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Design of the Catalyst for Partial Oxidation of Ethylene by Applying an Electrochemical Device

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The electrochemical device composed of the H_3PO_4-membrane on which various noble metals were attached, M/H_3PO_4/M', was demonstrated as a probe of the catalysts for partial oxidation of C_2H_4. On the basis of the results, we have designed the catalyst (Pd-Ru-Graphite-H_3PO_4) for the selective synthesis of CH_3CHO from C_2H_4.

Wacker type oxidation of ethylene into acetaldehyde over solid catalysts can be recognized, in general, to proceed through the two fundamental reactions, i.e., the oxidation of ethylene by water (Eq. 1) and the reduction of oxygen (Eq. 2).

$$C_2H_4 + H_2O \text{ ----> } CH_3CHO + 2H^+ + 2e^- \qquad (1)$$

$$(1/2)O_2 + 2H^+ + 2e^- \text{ ----> } H_2O \qquad (2)$$

The protons and electrons released on the oxidation site (Eq. 1) are transferred through the H^+-conducting medium and the electron-conducting one, respectively, existing in the catalyst system. For examples, the former could be Brönsted acid sites on the surface and the latter the bulk of the catalyst. Thus, we realize that the Wacker catalysts must fulfill the four functional elements, i.e., (1) the site for oxidation of ethylene (Eq. 1), (2) the site for reduction of oxygen (Eq. 2), (3) the H^+-conducting element, and (4) the e^--conducting element.

The first purpose in this work is to demonstrate a device in Fig. 1 which, as a whole, works as a catalyst for the partial oxidation of ethylene. Secondly, we design a new catalyst for the Wacker reaction on the basis of the information obtained by applying the device in Fig. 1.

The device in Fig. 1 was composed of the proton conducting membrane (a silica-wool disk with H_3PO_4 (85% aq., 0.70 g), 1 mm thickness) on which the electrode wafers, made from various noble metals (20 mg) mixed with graphite (50 mg) and teflon powder (5 mg), were attached as catalysts. The noble metals used were Pt and Pd blacks, and Ru, Rh, Os, and Ir. The

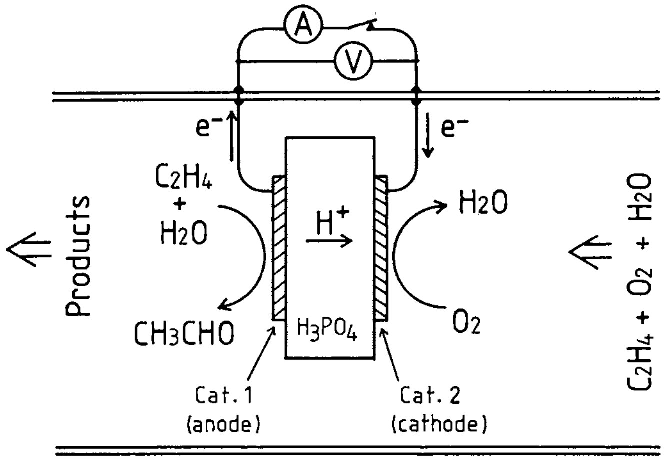

Fig. 1. The electrochemical device for the catalytic partial oxidation of C_2H_4.

latter four metals were prepared from their chlorides by reduction with hydrogen for 4 h at 573 K. The geometrical area of the electrodes was 2.0 cm^2. The electrodes on both sides of the membrane were shorted with an Au wire. The device was allowed to stand in a flow of the gas mixture of ethylene, oxygen and water vapor ($C_2H_4 : O_2 : H_2O = 16 : 4 : 5$) at 353 K under atmospheric pressure. The steady state results were obtained after about 2 hr of the time on stream of the gas mixture. The total flow rate of the gas mixture was 25 ml(STP)min^{-1}.

For various electrode combinations tested in the gas mixture of C_2H_4, O_2, and H_2O, we have confirmed that Pd is the unique anode material capable for catalyzing the selective acetaldehyde formation as suggested by many researchers.[1,2] Therefore, Pd was always used as anode for the following experiments. We have observed that the various metals in the cathode of the device, Pd(anode)/H_3PO_4/M(cathode), give voltages in the gas mixture under open circuit conditions. The voltages observed are indicated in Table 1. The electrode combination Pd/H_3PO_4/Pt was exceptional because Pd became cathode in this case giving -108 mV. The Pd/H_3PO_4/ without counter electrode catalyzed the selective formation of acetaldehyde. The reproducibility of the observed rate of acetaldehyde formation for each Pd electrode prepared (renewed for each experiment) was within 1.00 ± 0.20 µmol/min. The attachment of the counter electrode did not change the reaction rate under open circuit conditions within the experimental error. The shorting of the circuit enhanced the formation rate of acetaldehyde appreciably for the cathodes of Ru, Rh, Os, and Ir (Table 1). The enhanced rate of acetaldehyde formation corresponded to 80 to 88% of the current observed (current efficiency) assuming the electrocatalytic reactions (Eqs. 1 and 2). The results in Table 1 show that the best combination of the electrode material is Pd/H_3PO_4/Ru, giving the highest voltage, the highest current and the highest formation rate of

Table 1. Results for the synthesis of acetaldehyde with Pd/H_3PO_4/M under open and short circuit conditions

Counter electrode M	Conditions	Open voltage /mV	Formation rates of products/μmol·min^{-1} CH_3CHO	CO_2	Current /mA	Current efficiency /%
Ru	open	236	0.91	0		
	short		2.33	0	5.2	88
Rh	open	205	0.78	0		
	short		2.03	0	5.0	80
Os	open	160	0.89	0		
	short		1.37	0	1.8	84
Ir	open	103	1.15	0.10		
	short		1.85	0.07	2.8	80
Pt	open	-108	0.90	0.94		
	short		0.55	1.30	5.2	-

acetaldehyde under short-circuit conditions.

