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An Electrochemical Membrane Reactor for Selective Hydrogenation of Acetylene in Abundant Ethylene

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A membrane reactor, where acetylene and ethylene were separated from hydrogen by a phosphoric acid containing silica-wool disk, was applied to hydrogenation of acetylene in abundant ethylene at 353K. The hydrogen supplied onto the *d*-metal cathodes (Pt, Ir, Pd, Rh, and Ru) by electrochemical pumping through the membrane hydrogenates both ethylene and acetylene. The relative rate of hydrogenation of ethylene over all the *d*-metal cathodes was much greater than that of acetylene because ethylene was abundant compared to acetylene [$P(C_2H_4)/P(C_2H_2) = 51$]. However, the hydrogen pumped to Cu-cathode hydrogenates acetylene to ethylene very selectively with only a slight production of ethane. The gas mixture of hydrogen, acetylene, and ethylene did not cause any catalytic hydrogenation over the Cu cathode. This can be ascribed to the inability of Cu for hydrogen activation under the reaction conditions in this work. However, the electrochemical pumping of hydrogen easily generates active hydrogen onto this inactive catalyst. The results of kinetic studies on electrocatalytic hydrogenations of ethylene and acetylene over the Cu cathode have suggested that both hydrogenations occur independently each other. It is suggested that a stronger adsorption of acetylene than ethylene on Cu enables the preferential hydrogenation of acetylene.

INTRODUCTION

The production and polymerization of olefins must be regarded as one of the most important reactions in the chemical industry. In the presence of olefins, it is not surprising that organic impurities may be present. Among these impurities, acetylenic compounds are particularly troublesome because it is difficult to separate them from olefins to the levels required for polymerization feedstock. When we confine our attention to ethylene, a catalytic hydrogenation process has been developed in which acetylene is hydrogenated to ethylene with minimized formation of ethane. Although this subject has received considerable attention for many years (1, 2), the designers look for a better catalyst or a new process for this selective hydrogenation.

Conventional catalytic hydrogenation of unsaturated compounds is carried out by contact of hydrogen and substrate with a suitable catalyst. A new hydrogenation technique using the hydrogen supplied electrochemically through a proton-conducting membrane was first demonstrated by Langer *et al.* (3, 4). In this method, hydrogen is placed on one side of an electrolyte barrier, while an unsaturated hydrocarbon is placed on the other side. The electrolyte phase is sandwiched by porous, catalytic electrodes. Under operating conditions, hydrogen is dissociated at one electrode, being transformed into hydrogen ions and electrons. The hydrogen ions are conducted through the electrolyte, while electrons are conducted through the external circuit containing a potentiostat and an ammeter. Hydrogenation takes place on the counter catalytic electrode where unsaturated hydrocarbons, hydrogen ions, and electrons are combined. A part of the hydrogen ions transferred to the cathode is discharged, evolving as hydrogen into the gas phase. The rate and the selectivity to hydrogenation can be controlled easily by the potentiostat in the external circuit. The reactions described above may be represented as:

$$\text{anode:} \quad H_2 \rightarrow 2H^+ + 2e^-, \qquad [1]$$

$$\text{cathode:} \quad RCH{=}CHR' + 2H^+ + 2e^- \rightarrow RCH_2CH_2R' \qquad [2]$$

$$2H^+ + 2e^- \rightarrow H_2. \qquad [3]$$

Langer *et al.* claimed several advantages of this hydrogenation technique (3, 4). However, the application of this method for the selective hydrogenation of acetylene has not been reported yet.

The purpose of this work is to investigate the applicability of the electrocatalytic technique described above for selective hydrogenation of acetylene in the presence of abundant ethylene. First, favorable electrocatalysts for this reaction are sought. Second, the electrocatalytic functions of *d*-metals (such as Pt, Pd, and Ru) and *sp*-metals (Cu, Ag, and Au) for selective hydrogenation of acetylene are demonstrated in comparison with each metal group.

