

Hydroformylation of Ethylene via Spontaneous Cell Reactions in the Gas Phase

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Received May 22, 1996; revised September 16, 1996; accepted September 30, 1996

A new method for the hydroformylation of ethylene using a gas cell composed of (C₂H₄, CO, cathode |H₃PO₄ aq. | anode (Pt-black), H₂) has been examined at ca. 373 K and atmospheric pressure. Among many cathode electrocatalysts tested, H₂PtCl₆ showed the highest selectivity and high activity for the formation of C₂H₅CHO. However, H₂PtCl₆ did not catalyze the reaction at all under a gas mixture of C₂H₄, CO, and H₂. H₂PtCl₆ was specifically active for the electrocatalytic hydroformylation by separating H₂ from C₂H₄ and CO with a H₃PO₄-electrolyte membrane. The addition of Na₃PO₄ to the cathode enhanced the rate of C₂H₅CHO formation as well as the selectivity. The cell reaction does not require electrical energy input but takes place spontaneously and most efficiently under short-circuit conditions. The results from kinetic and electrochemical studies have suggested that the catalytic active species is the Pt²⁺-chloride supported on the host graphite. A stronger coordination of CO compared to those of C₂H₄ and hydride reduces both the hydrogenation and hydroformylation of C₂H₄. Therefore, a low partial pressure of CO and higher partial pressures of C₂H₄ and H₂ are recommended for the conversion of C₂H₄. The optimum temperature for the hydroformylation was 373 K. The results of transition response experiments have suggested a rapid reversible coordination of C₂H₄ but a slow conversion of the precursor of C₂H₅CHO on the Pt²⁺ sites. A tentative reaction mechanism assuming the formations of ethyl-carbonyl, ethyl-carbonyl hydride and acyl-carbonyl Pt complexes has been proposed on the bases of the results in this work.

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INTRODUCTION

The electrocatalytic synthesis of organic chemicals has several advantages compared to the thermal catalytic ones. These are (i) the electrocatalytic reactions can be operated at low temperatures by the control of potential at the electrode-substrate interface, thus serving as an alternative to a drive of catalytic reactions at high temperatures, which is favorable on the singular basis of catalytic selectivity because the application of elevated temperatures initiates undesirable reaction pathways; (ii) the product selectivities and the reaction rate are easily controlled by an externally applied potential; (iii) the electrocatalytic reaction can be performed by separating one of the reactants from the oth-

ers using an electrolyte membrane as the separator, which would diminish the danger of explosion (in the case of oxidation) or prevent undesirable side reactions, and (iv) the electrocatalytic synthesis can be operated as a cell reaction cogenerating useful chemicals and electric power output.

Hydroformylation of olefins, the reaction of olefins with synthesis gas, in the presence of homogeneous catalysts to form aldehydes containing an additional carbon atom is commercially applied for making higher aldehyde and alcohols from olefins (Oxo process). These include bulk products as well as high-value specialty products. In general, the hydroformylation reaction is operated under high pressures (15–300 atm). A variety of transition metal complexes catalyze the hydroformylation reaction, but only cobalt and rhodium carbonyl complexes are used in commercial Oxo plants.

As far as we know, no one has ever tested the electrocatalytic hydroformylation of olefins. We expect that the electrocatalytic reaction might occur under atmospheric pressure if we chose a suitable electrocatalyst. This novel technique, if it works, may meet the new requirements imposed upon industry for environmentally acceptable and energy saving routes, utilizing readily obtainable and less expensive materials. Thus, the purpose of this work is first to design an electrochemical cell for the hydroformylation of ethylene as an example of olefins in the gas phase. Second, the suitable catalysts for the reaction are explored extensively. The electrocatalytic performance of the best catalytic system is described in detail and the reaction mechanism for the hydroformylation of ethylene is discussed on the bases of kinetic and electrochemical studies on the reaction.

The hydroformylation of ethylene (Eq. [1]) is a highly exothermic ($\Delta H^\circ = -129.0$ kJ/mol) and downhill ($\Delta G^\circ = -56.9$ kJ/mol) reaction:



Therefore, we expect that this reaction can be operated as a cell reaction by separating hydrogen from ethylene and carbon monoxide by a membrane holding an acid electrolyte such as an aqueous H₃PO₄ where the anode

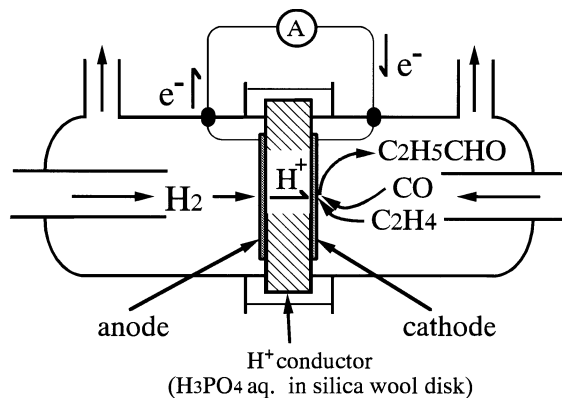
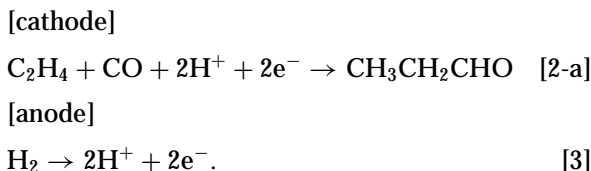


FIG. 1. Schematic diagram of the cell reactor and the principle of the method for hydroformylation of ethylene.

and cathode electrocatalysts are attached on both sides of the membrane. If we select an appropriate electrocatalyst at the cathode, the reaction must proceed spontaneously when the anode and the cathode is shorted with a lead wire as demonstrated in Fig. 1. The catalytic hydroformylation of ethylene has been divided into the cathode and anode reactions as follows:



Several advantages of the method of Fig. 1 may be worth noting here. (i) The catalyst for the hydroformylation of olefins is in general required to have the ability to activate of all the reactants, i.e., olefins, carbon monoxide, and hydrogen. The method of Fig. 1 would loosen this requirement for the catalyst, viz., the electrocatalyst at the anode is required only to activate hydrogen and that at the cathode to activate ethylene and carbon monoxide. (ii) Since the hydroformylation of ethylene in Fig. 1 is performed in the gas phase, the analysis and the separation of products are simplified. (iii) Application of a load in the outer circuit cogenerates electricity during the synthesis of propionaldehyde.

EXPERIMENTAL

The size of the cell (Fig. 1) in this study was of 10 cm length and 2.2 cm inner diameter. A detailed description of the cell setup has been described elsewhere (1). The silica-wool disk used as the separator of the two compartments in the cell was obtained from Toyo Filter Co. The wool disk was made from borosilicate (26 mm diameter, 1 mm thickness, and 114 mg weight). The pore volume of the wool disk was $4.1 \text{ cm}^3 \text{ g}^{-1}$. The silica-wool disk was impregnated with 0.8 g of 14.7 M H_3PO_4 aqueous solution. The electrolyte (H_3PO_4)

containing membrane was sandwiched by porous, catalytic electrodes. The cell was connected to a conventional gas-flow system.

