Electrochemical Hydrogenation of CFC-13 Using Metal-Supported Gas Diffusion Electrodes

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Chlorofluorocarbons(CFCs) are known to cause the depletion of the ozone layer at the stratosphere. A large amount of CFCs still in use should be collected and retreated to harmless compounds to the environment. Electrochemical hydrogenation of CFC-13 ($CClF_3$), which is the most stable of the C1 chlorofluorocarbons, was attempted with 13 kinds of metal-supported porous carbon gas diffusion electrodes (GDEs). In the case of the electrolysis at a Cu-supported GDE, both dechlorination and defluorination of CFC-13 proceeded, and methane was produced. With a Ag-supported GDE, dechlorination proceeded selectively, and HFC-23 (CHF_3) was produced. The faradaic efficiency for hydrogenation of CFC-13 depends on the current density, the pressure of CFC-13, the composition of the electrolyte solution, and the potential imposed on the GDE. If these factors are optimized, the faradaic efficiency for hydrogenation of CFC-13 was improved up to 77.7%.

Introduction

Chlorofluorocarbons (CFCs) are known to cause the depletion of the ozone layer at the stratosphere. Recently, the production of specified CFCs was discontinued. However, a large amount of CFCs are still in use as refrigerants, etc. It is a serious subject to recover these CFCs and to convert them into harmless compounds to the environment. Generally, decomposition of CFCs requires high energy, e.g., high temperature (*1*), plasma (*2*), supercritical state (*3*), etc. In a previous paper, we reported electrochemical hydrogenation of CFC-12 (CCl_2F_2) using metal-supported gas diffusion electrodes (GDEs) (*4*). A GDE has very porous structure and consists of two regions; a reaction region made of a hydrophilic carbon and a gas diffusion region made of a hydrophobic carbon (*5*, *6*). Electrolytic solution penetrates only into the reaction region, and a gaseous reactant is supplied through the gas diffusion region rapidly. Therefore, a GDE is appropriate for the electrochemical reaction with gaseous reactants. With this system, hydrogenation of CFC-12 proceeds in a very high faradaic efficiency at room temperature. In this paper, we attempted hydrogenation of CFC-13, which is the most stable and difficult to decompose among C1 chlorofluorocarbons (*3*, *7*–*9*), to extend this electrochemical method.

There are few reports of decomposition of CFC-13 as far as we know (*10*–*13*). Okazaki and Kurosaki carried out oxidative decomposition on an Fe_2O_3 catalyst supported on an activated carbon carrier (*10*). They reported that the temperature at which the conversion of CFC-13 reached 100% was more than 100 °C higher (570 °C) than that of CFC-12. Hydrogenation of CFC-13 to HFC-23 (CHF_3) by hydrogen was reported to proceed in a Cu tube and a Pd-lined tube at 650–720 °C with 70% efficiency (*11*). Hydrogenation of CFC-13 is also reported to be caused by methanol, used as a hydrogen source, in a Ni tube at 550 °C with a 66% conversion (*13*). Decomposition of CFC-13 was not so noted as that of CFC-12 because the amount of CFC-13 used was much less than that of CFC-12. However, CFC-13, which is more stable than CFC-12, is produced via disproportionation of CFC-12 (*14*) and the process of decomposition of CFC-12 (*15*). Therefore, decomposition of CFC-13 is also necessary to decompose CFC-12 completely.

In this work, we carried out electrochemical hydrogenation of CFC-13 using metal-supported GDEs at room temperature. The catalytic activity of hydrogenation of CFC-13 and products depended on the kind of metals supported on GDEs. Methane was produced from an electrolysis of CFC-13 at a Cu-supported GDE. By using a Ag-supported GDE, dechlorination of CFC-13 proceeded selectively, and HFC-23 (CHF_3) was produced.