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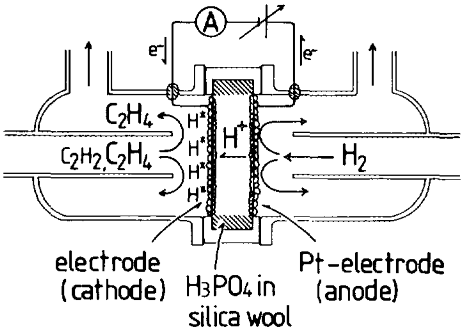

FIG. 1. The membrane reactor for selective hydrogenation of C_2H_2 in abundant C_2H_4.

Finally, the mechanism of hydrogenation of acetylene on Cu electrode is discussed on the basis of kinetic studies.

EXPERIMENTAL

The membrane reactor used and the principle of experimental procedure are shown schematically in Fig. 1. The method of preparation of the cathode, the anode, and the proton-conducting membrane was described in detail elsewhere (5). To be brief, the anode was prepared from Pt black (20 mg) mixed with graphite (Pt : carbon = 2 : 5 (weight ratio)) and Teflon powder (5 mg) by the hot-press method. The cathode prepared from the graphite containing various metal chlorides was reduced in hydrogen at 573 K. The content of the metals was adjusted to be 20 wt% against the weight of graphite. The proton-conducting membrane was made of a silica-wool disk (diameter 20 mm, thickness 1 mm) containing 1 g of H_3PO_4 aq. (14.7 *M*). The geometrical area of the electrodes was 2.0 cm^2. The reactor shown in Fig. 1 was connected to a conventional gas flow system.

A gas mixture of C_2H_4 and C_2H_2 ($C_2H_4 : C_2H_2$ = 51 : 1 kPa) was carried with helium to the cathode compartment. Hydrogen (81 kPa) with water vapor (20 kPa, added to keep the electrolyte being always wetted) was passed in the anode compartment. Total gas flow rate was 50 ml (STP) min^{-1} for both anode and cathode compartments. The total gas pressure for both cathode and anode sides was 101 kPa. The pumping rate of hydrogen through the membrane was controlled by means of externally applied potential between both electrodes. Polarization was slight for the hydrogen electrode (anode) in the range of currents observed in this work, and practically most of the polarization was observed at the counter electrode (cathode). The reactants (C_2H_2 and C_2H_4) and products (C_2H_4 and C_2H_6, respectively) were analyzed by on-line gas chromatography. The current and the open-circuit potential across the cell were monitored with a multimeter (Hewlett–Packard 3468A).

The reaction was carried out at the temperature range from 293 to 373 K. The essential feature of the reaction did not change with temperatures. Therefore, the results observed at 353 K are described unless otherwise stated. The data described below were obtained under steady-state conditions (with gases flowing) which were achieved 5 min after the current had been changed to a specified value.

The reproducibility in the preparation of electrodes was checked on the basis of the rates of hydrogenations of C_2H_2 and C_2H_4 under the same experimental conditions. Carefully prepared electrodes showed the reproducibility of ±20%. However, the reproducibility was better (within ±5%) when the same electrodes were used repeatedly under the same reaction conditions.

RESULTS AND DISCUSSION

Comparison of Various Metal Cathodes

The electrocatalyst favorable to remove acetylene in ethylene is the one which hydrogenates acetylene selectively with a limited conversion of ethylene into ethane. We have examined the catalytaic activity of various metal-added graphites for hydrogenation of gas mixture of acetylene and ethylene under the standard reaction conditions as follows: T = 353 K, flow rate = 50 ml (STP) min^{-1}, pumping rate of hydrogen from the anode to the cathode = 21.8 μmol · min^{-1} (corresponding to 70 mA), $P(C_2H_4)$ = 51 and $P(C_2H_2)$ = 1.0 kPa at the cathode, $P(H_2)$ = 81 kPa and $P(H_2O)$ = 20 kPa at the anode.

