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Synthesis of Methyl Formate by Electrocatalytic Oxidation of Methanol in the Gas Phase Using Heteropoly and Phosphoric Acids

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A simple method for electrocatalytic conversion of methanol to methyl formate in the gas phase has been demonstrated. The method using heteropoly acids and phosphoric acid in a flow of methanol vapor could be applied successfully for synthesizing methyl formate with high one-pass yield and selectivity.

Methyl formate has recently received much attention since it can be a versatile starting material to prepare a variety of important organic chemicals such as formic acid, acetic acid, acetic anhydride, dimethyl formamide, and ethylene glycol, and oxogas.1,2) Four methods for the catalytic synthesis of methyl formate have so far been presented:2) (i) the dehydrogenation of methanol in the absence of oxygen; (ii) the dimerization of formaldehyde (Tischenko reaction); (iii) the carbonylation of methanol with CO, and (iv) partial oxidation of methanol by oxygen. Very recently, we have demonstrated an electrocatalytic partial oxidation of methanol into dimethoxymethane and methyl formate in the gas phase using Pt-bonded solid polymer electrolyte (Pt-SPE).3) The electrocatalytic oxidation of methanol in the gas phase required neither a supporting electrolyte nor a solvent. Thus, it is not necessary to separate products from the solutions of the reactant and products. Moreover, one-pass conversion of the reactant could be increased by controlling the current (or potential) between the electrodes.3) Thus, when the yield of methyl formate is high, the electrochemical method in the gas phase is of great advantage for purifying the desired products from unreacted reactants and by-products. The electrochemical synthesis of methyl formate can be operated at room temperature. This is another advantage of the method compared to the catalytic method (i)-(iv) which required higher temperatures than 150 °C.

In this communication, we describe the synthesis of methyl formate by means of the electrocatalytic oxidation of methanol in the gas phase using heteropoly and phosphoric acids supported on a silica wool wafer. A schematic diagram of the reactor and the principle of the method are shown in Fig. 1. The Pt black-attached silica wool wafer holding a heteropoly acid (Pt/HPA/Pt) is suspended by Pt wires in a flow of methanol vapor.

The heteropoly acids tested as solid electrolytes were $H_4SiW_{12}O_{40}$, $H_3PW_{12}O_{40}$, and H_3PMoO_{40}. The heteropoly acid (5.0 g) or phosphoric acid (85%-H_3PO_4(aq.) 0.25 ml) was dissolved in 1 ml of water. The solution was soaked

