparged into the catholyte (flow rate: $ca. 50-140 \text{ mL min}^{-1}$) during the electrolyses; the catholyte was stirred at ca. 680 rpm with a magnetic stirrer. Gaseous products in the effluent gas from the cell were analyzed at 5 min intervals by gas chromatographs. The concentration of gaseous products in the effluent gas remained virtually constant during the electrolyses. Products soluble in the electrolyte solution were analyzed by a liquid chromatograph and a gas chromatograph using a PEG 400 column after the electrolyses. The limit of the quantitative analysis was 0.6 ppm for CH₄, 0.3 ppm for C₂H₄, and 3×10^{-6} mol dm⁻³ for C₂H₅OH and *n*-C₃H₇OH. Other details were described in the previous publication from our laboratory.³

The current limited by the diffusion of CO to the electrode was estimated as 4.1 mA cm⁻² under the present experimental conditions; CO at 1 atm and the temperature at 19 °C. The diffusion layer thickness, 0.0025 cm, was determined from a measurement of the limiting current of reduction of Fe(CN)₄^{3–} under identical hydraulic conditions with an equivalent geometrical size of a Pt plate electrode. Five electrons were assumed for reduction of one CO molecule as an average. All the present electrolytic measurements of CO reduction were conducted under the conditions that the sum of the partial currents of CO reduction was below 20% of the limiting current; most of the measurements were below 10% of the limiting

current. Thus the partial currents will not be affected by the transport process of CO to the electrode.

3. Results and Discussion

3.1. Product Distribution Affected by Concentration of HCO_3^- . Table 1 tabulates Faradaic efficiencies of the products in the cathodic reduction of CO at a constant current density of 2.5 mA cm⁻² in KHCO₃ solution of various concentrations. The total ionic concentration was kept at 0.3 mol dm⁻³ by addition of KCl.

Methane and ethylene are produced together with H₂ formed from water electrolysis as a competing parallel reaction. Various soluble products are formed as well in the electrolytes; ethanol, *n*-propanol, acetaldehyde, and propionaldehyde. Formaldehyde is not formed. The Faradaic yields of C₂H₄ and C₂H₅OH are high in dilute KHCO₃ solutions, whereas the CH₄ yield increases with increase of KHCO₃ concentration. The Faradaic production ratio C₂H₄/CH₄ significantly decreases with increase of KHCO₃ concentration.

Table 2 presents the result of the Cu electrode obtained in phosphate buffer solution ($KH_2PO_4 + K_2HPO_4$, pH 6.8); C_2H_4 and C_2H_5OH remarkably drop, whereas CH_4 is not much different compared with the value obtained in KHCO₃ solutions. No other soluble product was produced in phosphate buffer solution.

The dependence of C₂H₄/CH₄ on HCO₃⁻ concentration in electrochemical reduction of CO₂ was discussed in our previous publication in terms of the local high-pH region close to the electrode.³ The process is briefly described. OH⁻ is generated in cathodic reactions that involve water molecules such as CO and CO₂ reduction. OH⁻ thus produced will be instantaneously neutralized by HCO3⁻. The pH value will not rise at the electrode if a sufficient amount of HCO3⁻ is supplied by diffusion in concentrated HCO3⁻ solution. However, the transport of HCO₃⁻ to the electrode will not be enough in dilute HCO₃⁻ solutions, and the pH will be enhanced in the neighborhood of the electrode. The pH values at the electrode are estimated for a current density of 2.5 mA cm⁻² in various KHCO3 concentrations saturated with CO according to the procedure described in our previous publication:³ 9.5 in 0.03 mol dm^{-3} ; 9.0 in 0.1 mol dm^{-3} ; 8.5 in 0.3 mol dm^{-3} .

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Thus the present results are compatible with the fact that CH_4 formation in the electrochemical reduction of CO is favored in low-pH electrolytes, and C_2H_4 in high-pH ones as reported previously.³ The present results further confirm that the $C_2H_4/$ CH₄ ratio in CO reduction is affected by HCO_3^- concentration in a similar way with the electrochemical reduction of CO₂.