Table 1 shows the results for various metal-added cathodes under standard reaction conditions. Here, the ratio in the rates of conversions of C_2H_4 and C_2H_2 (R_E/R_A) and the current efficiency of hydrogenation were defined as follows:

$$R_E/R_A = \frac{(\text{rate of } C_2H_6 \text{ formation})}{(\text{rate of } C_2H_2 \text{ conversion})} \quad [4]$$

current efficiency

$$= \frac{\begin{array}{c}(\text{rate of } C_2H_2 \text{ conversion} \\ \text{plus that of } C_2H_6 \text{ formation})\end{array}}{(\text{pumping rate of } H_2)} \times 100\%. \quad [5]$$

It is to be noted that the rate of C_2H_4 conversion can be evaluated from the rate of C_2H_6 formation. The favorable cathodes are the ones giving a higher rate of C_2H_2 conversion with a lower R_E/R_A. The graphite cathode without metals showed only a slight electrocatalytic activity for the hydrogenation of acetylene. Because of the low rate of C_2H_6 formation, the reliable R_E/R_A could not be obtained for this cathode. Addition of metals to the graphite

TABLE 1

Hydrogenation of the Gas Mixture of C_2H_4 and C_2H_2 with the Hydrogen Pumped to the Cathode at 353 K

Cathode	C_2H_2 conversion (%)	R_E/R_A	Current efficiency (%)
Gr (graphite)	0.9	—[a]	<1
Ru/Gr	1.3	—[a]	3
Ir/Gr	3.4	14.2	51
Pd/Gr	17.9	6.1	117
Rh/Gr	4.4	5.3	26
Pt/Gr	8.4	11.4	98
Ni/Gr	1.8	1.8	5
Cu/Gr	11.8	0.01	11
Ag/Gr	1.0	—[a]	1
Au/Gr	1.6	0.7	2

[a] Not measurable due to the low conversions of C_2H_2 and C_2H_4.

cathode enhanced the conversion of C_2H_2 appreciably, as shown in Table 1. The high current efficiency and the high R_E/R_A observed for Pt/Gr, Pd/Gr, Rh/Gr, and Ir/Gr indicate that these metals are very active for hydrogenation of C_2H_4 as is well known. For *sp*-metals, Cu is specifically active for converting C_2H_2. The conversion of C_2H_2 observed for Ag/Gr and Au/Gr may be ascribed mostly to the catalytic function of graphite. Among the cathodes examined in Table 1, the second highest conversion of C_2H_2 and the lowest R_E/R_A were obtained for Cu/Gr, suggesting that Cu is the most favorable cathode for selective hydrogenation of C_2H_2 into C_2H_4 with the lowest conversion of C_2H_4 into C_2H_6.

Hydrogenation of C_2H_4–C_2H_2 Mixture over d-Metal Cathodes

Before we describe the hydrogenation over the Cu/Gr catalyst, it may be worth while to show some characteristics of the reaction caused by the hydrogen electrochemically generated on *d*-metal catalysts.

It is interesting to compare the reactivities of the hydrogen between the one generated on Pt/Gr by electrochemical pumping and the one supplied from the gas phase. This can be seen by comparing the results between the reaction with the electrochemically supplied hydrogen to the Pt/Gr cathode and that with hydrogen cofed with C_2H_4–C_2H_2 gas mixture into the cathode compartment under open circuit conditions. The latter is the usual catalytic hydrogenation over Pt/Gr. Hereafter, the former and the latter hydrogenations are denoted as electrocatalytic and catalytic hydrogenations, respectively.