Experimental Section

All the electrolyses were carried out in a stainless steel autoclave as described in a previous paper (*4*). A cell equipped with GDEs was made of poly(vinyl chloride), which is resistant to corrosion by HF. GDEs and Ru- and Pt-supported GDEs were purchased from Tanaka Noble Metal Ltd. and used as working electrodes. Other metals (Ni, Zn, Ag, Cu, Pd, Pb, Co, Fe, Sn, Cr, and In) were supported on the GDEs by the impregnation method (*16*). The potential of the working electrode was measured with respect to an Ag/AgCl/saturated KCl reference electrode. A Pt wire was used as a counter electrode. The electrolyte solution was a 1:1 volume mixture of water and methanol containing 1 M NaOH (GR Wako Pure Chemical) unless otherwise noted. Methanol (GR Wako Pure Chemical) was used without further purification. Purified N_2 gas was bubbled into the solution for at least 20 min to remove dissolved oxygen. CFC-13 (Syouwa Denko) was introduced directly into the autoclave. Electrolyses were carried out galvanostatically (passage of 250 °C) with the aid of a potentiostat–galvanostat (Hokuto model HA-305) connected in series with a coulomb–ampere–hour meter (Hokuto model HF-201). The potential of a cathode was corrected with an IR compensation instrument (Hokuto model HI-203). The sampled gas from the autoclave was analyzed by gas chromatography. An Ohkura GC-802 instrument equipped with an activated carbon column (4 mm × 2 m) and a thermal conductivity detector (TCD) for H_2, an Ohkura GC-202 instrument equipped with a VZ-10 column (4 mm × 2 m), and a flame ionization detector (FID) for hydrocarbons, an Ohkura GC-103 instrument equipped with a Porapak QS column (4 mm × 2 m), and a FID for HFC-23 were used for this purpose. Identification of fluorocarbons produced in electrolyses was curried out with a gas chromatograph–mass spectrometer (Hitachi model M-80) equipped with a Porapak Q column (4 mm × 2 m).

Results and Discussion

One of the differences between CFC-12 and CFC-13 is the solubility in water as well as stability. The solubility of CFC-12 in water is 0.026 g/100 g, whereas CFC-13 is hardly soluble

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TABLE 1. Faradaic Efficiencies for the Hydrogenation of CFC-13 and for Product Formation in Electrolyses of CFC-13 at Various Metal-Supported Gas Diffusion Electrodes[a]

supported metal	E^b (V)	faradaic efficiency (%)				
		hydrogenation	CH$_4$	CHF$_3$	H$_2$	total
Ni	−1.27	0.8	0.3	0.5	80.1	80.9
Pt	−0.92	1.7	1.3	0.4	79.3	81.0
Zn	−1.47	4.9	1.3	3.6	78.8	83.7
Ag	−1.13	60.3	3.3	57.0	19.1	79.4
Cu	−1.00	51.2	21.0	30.2	39.3	90.5
Ru	−1.03	2.0	1.5	0.5	69.2	71.2
Pd	−1.9	1.3	nd[c]	1.3	83.0	84.3
Pb	−1.51	0.5	0.5	nd	77.2	77.7
Co	−1.35	1.0	0.5	0.5	73.4	74.4
Fe	−1.30	0.3	0.3	nd	71.5	71.8
Sn	−1.49	6.6	0.6	6.0	67.1	73.7
Cr	−1.45	0.5	0.5	nd	72.3	72.8
In	−1.53	2.1	0.3	1.8	79.0	81.1

[a] Under the conditions: current density 31.9 mA cm^{-2} at 30 atm of CFC-13 and at room temperature. [b] Potential (V) corrected with an IR compensation instrument (vs Ag/AgCl). [c] Not detected.

in water (17). By use of a GDE, a gaseous reactant is supplied to the GDE through the gas diffusion layer and reacts at the catalyst layer of the electrode efficiently (5, 6). However, it seems difficult that an insoluble gas reacts efficiently at the GDE because the actual electrode reaction occurs at the interface between gas and liquid phases. In our electrochemical system, the adsorbed hydrogen on the electrode that hydrogenates CFCs is obtained from the reduction of water. Therefore, water is an indispensable solvent to the electrolyte solution in our system. As the electrolyte solution, we adopted a 1:1 volume mixture of water and methanol in which CFCs are relatively soluble, containing 1 M NaOH.