Tables 1 and 2 further indicate that the Faradaic efficiencies of C_2H_4 and the soluble products at the Cu electrode depend similarly upon pH at the electrode surface, whereas CH_4 formation depends differently upon pH.

3.2. Comparison of Cu, Fe, and Ni Electrodes with Regard to the Fischer–Tropsch Reaction. 3.2.1. Reduction Products from Cu, Fe, and Ni Electrodes. Table 2 presents the reaction products in the electrochemical reduction of CO with the Cu, Fe, and Ni electrodes at constant current 2.5 mA cm^{-2} . The Cu electrode shows very high activity. The Fe and Ni electrodes are much less active, but they can still reduce CO, forming small amounts of CH₄, C₂H₆, C₂H₄, CH₃OH, and C₂H₅OH. The product distributions from the Fe and Ni electrodes are not affected by pH at the electrode surface. The Faradaic efficiency of C₂H₆ and CH₃OH mostly exceeds that of C₂H₄ and C₂H₅OH respectively.

The Fischer–Tropsch reaction yields hydrocarbons and alcohols from CO–H₂ gas mixtures. Ni, Fe, Co, Ru, Rh, Pd, Pt, and Ir are active catalysts for this reaction, whereas Cu is inert.¹⁷ This reaction, as is well-known, proceeds with intermediate formation of carbon and hydrogen atoms adsorbed on the catalyst surface.¹⁷ These intermediates are converted to CH₂ and further to hydrocarbons and alcohols. In analogy with the Fischer–Tropsch reaction, the electrochemical reduction of CO at Fe and Ni electrodes may proceed with intermediate formation of carbon and hydrogen atoms adsorbed on the electrodes leading to the formation of hydrocarbons and alcohols.

Since Cu is inert in the Fischer-Tropsch reaction, we expect that the electrochemical reduction of CO proceeds with different intermediate species. On the Cu electrode, neither ethane nor methanol was produced in both 0.1 mol dm⁻³ KHCO₃ and phosphate buffer solutions. Hydrogen is adsorbed on the copper surface in a gas/solid system with some activation energy, and the heat of adsorption is much lower than on Ni and Fe.18,19 Thus the concentration of adsorbed hydrogen species on a copper electrode in aqueous solution will be much lower than that on nickel and iron. The ethylene formation would naturally be more advantageous than ethane formation due to the limited supply of adsorbed hydrogen compared with Ni and Fe electrodes. However, the Cu electrode surface will be enriched with adsorbed hydrogen species during CO reduction at low pH, at which methane formation and hydrogen evolution are predominant. Ethane was not detected under such conditions; the limit of detection was 0.05% or less in the Faradaic efficiency. The Cu electrode thus shows a unique electrocatalytic feature in addition to the high efficiency in hydrocarbon formation in CO and CO2 reduction, distinguished from other metal electrodes.

A surface-roughened Cu electrode was prepared by oxidation at 350 °C in the air and subsequent reduction with H₂ below 200 °C.²⁰ Repeated oxidation reduction treatments enhanced the surface area of the Cu electrode by more than 2 orders of magnitude according to a measurement of the double-layer charging current. The surface-roughened Cu electrode yielded a small amount of C₂H₆ with *ca*. 1% of Faradaic efficiency in CO₂ reduction at a constant current of 5 mA cm⁻². No C₂H₆ is formed from CO or CO₂ reduction with smooth Cu electrodes electrochemically polished in 85% phosphoric acid or etched with dilute HCl solution.



Figure 1. Partial current densities of C_2H_4 formation in electrochemical reduction of CO correlated with the electrode potential in various electrolyte solutions: pH 6.0–6.3 (\bigcirc), pH 7.1–7.7 (\triangle), pH 8.0–8.6 (\square), pH 8.7–8.9 (\times), pH 9.0–9.3 (\bullet), pH 10.5–11.3 (\blacktriangle), pH 12.2 (\blacksquare).