The anode was prepared from Pt-black (20 mg) mixed with graphite (50 mg) and Teflon powder (5 mg). The mixture was pressed and shaped into a round wafer (20 mm diameter and ca. 0.1 mm thickness) on a hot plate (393 K) with a stainless steel roller. Pt-black was always used as the anode electrocatalyst because its ability for the activation of hydrogen (Eq. [3]) was sufficiently high under the reaction conditions in this work.

The cathode was prepared by the same procedure as for the anode from a physical mixture of graphite and various metal blacks or powder. Various metal chlorides used as electrocatalysts were added to the graphite (70 mg) by the impregnation and dryness method using aqueous solutions of the chlorides. The metal chloride-added graphite (100 mg) mixed with Teflon powder (5 mg) was pressed and shaped to a wafer (superficial area 3.1 cm^2).

A gas mixture of ethylene and carbon monoxide was passed in the cathode compartment. Hydrogen and water vapor (added to keep the electrolyte wet) were passed through the anode compartment. The partial pressure of water vapor (16 kPa) was adjusted by passing hydrogen through a water evaporator at 328 K. All the experiments were carried out under atmospheric pressure for both compartments. Prior to each run of experiment, a gas mixture of ethylene and carbon monoxide had been passed for ca. 60 min under open-circuit conditions. The reaction was started after this treatment by applying potential across the cell or by shorting the circuit. The hydroformylation of ethylene was usually tested under the following standard conditions unless otherwise stated: short-circuit, reaction temperature = 393 or 353 K; anode; $P(\text{H}_2) = 85$, $P(\text{H}_2\text{O}) = 16$ kPa, total flow rate = 30 ml (STP) min^{-1} , cathode; $P(\text{C}_2\text{H}_4) = 90$, $P(\text{CO}) = 11$ kPa, total flow rate = 20 ml (STP) min^{-1} .

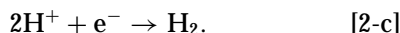
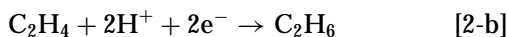
The effluents of reactant and product gases were analyzed by an on-line gas chromatography at different predetermined intervals. The current and the applied potentials across the cell were monitored by a multimeter (Yokokawa 2506A). The anode and the cathode potentials were measured during the reaction by a potentiostat-galvanostat (Hokuto HE-104) and a standard Ag/AgCl electrode (0.196 V vs NHE) with a KCl salt bridge capillary inserted to the electrolyte (H_3PO_4) in a silica-wool disk at the center of the cell (Fig. 1). A detailed setup of the system for the measurement of the potentials has been demonstrated elsewhere (2).

All the reagents used in this work were extrapure grade purchased from Wako Pure Chemical, Kanto Chemical, Soekawa Rikagaku, or Aldrich. The ethylene, carbon monoxide, hydrogen, and helium used were certified standard (purity >99.95%) obtained from Takachiho Chemical

Ind. The graphite (Wako) used as the supporter of the electrocatalysts as well as the current collector were pre-treated in HCl and HNO₃ aqueous solutions and thoroughly washed with distilled water.

All the experiments in this work were performed using fresh electrodes and silica-wool disks with a fresh electrolyte (H₃PO₄ aq.). The reproducibility for the preparation of a set of the electrode-electrolyte system was examined on the basis of the rate of the formation of each product under the same experimental conditions. Carefully prepared electrode-electrolyte systems showed a good reproducibility within the experimental error of ±10%.

The cathode reactions expected other than the hydroformylation are hydrogenation of ethylene (Eq. [2b]) and hydrogen evolution (Eq. [2c]).



The current measured under steady-state progress of the reaction, usually 30 min after shorting the outer circuit, corresponded well with the value calculated from the amounts of the products obtained at the cathode within the experimental error of ±5%. Thus, the current efficiency for the steady-state formation of propionaldehyde (denoted as PA C.E.) was evaluated from the rate of propionaldehyde formation and the current. The selectivity to propionaldehyde was defined by the percentage of the propionaldehyde in the total amount of products (C₂H₅CHO + C₂H₆).

RESULTS AND DISCUSSION

a. Look for an Effective Electrocatalyst

Because there is no information about an electrocatalyst ever reported for the electrochemical hydroformylation, we have first looked for the active electrocatalysts at the cathode for the formation of propionaldehyde. A Pt-black mixed with graphite was always used as an anode electrocatalyst as described under Experimental. The cathode electrocatalysts tested in this work were Pt-black, Pd-black, Rh-black, Co powder, H₂PtCl₆, H₂PtCl₄, PdCl₂, RhCl₃, RuCl₃, IrCl₃, OsCl₃, FeCl₂, MnCl₂, CoCl₂, NiCl₂, CuCl₂, AgCl, HAuCl₄, LaCl₃, SmCl₃, and EuCl₃. These catalysts (20 wt%) were mixed with graphite and Teflon powder. The mixture was pressed and shaped into a wafer by the hot-press method. The catalytic test was performed under standard experimental conditions at an externally applied voltage of 0.30 V. The first series transition metal chlorides, AgCl, and rare-earth metal chlorides did not catalyze the hydroformylation and hydrogenation of ethylene. Pt-black, Pd-black, RuCl₃, IrCl₃, and OsCl₃ catalyzed the hydrogenation of ethylene considerably but did not the hydroformylation at all. The results for noble metal-blacks and chlorides are summarized in Table 1. Among the cath-

TABLE 1

Electrocatalytic Function of the Cathodes with Various Additives for Hydroformylation of Ethylene

Cathode	Products (mmol h ⁻¹ m ⁻²)		CD ^a (A m ⁻²)	C ₂ H ₅ CHO select. (%)	CE ^b of C ₂ H ₅ CHO (%)
	C ₂ H ₄	C ₂ H ₅ CHO			
Gr	0	0	72.7	0	0
Pt-black/Gr	93.6	0	134.3	0	0
Pd-black/Gr	370.0	0	70.0	0	0
Rh-black/Gr	526.0	4.8	122.3	0.9	0.21
H ₂ PtCl ₄ /Gr	89.8	6.4	119.7	6.7	0.29
H₂PtCl₆/Gr	134.6	11.4	161.7	7.8	0.38
PdCl ₂ /Gr	1230.0	23.0	133.3	1.8	0.93
RhCl ₃ /Gr	166.0	5.8	127.3	3.4	0.24
RuCl ₃ /Gr	216.0	0	137.7	0	0
IrCl ₃ /Gr	169.8	0	136.0	0	0
OsCl ₃ /Gr	119.4	0	174.0	0	0
CoCl ₂ /Gr	0	0	43.0	0	0

Note. Temperature = 393 K. Applied voltage = +0.3 V. Cathode: [additives (30 wt%)/graphite] electrode, P(C₂H₄) = 90 kPa, P(CO) = 10 kPa, F = 20 ml/min. Anode: [Pt-black/graphite] electrode, P(H₂) = 85 kPa, P(H₂O) = 16 kPa, F = 30 ml/min.

