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Synthesis of Dimethyl Carbonate by Electrolytic Carbonylation of Methanol in the Gas Phase

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Electrolytic carbonylation of methanol has been attempted in the gas phase under atmospheric pressure at 343 K. The graphites added with $PdCl_2$ and $CuCl_2$ are favorable anodes for the synthesis of dimethyl carbonate (DMC). The formation of DMC occurs at a lower applied voltage than that for dimethoxy methane and methyl formate. However, a considerable CO_2 formation accompanies the DMC formation.

Dimethyl carbonate (DMC) is one of the important chemical intermediates in the current chemical industry especially because it can be substituted for phosgene in a variety of reactions. A major supplier of DMC, Enichem, uses technology based on the oxidative carbonylation of methanol (Eq. 1),$^{1,2)}$ as contrasted with the conventional synthesis from phosgene and methanol (Eq. 2).

$$2CH_3OH + CO + 1/2O_2 \xrightarrow{\text{catalysts}} (CH_3O)_2CO + H_2O \quad (1)$$

$$2CH_3OH + COCl_2 + 2NaOH \longrightarrow (CH_3O)_2CO + 2NaCl + 2H_2O \quad (2)$$

Many researchers have reported a study of chemistry concerning reaction (1) with transition metal compounds.$^{3-6)}$ However, reaction (1) requires higher pressures of CO (>20 atm) and temperatures higher than 400 K. Therefore, a new synthetic method for DMC under milder conditions is still worthy to be developed. In this report, we synthesize DMC by electrolysis in the presence of carbon monoxide and methanol under a pressure lower than 1 atmosphere at ambient temperature. As far as we know, the electrolytic carbonylation of alcohols in the gas phase has not been reported before.

The electrolytic carbonylation of methanol in the gas phase was conducted using the reactor schematically shown in Fig. 1. The cathode was prepared from Pt black (20 mg) mixed with graphite (50 mg) and Teflon powder (5 mg) by hot-press method.[7] The anode was prepared by the same procedure from the graphites added with various metal chlorides (5 wt%). The geometrical area of the electrodes was 3.1 cm^2. The proton-conducting membrane was made of a silica-wool disk containing 1 g of H_3PO_4 aqueous solution (14.7 M). A gas mixture of CO and CH_3OH and that of O_2 and H_2O were passed through the anode and the cathode compartments, respectively. Water vapor was added in the cathode compartment to keep the electrolyte being always wetted. The electrolysis was usually carried out under the following reaction conditions: Temperature=343 K, applied voltage=0.80 V, Anode; $P(CH_3OH)=43$ kPa, $P(CO)=58$ kPa, total flow rate=30 $ml \cdot min^{-1}$, Cathode; $P(O_2)=85$ kPa, $P(H_2O)=16$ kPa, total flow rate=30 $ml \cdot min^{-1}$.

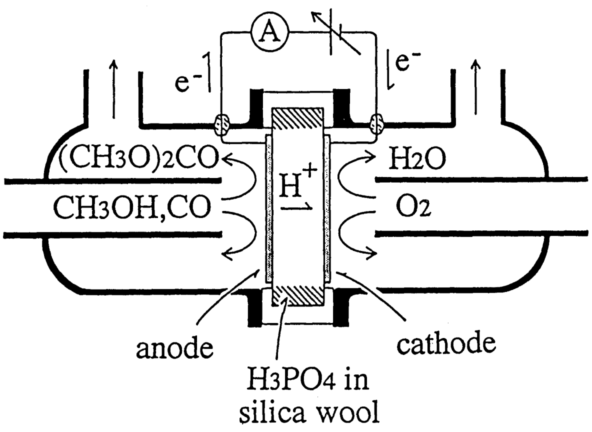

Fig. 1. Schematic diagram of the cell for electrolytic carbonylation of CH_3OH in the gas phase.

We have first looked for a favorable electrocatalyst for the synthesis of DMC under standard reaction conditions described above. Among the precious metal blacks tested as additives to the graphite cathode, Pd black was the only one that produced DMC, though its quantity was only a trace. However, the chloride of palladium remarkably enhanced the formation of DMC compared to the Pd black. Table 1 shows the results of the $PdCl_2$-added graphite cathode (denoted as $PdCl_2$/Gr) as well as those

Table 1. The anode for electrolytic carbonylation of methanol

Anode	Current/mA	Formation rate of products /$\mu mol \cdot min^{-1}$			
		DMC	DMM	MF	CO_2
Gr	0.2	<0.01	<0.01	<0.01	<0.01
$PdCl_2$/Gr	14.9	0.39	0.61	0.08	1.68
$CuCl_2$/Gr	3.4	0.18	<0.01	<0.01	0.57
$RhCl_3$/Gr	10.5	0.12	0.58	0.20	0.63
$HgCl_2$/Gr	3.8	0.05	0.11	0.16	0.50
$IrCl_3$/Gr	23.1	0.03	1.17	1.24	0.29
$RuCl_3$/Gr[a]	41.5	<0.01	2.25	2.44	0.52

[a] Applied voltage = 0.60 V.