These experimental facts strongly suggest that adsorption of hydrogen species is structure sensitive. In rationalization of the product distribution on the Cu electrode, we presume that hydrogen species composed of two hydrogen atoms is involved with the CO reduction on smooth copper electrodes. Atomically adsorbed hydrogen may be involved on roughened copper surfaces as well as nickel and iron electrodes. Surface roughening likely introduced surface defects such as steps and vacancies favorable for reaction of adsorbed hydrogen atoms.

3.2.2. Catalytic Activity in the Electrochemical Reduction of CO and CO₂. The Cu electrode is markedly active in CO reduction compared with Ni and Fe as shown in Table 2. We previously demonstrated that the adsorption strength of CO on an electrode relates closely with the electrocatalytic activity of electrode metals in CO and CO₂ reduction. Adsorption of CO on Cu is exothermic, and the heat of adsorption is much lower than that on Ni and Fe. Such moderate strength of CO adsorption bond to Cu facilitates the reduction of CO, leading to efficient formation of hydrocarbons.²¹

We have reported infrared absorption spectra of the CO molecule adsorbed on Cu, Ni and Fe in a separate paper.²² The infrared absorption of C–O stretching occurs in the following order in wavenumber units: Cu > Ni(linear) > Fe > Ni-(bridged). In accordance with Blyholder's relation between the C–O stretching band frequency and the adsorption bond strength of adsorbed CO,²³ weak adsorption will lead to high C–O stretching frequency, approaching the value of the free CO molecule. Thus the order of the C–O stretching frequency, or the reverse of the adsorption strength of CO, again agrees with the activity order in CO reduction, Cu > Ni \cong Fe.

3.3. Partial Currents of the Products in the Electrochemical Reduction of CO. The partial currents of the products are calculated from the Faradaic efficiency and the total electrolysis current with various electrolytes of pH 6.0-12.2. The logarithms of the partial currents of CH₄, or log *i*(CH₄), plotted against the potential are widely scattered. However, the values of log *i*(CH₄) that were obtained in the electrolyte solutions of the same composition were relatively well correlated. This fact strongly suggests that *i*(CH₄) depends on pH.

Figures 1 and 2 illustrate the partial currents for C_2H_4 and C_2H_5OH as a function of the electrode potential. Figures 1 and 2 show relatively good correlations regardless of pH. Thus the partial currents for C_2H_4 and C_2H_5OH do not depend on the pH of the electrolytes.



Figure 2. Partial current densities of C₂H₅OH formation in electrochemical reduction of CO correlated with the electrode potential in various electrolyte solutions: pH 6.0−6.3 (\bigcirc), pH 7.1−7.7 (\triangle), pH 8.0−8.6 (\square), pH 8.7−8.9 (×), pH 9.0−9.3 (\bullet), pH 10.5−11.3 (\blacktriangle), pH 12.2 (\blacksquare).

The Tafel equation will hold in electrochemical reactions when an electrochemical process determines the overall rate. Figure 1 gives a linear correlation between $\log i$ and E, and the partial current of C_2H_4 formation is expressed in the form of the Tafel equation.

$$i(C_2H_4) = A \exp[-\alpha_e F(E - E^\circ)/RT]$$
(1)

where A is a constant, α_e is the transfer coefficient for C_2H_4 formation, and the other symbols have the usual meanings. α_e is estimated at 0.35 from Figure 1.

If the partial current for CH_4 is proportional to *j*th power of proton activity $[H^+]$ and expressed in the form of the Tafel equation, the following equation may be obtained

$$i(\mathrm{CH}_4) = B[\mathrm{H}^+]^j \exp[-\alpha_{\mathrm{m}} F(E - E^\circ)/RT]$$
(2)

where *B* is a constant and α_m is the transfer coefficient in CH₄ formation. Taking the logarithm of both sides of the equation, one obtains

$$\log i(CH_4) - j \log[H^+] = -\alpha_m F(E - E^\circ)/2.303RT + \log B$$
(3)

or

$$\log i(CH_4) + pH = -\alpha_m F(E - E^\circ)/2.303RT + \log B \text{ for } j = 1 (4)$$

or

$$\log i(CH_4) + 2pH = -\alpha_m F(E - E^\circ)/2.303RT + \log B \text{ for } j = 2 (5)$$