The electrocatalytic and catalytic hydrogenations over Pt/Gr are compared in Fig. 2. For the electrocatalytic hydrogenation (open symbols), the conversion rate of C_2H_2 and the formation rate of C_2H_6 are plotted as functions of the current or of the pumping rate of hydrogen (upper abscissa) from the anode to the cathode. The reaction was carried out under standard conditions except for varying the rate of hydrogen pumping. Over the Pt/Gr cathode, the reaction took place under short-circuit conditions (half-closed symbols) or even in the presence of a load in the outer circuit. Under these conditions, we can generate electricity during hydrogenation (3, 4). Both the conversion rate of C_2H_2 and the formation rate of C_2H_6, probably due to the hydrogenation of C_2H_4, increase roughly linearly with a rise in the pumping rate of hydrogen. However, the rate of C_2H_6 formation is one order of magnitude greater than that of C_2H_2 conversion at all the currents examined. Thus, the R_E/R_A was always greater than 8.

The closed symbols in Fig. 2 show the results for the catalytic hydrogenation. The experiment was carried out under open circuit conditions at 353 K and at a total flow rate of 50 ml (STP) min^{-1} for the gas mixtures of C_2H_4(51), C_2H_2(1.0), H_2, and He (H_2 + He = 49 kPa) in the cathode compartment. The rate of C_2H_2 conversion and that of C_2H_6 formation are plotted as functions of the feed rate of hydrogen (upper abscissa in Fig. 2). The curves for catalytic hydrogenation in Fig. 2 indicate the acceleration in both rates for C_2H_2 conversion and C_2H_6 formation. This may be ascribed to the saturation of active sites with adsorbed C_2H_2 and C_2H_4 in the absence of gaseous hydrogen. In the presence of gaseous hydrogen, hydrogen may substitute the adsorbed C_2H_2 and C_2H_4 on the active sites, accelerating the hydrogenation of both substrates by the L–H mechanism with a rise in the feed rate (or in the partial pressure) of hydrogen. The comparison between the results of electrocatalytic and catalytic hydro-

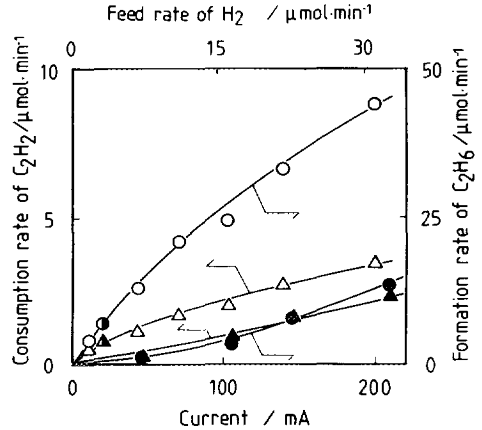

FIG. 2. Comparison between electrocatalytic and catalytic hydrogenations over Pt/Gr. Open symbols, electrocatalytic; closed symbols, catalytic; ◑ and ◭, short-circuit conditions; ○ and ●, formation rate of C_2H_6; and △ and ▲, conversion rate of C_2H_2.

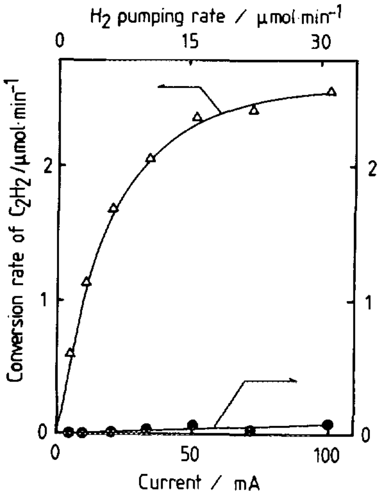

FIG. 3. Electrocatalytic hydrogenation on Cu/Gr as functions of current or hydrogen pumping rate. △, conversion rate of C_2H_2; ●, formation rate of C_2H_6.

genations in Fig. 2 clearly shows that both hydrogenations are enhanced considerably by electrochemically pumped hydrogen from the anode to the cathode. The enhancement is greater for the hydrogenation of C_2H_4 compared to that of C_2H_2.