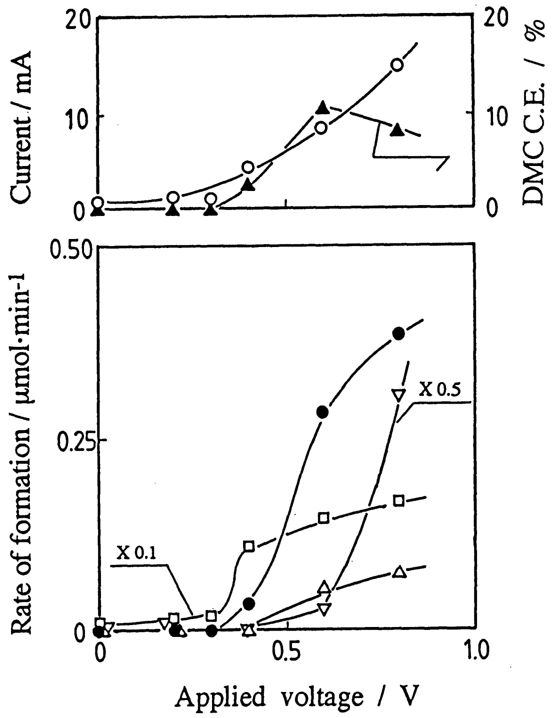

Fig. 2. Effect of applied voltage for $PdCl_2$/Gr anode: (●), DMC ; (▽), DMM; (△), MF; (□), CO_2; (○), current; (▲), current efficiency.

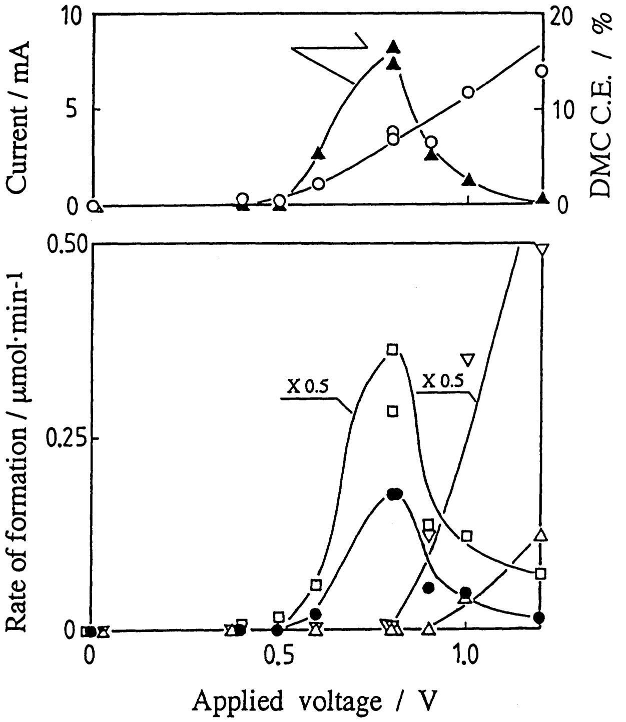

Fig. 3. Effect of applied voltage for $CuCl_2$/Gr anode: (●), DMC ; (▽), DMM; (△), MF; (□), CO_2; (○), current; (▲), current efficiency.

for the other metal chloride-added anodes. The products other than DMC obtained for these anodes were dimethoxy methane (DMM), methyl formate (MF), and CO_2. Among the anodes in Table 1, $PdCl_2$/Gr is most active for the formation of DMC. However, the selectivity to DMC is not quite high. The DMC selectivity is the highest for $CuCl_2$/Gr among the anodes in Table 1, though the electrocatalytic activity for DMC formation is lower than that for $PdCl_2$/Gr. The results in Table 1 suggest that $PdCl_2$ and $CuCl_2$ are favorable electrocatalysts for electrolytic carbonylation of methanol.

The effects of applied voltage on the formations of products for $PdCl_2$/Gr and $CuCl_2$/Gr are demonstrated in Figs. 2 and 3, respectively. The experiments were performed under the standard reaction conditions except for varying the applied voltage. Deactivation of the electrodes was only a slight within 10 h. The results in Fig. 2 indicate that the formation of DMC over $PdCl_2$/Gr takes place at an applied voltage greater than 0.3 V. A slow formation of CO_2 is observed even under short circuit conditions (applied voltage = 0 V). The rate of CO_2 formation is increased gradually with the applied voltage till 0.3 V, but a steep increase is observed above this voltage when DMC formation becomes obvious. On the other hand, the formations of DMM and MF are not initiated till about 0.5 V. The current efficiency for the formation of DMC, assuming the following electrolytic carbonylation of methanol (Figs. 3 and 4), shows the maximum at 0.6 V.

$$\text{(Anode):}\quad 2CH_3OH + CO \longrightarrow (CH_3O)_2CO + 2H^+ + 2e^- \qquad (3)$$

$$\text{(Cathode):}\quad 2H^+ + 2e^- + 1/2O_2 \longrightarrow H_2O \qquad (4)$$

The formation of DMM becomes dominant above this voltage as can be seen in Fig. 2. Therefore, the optimum applied voltage for DMC formation should be around 0.6 V.

The results for $CuCl_2$/Gr (Fig. 3) indicate that this anode requires higher anodic potential for the synthesis of DMC. DMC is formed at an applied voltage greater than 0.5 V and the maximum rate is observed at 0.8 V. The maximum current efficiency for DMC is also obtained at this applied voltage. The formations of DMM and MF initiate at >0.8 V with a decrease in the rate of DMC formation. The parallel curves for the formations of CO_2 and DMC suggest that the former accompanies the latter. The results in Fig. 3 suggest that the optimum applied voltage for DMC synthesis is around 0.8 V under standard reaction conditions.

For both $PdCl_2$/Gr and $CuCl_2$/Gr, the results in Figs. 2 and 3 suggest that the formation of DMC occurs independently of those of DMM and MF. Therefore, it is not difficult to find the experimental conditions that can avoid the formations of DMM and MF. However, the formation of DMC was always accompanied by a considerable formation of CO_2. Further studies on these reactions are under way to have a detailed knowledge of the reaction mechanism and of the optimum conditions for selective synthesis of DMC.

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