^a Current density.

^b Current efficiency.

odes listed in Table 1, the cathodes of PdCl₂, H₂PtCl₆, and H₂PtCl₄ showed relatively high rate of C₂H₅CHO formation. Although the formation rate was the highest for the PdCl₂ cathode, the selectivity to C₂H₅CHO was quite low because of a rapid formation of C₂H₆. In contrast, the selectivity to C₂H₅CHO was the highest for H₂PtCl₆. The formation rate of C₂H₅CHO for this cathode was the second highest in Table 1. Therefore, we have selected the H₂PtCl₆/Gr as the most suitable cathode for the synthesis of C₂H₅CHO.

The optimum content of H₂PtCl₆ in the graphite for the formation rate and the selectivity of C₂H₅CHO was investigated under an applied voltage of 0.30 V. The rates of C₂H₅CHO formation increased linearly with the content of H₂PtCl₆ in the range of 0 to 50 μmol in 50 mg of graphite. The rate showed maximum at 50 μmol of H₂PtCl₆ and decreased above this content. Therefore, the content of H₂PtCl₆ hereafter was adjusted to be 50 μmol (29 wt%) in 50 mg of graphite.

b. Catalytic (Nonelectrochemical) Hydroformylation of Ethylene

There are many reports concerning the heterogeneous catalytic hydroformylation of ethylene using Rh-based catalysts (3–7). However, H₂PtCl₆ has not been recognized as a catalyst for the hydroformylation of ethylene. We have examined the nonelectrochemical catalytic abilities of the two electrodes (RhCl₃ (30 wt%)/Gr and H₂PtCl₆ (30 wt%)/Gr) in a gas mixture of C₂H₄, CO, and H₂ (C₂H₄:CO:H₂ = 61:7:7 (kPa) to 61:7:33 (kPa)) in the

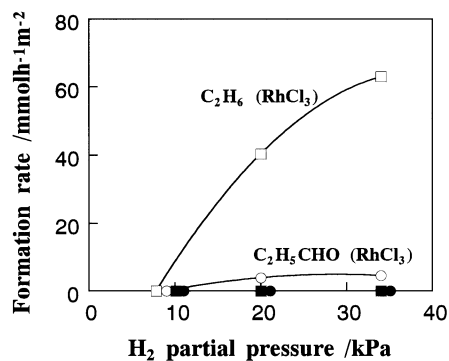


FIG. 2. Catalytic hydroformylation of ethylene in a mixture of C_2H_4 , CO, and H_2 . H_2PtCl_6/Gr (●, ■); $RhCl_3/Gr$ (○, □). Formation rate of C_2H_5CHO (●, ○); formation rate of C_2H_6 (■, □).

cathode compartment of the same reactor in Fig. 1. The reaction was tested under open circuit conditions at 393 K by changing the partial pressure of hydrogen. Helium (85 kPa) and water vapor (16 kPa) were passed through the anode compartment of Fig. 1. The rates of product formation observed are plotted as functions of the partial pressure of hydrogen in Fig. 2. The catalytic reaction over the H_2PtCl_6/Gr did not occur under the experimental conditions in Fig. 2. However, the catalytic hydroformylation and hydrogenation of ethylene proceeded over the $RhCl_3/Gr$ at a partial pressure of hydrogen greater than 20 kPa in Fig. 2. In contrast with these nonelectrocatalytic results, the electrocatalytic activity of the H_2PtCl_6/Gr for the formation of C_2H_5CHO was twice as great as that of the $RhCl_3/Gr$.

c. Effect of Various Additives

For the homogeneous catalytic systems based on Co or Rh complexes, the presence of an excess amount of triphenyl phosphine (PPh_3) is indispensable for the stability of the catalysts as well as for high catalytic performance of the complexes (8, 9). Therefore, it is interesting to examine the effect of PPh_3 added to the H_2PtCl_6/Gr and $RhCl_3/Gr$ cathodes. The addition of PPh_3 with 10 to 100 μmol to H_2PtCl_6 (50 μmol)/Gr completely diminished the electrocatalytic activity of the H_2PtCl_6 for the formation of C_2H_5CHO . The same was true of $RhCl_3/Gr$. Therefore, it seems that no enhancing effect of PPh_3 is expected on the electrochemical hydroformylation for ethylene using the H_2PtCl_6 or $RhCl_3$ cathode.

The effects of additives of various metal chlorides instead of PPh_3 were investigated by adding 30 μmol of the additives to the H_2PtCl_6 (50 μmol)/Gr cathode under standard reaction conditions. The chlorides of Fe, Co, Ni, Sm, Pd, Au, and Sn enhanced both reactions, i.e., hydrogenation and hydroformylation of ethylene as well as current density. However, these compounds reduced the current efficiency of the formation of C_2H_5CHO . The additives improving both the formation rate and the current efficiency

of C_2H_5CHO were NaCl and other Na salts. The results for the Na salts are summarized in Table 2. The experiments were performed at 353 K and under short-circuit conditions. As can be seen in this table, NaCl, Na_3PO_4 , Na_2HPO_4 , NaOH, Na_2CO_3 , and Na_2SO_4 enhanced the rate of C_2H_5CHO formation, the current efficiency, and the selectivity of C_2H_5CHO . Among the cathodes with these additives, the Na_3PO_4 -added H_2PtCl_6/Gr showed reproducible and stable electrocatalytic activity compared to the others.

The electrocatalytic performance of the H_2PtCl_6 (50 μmol)/Gr cathode as a function of the amount of Na_3PO_4 added were examined under standard reaction conditions. The results are shown in Fig. 3. As can be seen from this figure, the addition of Na_3PO_4 enhanced the rate of C_2H_5CHO formation as well as the selectivity and the current efficiency of C_2H_5CHO . In contrast with C_2H_5CHO formation, the hydrogenation of ethylene was enhanced only slightly with the amount of Na_3PO_4 at <100 μmol , but decreased considerably at >100 μmol . The results in Fig. 3 indicate that the maximum in the formation rate of C_2H_5CHO and in the current efficiency of C_2H_5CHO are obtained at 200 μmol of Na_3PO_4 . Therefore, we have chosen the H_2PtCl_6 (50 μmol)/graphite (50 mg) added with 200 μmol of Na_3PO_4 as the most favorable electrocatalyst for the electrolytic hydroformylation of ethylene. This cathode is denoted as $H_2PtCl_6 \cdot Na_3PO_4/Gr$, hereafter.

d. Hydroformylation as a Function of the Applied Voltage

The effects of applied voltage across the cell on the hydroformylation and hydrogenation of ethylene over the $H_2PtCl_6 \cdot Na_3PO_4/Gr$ cathode are indicated in Fig. 4. The rates of both reactions were enhanced with increasing

