Temperature Dependence of the Probability of Chain Growth for Hydrocarbon Formation by Electrochemical Reduction of CO_2

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The temperature dependence of the probability of chain growth was studied for hydrocarbons formed at Fe and Ni electrodes by electrochemical CO_2 reduction. The faradaic efficiency for hydrocarbons increased with increasing temperature. The distribution of the produced hydrocarbons followed well the Schultz Flory equation. The probability of chain growth increased with increasing temperature. Based on the temperature dependence of the probability of chain growth, the mechanism of the electrochemical Fischer Tropsch reaction is discussed.

In the electrochemical reduction of CO_2, the selectivity control of the reduction products is one of the important problems to develop its technology. It is known that hydrocarbons such as methane, ethane and propane are produced by the electrochemical reduction of CO_2 under high pressure at transition metal electrodes such as Fe, Co, Pd and Ni.[1,2,3,4] Cook et al. analyzed the distribution of hydrocarbons produced by the electrochemical reduction of CO_2 at a Pd electrode and discovered that it can be well explained by the Schultz–Flory distribution. From this result, they suggested that hydrocarbons are produced by the Electrochemical Fischer Tropsch mechanism,[1] which resembles the Fischer Tropsch reaction in catalysis in which hydrocarbons are produced catalytically on catalyst surfaces from CO and hydrogen.

Following a report by Cook et al.,[1] Kudo et al. reported that hydrocarbons are also produced according to the Schultz–Flory distribution at Ni, Co and Rh electrodes.[2]

In the technology of electrochemical conversion of CO_2 into more valuable chemicals, it is very important to develop a method to control the length of the hydrocarbon chain. Most Fischer Tropsch reactions take place on catalyst surfaces in C_1 chemistry higher than 250 °C. On the other hand, hydrocarbons are produced at room temperature in the electrochemical Fischer Tropsch reaction, although the current efficiency is low.[2]

It is interesting to elucidate the mechanism of this unique reaction on the electrode surface. An important factor related to the electrochemical Fischer Tropsch reaction is the probability of chain growth (α), which represents the growth probability of the carbon chain in a hydrocarbon. As far as we know, temperature dependence of the probability of α in the Fischer Tropsch reaction has not been studied so far.

In the present study, we analyzed the temperature dependence of the probability of the chain growth (α) in the electrochemical Fischer Tropsch reaction of CO_2 under high pressure at Fe and Ni electrodes where hydrocarbons are produced electrochemically.[2,3]

Table 1. CO_2 Pressue to Keep the Solubility of CO_2 at 0.6 M in Aqueous Electrolyte Solutions at Various Temperatures

T/°C	P/atm
5	10
25	21
30	24
35	27
40	31
50	38
75	55

Experimental

The electrochemical reduction of CO_2 was carried out in a 0.5 M $KHCO_3$ aqueous electrolyte solution by using a high-pressure electrochemical cell after preliminary electrolysis. In the experiments, a Fe plate (purity, 99.99% ; 1 cm × 1 cm) and a Ni wire (diameter, 0.1 mm; Nilaco ; purity, 99.7%) were used as electrodes, because they are known to produce hydrocarbons according to the Schultz–Flory distribution by electrochemical reductions of CO_2 under high pressure of several tens of atmospheres.[2,3]

Before electrolysis, CO_2 gas (purity: 99.95%) was bubbled through the $KHCO_3$ solution. In order to control the temperature of the electrochemical cell, the electrochemical cell was immersed in a water bath whose temperature was controled from 5 °C to 75 °C.

The solubility of CO_2 into an aqueous electrolyte solution depends on the temperature. In the experiments, the CO_2 pressure was regulated to keep the CO_2 concentration in the aqueous electrolyte solution at 0.6 M. Table 1 gives the CO_2 pressure that is necessary to keep the CO_2 concentration in the aqueous electrolyte solution at 0.6 M.

