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WACKER TYPE AND π-ALLYL TYPE OXIDATIONS OF PROPYLENE CONTROLLED BY FUEL CELL SYSTEM IN THE GAS PHASE

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Oxidation of propylene applying the (C_3H_6, Pd/H_3PO_4/Pt, O_2) fuel cell system in the gas phase produced acrolein and acrylic acid, the π-allyl type oxidation products. However, addition of H_2PdCl_4 or HCl to the electrolyte reduced the π-allyl oxidation, but enhanced Wacker type oxidation producing acetone. Direction to either Wacker type or π-allyl type oxidation can easily be controlled electrochemically by applying the fuel cell system in the gas phase.

Wacker oxidation, π-allyl oxidation, propylene, fuel cell

1. Introduction

Two types of catalytic oxidation of olefins by palladium are well known. Olefin oxidation catalyzed by palladium black proceeds via π-allyl complex of the olefin on palladium metal surface [1], which is distinguished from the Wacker type oxidation catalyzed by Pd^{2+} where redox of the palladium ($Pd^{2+} \rightleftharpoons Pd^0$) is essential [2]. When we choose propylene as a reactant olefin, acrolein and acrylic acid are the expected products over palladium black according to the π-allyl type oxidation. On the other hand, acetone is the main product in the Wacker type reaction. In this communication we will describe the electrochemical control on the Wacker type and π-allyl type oxidation of propylene using the fuel cell reactor [3].

2. Experimental

A schematic diagram of the fuel cell reactor is shown in fig. 1. A silica wool disk (1.0 mm thickness, 21 mm diameter) containing phosphoric acid [85% H_3PO_4(aq.) 0.25 ml] was used both as a H^+ conductor and a separator for the right and left compartments of the reactor. Pd-black (20 mg) and Pt-black (20 mg) as electrodes were attached on the both sides of the silica wool disk. The apparent areas of the electrodes were 2 cm^2. All the reactions were operated

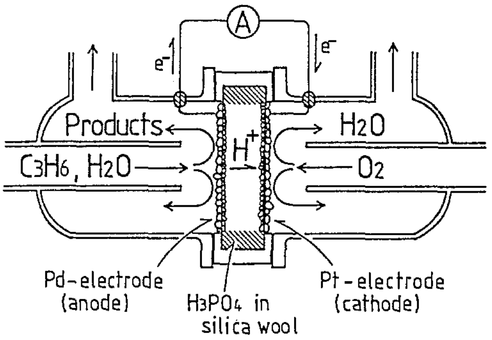


Fig. 1. Schematic diagram of the fuel-cell reactor.

under atmospheric pressure for both compartments at 365 K. The experimental conditions were as follows: for anode side; $C_3H_6 : H_2O : He = 2 : 1 : 2$, total flow rate = 30 ml · min^{-1}: for cathode side; pure O_2 (20 ml · min^{-1}). Quantitative analysis of the products were carried out by gas chromatography using Porapack-Q, PEG-20M and active carbon columns. No leakage of the reactants through the membrane was observed. The open circuit cell potential under the conditions described above was 0.70 V. Usually it took one hour to rearch steady state conditions after closing the circuit.

3. Results and discussion

Under open circuit conditions at 365 K, 2-propanol (0.044×10^{-6} mol · min^{-1}) and a trace of CO_2 (0.008×10^{-6} mol · min^{-1}) were observed. The former was produced via catalytic hydration of propylene by H_3PO_4. When the circuit was closed without any external load, current flowed (6.5 mA) and acrolein, acrylic acid and acetone were produced. The formation rate of each product was as follows: $CH_2{=}CHCHO$ (0.33), $CH_2{=}CHOOCH$ (0.21), CH_3COCH_3 (0.02), CO_2 (0.079) and $CH_3CH(OH)CH_3$ (0.042) (unit of the values is 10^{-6} mol · min^{-1}). The formation rate of the acid catalyzed products ($CH_3CH(OH)CH_3$) did not change after closing the circuit. Assuming the following half-cell reactions at anode, the total current efficiency for the electrochemically-oxidized products was evaluated as 99%. Thus, total formation rate of the oxidation products (eqs. (1–4)) corresponded well to the current observed.