TABLE 2
Effect of Additives on the Electrocatalytic Function of H_2PtCl_6/Gr

Cathode	Products (mmol h ⁻¹ m ⁻²)		CD ^a (A m ⁻²)	C ₂ H ₅ CHO select. (%)	CE ^b of C ₂ H ₅ CHO (%)
	C ₂ H ₆	C ₂ H ₅ CHO			
H_2PtCl_6/Gr	89.4	9.6	13.0	9.6	3.9
H_2PtCl_6/Gr with additives					
+ NaCl	98.4	13.4	13.3	11.9	5.4
+ Na_3PO_4	79.4	12.2	13.8	13.4	4.7
+ Na_2HPO_4	71.0	13.6	15.0	16.1	4.9
+ NaOAc	74.2	10.4	15.0	12.4	3.8
+ NaOH	92.8	14.4	17.0	13.4	4.6
+ Na_2CO_3	72.0	10.8	12.7	13.1	4.6
+ Na_2SO_4	112.2	15.2	17.7	11.9	4.6

Note. Short-circuit conditions; temperature = 353 K. Cathode: [H_2PtCl_6 (50 μmol) + Na salts (30 μmol)/graphite] electrode, $P(C_2H_4) = 90$ kPa, $P(CO) = 10$ kPa, $F = 20$ ml/min. Anode: [Pt-black/graphite] electrode, $P(H_2) = 85$ kPa, $P(H_2O) = 16$ kPa, $F = 30$ ml/min.

^a Current density.

^b Current efficiency.

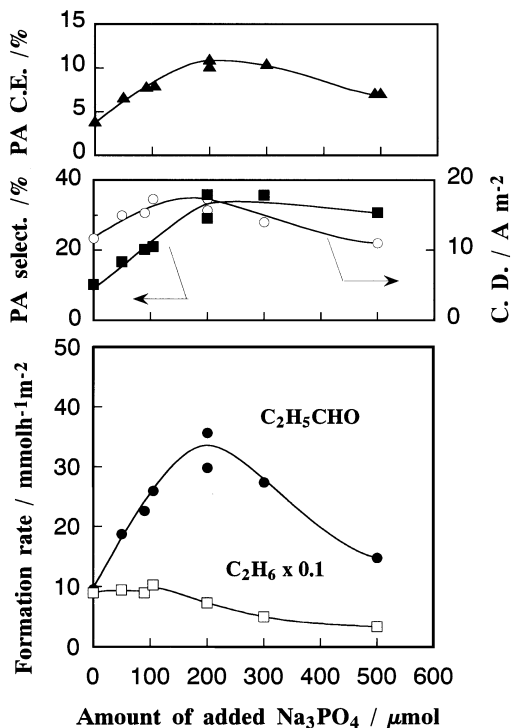


FIG. 3. Effect of Na_3PO_4 on the electrocatalytic hydroformylation of ethylene with $\text{H}_2\text{PtCl}_6/\text{Gr}$ at 353 K. Standard reaction conditions (see text). Formation rate of $\text{C}_2\text{H}_5\text{CHO}$ (●); formation rate of C_2H_6 (□); $\text{C}_2\text{H}_5\text{CHO}$ selectivity (■); current density (CD) (○); current efficiency (CE) for $\text{C}_2\text{H}_5\text{CHO}$ formation (▲).

applied voltage. The selectivity to $\text{C}_2\text{H}_5\text{CHO}$ did not change appreciably, but the current efficiencies for the formation of $\text{C}_2\text{H}_5\text{CHO}$ and for the total products ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_5\text{CHO}$) were dramatically decreased with the applied voltage because most of the current under applied voltage can be ascribed to the pumping of hydrogen from the anode to the cathode through H_3PO_4 -electrolyte in a silica-wool disk used as the separator for the two compartments. The amount of hydrogen evolved into the cathode compartment without reacting with ethylene was quantitatively analyzed during the electrolysis. The sum of the amount of hydrogen thus measured and those of C_2H_6 and $\text{C}_2\text{H}_5\text{CHO}$ produced corresponded well to the charge passed. The hydroformylation of ethylene under an externally applied voltage should be avoided because the current efficiency becomes extremely low as described above. Therefore, further studies will be performed always under short-circuit conditions.

e. Effect of the Concentration of the Electrolyte (H_3PO_4)

In order to know the optimum concentration of the electrolyte in a silica wool disk for the hydroformylation of ethylene, the reaction was examined at different concentration of H_3PO_4 at 353 K. The results indicated that the

rate of hydroformylation, the selectivity to $\text{C}_2\text{H}_5\text{CHO}$, and the current efficiency were all improved with a rise in the concentration of H_3PO_4 from 7.4 to 14.7 M.

f. Effects of the Partial Pressures of H_2 , CO , and C_2H_4

The partial pressure of hydrogen in the anode compartment markedly affected the current and the rates of both reactions under short-circuit conditions at 353 K. The current density and the rates of hydrogenation and hydroformylation increased about five times with a rise in the pressure of hydrogen at the anode from 10 to 85 kPa. However, the current efficiency and the selectivity to $\text{C}_2\text{H}_5\text{CHO}$ was not influenced appreciably by the pressure of hydrogen.

The effects of CO pressure in the cathode compartment on both reactions are shown in Fig. 5. The rates of both reactions as well as the current were reduced with increasing the partial pressure of CO . However, the selectivity to $\text{C}_2\text{H}_5\text{CHO}$ was not affected appreciably.

In contrast with the effect of CO pressure, the formation rates of both $\text{C}_2\text{H}_5\text{CHO}$ and C_2H_6 were enhanced markedly with a rise in the partial pressure of C_2H_4 (Fig. 6). The increase in the current, however, was not appreciable in contrast with the marked enhancements in the formations of both products. Thus, the current efficiencies for both products were improved at high partial pressure of C_2H_4 .

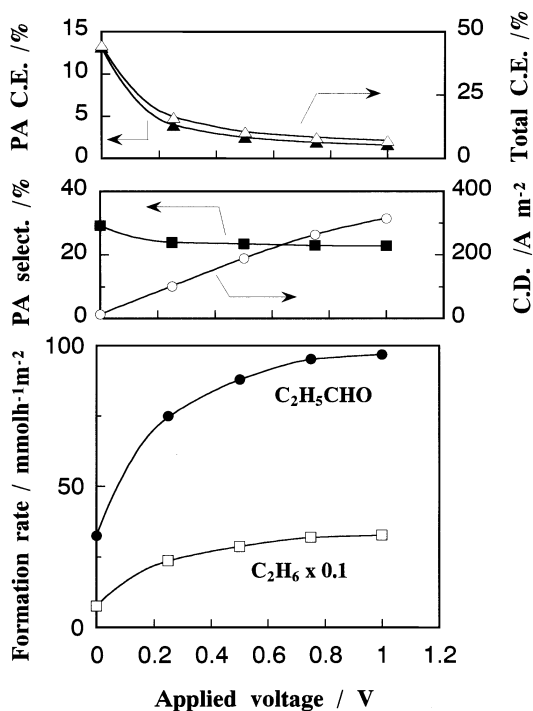


FIG. 4. Hydroformylation and hydrogenation of ethylene over $\text{H}_2\text{PtCl}_6 \cdot \text{Na}_3\text{PO}_4/\text{Gr}$ at 353 K as functions of applied voltage. Under standard conditions. Formation rate of $\text{C}_2\text{H}_5\text{CHO}$ (●); formation rate of C_2H_6 (□); $\text{C}_2\text{H}_5\text{CHO}$ selectivity (■); current density (CD) (○); current efficiency (CE) for $\text{C}_2\text{H}_5\text{CHO}$ formation (▲); current efficiency for the sum of $\text{C}_2\text{H}_5\text{CHO}$ and C_2H_6 (△).