The reduction products of CO_2 were detected and analyzed quantitatively by gas chromatographs (Ohkura Model-802; TCD, MS-13X column for CO and active carbon for H_2 and Ohkura GC202; FID, VZ-10 column for hydrocarbons). The reduction products in

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Table 2. Temperature Dependence of Faradaic Efficiecies of the Electrochemical Reduction Products of CO_2 (Pressure: 10 atm)

T/°C	P/atm	H_2	CO	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	i-C_4H_{10}	n-C_4H_{10}	H.C. Total	HCOOH	Total	α
5	10	80.1	t	0.76	0.12	0.05	0.05	0.02	0.02	t	1.02	10.20	92.3	0.304
25	21	66.5	0.07	1.00	0.34	0.25	0.25	0.12	0.10	0.02	1.96	26.35	96.9	0.344
35	27	54.9	n	0.97	0.33	0.23	0.23	0.13	0.10	0.02	1.90	23.54	82.5	0.355
40	31	76.6	t	2.14	0.62	0.38	0.38	0.24	0.09	t	3.51	19.56	104.0	0.348
50	38	63.6	n	1.23	0.48	0.39	0.39	0.20	0.15	0.03	2.69	30.54	99.6	0.371
75	55	68.6	0.08	1.26	0.54	0.52	0.52	0.24	0.24	0.04	3.06	23.59	98.6	0.429

H.C.Total: Hydrocarbon Total, n: not detected, t: trace.

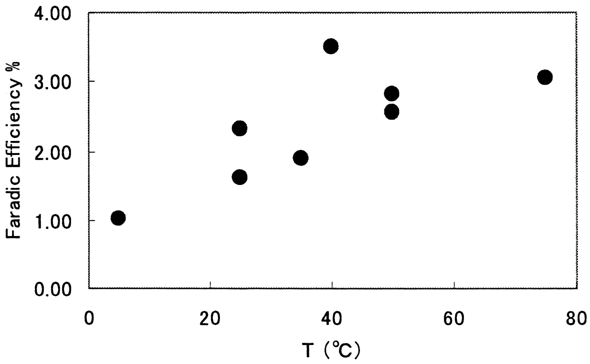

Fig. 1. Temperature dependence of hydrocarbons formed by electrochemical reduction of CO_2 under high pressure at Fe electrode.

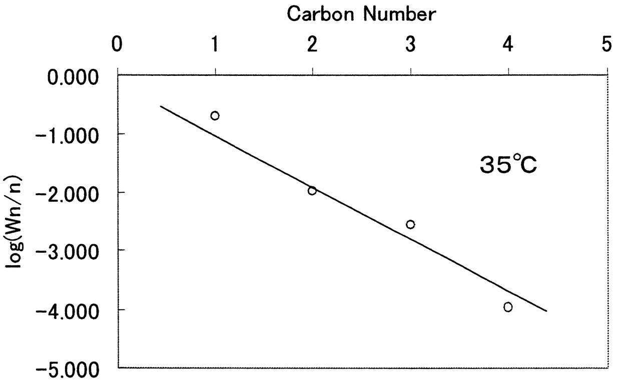

Fig. 2. $\log\left(\frac{m_p}{P}\right)$ vs P plot of hydrocarbons produced by electrochemical reduction of high pressure CO_2 (Pressure: 30 atm) at 35 °C on Fe electrode.

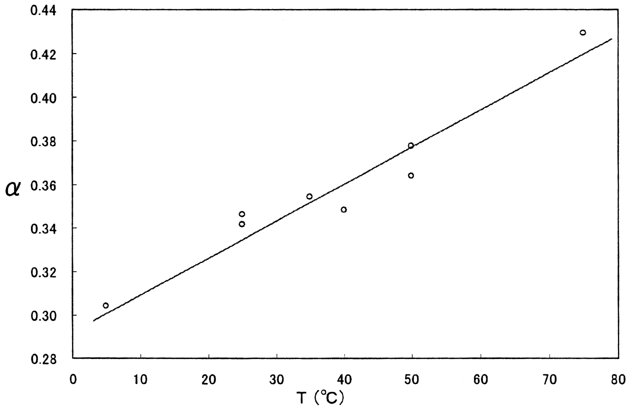

Fig. 3. Temperature dependence of the probability of chain growth α on Fe electrode (CO_2 pressure: 30 atm).

aqueous solutions, like formic acid, were analyzed by HPLC (Shimadzu LC-4A, Shodex Ionpack KC-811 column).

