Selective Carbonylation of Methanol to Dimethyl Carbonate by Gas–Liquid–Solid-Phase Boundary Electrolysis

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Selective and efficient electrochemical carbonylation of MeOH to DMC was performed over $PdCl_2$/VGCF (vapor grown carbon fiber) anode by utilizing the three-phase boundary electrolysis at 1 atm (CO) and 298 K.

Dimethyl carbonate (DMC) is one of the important chemicals in the current chemical industry because DMC is expected to be a safe carbonylation reagent to substitute for strong toxic phosgene and dimethyl sulfate for the synthesis of carbamates, isocyanates, etc. However, the DMC production of more than 20% is manufactured by the phosgene method in the world. Parts of the DMC production are manufactured by the EniChem method[1] and the Ube method[2] from CO and MeOH. The two industrial processes have a great advantage of no use of phosgene, compared with the phosgene method, but have disadvantages such as severe conditions, multi-steps operations, and so on. Therefore, it has been desired to develop a new reaction system for the one-step synthesis of DMC from MeOH and CO under mild conditions.

We have reported the electrochemical carbonylation method for the DMC synthesis over the $PdCl_2$/graphite anodes in the gas phase at atmospheric pressure and 343 K (eq 1).[3] However, the performance for the DMC formation was not excellent because partial pressures (concentrations) of MeOH and CO on the anode were limited at atmospheric conditions.

$$2CH_3OH + CO \rightarrow (CH_3O)_2CO + 2H^+ + 2e^- \qquad (1)$$

We have concluded that the increase in the both concentrations of CO and MeOH at the anode is essential for a drastic advance in the DMC formation.

We propose a new concept and a new cell structure for the electrochemical carbonylation to enable to increase the both concentrations of CO and MeOH at the same time. Our idea is utilization of the three-phase boundary of the gas phase (CO), liquid phase (MeOH), and solid phase (anode) for the electrochemical carbonylation, as shown in Fig. 1. Solution of MeOH and electrolyte fills a space between gas-diffusion anode and cathode (2 ml). A high partial pressure of CO (101 kPa), and a high concentration of MeOH (24.8 mol l^{-1}) should be supplied to the active site at the three-phase boundary.

Figure 2 shows the effect of electrolytes dissolved in MeOH on the carbonylation over $PdCl_2$/VGCF (vapor grown carbon fiber) anode at a constant applied voltage of 3.5 V and 298 K. The anode (1.5 cm^2) was prepared by the hot-press method from electrocatalyst powder (1.1 μmol-Pd/g-VGCF) and PTFE powder. Products, dimethyl carbonate (DMC), dimethyl oxalate (DMO), dimethoxymethane (DMM), methyl formate (MF), and CO_2 were determined by GC, HPLC and GC-mass techniqes. When acidic ($HClO_4$) or basic (NaOH) electrolyte was used for the carbonylation, formation rate of (DMM + MF) was very high though DMC was exactly produced. An electrochemical activation of MeOH in acidic or basic conditions should be too strong for the carbonylation.

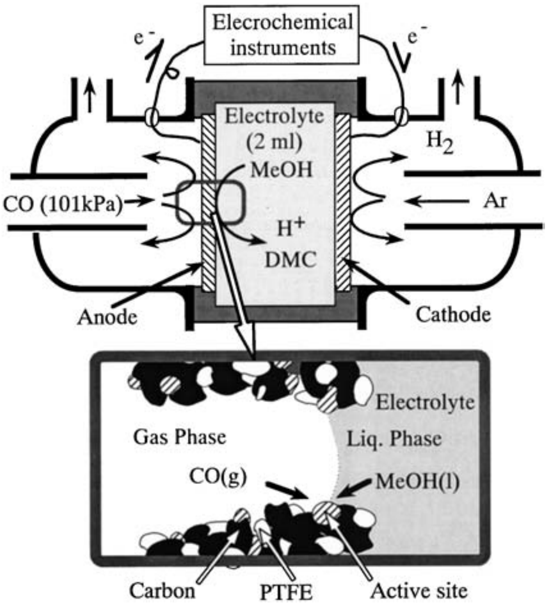

Figure 1. Concept of the three-phase boundary electrolysis for the carbonylation of methanol to dimethyl carbonate.