Figure 3 presents the relationship between log $i(CH_4) + pH$ and E, and Figure 4 that between log $i(CH_4) + 2pH$ and E. Figure 3 apparently gives a well-correlated straight line, whereas Figure 4 gives a curved line. Thus only j = 1 fits the experimental data with the α_m values 1.33 as calculated from the linear correlation of Figure 3.

3.4. Hydrogen Species. In connection with the mechanism of the Fischer–Tropsch reactions, Brady and Pettit studied gaseous reactions of diazomethane on transition metal surfaces.²⁴ They showed that CH_2N_2 diluted in He rapidly and quantitatively



Figure 3. log *i*(CH₄) + pH correlated with the electrode potential: pH 6.0−6.3 (\bigcirc), pH 7.1−7.7 (\triangle), pH 8.0−8.6 (\square), pH 8.7−8.9 (×), pH 9.0−9.3 (**●**), pH 10.5−11.3 (**▲**), pH 12.2 (**■**).



Figure 4. log *i*(CH₄) + 2pH correlated with the electrode potential: pH 6.0−6.3 (\bigcirc), pH 7.1−7.7 (\triangle), pH 8.0−8.6 (\square), pH 8.7−8.9 (×), pH 9.0−9.3 (**●**), pH 10.5−11.3 (**▲**), pH 12.2 (**■**).

decomposed on Ni, Pd, Fe, Co, Ru, and Cu at 1 atm and 25– 200 °C, forming C_2H_4 and N_2 as the predominant products in each case. The principal reaction is a simple dimerization of CH₂ fragments formed in the decomposition of CH₂N₂. When CH₂N₂ mixed with H₂ was passed over these materials, the nature of the product changed markedly. CH₄, C₂H₆, and higher hydrocarbons up to C₁₈ are produced on the metals other than Cu. The authors concluded that CH₂ groups were polymerized on these surfaces, initiated by metal-hydride bonds (adsorbed hydrogen). However, Cu metal still gave C₂H₄ as the predominant product in the reaction of CH₂N₂ and H₂. Cu does not readily dissociatively chemisorb H₂, and adsorbed hydrogen is not sufficiently provided to the initiation step in the oligomerization of CH₂. Thus the reaction of CH₂N₂ and H₂ on Cu leads predominantly to dimerization and ethylene formation.

Hydrogen evolution reaction at the Cu electrode proceeds in the Heyrovsky reaction.^{25,26}

$$H(ads) + H^+ + e^- \rightarrow H_2 \tag{6}$$

Horiuti et al. advocated in accordance with their quantum mechanical calculations that the Heyrovsky reaction proceeds with intermediate species H_2^+ , which follows formation of adsorbed hydrogen.²⁷

$$H^+ + e^- \rightarrow H(ads)$$
(7)

$$H(ads) + H^+ \rightarrow H_2^+(ads)$$
 (8)

Reactions 7 and 8 readily proceed, and the rate-determining step is

$$\mathrm{H_2}^+(\mathrm{ads}) + \mathrm{e}^- \to \mathrm{H_2} \tag{9}$$

If step 9 is the rate-determining step, $H_2^+(ads)$ will be abundant on the electrode surface. However, the presence of H_2^+ was disputed by many workers and has not yet received experimental confirmation.^{28, 29} The process may be preferably considered as a combined proton and electron transfer (eq 6), similar to the discharge step 7, in which the active surface site is an adsorbed hydrogen atom rather than a bare metal atom.²⁸ In this model, $H_2^+(ads)$ is a transient transition state, rather than a stable species with a comparatively long life time.