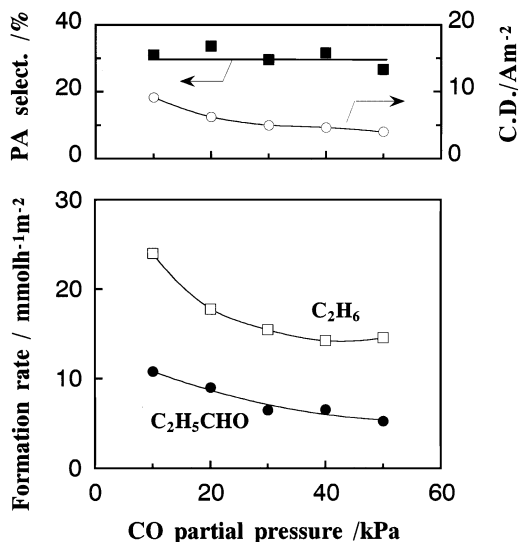


FIG. 5. Effect of the partial pressure of CO under standard conditions ($T = 353$ K). Formation rate of C_2H_5CHO (●); formation rate of C_2H_6 (□); C_2H_5CHO selectivity (■); current density (CD) (○).

g. Effect of Temperature

Figure 7 shows the temperature effect on the reactions under standard conditions except for changing temperature. C_2H_5CHO was not formed when temperature was decreased to 313 K. The formation of C_2H_5CHO depended

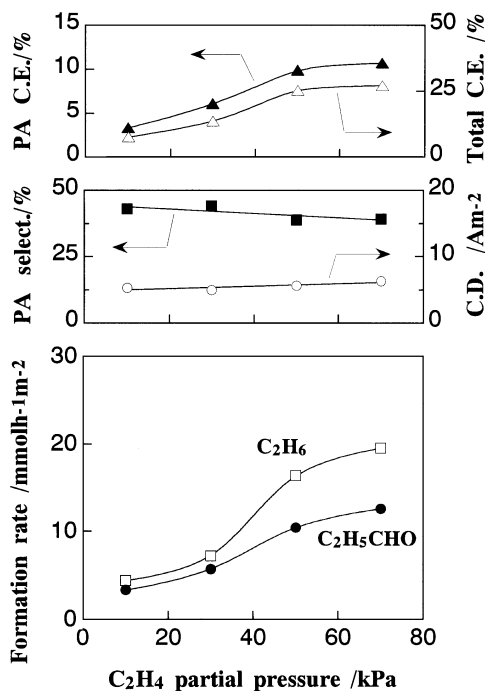


FIG. 6. Effect of the partial pressure C_2H_4 . Formation rate of C_2H_5CHO (●); formation rate of C_2H_6 (□); C_2H_5CHO selectivity (■); current density (CD) (○); current efficiency (CE) for C_2H_5CHO formation (▲); current efficiency for the sum of C_2H_5CHO and C_2H_6 (△).

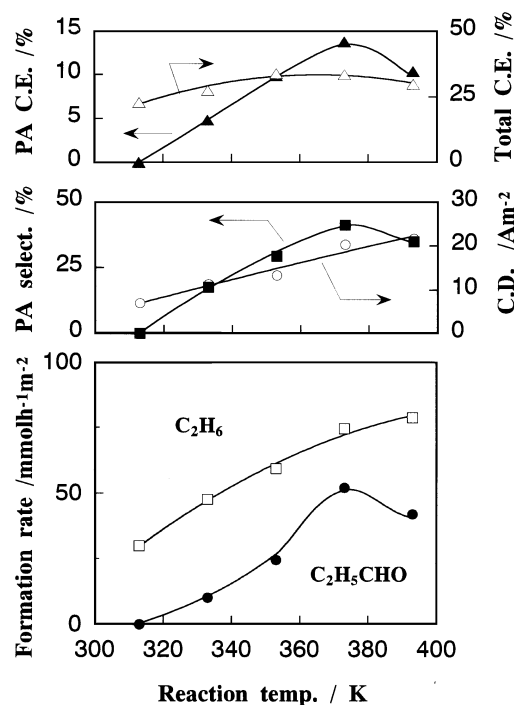


FIG. 7. Effect of reaction temperature. Formation rate of C_2H_5CHO (●); formation rate of C_2H_6 (□); C_2H_5CHO selectivity (■); current density (CD) (○); current efficiency (CE) for C_2H_5CHO formation (▲); current efficiency for the sum of C_2H_5CHO and C_2H_6 (△).

strongly on temperature compared to that of C_2H_6 . The plot of logarithm of the rate against $1/T$ for the data in the temperature range of 333 to 373 K in Fig. 7 gave the apparent activation energies of 12 and 43 kJ mol^{-1} for hydrogenation and hydroformylation of ethylene, respectively. The C_2H_5CHO formation has quite higher apparent activation energy than that of C_2H_6 . However, the formation rate of C_2H_5CHO did not increase but decreased at >373 K. The reason for this phenomenon is not known at the moment. The results in Fig. 7 indicate that the optimum temperature for the formation of C_2H_5CHO is 373 K. The maximum current efficiency (13%) and the maximum selectivity (42%) to C_2H_5CHO were obtained at this temperature.

Studies on the Reaction Mechanism

i. The working state of Pt-chloride. The cathode and anode potentials under standard reaction conditions at 353 K were measured with reference to a $Ag/AgCl$ reference electrode (0.196 vs NHE). Under open-circuit conditions at the same temperature and under the same gas flow conditions, the cathode ($H_2PtCl_6 \cdot Na_3PO_4/Gr$) and anode (Pt-black/Gr) potentials were 0.05 and -0.13 V (vs $Ag/AgCl$), respectively. Thus, the terminal voltage across the cell was 0.18 V. The shorting of the circuit decreased the cathode potential considerably and increased the anode potential slightly to -0.11 V (vs $Ag/AgCl$). These results indicate a greater overpotential at the cathode side than that at the

anode during the hydroformylation under standard reaction conditions.

The standard redox potential of Pt^{2+} and Pt^{4+} were indicated as follows (10).

