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Partial Oxidation of Methanol Using a Fuel Cell System at Room Temperature

Ichiro YAMANAKA and Kiyoshi OTSUKA*
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

Partial oxidation of methanol in the gas phase applying the fuel cell system using Pt-bonded solid polymer electrolyte membrane produces methyl formate and methylal selectively with a trace of CO_2 at room temperature. The effect of pressures of O_2 (cathode), CH_3OH (anode) and of H_2O were examined. The increases in these pressures enhanced the rate of partial oxidation. In particular, the selectivity to methyl formate was improved with increasing the pressures of O_2 and H_2O.

Partial oxidation of methanol is expected to give important chemicals such as formaldehyde, methylal, methyl formate, etc. Recently we have demonstrated an electrocatalytic partial oxidation of methanol in the gas phase by a simple method using precious metals-bonded electrolytes suspended in the flow of methanol vapor.[1-3] The advantage of this method has already been described.[1,2] However, the electrocatalytic oxidation of methanol requires, of course, electricity. A number of investigators have focused a great deal of effort on inorganic and organic oxidation in fuel cells. The purpose of the programs was the rapid and complete oxidation of cheap feed stocks for generating electricity and heat. However, some of the investigators have demonstrated that fuel cells could also be used for cogenerating electricity and industrial chemicals.[4-7] The purpose in this work is to apply this idea to partial oxidation of methanol using a platinum-bonded solid polymer electrolyte (SPE) cell at 298 K. A schematic diagram of the fuel cell reactor and the gas flow system is shown in Fig. 1. An external load was not applied in order to gain chemicals exclusively. A platinum-bonded Nafion 117 (Du Pont) membrane was used as the SPE material. The Pt-SPE was prepared by the Takenaka and Torikai method.[8] The geometrical area of the platinum-bonded SPE was 2.5 cm^2 for both side of the membrane. The apparent density of the platinum was 10 mg cm^{-2}. The apparatus used was a conventional gas-flow system at atmospheric pressure. The vapor of the fuel (CH_3OH) with helium was flowed into left compartment (anode) in Fig. 1. Oxygen was diluted and carried by helium into the right compartment (cathode) of the cell in Fig. 1. The flow rate of gas mixtures into anode and cathode compartments was 20 ml min^{-1}. Quantitative analysis of the products were carried out

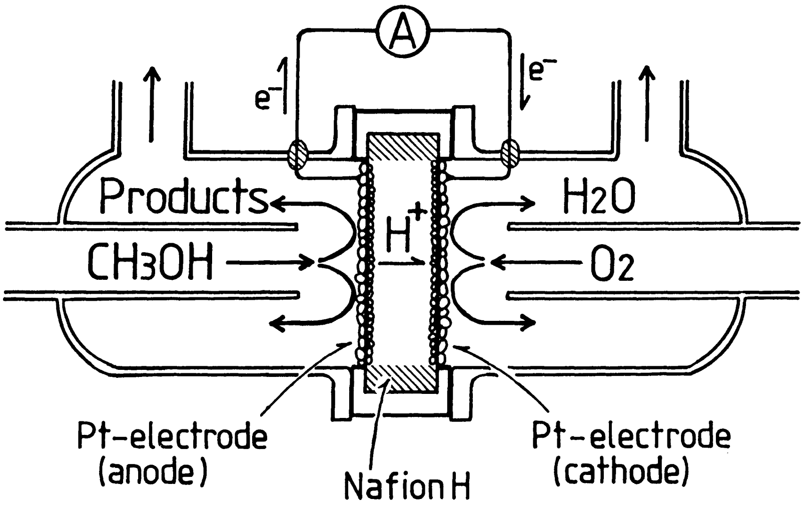

Fig. 1. Schematic diagram of the fuel cell reactor and the gas flow system.

by gas chromatography. The selectivity to the product was calculated on the basis of the carbon number of methanol reacted. All the experiments were carried out at 25 °C.