In CO-saturated solution, hydrogen evolution is greatly prevented at Cu electrodes, and the coverage of CO on the electrode surface amounts to 90% at -1.0 V,¹³ where the reduction of CO starts. We presume under such a specific situation that the existence of H₂⁺(ads) is possible at the sites not covered with CO, or the hydrogen species reacts as a group of H(ads) + H⁺ in stead of H(ads) in the subsequent reactions. Thus H₂⁺(ads) or H(ads) + H⁺ is involved with CO reduction, leading to the unique product distribution in CO reduction on Cu electrodes. The hydrogen species, H₂⁺(ads), or combined H(ads) + H⁺ is tentatively represented as H₂⁺(ads) for brevity hereafter.

3.5. Rate-Determining Step of Ethylene Formation. We reported in the previous paper that adsorption of CO on a Cu electrode is accompanied with an electron transfer according to voltammetric measurements.¹⁴ *In-situ* infrared spectroscopy at a Cu electrode showed an absorption of adsorbed CO at 2087 cm⁻¹ at -0.95 V, which corresponds to CO linearly adsorbed on a metal surface without electron transfer to a CO molecule. We suggested some cluster-like substance as an intermediate species adsorbed on the surface in CO reduction on the basis of the voltammetric measurements.

However, electrolytic measurements using single-crystal copper electrodes revealed that the Cu(111) surface can reduce CO_2 and CO to methane, whereas any charge transfer voltammetric peak does not appear with a Cu(111) electrode.³⁰ We then carried out an *in-situ* infrared spectroscopic measurements of a Cu electrode surface, and observed that anion and CO are competitively adsorbed on the surface. Thus we presumed that the apparent charge transfer is derived from charge displacement of specifically adsorbed anions by the adsorption of CO on the electrode surface. The details will appear elsewhere. At present we cannot propose a definite intermediate species for the CO reduction. We discuss the reaction scheme under a hypothesis that adsorbed CO molecules are involved in the reaction.

The formation of hydrocarbons and other products from CO at a Cu electrode will proceed in a series of consecutive multistep process. We assume that a rate-determining step determines the overall rate of the reaction, and the steps prior to the rate-determining one are in equilibrium. The partial current for each product will follow the Tafel relationship, as given below for the cathodic current

$$i = i_0 \exp[-\alpha F(E - E^\circ)/RT]$$
(10)

where i_0 denotes the exchange current, α is the transfer coefficient and other symbols have their usual meanings.

 α is related to the symmetry factor of the rate-determining step β^{31}

$$\alpha = s/\nu + \beta r \tag{11}$$

where *s* is the number of electrons passing before the ratedetermining step, and ν is the stoichiometric number and *r* the number of electrons both in the rate-determining step. Conway and Bockris showed that *r* should be 1 in electrochemical charge transfers in accordance with their theoretical calculations of heats of activation.³²

The value of ν in ethylene formation will be 1 or 2, as shown later in connection with the reaction scheme. The transfer coefficient of ethylene formation α_e is 0.35 as determined from Figure 1. Thus the value of *s* must be zero, and α_e is equal to β_e , where the suffix e denotes ethylene formation. The partial current of ethylene formation is not affected by proton activity as described above. Therefore the rate-determining step of ethylene formation may be the first electron transfer process or simply the electron transfer to adsorbed CO.

$$CO + e^{-} \rightarrow CO^{\bullet-} \tag{12}$$

We previously depicted a reaction scheme of the electrochemical reduction of CO_2 in analogy with Fischer–Tropsch reaction, in which atomic carbon is a precursor of hydrocarbons.³ Intermediate formation of carbon at a Cu electrode surface in electrochemical reduction of CO_2 was reported on the basis of XPS measurement,^{6a} but it has not yet been confirmed by other workers.

Kim et al. discussed electrochemical methanation of adsorbed CO during CO₂ reduction on the basis of their thermochemical calculations. They concluded that CO is thermally dissociated to form surface carbon atoms at the Ru electrode.⁵ As mentioned in the previous section, formation of surface carbon atoms has been established as an intermediate step in the Fischer–Tropsch reaction.¹⁷ Thus it is accepted that a surface carbon atom is formed as a precursor to hydrocarbons in the electrochemical reduction of CO on Ru, Ni, and Fe, catalytically active metals in the Fischer–Tropsch reaction.