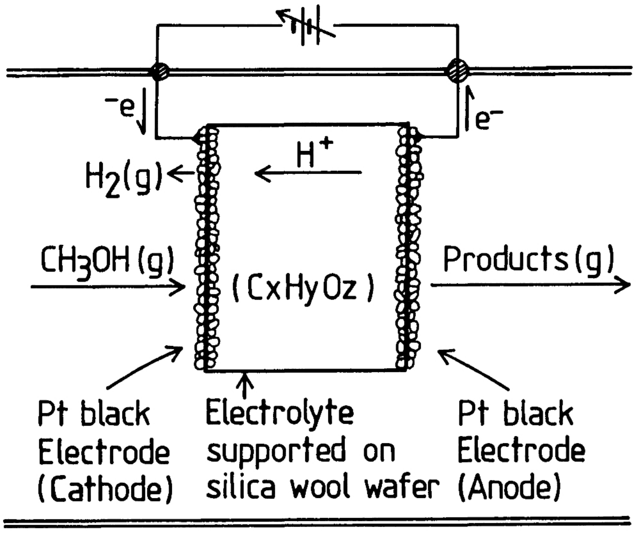


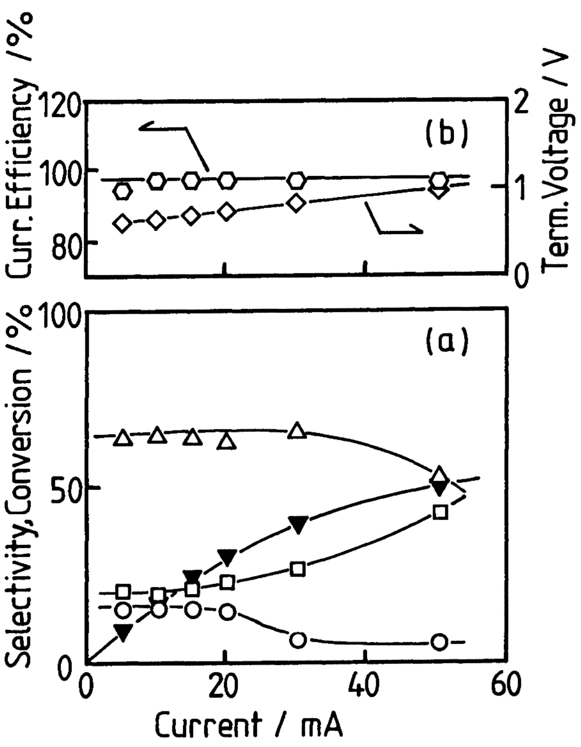
Fig. 1. Schematic diagram of the reactor and the principle of the electrocatalytic oxidation of CH_3OH in the gas phase. $(C_xH_yO_z)$ means a reaction intermediate.

into a silica wool wafer (1.0 mm thickness, 21 mm diameter). The Pt-black catalyst(20 mg) was spread uniformly on both sides of the wafer. The Pt black were adhered to the wafer after evaporating the water. The Pt-attached wafer was sandwiched between the Teflon plates (bored with many small holes) to prevent the catalysts from detaching from the wafer. The apparatus used was a conventional gas-flow system at atmospheric pressure. The vapors of the reactant and products were carried by helium. Water vapor was carried with methanol to keep the electrolytes always being wet with water. The partial pressures of methanol and water vapor at the inlet of the reactor were 3.3 and 1.2 kPa, respectively. The flow rate of the gas mixture was 20.6 ml min^{-1}. Quantitative analysis of the products were carried out by gas chromatography. All the experiments were carried out at 20 °C.

Figure 2 shows the conversion of methanol and the selectivities of the products as a function of the currents between the electrodes for the $Pt/H_4SiW_{12}O_{40}/Pt$. The terminal voltage and the current efficiency for the sum of the products ($HCOOCH_3+CH_2(OCH_3)_2+CO_2$) are also plotted at the upper part in Fig. 2. The electrocatalytic oxidation of methanol occurred when the terminal voltage was increased above 0.55 V. The products were methyl formate, dimethoxymethane, CO_2, H_2O, and hydrogen. The conversion of methanol increased to 50% with a rise of the current and terminal voltage. As can be seen in Fig. 2, the selectivity to methyl formate is fairly high (65%) at the current below 30 mA. The yield of methyl formate at the current of 50 mA reached to 26% which was higher than the value observed for the Pt-SPE (maximum 21%).[3)]

The experiments for the $Pt/H_3PW_{12}O_{40}/Pt$ gave the results (not shown) similar to Fig. 2. High conversion of methanol (41% at a current 50 mA) and high selectivity to methyl formate (74-65%) were also observed in this case. The maximum yield of methyl formate was 30% at a current 50 mA (terminal voltage 1.0 V).