Results and Discussion

Table 2 shows temperature dependence of the Faradaic efficiecies of the reduction products at the Fe electrode. As the reduction products, formic acid, hydrocarbons (methane, ethane, ethylene, propane, propylene, butane and iso-butane) and a small amount of CO were detected, as is listed in this table. Although the quantity could not be evaluated because of the detection limit, a very small amount of pentane was detected on the gas chromatograph. The Faradaic efficiency of hydrogen and formic acid does not depend very much on temperature, as is shown in Table 2. However, the Faradaic efficiency of hydrocarbon increases with increasing temperature, as shown in Fig. 1.

The distribution of the produced hydrocarbons was analyzed by using the Schultz–Flory equation (see Appendix). Schultz–Flory equation is expressed by the following equation.[2,5,6]

$$\log\left(\frac{m_p}{P}\right) = P\log\alpha + \log\frac{(1-\alpha)^2}{\alpha}, \tag{1}$$

where P represents the carbon number of the hydrocarbon, m_p is the weight fraction of the hydrocarbon with carbon number P, and α represents the probability of chain growth.

If the hydrocarbons are formed according to the Fischer Tropsch mechanism, $\log\left(\frac{m_p}{P}\right)$ plotted vs P forms a straght line.[1,2] The probability of chain growth (α) can be obtained from the slope. $\log\left(\frac{m_p}{P}\right)$ was plotted against P in order to confirm whether the hydrocarbons are formed according to the Fischer Tropsch mechanism on an Fe electrode. Fig. 2 shows the result of a $\log\left(\frac{m_p}{P}\right)$ vs P plot at 35 °C on an Fe electrode.

As can be seen in Fig. 2, the distribution of the produced hydrocarbons is well explained by the Schultz–Flory equation. The distribution of the produced hydrocarbons produced at each temperature was analyzed by this method. All of the results were found to be explained well by the Schultz–Flory equation. The probability of chain growth (α) was obtained from the slope of a $\log\left(\frac{m_p}{P}\right)$ vs P plot. Fig. 3 shows the temperature dependence of α on an Fe electrode. Similarly α was obtained from a Schultz–Flory distribution analysis of hydrocarbons produced on a Ni electrode.

Fig. 4 shows the temperature dependence of α on a Ni elec-

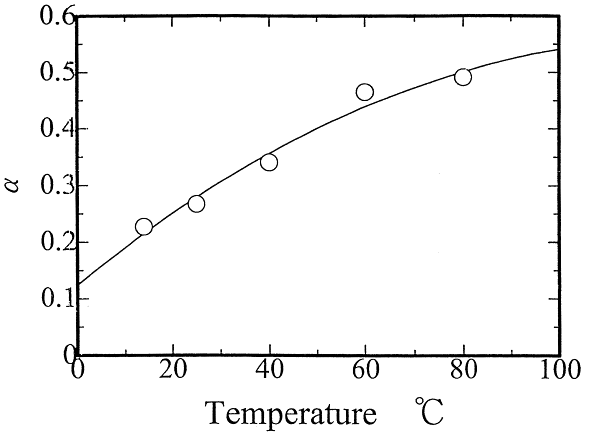

Fig. 4. Temperature dependence of the probability of chain growth α on Ni electrode (CO_2 pressure: 30 atm).