Results similar to those in Fig. 2 were also obtained for the cathodes of Pd/Gr, Rh/Gr, Ru/Gr, Ir/Gr, and Ni/Gr, i.e., the electrochemical supply of hydrogen through H_3PO_4 electrolyte enhanced the hydrogenations of C_2H_4 and C_2H_2 compared to the usual catalytic hydrogenation with gas mixtures of C_2H_4, C_2H_2, and hydrogen. Moreover, the enhancement was more emphasized for C_2H_6 formation than C_2H_2 hydrogenation.

Thus, *d*-metals are not suitable as the cathode for selective hydrogenation of C_2H_2 in C_2H_4 by applying a membrane-reactor technique demonstrated in Fig. 1.

Hydrogenation over the Cu/Gr Cathode

As pointed out earlier, Cu/Gr is a promising electrocatalyst for selective hydrogenation of C_2H_2 (Table 1). We describe the kinetic studies on the hydrogenations of C_2H_2 and C_2H_4 over Cu/Gr in detail below.

Figure 3 shows the rate of C_2H_2 conversion and that of C_2H_6 formation as functions of the current or of the pumping rate of hydrogen from the anode to the Cu/Gr cathode. The experiments were carried out under standard conditions with varying the rate of hydrogen pumping. The results in Fig. 3 indicate that the electrochemically supplied hydrogen onto Cu/Gr hydrogenates C_2H_2 preferentially even though a quantity of C_2H_4 51 times larger than that of C_2H_2 is present in the cathode compartment. The R_E/R_A was remarkably low ($R_E/R_A < 0.03$) at all the currents examined. The increase in the rate of C_2H_2 conversion with a rise in the current appears to level off at > 70 mA in Fig. 3. Thus the current efficiency of hydrogenation decreases from 35% (at the lowest current) to 8% (at 100 mA). Most of the hydrogen pumped to the cathode evolves into the gas phase without hydrogenating unsaturates at high current conditions.

When the hydrogen was not pumped electrochemically to Cu/Gr cathode, addition of hydrogen to the gas mixture in the cathode compartment caused neither the hydrogenation of C_2H_2 nor that of C_2H_4. This was confirmed by adding hydrogen with a flow rate of 187 µmol/min which was six times greater than the highest pumping rate of hydrogen in Fig. 3 (100 mA or 31 H_2 µmol/min). This is not surprising because the low catalytic activity of Cu has already been pointed out by many researchers (1). However, it should be emphasized that the active hydrogen generated on the Cu/Gr cathode by the electrochemical pumping can hydrogenate C_2H_2 into C_2H_4 very selectively.

The turnover numbers per copper atom for the hydrogenation of C_2H_2 in Fig. 3 were $3.8 \times 10^{-3} \cdot \text{min}^{-1}$ for the lowest and $1.63 \times 10^{-2} \cdot \text{min}^{-1}$ for the highest. These values, however, cannot be the true turnover numbers because we have no information about what fraction of the cathode surface is being utilized in the reaction. In general, it is believed that electrocatalytic reactions take place at the three-phase boundary (gas, electrolyte, and electrode). Therefore, we speculate that only a very low fraction of the copper added in the cathode might be working during the reaction.

In order to obtain information about the specific hydrogenation over the Cu/Gr cathode, we have examined the effects of partial pressures of C_2H_2 and C_2H_4 on the rates of C_2H_2 conversion and of C_2H_6 formation.