Faradaic efficiencies for hydrogenation of CFC-13 and that for the formation of products in electrolyses at 13 kinds of metal-supported GDEs are summarized in Table 1. Faradaic efficiency is defined as the ratio of the charge used for hydrogenation or the formation of the product to the total charge passed during the electrolysis. None of the metal-supported GDEs showed electrocatalytic activity for hydrogenation of CFC-13 except for Cu- and Ag-supported GDEs; i.e., the main product of electrolyses at metal-supported GDEs other than Cu and Ag was hydrogen produced by the reduction of water. Ag- and Cu-supported GDEs carried out hydrogenation of CFC-13 with a faradaic efficiency of 51−60%. The efficiency for hydrogenation of CFC-13 was about 25% lower than that of CFC-12 (4). Instead of hydrogenation of CFC, the faradaic efficiency for hydrogen formation increased. Products of electrolyses were also dependent on the kind of metals that were supported on GDEs. At a Cu-supported GDE, methane was produced with a faradaic efficiency of 21.0%. This result indicates that the C−F bond of CFC-13 can be broken at room temperature in an electrolysis at the metal-supported GDE. Among the C1 chlorofluorocarbons, whose C−F bond is known to be very strong, the C−F bond of CFC-13 is the strongest one, and a lot of energy is needed to break it (2, 7−9). There has been no report of decomposition of CFC-13 at room temperature as far as we know. Therefore, a Cu-supported GDE has a high electrocatalytic activity even for decomposition of CFC-13. By using a Ag-supported GDE, we produced HFC-23 (CHF$_3$) with a faradaic efficiency of 57.0%, and methane was hardly produced. This result shows that dechlorination of CFC-13 proceeds selectively at a Ag-supported GDE.

From the results mentioned above, it became clear that Cu- and Ag-supported GDEs have electrocatalytic activity for hydrogenation of CFC-13. However, the activity is not so high under the present condition as in the case of CFC-12. Therefore, we sought good conditions for the electrolysis of CFC-13 at metal-supported GDEs by investigating the effect
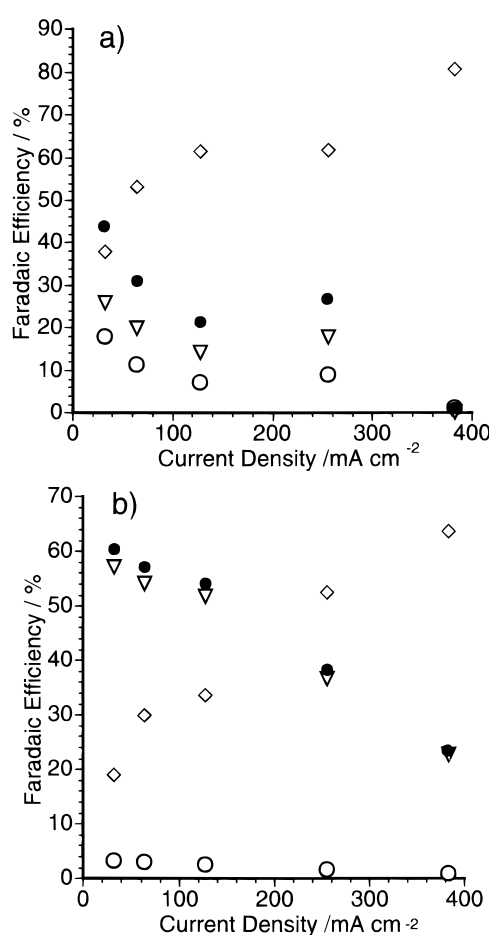

FIGURE 1. Relationship between current density and the faradaic efficiencies for the hydrogenation of CFC-13 and for product formation at (a) Cu-supported GDE and (b) Ag-supported GDE at 30 atm of CFC-13 in 1:1 mixed solvent of methanol and water. ●, hydrogenation of CFC-13; ○, methane formation; ▽, HFC-23 formation; ◇, hydrogen formation.