$$\text{At anode}: C_3H_6 + H_2O \longrightarrow CH_2{=}CHCHO + 4H^+ + 4e^- \quad (1)$$

$$C_3H_6 + 2H_2O \longrightarrow CH_2{=}CHCOOH + 6H^+ + 6e^- \quad (2)$$

$$C_3H_6 + H_2O \longrightarrow CH_3COCH_3 + 2H^+ + 2e^- \quad (3)$$

$$C_3H_6 + 6H_2O \longrightarrow 3CO_2 + 18H^+ + 18e^- \quad (4)$$

$$\text{At cathode}: 4H^+ + 4e^- + O_2 \longrightarrow 2H_2O. \quad (5)$$

Table 1
Effects of various additives on the rates of formations of acetone and acrolein

additives [a]	current/mA	rate of formation/ [b]	
		acetone	acrolein
None	6.5	0.02	0.33
H_2PdCl_4	4.1	1.29	0.00
H_2SO_4	6.6	0.34	0.29
HCl	6.2	1.83	0.03
NaCl	10.2	0.22	0.54

[a] Amount of additives was 2.5×10^{-6} mol.
[b] 10^{-6} mol·min^{-1}.
Experimental conditions were described in the text.

As described above, the main products under closed circuit conditions were acrolein and acrylic acid. This observation suggests that the main oxidation proceeds not via Wacker type mechanism but via π-allyl type reaction. However, when we added H_2PdCl_4 or HCl into the H_3PO_4-impregnated membrane, the selectivity to acetone increased dramatically up to 99 ± 2%. The effects of various additives were shown in table 1. All data in table 1 were observed at time on stream of 2 h. Although acrylic acid was not measured at the same time in this experimental series, separate experiments showed that the rate of formation of acrylic acid was generally less than that of acrolein. The results in table 1 show that all the additives tested here enhance the rate of formation of acetone and reduce the rate of formation of acrolein. These effects were remarkable for H_2PdCl_4 and HCl. It is to be noted that the Wacker reaction in the presence of these additives ceased within 2 min after the circuit was opened. This observation suggests that electrochemical oxidation of Pd^0 to Pd^{2+} is essential for continuous progress of the Wacker reaction.

Figure 2 shows the effect of externally applied potential between anode and cathode electrodes on the rates of formation of products and current. The formation rate of acrylic acid is not plotted here because of difficulty in simultaneous determination of the quantity of the acid. Zero applied voltage on the abscissa in fig. 2 means the closed circuit condition without any external load. Application of positive voltage enhanced the formation of acetone but reduced that of acrolein markedly. The increase in the rate of formation of CO_2 was not so appreciable. The selectivity to acetone was greater than 90% at the applied voltage larger than 0.15 V. On the other hand, application of negative voltage (or of external load) decreased the rates of formations of both acetone and CO_2 sharply with the voltage, while that of acrolein decreased gradually. Thus, the selectivity to acrolein increases when negative voltage or external load is applied in the circuit. The results in fig. 2 show that positive applied voltage enhances Wacker type oxidation but reduces π-allyl type oxidation, while application of negative voltage enhances the selectivity to the latter oxidation.

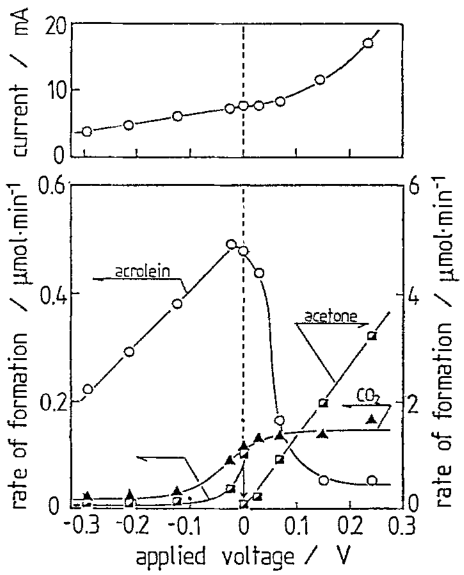


Fig. 2. Effects of applied potential between anode and cathode on the rates of Wacker and π-allyl oxidations of propylene.

Separate experiments for evaluating the quantity of the acrylic acid formed under the same experimental conditions in fig. 2 at -0.2 and $+1.5$ V have been carried out. The current efficiencies for the products at these voltages including acrylic acid thus measured became 100% within experimental error of $\pm 2\%$. These observations support the electrochemical reactions of eqs. (1) to (5) for the oxidations in fig. 2.