Copper is inert in the Fischer–Tropsch reaction. The infrared spectroscopic measurements showed that CO is weakly adsorbed on Cu with a C–O stretching band frequency closer to that of a gaseous CO molecule than on Ni and Fe. Thus thermal dissociation of CO to C and O atoms will not readily take place on Cu.

By electronation (eq 12) in the gas phase, however, CO is readily decomposed to carbon atoms and O^- ions.³³ Thus CO is possibly decomposed to a carbon atom and an O^- ion, when an electron is transferred to CO adsorbed on a Cu electrode. Kim et al. proposed "electrochemical splitting of CO" in CO reduction on a Cu electrode. They assumed the elementary step of surface carbon atom formation on a Cu electrode.⁵

$$CO(ads) + H_2O + e^- \rightarrow C(ads) + OH(ads) + OH^-$$
 (13)

They calculated the binding energies of adspecies, such as CO, C, and OH, and rationalized the onset potential value in the voltammogram of CO reduction.

Thus the electrochemical splitting of CO may possibly take place as an intermediate step in the present ethylene formation in the electrochemical reduction of CO on Cu. Since the ethylene formation is independent of pH, $H_2^+(ads)$ or H^+ + H(ads) will not be involved in the process. Thus the ratedetermining step of ethylene formation may be eq 13 followed by electronation of OH(ads).

$$OH + e^- \rightarrow OH^-$$
(14)

C(ads) may further be reduced to CH_2 , the presence of which is confirmed in the study of the dissociation of CH_2N_2 ,²⁴ as mentioned above.

$$C(ads) + H_2^+ + e^- \rightarrow CH_2$$
(15)

3.6. Rate-Determining Step of Methane Formation. Methane formation is proportional to proton activity with the transfer coefficient 1.33 as shown in Figure 3. ν for methane formation may be taken as 1, and *r* should be 1 as discussed above. The transfer coefficient between 1 and 2 means on the basis of eq 11 that an electron transfer process is in equilibrium prior to the rate-determining step. We attempt to rationalize the following reaction scheme by introducing a hypothetical reaction intermediate COH.

The reaction

$$CO(ads) + H^+ + e^- \rightleftharpoons COH(ads)$$
 (16)

may be in electrochemical equilibrium. The coverage θ (COH) will be given by

$$\theta(\text{COH}) = K_i \theta(\text{CO})[\text{H}^+] \exp(-FE/RT)$$
 (17)

with K_i the equilibrium constant of eq 16, under the assumption that θ (COH) is very low in comparison with θ (CO). The rate-determining process is

$$COH(ads) + e^- \rightarrow [COH]^- (RDS)$$
 (18)

The reaction will further proceed consecutively. The rest of the process may be expressed comprehensively as shown below:

$$[COH]^{-} + 2H_2^{+} + 2e^{-} \rightarrow CH_4 + OH^{-}$$
 (19)

The rate of methane formation is given by

$$R(CH_4) = k_i \theta(COH) \exp(-\beta_m FE/RT) = k_i K_i \theta(CO) [H^+] \exp[-(1 + \beta_m) FE/RT]$$
(20)

where k_i denotes the rate constant and β_m the symmetry factor in the electrode process (eq 18). θ (CO) can be taken as 1, and the partial current *i*(CH₄) is written as

$$i(CH_4) = FR(CH_4) = Fk_i K_i [H^+] \exp[-(1 + \beta_m)FE/RT]$$
(21)

We obtain $\alpha_m = 1 + \beta_m$ as a result of comparing eqs 21 and 4. The symmetry factor β_m is between 0 and 1 or probably close to 0.5. Thus eq 21 is compatible with the experimental transfer coefficient 1.33.