of current density, pressure of CFC-13, and electrolyte solution on the faradaic efficiency for hydrogenation of CFC-13. Figure 1 shows the relationship between the current density and faradaic efficiencies for hydrogenation and for product formation in electrolyses of CFC-13 at Ag- and Cu-supported GDEs. At a Cu-supported GDE, the faradaic efficiencies for hydrogenation of CFC-13 decreased with an
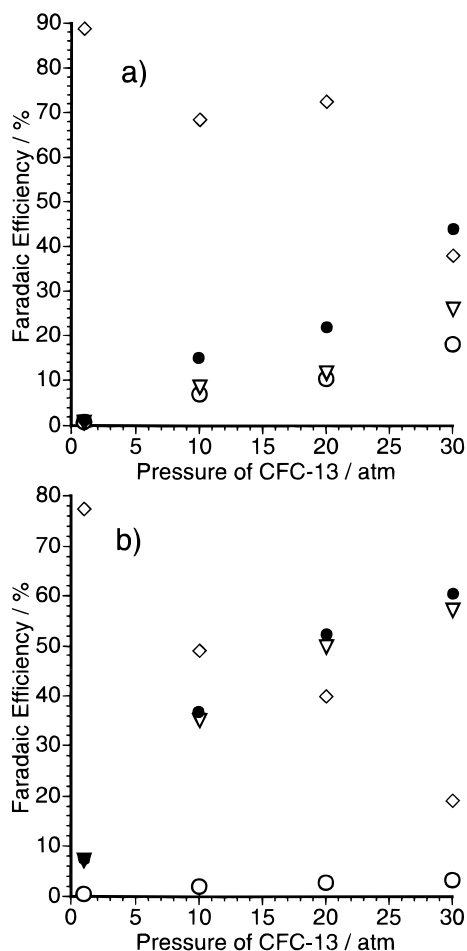
FIGURE 2. Relationship between pressure of CFC-13 and the faradaic efficiencies for the hydrogenation and for product formation of CFC-13 at (a) Cu-supported GDE and (b) Ag-supported GDE at 31.9 mA cm^{-2} in 1:1 mixed solvent of methanol and water. ●, hydrogenation of CFC-13; ○, methane formation; ▽, HFC-23 formation; ◇, hydrogen formation.
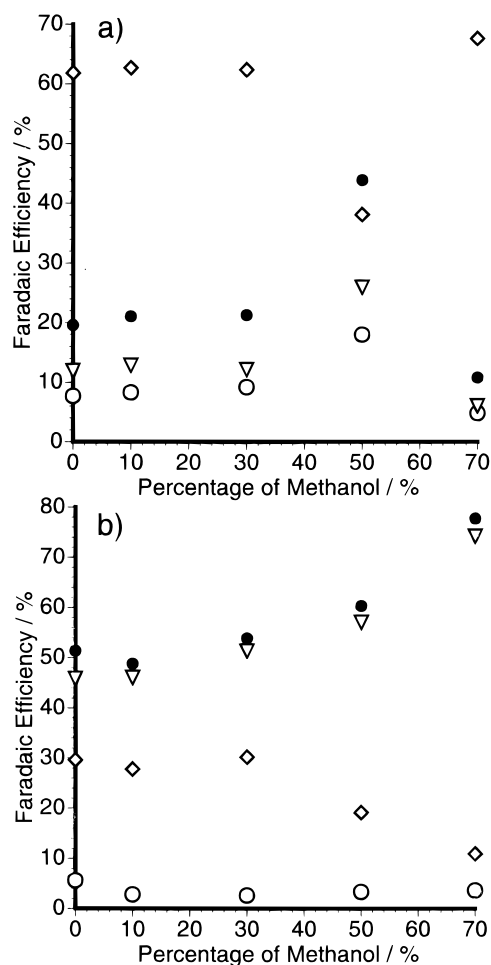

FIGURE 3. Relationship between the percentage of methanol in the electrolyte solution and the faradaic efficiencies for the hydrogenation of CFC-13 and for product formation at (a) Cu-supported GDE and (b) Ag-supported GDE at 31.9 mA cm^{-2} at 30 atm of CFC-13. ●, hydrogenation of CFC-13; ○, methane formation; ▽, HFC-23 formation; ◇, hydrogen formation.

increase in the current density and reached almost 0% at 380 mA cm^{-2}. The faradaic efficiency for the formation of hydrogen increased with an increase in current density. Hydrogen was the major product in the region where the current density was higher than 50 mA cm^{-2}. In the case of a Ag-supported GDE, the faradaic efficiency for hydrogenation also decreased with an increase in the current density with the slower rate of decrease in the faradaic efficiency than at the Cu-supported GDE; the faradaic efficiency for hydrogenation was approximately 55% at 120 mA cm^{-2} and 25% at 380 mA cm^{-2}.

Figure 2 shows the relationship between the pressure of CFC-13 and the faradaic efficiencies for hydrogenation and for product formation in electrolyses of CFC-13 at Cu- and Ag-supported GDEs. At both Ag- and Cu-supported GDEs, hydrogenation of CFC-13 hardly occurred at atmospheric pressure. Faradaic efficiencies for the formation of products in the electrochemical hydrogenation of CFC-13 increased with an increase in the pressure of CFC-13. This result could be attributable to the increase in the concentration of CFC-13 in the electrolyte solution with an increase in the pressure of CFC-13. Because of the low solubility of CFC-13, the production of hydrogen should be dominant at atmospheric pressure. As the concentration of CFC-13 in the solution increases in proportion to the pressure of CFC-13, according to Henry's law, reduction of CFC-13 would proceed more efficiently.