	Standard potential/V (vs Ag/AgCl)
$\text{PtCl}_4^{2-} + 2e^- = \text{Pt}^0 + 4\text{Cl}^-$	0.56
$\text{PtCl}_6^{2-} + 2e^- = \text{PtCl}_4^{2-} + 2\text{Cl}^-$	0.53

On the bases of these potentials, thermodynamically, the Pt^{4+} added to the cathode could be reduced to Pt^0 under standard reaction conditions because the cathode potential was -0.11 V (vs Ag/AgCl) as described above. However, if the working species in the H_2PtCl_6 -added cathode is the platinum metal, we cannot expect the formation of $\text{C}_2\text{H}_5\text{CHO}$ because the Pt-black/Gr cathode cannot produce $\text{C}_2\text{H}_5\text{CHO}$ at all (see Table 1). Moreover, it should be noted that the $\text{H}_2\text{Pt(II)Cl}_4/\text{Gr}$ cathode in Table 1 showed comparable selectivity and current efficiency of the $\text{C}_2\text{H}_5\text{CHO}$ formation with those for the $\text{H}_2\text{Pt(IV)Cl}_4/\text{Gr}$ cathode. These observations suggest that the oxidation state of platinum in the $\text{H}_2\text{PtCl}_6 \cdot \text{Na}_3\text{PO}_4/\text{Gr}$ cathode could be Pt^{2+} effective for the electrocatalytic synthesis of $\text{C}_2\text{H}_5\text{CHO}$.

ii. Cathode reaction with CO or C_2H_4 alone. The electrocatalytic reaction of CO or C_2H_4 alone in the cathode compartment might provide useful information for the reactions in the presence of both reactants. Figure 8 shows the response of the current density after switching on and off the CO gas flow under short-circuit conditions at 353 K, where hydrogen (85 kPa) has always been passed through the anode compartment. When pure helium was passed through the cathode compartment at the time on stream of 0 to 1 h, a considerable current flowed due to the hydrogen transfer from the anode to the cathode driven by the

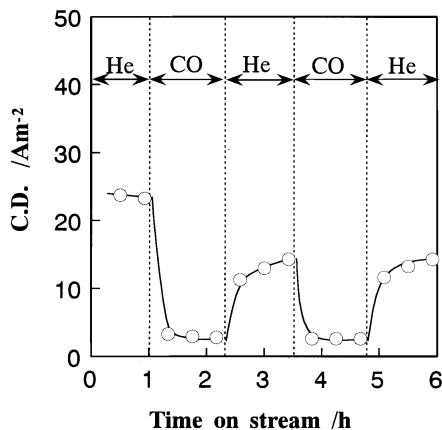


FIG. 8. The response of current to switching on and off the CO gas flow under standard conditions ($T = 353$ K).

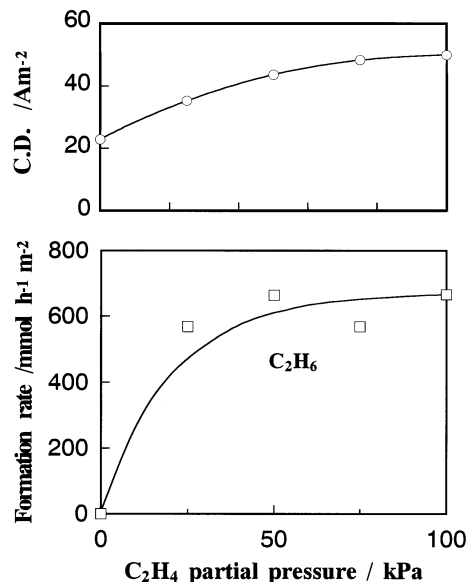


FIG. 9. Hydrogenation of C_2H_4 as a function of the partial pressure of C_2H_4 in the absence of CO. Formation rate of C_2H_6 (\square); current density (\circ).

difference in hydrogen pressure between the anode and the cathode. The addition of CO (30 kPa) to helium (total pressure, 101 kPa) at a time on stream of 1 h markedly decreased the current as can be seen in Fig. 8. The switching off CO at 2.3 h recovered the current to ca. 60% of the initial value. The current responded reversibly to the subsequent addition and removal of CO as indicated in Fig. 8. The results of Fig. 8 suggest that the CO adsorbed on the cathode strongly retards the evolution of hydrogen from the cathode. However, a part of the CO adsorbed can desorb by switching off the stream of CO. It was confirmed that no product due to the hydrogenation of CO was obtained during the experiments of Fig. 8.

The addition of C_2H_4 to the helium carrier at the cathode compartment in the absence of CO but in the presence of hydrogen (85 kPa) at the anode initiated the hydrogenation of C_2H_4 under short-circuit conditions. The change in the rate of C_2H_6 formation and in the current density observed are plotted in Fig. 9 as functions of the partial pressure of C_2H_4 in the cathode compartment. The feeding of C_2H_4 increased the current due to the hydrogenation of C_2H_4 to C_2H_6 .

iii. Transient response of the products after cut off C_2H_4 or CO. A dynamic response of the formation of products after switching off or on the stream of the reactants (C_2H_4 and CO) at the cathode might give us useful information about the reaction mechanism. Therefore, we have observed the responses in the current and in the formation rates of the products (C_2H_6 and $\text{C}_2\text{H}_5\text{CHO}$) after cut off or resumption of a flow of C_2H_4 or CO under standard reaction conditions at 353 K. The total flow rate was always

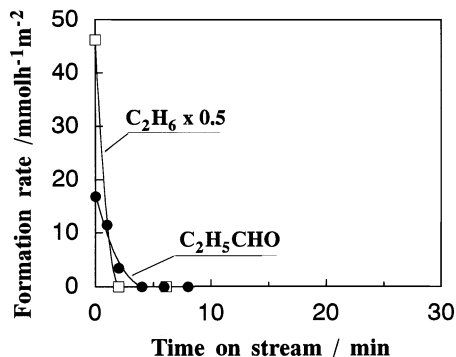


FIG. 10. Changes in the apparent formation rates of C_2H_6 and C_2H_5CHO after opening the external circuit under standard conditions ($T = 353$ K). C_2H_5CHO (●); C_2H_6 (□).

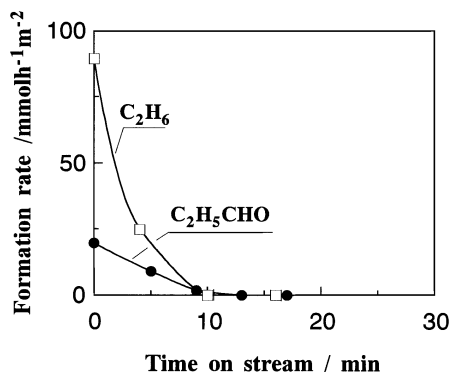


FIG. 11. Transient response of the formations of C_2H_5CHO and C_2H_6 after switching off C_2H_4 flow. C_2H_5CHO (●); C_2H_6 (□).

kept constant (20 ml min^{-1}) in these experiments by compensating with helium flow.