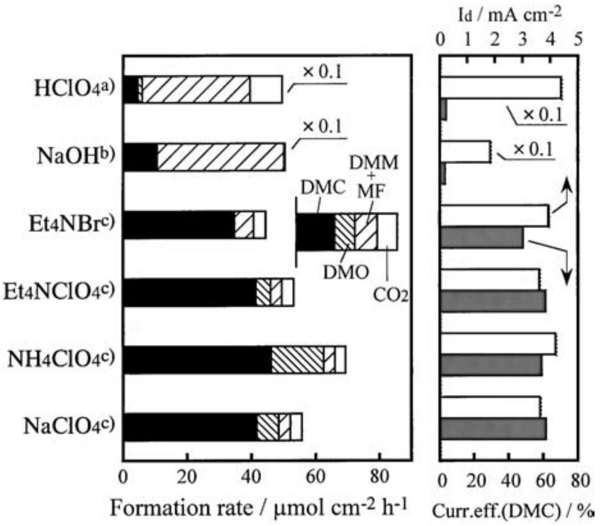

Figure 2. Effects of various electrolytes on the electrochemical carbonylation of methanol over $PdCl_2$/VGCF anode. T = 298 K, appl.volt. = 3.5 V, anode; $PdCl_2$ (1.1 μmol cm^{-2})/VGCF, CO (101 kPa), cathode; Pt/graphite, He (101 kPa). a) 0.9 mol l^{-1}, b) 0.7 mol l^{-1}, c) 0.05 mol l^{-1}.

Thus, MeOH easily oxidized to DMM and MF before the addition of CO in acidic and basic conditions.[3] As you can see clearly, neutral electrolytes, Et_4NBr, Et_4NClO_4, NH_4ClO_4 and $NaClO_4$, showed very good performances for the DMC formation. The DMC selectivities based on MeOH were reached to 80%. Among the neutral electrolytes, $NaClO_4$ was most expected one for the DMC formation because a high formation rate of $41\,\mu mol\,h^{-1}cm^{-2}$ ($TON = 37\,h^{-1}$), a high current efficiency ($CE = 60\%$) and a high CO-selectivity ($CO\text{-sel} = 70\%$). This performance was drastically improved compared with the result obtained in our previous work ($TON = 1\,h^{-1}$, $CE = 11\%$, and $CO\text{-sel} = 14\%$).[3] These results strongly show the advantage of the new electrolysis cell system for the carbonylation.

Effects of the concentration of $NaClO_4$ ($0.05–0.5\,mol\,l^{-1}$) on the carbonylation were studied. The formation rates of DMC increased with increasing in the concentration of $NaClO_4$, corresponding to the increase in current density. A higher formation rate of DMC ($TON = 100\,h^{-1}$) was obtained at $0.5\,mol\,l^{-1}$ but the formation rates of by-products also increased. Thus, a high CE of 59% and a high CO-sel of 66% were obtained at $0.1\,mol\,l^{-1}$.

Figure 3 shows effects of $PdCl_2$ loading over VGCF on the carbonylation at 3.5 V. The current densities were almost constant without dependence of $PdCl_2$ loading. The formation rate of DMC increased with increasing in $PdCl_2$ loading. In contrast, the formation rate of DMO increased with decreasing in the $PdCl_2$ loading. On the other hand, the formation rates of CO_2 and the oxidation product of MeOH (DMM and MF) increased slightly with increasing in the $PdCl_2$ loading. A very high TON of $192\,h^{-1}$ for the DMC formation was obtained at the $PdCl_2$ loading of $0.27\,\mu mol\,cm^{-2}$ though the formation rate of DMO was fairly large. The most effective $PdCl_2$ loading is around $2.1\,\mu mol\,cm^{-2}$ because the highest formation rate of DMC, the highest CE of 65% and the highest CO-sel of 83% were obtained. This $PdCl_2$/VGCF anode could be repeatedly used for the carbonylation for 3 times. This fact proposed that Pd species should be held on the VGCF during the carbonylation. However, we have not obtained any information for formula and state of Pd species, yet.