In the case of $Pt/H_3PMoO_{40}/Pt$, the reaction occurred at an applied potential



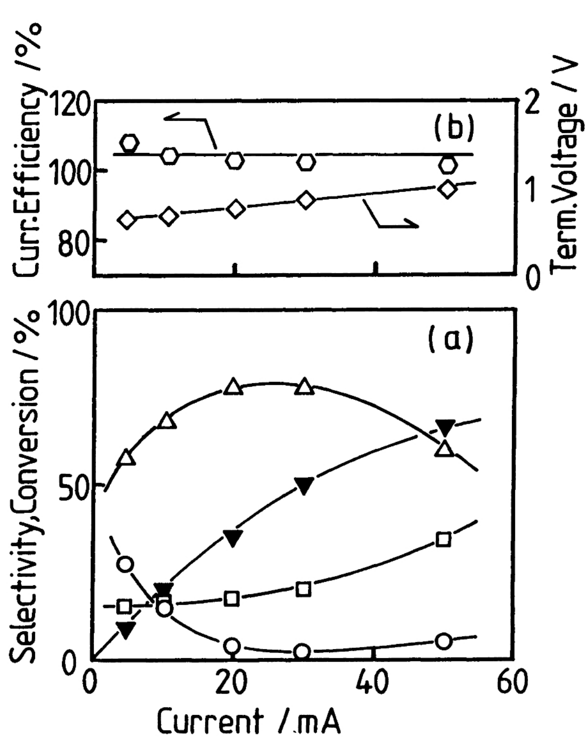


Fig. 2. The electrocatalytic oxidation of CH_3OH over $Pt/H_4SiW_{12}O_{40}/Pt$.

Fig. 3. The electrocatalytic oxidation of CH_3OH over $Pt/H_3PO_4/Pt$.

The following figure captions are common to Figs. 2 and 3: (a) conversion of CH_3OH (▼), selectivities to $HCOOCH_3$ (△), $CH_2(OCH_3)_2$ (○), and CO_2 (□) as a function of current. (b) current efficiency (⬡) and terminal voltage (◇).

lower than 0.5 V, but the maximum conversion was only 19% at a current of 15 mA (terminal voltage 9.3 V). The selectivity to methyl formate was higher than 51%. However, the maximum yield of methyl formate was 9% at a current of 10 mA.

Figure 3 shows the results observed for H_3PO_4 as an electrolyte in the silica wool wafer. The selectivity to methyl formate was fairly high (78%) at a current around 25 mA. The reaction started at the applied potential above 0.60 V. The terminal voltage at the largest current in Fig. 3 was 1.05 V. The conversion of methanol increased to 66% at 50 mA. The yield of methyl formate at 30 mA gave the highest value of 39%.

The current efficiencies for the sum of the products for most of the experiments described above were 100% within the experimental error ±5%. The only exception was for the $Pt/H_3PW_{12}O_{40}/Pt$: the current efficiency of the products for this electrocatalyst decreased from 100 to 53% when the current increased from 15 to 50 mA.

Mineral acids such as sulfuric, nitric, and hydrochloric acids could not be used as electrolytes in the silica wool wafer because they evaporated during reaction under the flow of the carrier gas. In this sense, phosphoric acids and heteropoly acids are the most suitable electrolytes for the electrochemical synthesis of the chemicals in the gas phase by the method proposed in this work. The reproducibility of the data was better than 90% for every Pt-heteropoly acids and Pt-H_3PO_4 systems tested in this work.

The reaction mechanism may be written as follows:

Anode:

$$CH_3OH \rightarrow HCHO + 2H^+ + 2e^- \quad (1)$$

$$HCHO + H_2O \rightarrow HCOOH + 2H^+ + 2e^- \quad (2)$$

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \quad (3)$$

Cathode:

$$2H^+ + 2e^- \rightarrow H_2 \quad (4)$$

In electrolytes: Fast acid catalyzed reaction by the electrolytes,

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

$$HCOOH + CH_3OH \rightarrow HCOOCH_3 + H_2O \quad (6)$$

where the HCHO and HCOOH were assumed as reaction intermediates. A trace of HCHO and HCOOH was actually observed during oxidation. The rate of evolution of hydrogen observed agreed well with the rate calculated from the current. The selectivities to $CH_2(OCH_3)_2$, $HCOOCH_3$, and CO_2 are determined by the relative rates of oxidations (1), (2), and (3). Further work is under way to support the reaction mechanism written above.

References

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