Before demonstrating the results after cutting off either of the reactants, it is necessary to estimate the required time for displacing the products by a feed gas flow from the cathode compartment as well as from the gas line from the exit of the reactor to the sampling position at standard reaction conditions in this work. From the results in Fig. 10, we can evaluate the time on stream needed for a gas to be expelled from the cathode compartment and the gas line to the sampling position. The results in Fig. 10 show the changes in the apparent formation rates of C_2H_6 and C_2H_5CHO measured at the sampling position after opening the external circuit under standard conditions at 353 K. As can be seen from this figure, C_2H_6 and C_2H_5CHO have not been detected after 2 and 4 min, respectively. Since the electrochemical reaction never occurs at open circuit conditions, the results in Fig. 10 indicate that the displacement of the products from the cathode compartment under our experimental conditions requires less than 4 min. The fact that a longer time is necessary to remove C_2H_5CHO than that for C_2H_6 may suggest a slower desorption of C_2H_5CHO compared to that of C_2H_6 from the cathode.

When a flow of C_2H_4 was cut off after a steady-state reaction of C_2H_4 with CO had been established, both products (C_2H_6 and C_2H_5CHO) in the cathode compartment became undetectable within 8 min. The resumption of the flow of C_2H_4 recovered the same current and the same formation rate for both products within 5 min as those observed before the cut off C_2H_4 . The response for the formations of C_2H_6 and C_2H_5CHO after cutting off the flow of C_2H_4 are indicated in Fig. 11. After the reaction under standard conditions at 353 K for 2 h, the flow of C_2H_4 was stopped at zero time in Fig. 11. The formation of both products terminated in 8 min after this operation, as can be seen in this figure. If one compares the kinetic curves in Fig. 11 with those in Fig. 10, it is suggested that formations of both C_2H_6 and C_2H_5CHO continue for several minutes under short-circuit conditions after cutting off the flow of C_2H_4 .

Figure 12 shows the response of the formation rates of C_2H_6 and C_2H_5CHO under short-circuit conditions after switching off only the flow of CO from the mixture of CO, C_2H_4 , and He. It should be noted that the formation rate of C_2H_5CHO does not decrease but rather increases at 5 min and then decreases gradually with the time on stream. The formation of C_2H_5CHO continued for 23 min as can be seen in Fig. 12. The formation of C_2H_6 was enhanced remarkably with the decrease in the formation of C_2H_5CHO . The formation rate of C_2H_6 reached a plateau when the formation of C_2H_5CHO terminated. These observations strongly suggest that the electrocatalytic active sites or the reaction intermediates are identical for the two products. The continuous formation of C_2H_5CHO after cutting off the flow of CO suggests that one of the precursors of C_2H_5CHO is accumulated on the catalytic active sites without quickly converting into C_2H_5CHO or back into the reactants (C_2H_4 and CO). The precursor must be reduced electrochemically during the stay on the active site. The dramatic enhancement in the formation of C_2H_6 when CO has been removed suggests the competitive coordination of CO and C_2H_4 to the active platinum chloride during the hydroformylation of C_2H_4 . The results in Fig. 11 and those from separate experiments

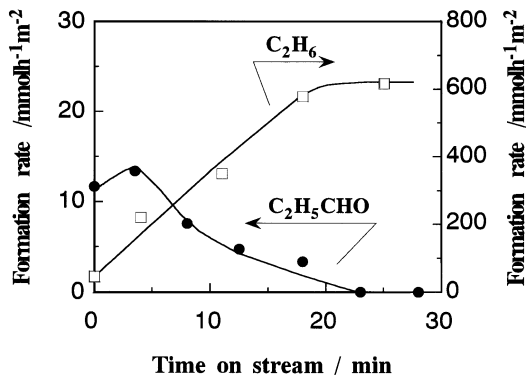


FIG. 12. Transient response of the formations of C_2H_5CHO and C_2H_6 after switching off CO flow. C_2H_5CHO (●); C_2H_6 (□).

indicated that the formation of C_2H_6 was terminated within 6 min after cutting off a flow of C_2H_4 . Resuming the C_2H_4 flow recovered the same formation rate of C_2H_6 within 2 min as that obtained before cutting off the flow of C_2H_4 . If one compares these observations with the quite longer durability in the formation of C_2H_5CHO in Fig. 12, it can be suggested that the coordination or adsorption of C_2H_4 to the active site is reversible and its rate is faster than that of CO. The coordination of CO must be stronger than that of C_2H_4 , reducing the concentration of the coordinated C_2H_4 , which decreases the rates of both reactions (hydrogenation and hydroformylation) at high partial pressures of CO (Fig. 5).

iv. Effect of reactant gases on the cathode potential. The open-circuit cathode potentials in a flow of C_2H_4 , CO, or a mixture of them would give some information about the change in the state of the cathode. The measurements of the cathode potentials were carried out using the same reactor used in this work with a KCl salt-bridge capillary inserted to the center of the silica-wool disk containing H_3PO_4 electrolyte. The cathodes concerned in this experiments were Pt-black/Gr, H_2PtCl_6/Gr , and $(H_2PtCl_6 \cdot Na_3PO_4)/Gr$. The electrocatalytic performance of these cathodes have already been described earlier and in Table 1.

The potentials of these cathodes (vs Ag/AgCl) have been monitored after passing He, C_2H_4 , and the mixture of C_2H_4 and CO by turns for 25 min through the cathode compartment under open-circuit conditions. In the case of Pt-black/Gr, a steady-state potential was obtained within 10 min after introducing C_2H_4 (90 kPa) or the mixture of C_2H_4 (90 kPa) and CO (11 kPa). The cathode potentials in C_2H_4 and in the mixture of CO and C_2H_4 were 0.12 and 0.11 V (vs Ag/AgCl). For H_2PtCl_6/Gr and $H_2PtCl_6 \cdot Na_3PO_4/Gr$, a steady-state cathode potential was obtained in 5 min after passing a flow of C_2H_4 ; the potentials were 0.67 and 0.72 V (vs Ag/AgCl) for H_2PtCl_6/Gr and $H_2PtCl_6 \cdot Na_3PO_4/Gr$, respectively. However, the addition of CO to the C_2H_4 flow changed the potential gradually and reached a steady-state after ca. 50 min for both H_2PtCl_6 -based cathodes. In the case of H_2PtCl_6/Gr , the cathode potential decreased from 0.47 V (at 5 min) to 0.06 V vs Ag/AgCl (at 50 min). The similar decrease in the cathode potential from 0.57 (at 5 min) to 0.05 V vs Ag/AgCl (at 50 min) was observed for $H_2PtCl_6 \cdot Na_3PO_4/Gr$. These changes in the potential for the H_2PtCl_6 -based cathodes may suggest the change in the oxidation state of platinum from Pt^{4+} to Pt^{2+} in a flow of CO. In fact, the similar drop in the cathode potentials for both H_2PtCl_6 -based cathodes was observed in a flow of CO (11 kPa) in the absence of C_2H_4 . As described earlier, before the electrolytic hydroformylation of C_2H_4 , a gas mixture of C_2H_4 and CO had been passed through the cathode for 60 min under open circuit conditions. In these circumstances, Pt^{2+} could be the active sites from the beginning for the electrochemical