trode. As is shown Figs. 3 and 4, α increases with increasing temperature. In the Fischer Tropsch reaction carbene is considered as the intermediate.[4,5] It is considered that the thermal movement of carbene species and CO and their collision for the reaction are activated on the electrode surface with increasing temperature. Consequently, the results of Figs. 3 and 4 suggest that the polymerization between carbene species or the reactions between CO and carbene species are activated thermally. Lee et al. have reported that hydrocarbons are formed according to the Schultz–Flory distribution with $\alpha = 0.39$ in the hydrogenation of CO_2 at 400 °C on an Fe catalyst.[7] On the other hand, $\alpha = 0.429$ is achieved at a relatively low temperature of 75 °C on an Fe electrode in the electrochemical reduction of CO_2, as can be seen in Fig. 3 and Table 2.

This result indicates that an electrochemical Fischer Tropsch reaction gives a larger probability of chain growth (α) at a lower temperature in compared with the catalytic Fischer Tropsch reaction. This interesting result might be reasonably explained as follows.

In the electrochemical reduction of CO_2 in an aqueous electrolyte solution a large number of atomic hydrogens can be easily formed at room temperature and supplied on the electrode surfaces by the electrochemical reduction of a proton of Eq. 2.

$$H^{+}_{aq} + e \rightarrow H_{ad}, \tag{2}$$

where H^{+}_{aq} represents the proton in the aqueous medium, e is an electron from the cathode, and H_{aq} is the atomic hydrogen adsorbed on the electrode surface.

Because of the atomic hydrogen hydrocarbon can be produced even at room temperature by a reaction with CO, which is produced electrochemically at room temperature. This is an advantageous aspect of the electrochemical reduction of CO_2.

Fig. 5 illustrates schematically the mechanism of the electrochemical Fischer Tropsch reaction.

On the other hand, in the catalytic hydrogenation reaction of CO_2, hydrogen molecules are supplied on the catalyst surface. Chemically active atomic hydrogens are produced thermally on the catalyst surface by the dissociation of molecular hydrogen at relatively higher temperatures.

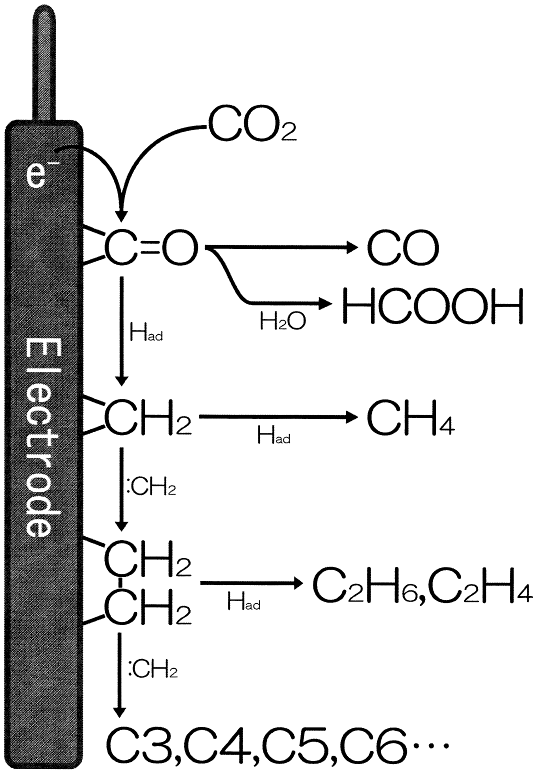

Fig. 5. Schematic illustration of electrochemical Fischer Tropisch reaction mechanism for CO_2 reduction.

The dissociation energy of the hydrogen molecule is 4.48 eV.[8] Because of this large dissociation energy, thermal activation on the catalyst surface is indispensable in the catalytic hydrogenation reaction of CO_2. It is well known that adsorbed atomic hydrogen is formed on the surface of transition- metal surface such as Ni and Pt.