Judging from the effect of the pressure of CFC-13 on the efficiency for hydrogenation mentioned above, the proportion of methanol to water in the electrolyte solution is expected to affect the faradaic efficiency for hydrogenation. CFC-13 is relatively more soluble in methanol than in water. Therefore, the faradaic efficiency for hydrogenation of CFC-13 is expected to increase with an increase in the ratio of methanol in the electrolyte solution. Figure 3 shows the dependence of faradaic efficiencies for hydrogenation and for product formation in electrolyses of CFC-13 at Cu- and Ag-supported GDEs on the percentage of methanol in the electrolyte solution. At a Ag-supported GDE, the faradaic efficiency for hydrogenation of CFC-13 was 50% in water and increased with an increase in the percentage of methanol in the electrolyte solution, as was expected. In an electrolyte solution containing 70% methanol, the faradaic efficiency for hydrogenation of CFC-13 increased to 77.7%, with a high selectivity for HFC-23 formation (74.1% in faradaic efficiency). In a solution that contains more than 70% methanol, the electrolyte (1 M NaOH) was not soluble. The moderate activity for hydrogenation of CFC-13 in water could be attributed to a certain extent of the concentration of CFC-13 in water under high pressure. At a Cu-supported GDE, the faradaic efficiency for hydrogenation of CFC-13 increased with an increase in the percentage of methanol in the electrolyte solution until 50%. In the solution of 70% methanol, the faradaic efficiency for hydrogenation decreased
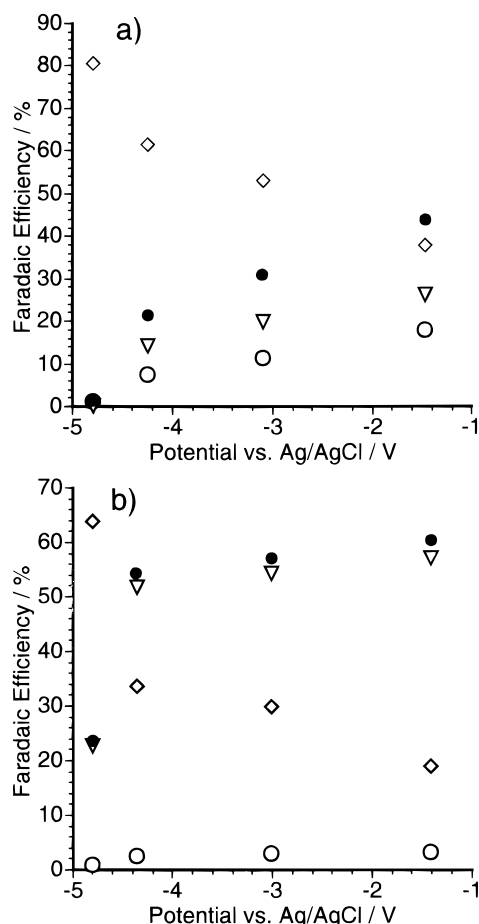
FIGURE 4. Relationship between the potential imposed on a GDE vs Ag/AgCl and the faradaic efficiencies for the hydrogenation of CFC-13 and for product formation at (a) Cu-supported GDE and (b) Ag-supported GDE at 30 atm of CFC-13 in 1:1 mixed solvent of methanol and water. ●, hydrogenation of CFC-13; ○, methane formation; ▽, HFC-23 formation; ◇, hydrogen formation.

suddenly. The activity of a Cu-supported GDE in water is lower than that of a Ag-supported GDE. This suggests that the adsorption of CFC-13 on the surface of Cu is weaker than that of Ag. The result in the solution of 70% methanol cannot be explained by the concentration of CFC-13. This would be elucidated by knowledge of the potential imposed on the GDEs during electrolyses. Figure 4 is the relationship between the steady potential during the electrolyses and the faradaic efficiencies for hydrogenation and for product formation. The faradaic efficiencies in Figure 1 are plotted again in Figure 4 vs the potential imposed on the GDE during electrolyses. At a Ag-supported GDE, the efficiency for hydrogenation of CFC-13 decreased gradually as the potential imposed on the cathode GDE was made more negative, until it reached −4.4 V. When the cathode potential was made more negative, the efficiency for hydrogenation of CFC-13 decreased steeply. The efficiency for hydrogenation of CFC-13 at a Cu-supported GDE decreased more rapidly with an increasingly negative potential than at a Ag-supported GDE. The efficiency for hydrogenation at a Cu-supported GDE at −4.3 V was about 20%, whereas that at a Ag-supported GDE was 50% at −4.4 V; i.e., a Ag-supported GDE is able to hydrogenate CFC-13 more efficiently at very negative potential than a Cu-supported GDE. The increasing negative potential shown in Figure 4 is accompanied by an increase in the current density at the GDE. The increasing negative potential is also related to the change in the electrolyte solution. The potential imposed on a GDE became more