The results in table 1 and fig. 2 can be explained as follows: Let us assume that the Wacker type reaction proceeds on Pd^{2+} cations dissolved at the interface of Pd electrode and H_3PO_4(aq.);

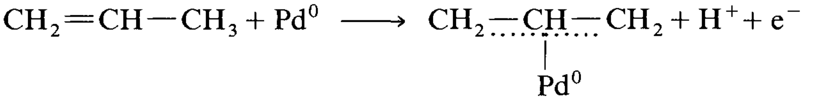
$$\mathrm{Pd^0} \longrightarrow \mathrm{Pd^{2+}} + 2\mathrm{e^-} \tag{6}$$

$$\mathrm{Pd^{2+}} + \mathrm{C_3H_6} \longrightarrow \mathrm{Pd^{2+}} \ldots \mathrm{C_3H_6} \tag{7}$$

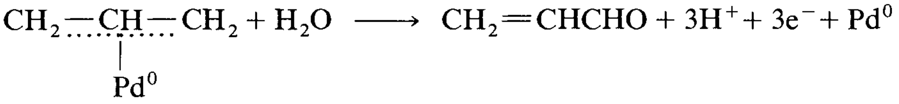
$$\mathrm{Pd^{2+}} \ldots \mathrm{C_3H_6} + \mathrm{H_2O} \longrightarrow \mathrm{Pd^+}-\mathrm{CH_2CH(OH)CH_3} + \mathrm{H^+} \tag{8}$$

$$\mathrm{Pd^+}-\mathrm{CH_2CH(OH)CH_3} \longrightarrow \mathrm{CH_3COCH_3} + \mathrm{H^+} + \mathrm{Pd^0}. \tag{9}$$

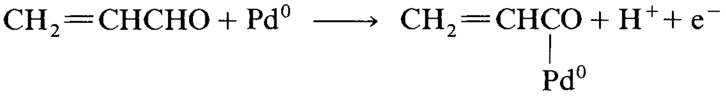
On the other hand, the π-allyl type oxidation occurs on Pd metal electrode;



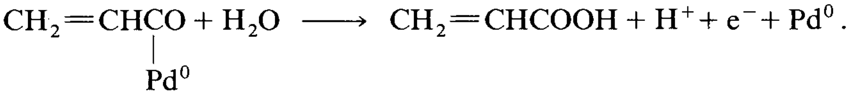
$$\mathrm{CH_2{=}CH{-}CH_3 + Pd^0 \longrightarrow CH_2 \cdots \underset{\underset{\textstyle Pd^0}{|}}{CH} \cdots CH_2 + H^+ + e^-} \qquad (10)$$



$$\mathrm{CH_2 \cdots \underset{\underset{\textstyle Pd^0}{|}}{CH} \cdots CH_2 + H_2O \longrightarrow CH_2{=}CHCHO + 3H^+ + 3e^- + Pd^0} \qquad (11)$$



$$\mathrm{CH_2{=}CHCHO + Pd^0 \longrightarrow CH_2{=}CH\underset{\underset{\textstyle Pd^0}{|}}{C}O + H^+ + e^-} \qquad (12)$$



$$\mathrm{CH_2{=}CH\underset{\underset{\textstyle Pd^0}{|}}{C}O + H_2O \longrightarrow CH_2{=}CHCOOH + H^+ + e^- + Pd^0.} \qquad (13)$$

These mechanisms are mainly based on those proposed in the references [1,2]. Addition of H_2PdCl_4, H_2SO_4, HCl or NaCl to the membrane must increase the concentration of Pd^{2+} dissolved in the membrane, enhancing the Wacker type reaction (table 1). Addition of positive potential between the electrodes may enhance the electrochemical oxidation of Pd^0 into Pd^{2+} (eq. (6)) favorably for the Wacker type oxidation. Negative potential would reduce the oxidation of Pd^0 to Pd^{2+}, decreasing the rate of formation of acetone markedly. These assumptions well explain the observations in table 1 and fig. 2.

The method described above may generally be applicable to various Wacker type and π-allyl type oxidations.

References

[1] T. Seiyama, N. Yamazoe, J. Hojo and M. Hayakawa, J. Catal. 24 (1972) 173;
K. Fujimoto, H. Yoshino and T. Kunugi, Nippon Kagaku Kaishi, 1972 (1972) 507;
J.E. Lyons, G. Suld and C.-H. Hsu, in: *Catalysis of Organic Reactions* (Marcel Dekker, Inc., New York and Basel, 1988) p. 1.

[2] J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Seiber and H. Kojer, Angew. Chem. 71 (1959) 176;
E.W. Stern, Catal. Rev. 1 (1968) 105.

[3] K. Otsuka, Y. Shimizu and I. Yamanaka, J. Chem. Soc. Chem. Commun. 1988 (1988) 1272.