Figure 2 shows the changes in the rate of formation of acetaldehyde as functions of the amount of Ru(cathode) under open and short-circuit conditions. The current was also indicated in the figure. The results in Fig. 2 show that the increase in the amount of Ru does not change the rate of reaction at all under open circuit conditions, but remarkably enhances the current and the formation rate of acetaldehyde under short-circuit conditions. However, the increase in the rate and current was depressed at high Ru loading probably due to insufficient contact of Ru particles with the electrolyte (H_3PO_4). The current efficiencies calculated for the enhanced formation of acetaldehyde for all the data in Fig. 2 were 100% within the experimental error of ±10%. These results support the reaction

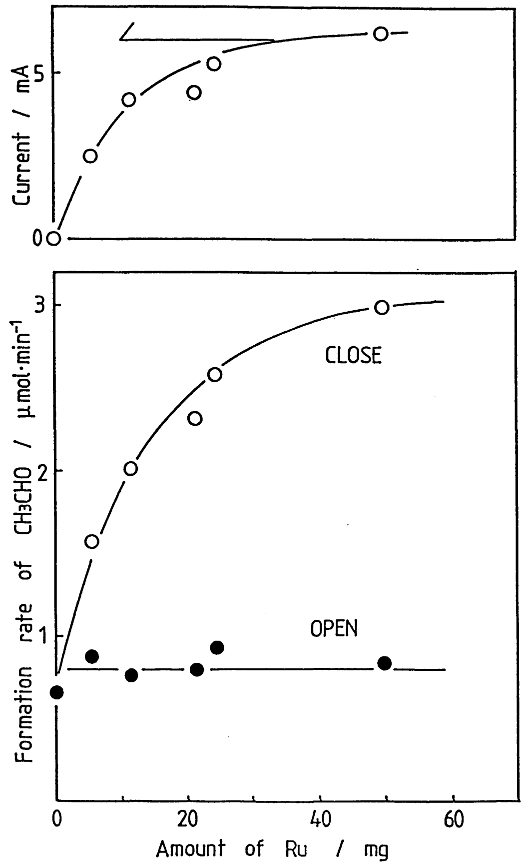

Fig. 2. Effect of the amount of Ru in the cathode on the formation rate of CH_3CHO. Ru + Graphite=70 mg, Pd(anode)=20 mg.

Table 2. Design of the catalyst for Wacker oxidation

Catalyst[a]	Formation rates of products/ μmol·min^{-1}	
	CH_3CHO	CO_2
Pd-Ru-Gr-H_3PO_4	3.18	0
Pd-Gr-H_3PO_4	0.64	0.05
Ru-Gr-H_3PO_4	0	0
Pd-Ru-Gr	0.29	0
Pd-Gr	0.01	0.04
Ru-Gr	0	0
H_3PO_4	0	0

[a] H_3PO_4(85%, aq.)(0.70 g loaded in a silica wool disk), Pd-Gr(Pd 20 + Graphite 50 mg), Ru-Gr(Ru 20 + Graphite 50 mg), Pd-Ru-Gr(Pd 20 + Ru 20 + Graphite 30 mg).

model hypothesized earlier (Eqs. 1 and 2). The enhanced reaction by shorting the circuit can be ascribed to the beginning of the reactions (Eqs. 1 and 2) due to the electron flow enabled through the outer circuit.

On the basis of the results described above, we have designed a catalyst for the synthesis of acetaldehyde from ethylene by combining the four functional elements, viz., (1) Pd as the oxidation sites for C_2H_4, (2) Ru as the reduction sites for O_2, (3) H_3PO_4(aq.) as H^+-conductor and (4) to maintain the contact between the particles of Pd and Ru to ensure the electron flow from Pd to Ru. Table 2 shows the results observed for the elements combined or singly used as the catalyst for the oxidation of ethylene. Here, the graphite (Gr) was added to the metals to make sure the electronic contact between metal particles. The catalyst composed of the four functional elements (Pd-Ru-Gr-H_3PO_4) showed the highest catalytic activity in the selective oxidation of ethylene to acetaldehyde. The lack of one of the four elements reduced the catalytic activity drastically.

In conclusion, the electrocatalytic device demonstrated in Fig. 1 is applicable to the search for the elemental functional elements, viz., the oxidation and reduction sites, which is essential for designing the catalyst for partial oxidation of olefins. We believe that this concept is not limited only to the oxidation of olefins but is generally applicable to many catalytic oxidations.

References

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