The effects of partial pressure of C_2H_4 are plotted in

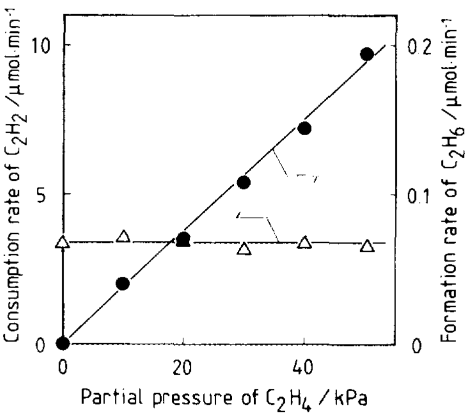

FIG. 4. Effect of C_2H_4 partial pressure on the rate of electrocatalytic hydrogenation over Cu/Gr. current = 70 mA, $P(C_2H_2)$ = 1 kPa. △, conversion rate of C_2H_2; ●, formation rate of C_2H_6.

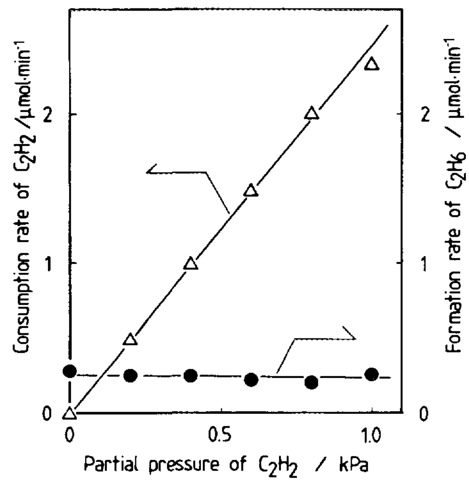

FIG. 5. Effect of C_2H_2 partial pressure (0–1.0 kPa). Cu/Gr, current = 70 mA, $P(C_2H_4)$ = 50 kPa. △, conversion rate of C_2H_2; ●, formation rate of C_2H_6.

Fig. 4. The experiments were carried out under a constant partial pressure of C_2H_2 (1.0 kPa) and a constant hydrogen pumping rate of 70 mA. The rate of C_2H_6 formation depends on the pressure of C_2H_4 (10–50 kPa) by first order. However, the conversion rate of C_2H_2 is not affected by changing the pressure of C_2H_4. The presence and absence of C_2H_2 did not affect the rate of C_2H_4 hydrogenation at all the pressures of C_2H_4 examined in Fig. 4. These results strongly suggest that both hydrogenations on Cu/Gr are independent each other.

The effects of partial pressure of C_2H_2 (0–1.0 kPa) on the rates of C_2H_2 conversion and of C_2H_6 formation are plotted in Fig. 5. The experiments were carried out at a constant partial pressure of C_2H_4 (51 kPa) and a constant current (70 mA). The results in Fig. 5 show that the rate of C_2H_2 conversion increases proportionally with the partial pressure of C_2H_2. However, the rate of C_2H_6 formation was not affected by increasing the C_2H_2 pressure. These observations support the suggestion that the hydrogenations of C_2H_2 and C_2H_4 proceed independently each other. Therefore, direct formation of C_2H_6 from C_2H_2 by multiple hydrogenation of C_2H_2 during the stay on the surface can be excluded.

The effect of partial pressure of C_2H_2 was examined at a higher pressure range than that of Fig. 5. The results are shown in Fig. 6. It should be noted that the increase in the rate of C_2H_2 conversion is decelerated with a rise in the pressure of C_2H_2 at > 5 kPa. The rate of C_2H_2 conversion, $R(C_2H_2)$, can be expressed well by an L–H type rate equation as far as the pressure of C_2H_2 is concerned.

$$R(C_2H_2) \propto \frac{K \cdot P(C_2H_2)}{1 + K \cdot P(C_2H_2)}, \qquad [6]$$