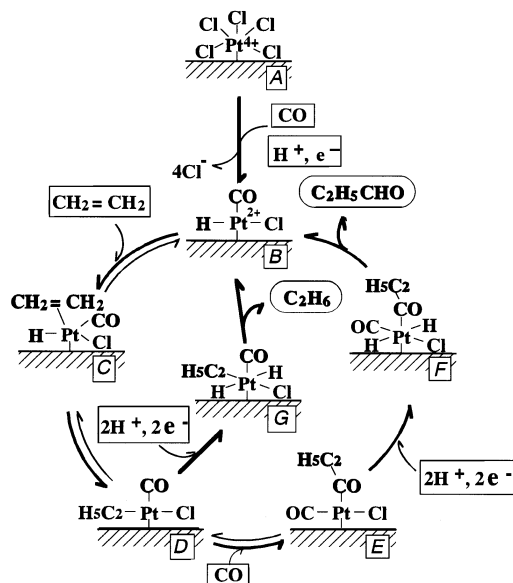


FIG. 13. Reaction scheme.

hydroformylation and hydrogenation of C_2H_4 . However, the possibility that a fast electrochemical reaction of Pt^{4+} to Pt^{2+} occurs after shorting the circuit cannot be excluded. As described above, the cathode potentials for the Pt-black/Gr and the H_2PtCl_6 -based cathodes in C_2H_4 atmosphere and in a mixture of C_2H_4 and CO are quite different, which supports the suggestion that platinum metal could not be the catalytic species for the formation of C_2H_5CHO .

v. Reaction scheme. On the bases of the results obtained in this work and with reference to the reaction models proposed so far (8, 9, 11–15), we propose a tentative reaction mechanism in Fig. 13.

The H_2PtCl_6 in the cathode may be anchored or adsorbed on surface functional groups such as $-COOH$ or $-OH$ of the host graphite. The adsorbed Pt^{4+} -chloride (A) would be reduced by CO or by electrochemically with protons and electrons and eventually forming a $Pt^{2+}(CO)(H)$ surface complex B. Coordination of C_2H_4 (complex C) and addition of hydride to the C_2H_4 forms the ethyl-carbonyl complex D. Insertion of CO to the $C_2H_5-Pt^{2+}$ or intramolecular transfer of the ethyl group to the carbonyl forms acyl-carbonyl complex E. Electrochemical addition of hydrogen to the complexes E and D generates hydride complexes F and G, respectively. Reductive elimination of the acyl group from F and that of alkyl group from G give C_2H_5CHO and C_2H_6 , respectively, regenerating the electrocatalytic active species B.

Quite similar dependencies of the formations of C_2H_5CHO and C_2H_6 on the kinetic parameters in Figs. 5 and 6 support that the two products are formed through the same reaction intermediates (B~D) as demonstrated in Fig. 13. The higher apparent activation energy for the formation of C_2H_5CHO suggests that either one of the steps

after the complexes **D**, **E**, and **F** in Fig. 13 has higher activation energy compared to those in the route for C_2H_6 formation. As suggested before, a strong coordination of CO to the Pt^{2+} complexes must hinder the coordinations of C_2H_4 and hydride; thus, lower partial pressure of CO (Fig. 5) and higher pressures of C_2H_4 (Fig. 6) and H_2 are preferable for the formations of both C_2H_5CHO and C_2H_6 under short-circuit conditions.

The results for the transient response of the products after the removal of gaseous C_2H_4 in Fig. 11 suggest that the desorption of ethylene and ethyl groups through the reverse steps from **E** to **D** to **C** are fast and reversible. In contrast, the results in Fig. 12 suggest that the desorption of CO is slow after the removal of gaseous CO and that may be most of the CO coordinated to the complexes is converted into C_2H_5CHO in the presence of gaseous C_2H_4 under short-circuit conditions. The formation of C_2H_5CHO can be accelerated just after the removal of gaseous CO (Fig. 12) because the coordination sites are left open for C_2H_4 and hydride due to the consumption of the coordinated CO to C_2H_5CHO .

Normally platinum complexes do not catalyze the hydroformylation of olefins. Rhodium and cobalt complexes are much more active catalysts than platinum complexes in homogeneous catalytic systems (8, 9). However, as described earlier, platinum chlorides are most active and selective for the electrolytic hydroformylation of C_2H_4 under the experimental conditions in this work. Although the explanation of this fact is not easy, we speculate that the electrolytic method makes it possible to coordinate hydride to the Pt^{2+} complexes in Fig. 13. As indicated in Fig. 2, the H_2PtCl_6/Gr did not catalyze both reactions (hydrogenation and hydroformylation) of C_2H_4 in the presence of CO and H_2 in the cathode compartment under open-circuit conditions. This fact strongly suggests that Pt^{2+} complexes cannot activate hydrogen; thus, the formation of Pt^{2+} -hydride complexes does not occur. However, if we perform the electrolytic hydroformylation with hydrogen in the anode compartment, it is quite easy to activate or dissociate H_2 on the Pt-black anode. Moreover, electric potential must greatly enhance the formation of hydride of Pt chloride at the cathode. We believe this explains the specific, electrocatalytic ability of the Pt-chloride in the electrolytic hydroformylation of C_2H_4 observed in this work.

vi. The role of Na_3PO_4 . The addition of sodium salts to the H_2PtCl_6/Gr cathode enhanced the selectivity and current efficiency for the formation of C_2H_5CHO (Table 2 and Fig. 3). This favorable effect of sodium salts irrespective of their counteranions suggests that the sodium cation would work as a promoter for the formation of C_2H_5CHO . One of the key steps to improving the selectivity to C_2H_5CHO is accelerating the formation of acyl group on complex **E**.

The polarization of the coordinated CO by Na^+ might accelerate the insertion of CO to the $C_2H_5-Pt^{2+}$ bond or the intramolecular transfer of ethyl group to the nucleophilic carbon of CO. However, at this moment, we need a lot of further investigations to clarify the role of sodium salts in the reaction mechanism.

CONCLUSION

Hydroformylation of ethylene occurred spontaneously using a gas cell composed of (C_2H_4 , CO, H_2PtCl_6 cathode [H_3PO_4 aq.] Pt-black anode, H_2) under short-circuit conditions at >320 K and atmospheric pressure.

Electrochemical studies have suggested that the catalytic active species at the cathode is Pt^{2+} -chloride. Platinum chlorides are specifically active for this electrochemical hydroformylation in contrast with rhodium and cobalt chlorides in homogeneous catalytic systems. Addition of sodium salts, especially Na_3PO_4 , improved the selectivity and the rate of C_2H_5CHO formation. A strong coordination of CO to the active site reduces the rate of hydroformylation. Thus a lower pressure of CO and higher pressure of C_2H_4 and H_2 enhanced both the hydrogenation and the hydroformylation of C_2H_4 . The proposed reaction mechanism well explains the kinetic and transient response results in this work.

Although the results obtained in this approach are far from commercial application, a better preparation method for the electrocatalyst and a better design of electrode-electrolyte system must remarkably improve the production of C_2H_5CHO .

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