Therefore it might be possible that the adsorbed hydrogen atom and CO react with each other to form hydrocarbons on a catalyst surface at room temperature. However, as far as we know, there is no clear result reported conscerning a Fischer Tropsch reaction at room temperature on catalyst surfaces. Further study would be necessary to elucidate the difference-between a catalytic Fischer Tropsch reaction and an electrochemical Fischer Tropsch reaction.

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Appendix

Schultz–Flory Equation. The probability of chain growth (α) in the Fischer Tropsch reaction is defined as

$$\phi_p = \phi_1 \alpha^{p-1}, 0 < \alpha < 1. \tag{A1}$$

Here ϕ_p represents the molar fraction of a hydrocarbon with carbon number p. Eq. A1 gives

$$\phi_{p+1} = \alpha\phi_p. \tag{A2}$$

Eq. A2 represents the physical meaning of probability of chain growth (α).

Now, the weight fraction m_p of a hydrocarbon with carbon number p can be expressed approximately as

$$m_p = \frac{p\phi_p}{\sum\limits_{p=1}^{\infty} p\phi_p}. \tag{A3}$$

It should be noted that the weight of hydrogen atoms in the hydrocarbon is neglected in this approximate equation.

Eq. A1 yields

$$\sum_{n=1}^{\infty} p\phi_p = \sum_{p=1}^{\infty} p\phi_1\alpha^{p-1}. \tag{A4}$$

Here, the following relation holds:

$$\sum_{n=1}^{\infty} p\phi_1\alpha^{p-1} = \frac{\partial}{\partial\alpha}\sum_{p=1}^{\infty}\phi_1\alpha^p. \tag{A5}$$

On the right -hand side equation of Eq. A5,

$$\sum_{p=1}^{\infty}\phi_1\alpha^p = \sum_{p=0}^{\infty}\phi_1\alpha^p - \phi_1 \tag{A6}$$

holds. Since $\sum_{p=0}^{\infty}\phi_1\alpha^p$ is the sum of a geometric series, we can calculte the right hand equation of Eq. A6 as follows:

$$\sum_{p=1}^{p}\phi_1\alpha^p - \phi_1 = \frac{\phi_1(1-\alpha^p)}{1-\alpha} - \phi_1 = \frac{\alpha\phi_1(1-\alpha^{p-1})}{1-\alpha}. \tag{A7}$$

Eqs. A6 and A7 give

$$\sum_{p=1}^{\infty}\phi_1\alpha^p = \lim_{p\to\infty}\frac{\alpha\phi_1(1-\alpha^{p-1})}{1-\alpha} = \frac{\alpha\phi_1}{1-\alpha}. \tag{A8}$$

By differentiating Eq. A8 by α, we obtain

$$\sum_{p=1}^{\infty} p\phi_1\alpha^{p-1} = \frac{\phi_1}{(1-\alpha)^2}. \tag{A9}$$

By using Eq. A9 for the right hand side of Eq. A4

$$\sum_{p=1}^{\infty} p\phi_p = \frac{\phi_1}{(1-\alpha)^2} \tag{A10}$$

is obtained. When Eq. A10 is used for the denominator of Eq. A3

$$m_p = \frac{p\phi_p}{\dfrac{\phi_1}{(1-\alpha)^2}} = p(1-\alpha)^2\cdot\frac{\phi_p}{\phi_1} \tag{A11}$$

is obtained. When Eq. A1 is used for the right- hand side of Eq. A11, we obtain

$$m_p = p(1-\alpha)^2\cdot\frac{\phi_p}{\phi_1} = p(1-\alpha)^2\alpha^{p-1} = p\alpha^p\frac{(1-\alpha)^2}{\alpha}. \tag{A12}$$

After taking the logarithm of Eq. A12 we obtain the following Schultz–Flory Equation:

$$\log\left(\frac{m_p}{p}\right) = P\log\alpha + \log\frac{(1-\alpha)^2}{\alpha}. \tag{A13}$$

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