Figure 2 shows the effect of oxygen pressure on the formation rates of the products observed at anode side and on the current flowed through the external Pt wire. The oxidized products of methanol were methyl formate, methylal, carbon dioxide and water. The sum of the oxidized products at anode side ($HCOOCH_3$ + $CH_2(OCH_3)_2$ + CO_2) corresponded well to the current observed. The open circuit voltage at oxygen pressure of 101 kPa, for an example, was 0.2 V. It is to be noted that the selectivity to the partial oxidation products ($HCOOCH_3$ + $CH_2(OCH_3)_2$) was almost 100% at low pressure of oxygen (<10 kPa) or at low current. The formation rate and selectivity of methyl formate, one of the most valuable products of partial oxidation of methanol,[9,10] increased considerably as a rise in oxygen pressure. However, the increase in the rate of deep oxidation is not so appreciable. Under open circuit conditions, the oxidation of methanol with oxygen has been tested by introducing the mixture of the gases (CH_3OH(4 kPa) + O_2(97 kPa)) in the right compartment of Fig. 1 at 25 °C. The conversion rate of CH_3OH was 0.15 μmol min^{-1} and the main product was CO_2 (>95% selectivity) and traces of methylal and methyl formate. Thus, the method using fuel cell system (Fig. 1) remarkably improves the selectivity to partial oxidation.

The effects of the methanol pressure in the anode compartment on the formation rates of products and on the current are shown in Fig. 3. The rate of deep oxidation did not increase with methanol pressure (>4.0 kPa). The results in Fig. 3 show that the partial oxidation occurred selectively as increasing metha-

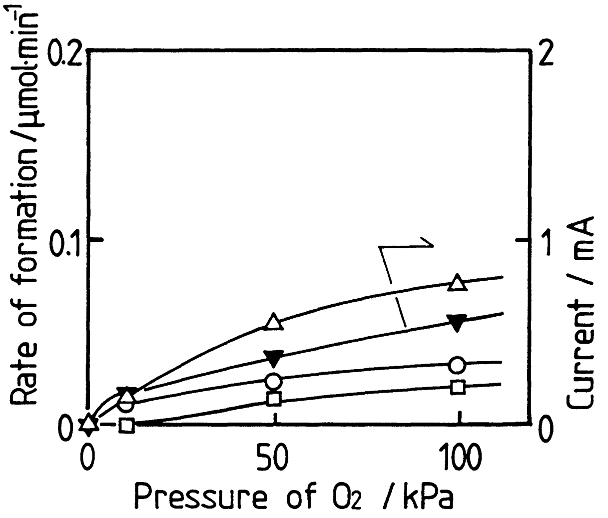

Fig. 2. Effect of oxygen pressure on the formation rates of products and on the current: (△) $HCOOCH_3$, (○) $CH_2(OCH_3)_2$, (□) CO_2, (▼) current, $P(CH_3OH)=4$ kPa, T=298 K.

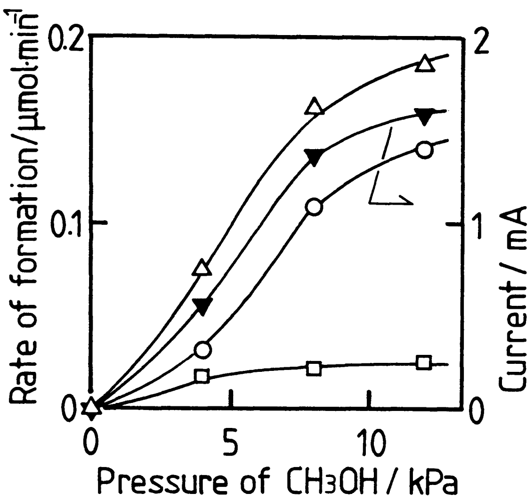

Fig. 3. Effect of methanol pressure on the formation rates of products and on the current: (△) $HCOOCH_3$, (○) $CH_2(OCH_3)_2$, (□) CO_2, (▼) current. $P(O_2)=101$ kPa, T=298 K.

nol pressure. It was confirmed that the current well corresponded to the sum of formation rates of the products.

The mechanism of electrocatalytic oxidation of methanol proposed previously was as follows.[1,2]

Anode;

$$CH_3OH \rightarrow HCHO + 2H^+ + 2e^- \quad (1)$$
$$HCHO + H_2O \rightarrow HCOOH + 2H^+ + 2e^- \quad (2)$$
$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \quad (3)$$

By acid catalysis of SPE;

$$HCHO + 2CH_3OH \rightarrow CH_2(OCH_3)_2 + H_2O \quad (4)$$
$$HCOOH + CH_3OH \rightarrow HCOOCH_3 + H_2O \quad (5)$$

where the HCHO and HCOOH were assumed as reaction intermediates.