3.7. Formation of Aldehydes and Alcohols. Figure 2 presents the partial current density of ethanol formation in various pH solutions as a function of the potential. The partial currents are low and not well correlated. If we attempt a linear correlation, the value of transfer coefficient is ca. 0.6 and the partial current is independent of pH. Ethanol may be formed in a reaction process similar to ethylene formation. A small amount of propanol was also produced in addition to ethanol.

Aldehydes are electrochemically reduced to the corresponding alcohols at some metal electrodes.³⁴ We studied the reduction

TABLE 3: Current Efficiencies of the Products in Electrochemical Reduction of Aldehydes at a Cu Electrode in 0.1 M KHCO₃^a

	concn/	potential/	products (%)						
aldehyde	mM	V	H_2	CH_4	C_2H_4	alcohols			
НСНО	61	-1.23	89.8	0.7	0.1	10.1 (CH ₃ OH)			
CH ₃ CHO	18	-1.09	6.3	0.0	0.1	91.8 (C ₂ H ₅ OH)			
C ₂ H ₅ CHO	27	-1.12	45.1	0.2	0.0	57.7 (<i>n</i> -C ₃ H ₇ OH)			

^{*a*} Potentials vs SHE. Temperature 18 °C, 2.5 mA cm⁻². pH is estimated at 9.0 at the electrode surface during the reactions.



Figure 5. Molecular reaction pathway diagram of the electrochemical reduction of CO. H_2^+ represents H_2^+ or a combined $H(ads) + H^+$. The \rightarrow with a \land through it denotes a rate-determining step. The H_2O and OH^- resulting from the reactions are excluded for brevity.

of HCHO, CH₃CHO, and C₂H₅CHO using the Cu electrode in 0.1 M KHCO₃. The results are given in Table 3. CH₃CHO was easily reduced to C₂H₅OH at the current density of 2.5 mA cm⁻², and C₂H₅CHO to *n*-C₃H₇OH. HCHO was reduced to CH₃OH with less current efficiency.

Table 1 shows that the alcohol formations are accompanied by the corresponding aldehydes. We can reasonably conclude that the alcohols are yielded with intermediate formation of the corresponding aldehydes. Neither HCHO nor CH₃OH is produced at the Cu electrode.

3.8. Molecular Reaction Pathway Diagram. We proposed a molecular reaction pathway diagram for the electrochemical reduction of CO₂ at a Cu electrode.³ The diagram showed that both CH₄ and C₂H₄ were formed with common intermediate species of CH₂ adsorbed on the electrode surface. Alcohol formations were supposed to proceed with insertion of CO to adsorbed CH₂ with reference to ethanol formation in the gas phase from CO + H₂ catalyzed by Rh/TiO₂ reported by Takeuchi and Katzer.³⁵

In the light of the present experimental results, we revise the molecular reaction pathway diagram as illustrated in Figure 5.

The reaction paths of methane and ethylene formations are separated at the very early stage of CO reduction in accordance with the discussion given above. We presume that insertion of CO to CH₂(ads) leads to formation of CH₂-CO(ads). H₂⁺ or H(ads) + H⁺ will be involved in all the hydrogenation processes. CH₂-CO(ads) will be reduced to CH₂=CH₂.

$$CH_2 - CO(ads) + 2H_2^+ + 2e^- \rightarrow CH_2 = CH_2 + H_2O$$
 (22)

Ethylene may possibly be formed by dimerization of CH_2 . CH_2 -CO(ads) will be further reduced to acetaldehyde and eventually to ethanol.

A small fraction of acetaldehyde may be transformed to vinyl alcohol CH_2 =CHOH by keto-enol tautomerization equilibrium. Vinyl alcohol is labile but will be possibly present at low concentration.³⁶ An intermediate substance vinyl alcohol may be hydrogenated to CH_3 -CH(ads), a homologue of CH_2 (ads).

$$CH_2 = CHOH + H_2^+ + e^- \rightarrow CH_3 - CH(ads) + H_2O \quad (23)$$

CO is inserted in to CH_3 -CH(ads) in a similar way as $CH_2(ads)$, further reduced to CH_3 -CH₂-CHO and eventually to *n*-propanol.

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