negative with the increase in the ratio of methanol in the electrolyte solution due to the higher electrical resistance of a methanol solution as compared with that of an aqueous solution. The potential imposed on a Cu-supported GDE changed from −1.5 V in 50% methanol electrolyte solution to −3.2 V in 70% methanol electrolyte solution, whereas the potential on a Ag-supported GDE changed from −1.4 V in 50% methanol to −2.6 V in 70% methanol. As was shown in Figure 4, a Ag-supported GDE is able to hydrogenate CFC-13 even at −3 V. Therefore, the faradaic efficiency for hydrogenation of CFC-13 at a Ag-supported GDE should increase with an increase in the percentage of methanol in the electrolyte solution because of the increase in the concentration of CFC-13 in the electrolyte solution, even in 70% methanol electrolyte solution (Figure 3). At a Cu-supported GDE in the 70% methanol solution, it is disadvantageous to hydrogenate CFC-13 at −3.2 V, and the faradaic efficiency for hydrogenation decreases suddenly as was shown in Figure 3 in spite of the increase in the concentration of CFC-13 in the electrolyte solution.

In a previous paper (4), we presumed that the mechanism for the electrochemical hydrogenation of CFC-12 is as follows: (i) the adsorption of a CFC on the surface of the fine grain of metal on a GDE, (ii) the elimination of Cl^- ion induced by electron transfer from the GDE, and (iii) the elimination of F^- ion induced by electron transfer from the GDE. The second and third processes would be accompanied by hydrogenation due to the adsorbed hydrogen on the electrode surface. The first process would determine the electrocatalytic activity of metals supported on GDEs, and the third process would determine the final products of the electrolysis. The results of hydrogenation of CFC-13 can also be explained by this mechanism. In the electrochemical hydrogenation of CFC-12, a Cu-supported GDE produced methane and HFC-32 (CH_2F_2) with faradaic efficiencies of 36.6% and 15.5%, respectively. At a Ag-supported GDE, methane and HFC-32 were produced with faradaic efficiencies of 16.3% and 50.8%, respectively. HFC-32 was produced by the selective electrochemical dechlorination of CFC-12 in a manner similar to the production of HFC-23 in the electrolysis of CFC-13. In the electrochemical hydrogenation of CFC-13, as summarized in Table 1, faradaic efficiencies for methane formation and HFC-23 formation were 21.0% and 30.2% at a Cu-supported GDE and 3.3% and 57.0% at a Ag-supported GDE, respectively. For these metals, the faradaic efficiency for methane formation in hydrogenation of CFC-13 decreased as compared to that of CFC-12, whereas the faradaic efficiency for formation of HFCs (the faradaic efficiency for the selective dechlorination) increased. This change in electrocatalytic activity is explained according to the mechanism mentioned above. (i) CFC-13 would be adsorbed on the surface of these metals to a certain extent. (ii) Dechlorination would proceed efficiently, because dechlorination requires a smaller energy than does defluorination. (iii) Due to the stronger C−F bond of CFC-13 than that of CFC-12 (7−9), the defluorination of CFC-13 would proceed less efficiently than in the case of CFC-12. As a result of these three steps, the efficiency for the dechlorination increased, whereas that of the defluorination decreased. Pb and In, which showed no electrocatalytic activity for hydrogenation of CFC-13, exhibited high activity for the hydrogenation of CFC-12. Concerning these metals, the change in electrocatalytic activity might be attributable to the degree of adsorption on the surface of metals, i.e., CFC-13 seems hardly to be adsorbed on the surface of In and Pb.

From the results mentioned above, it is concluded as follows. Cu- and Ag-supported GDEs show electrocatalytic activity for hydrogenation of CFC-13. At a Cu-supported GDE, methane and HFC-23 are produced, whereas HFC-23 is produced selectively at a Ag-supported GDE. Optimizing

some of the experimental factors causes the faradaic efficiency for hydrogenation of CFC-13 to be improved up to 77.7%.

Acknowledgments

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