Cathode;

$$2H^+ + 2e^- + 1/2O_2 \rightarrow H_2O \quad (6)$$

Figure 4 shows the effect of the partial pressure of H_2O added to the cathode compartment with oxygen. The content of the water absorbed in SPE increases as increasing the pressure of H_2O irrespective of the sides of the compartments to which H_2O vapor was added. The formation rates of $HCOOCH_3$ and CO_2 and the current increase as a rise in H_2O pressure. In contrast to this, the formation rate of $CH_2(OCH_3)_2$ decreases with H_2O pressure. These results suggest that the increase in the content of water in the SPE at higher pressures enhances the deeper oxidation of methanol to $HCOOCH_3$ (through Eqs. 2 and 5) and to CO_2 (through Eqs. 2, 3 and 5). In particular, the increase in H_2O pressure exerted the most favorable effect on the formation of $HCOOCH_3$ probably due to the oxidation of the intermediate HCHO by H_2O according to reaction 2, accompanied by rapid reaction 5. The selectivity to $HCOOCH_3$ at 2.7 kPa of H_2O vapor reached to 68%. The current observed in Fig. 4 also corresponded to the sum of the formation rates of the oxidized products.

It should be mentioned here that the SPE used in this work absorbs methanol and water considerable amount.[1] Therefore, we cannot neglect the leakage of methanol vapor from the anode to the cathode compartment and the oxidation by gaseous oxygen on the Pt electrode. However, as described earlier, the oxidation of the leaked CH_3OH with O_2 under the experimental conditions in this work was not so appreciable. For an example the conversion rate of the leaked CH_3OH at the cathode was 0.05 μmol min^{-1} under the highest pressure of CH_3OH at the anode compartment (12kPa in Fig. 3).

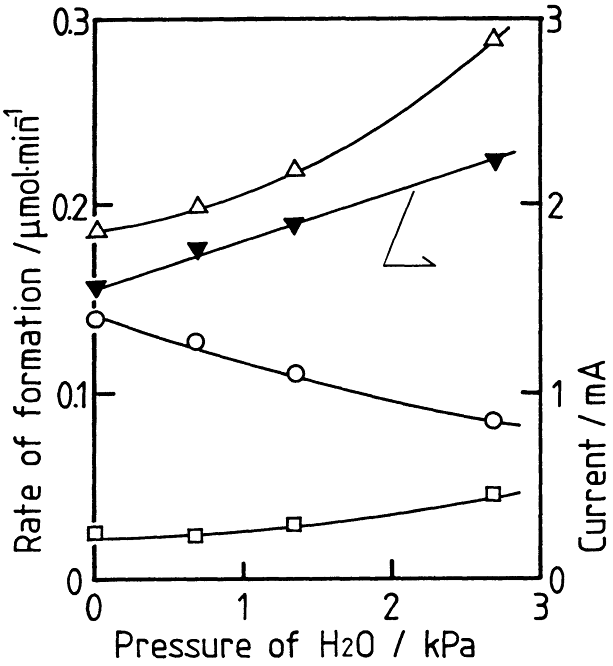

Fig. 4. Effect of water pressure on the formation rates of products and on the current: (△) $HCOOCH_3$, (○) $CH_2(OCH_3)_2$, (□) CO_2, (▼) current. $P(CH_3OH)$=12 kPa, $P(O_2)$=101 kPa, T=298 K.

References

1) K. Otsuka and I. Yamanaka, Appl. Cat., 26, 401(1986).
2) K. Otsuka, I. Yamanaka, and K. Suga, Chem. Lett., 1987, 1087.
3) K. Otsuka and I. Yamanaka, Chem. Lett., 1987, 1945.
4) C. G. Vayenas and R. D. Farr, Science, 208, 593(1980).
5) H. Iwahara, H. Uchida, and S. Tanaka, J. Appl. Electrochem., 16, 663(1986).
6) N. Kiratzis and Stoukides, J. Electrochem. Soc., 134, 1925(1987).
7) G. R. Stafford, Electrochim. Acta, 32, 1137(1987).
8) H. Takenaka and E. Torikai, Kokai Tokkyo Koho (Japan Patent), 55(1980) 38934.
9) T. Hiratani and S. Noziri, Chem. Economy Engng. Rev., 17, 21(1985).
10) M. Orisaku, Shokubai (Catalysis), 28, 211(1986).

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