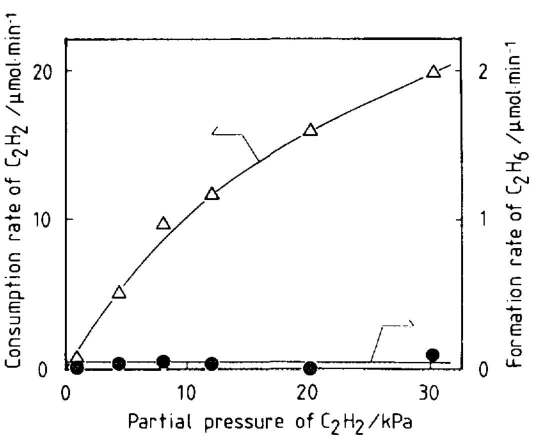

FIG. 6. Effect of C_2H_2 partial pressure (1–31 kPa). Cu/Gr, current = 70 mA, $P(C_2H_4)$ = 50 kPa. △, conversion rate of C_2H_2; ●, formation rate of C_2H_6.

where K is the constant at a fixed temperature. This is in contrast to the observation for hydrogenation of C_2H_4 in Fig. 4, viz., the rate of C_2H_6 formation still increases linearly at the pressure of C_2H_4 higher than 50 kPa. The comparison of these observations in Figs. 4 and 6 suggests that C_2H_2 adsorbs more strongly than C_2H_4 on Cu. The selective hydrogenation of C_2H_2 with a minimized hydrogenation of C_2H_4 over Cu/Gr can be ascribed to the stronger interaction of C_2H_2 with Cu than that between C_2H_4 and Cu.

Temperature effects on the rates of C_2H_2 conversion and C_2H_6 formation have been examined at the temperature range of 293 to 373 K. The reaction was carried out under standard conditions except for changing temperature. The whole reactor in Fig. 1 was maintained in a thermostat for this experiment. Figure 7 shows the logarithm of the rates plotted against the reciprocal of the reaction temperature. The apparent activation energies

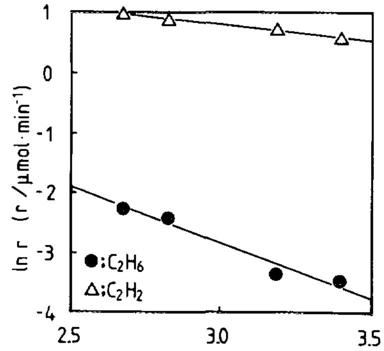

FIG. 7. Logarithm of the rate of hydrogenation as functions of 1/T. The rates were measured at a current of 70 mA, $P(C_2H_2)$ = 1 kPa, $P(C_2H_4)$ = 51 kPa, and flow rate = 50 ml (STP) min^{-1}. △, conversion rate of C_2H_2; ●, formation rate of C_2H_6.

for the hydrogenatiosn of C_2H_2 and C_2H_4 were calcualted from the slopes of the lines as 4.5 and 15.4 kJ · mol^{-1} respectively. Very small activation energies observed here may be ascribed to the interaction between adsorption energy for the substrates and the activation energy for hydrogenation (6). The results in Figs. 4 and 6 suggest that both adsorptions of C_2H_4 and C_2H_2 are not quite strong because higher pressures than those applied in this work are needed for the saturation of active sites by C_2H_2 and C_2H_4. Therefore, the apparent activation energies obtained for both hydrogenations at the partial pressures of C_2H_4 and C_2H_2 used for the experiments in Fig. 7 must embrace the true activation energy and the enthalpy change in adsorption (negative). Although the heats of adsorption for both substrates are not high, the true activation energies must well be small because the electrochemically generated hydrogen is quite active for both hydrogenations.

As described earlier, gaseous hydrogen in the cathode compartment did not induce both hydrogenations over Cu/Gr at 353 K. These may be ascribed to the inability of Cu for hydrogen activation at low temperatures. However, the catalytic hydrogenation was observed at $>$ 473K, though the hydrogenation of C_2H_4 occurred preferentially.

In conclusion, the electrochemically generated active hydrogen on Cu can catalyze the selective hydrogenation of C_2H_2 in abundant ethylene at lower temperatures than 293 K (Fig. 7). We believe that the membrane reactor demonstrated in Fig. 1 can be applied to many specific hydrogenations.

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