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

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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.<sup>1-3)</sup> The advantage of this method has already been described.<sup>1,2)</sup> 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 However, some of the investigators have demonstrated that fuel cells and heat. 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. An external load was not applied in order to gain chemicals exclusively. A 1. platinum-bonded Nafion 117 (Du Pont) membrane was used as the SPE material. The Pt-SPE was prepared by the Takenaka and Torikai method.<sup>8)</sup> The geometrical area of the platinum-bonded SPE was  $2.5 \text{ cm}^2$  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<sub>3</sub>OH) 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<sup>-1</sup>. 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  $^{\rm O}$ 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 The oxidized products of methanol were methyl formate, methylal, carbon wire. 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<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>) was almost 100% at low pressure of oxygen (<10 kPa) or at low cur-The formation rate and selectivity of methyl formate, one of the most rent. valuable products of partial oxidation of methanol, 9,10) increased considerably However, the increase in the rate of deep oxidaas a rise in oxygen pressure. tion is not so appreciable. Under open circuit conditions, the oxidation of methanol with oxygen has been tested by introducing the mixture of the gases (  $CH_3OH(4 \text{ kPa}) + O_2(97 \text{ kPa}))$  in the right compartment of Fig. 1 at 25 <sup>O</sup>C. The conversion rate of CH<sub>3</sub>OH was 0.15  $\mu$ mol min<sup>-1</sup> and the main product was CO<sub>2</sub> (>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-

Rate of formation/µmol·min<sup>1</sup> 0.2 ЧЧ 0.1 Current 04 0 100 0 50 Pressure of O<sub>2</sub> / kPa



Fig. 2. Effect of oxygen pressure on the formation rates of products and on the current: ( $\Delta$ ) HCOOCH<sub>3</sub>, (O) CH<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>, (□) CO<sub>2</sub>, (▼) current, (O) CH<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>, (□)CO<sub>2</sub>, (▼) 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: ( $\Delta$ ) HCOOCH<sub>3</sub>,

 $P(O_2)=101 \text{ kPa}, T=298 \text{ K}.$ 

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

The mechanism of electrocatalytic oxidation of methanol proposed previously was as follows.<sup>1,2)</sup>

Anode;

 $CH_{3}OH \rightarrow HCHO + 2H^{+} + 2e^{-}$ (1) HCHO +  $H_2O \rightarrow HCOOH + 2H^+ + 2e^-$ (2) $HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$ (3)

 $\text{HCHO} + 2\text{CH}_3\text{OH} \rightarrow \text{CH}_2(\text{OCH}_3)_2 + \text{H}_2\text{O}$ (4) (5)

where the HCHO and HCOOH were assumed as reaction intermediates.

Cathode;

 $2H^{+} + 2e^{-} + 1/20_{2} \rightarrow H_{2}O$ (6)

Figure 4 shows the effect of the partial pressure of H<sub>2</sub>O 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  ${\rm H_2O}$  vapor was added. The formation rates of  ${\rm HCOOCH_3}$  and  $CO_2$  and the current increase as a rise in  $H_2O$  pressure. In contrast to this,

the formation rate of CH2(OCH3)2 decreases with H<sub>2</sub>O 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<sub>3</sub> (through Eqs. 2 and 5) and to CO2 (through Eqs. 2, 3 and In particular, the increase in  $H_2O$ 5). pressure exerted the most favorable effect on the formation of HCOOCH3 probably due to the oxidation of the intermediate HCHO by H2O according to reaction 2, accompanied by rapid reaction The selectivity to HCOOCH<sub>3</sub> at 2.7 5. 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.<sup>1)</sup> 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.



Fig. 4. Effect of water pressure
on the formation rates of products
and on the current: (△) HCOOCH<sub>3</sub>,
(○) CH<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>, (□) CO<sub>2</sub>,
(▼) current. P(CH<sub>3</sub>OH)=12 kPa,
P(O<sub>2</sub>)=101 kPa, T=298 K.

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<sup>-1</sup> under the highest pressure of  $CH_3OH$  at the anode compartment (12kPa in Fig. 3).

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