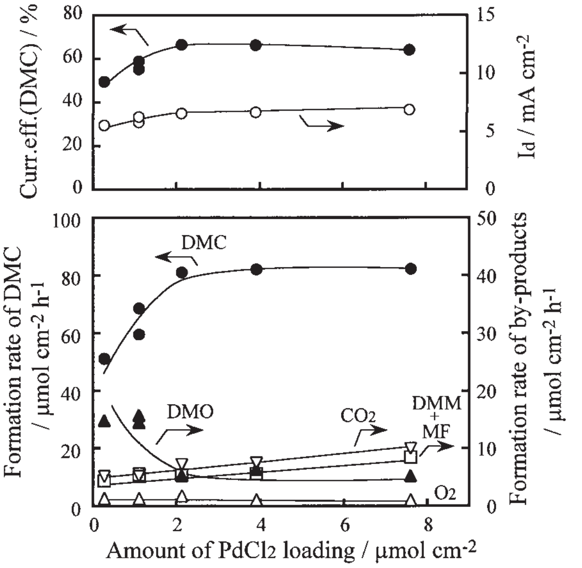

Figure 3. Effects of $PdCl_2$ loading on the carbonylation of methanol over the $PdCl_2$/VGCF anode. $T = 298\,K$, appl.volt. = 3.5 V, anode; CO (101 kPa), electrolyte; $NaClO_4$ ($0.1\,mol\,l^{-1}$)/CH_3OH.

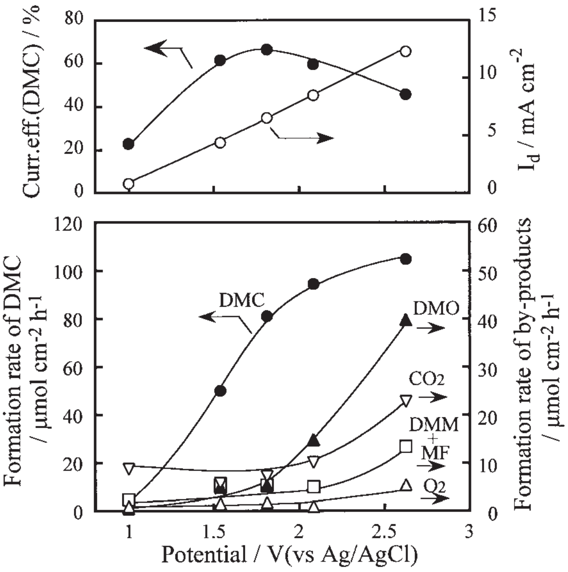

Figure 4. The carbonylation of methanol over $PdCl_2$/VGCF anode as functions of anode potentials. $T = 298\,K$, anode; $PdCl_2$ ($2.1\,\mu mol\,cm^{-2}$)/VGCF, CO (101 kPa), electrolyte; $NaClO_4$ ($0.1\,mol\,l^{-1}$)/CH_3OH.

Figure 4 shows the effect of anode potentials on the carbonylation of MeOH over $PdCl_2$/VGCF anode under potentiostatic conditions. The anode potential at the applied voltage of 3.5 V was 1.80 V (vs Ag|AgCl). The carbonylation of MeOH began from 1.0 V (Ag|AgCl). The formation rate of DMC linearly increased with increasing in anode potentials until 2.0 V, but decelerated above 2.0 V. In contrast to the DMC formation, the formation rate of DMO accelerated above 2.0 V. The formation rates of CO_2, DMM + MF, and O_2 also increased above 2.0 V. These observations recommend the change of the electrocatalysis of $PdCl_2$/VGCF anode at around 2.0 V. We didn't obtain detail information on the reaction mechanism in this system. On the basis of previous work,[3,4] Pd^{2+}/Pd^0 redox should catalyze the electrochemical carbonylation of MeOH (eq 1) and the electrochemical oxidation of MeOH (eq 2-3).[5] However, we did not observe the formation of DMO (eq 4) over $PdCl_2$/graphite anode in our previous work.[3] Equivalent H_2 corresponding to the carbonylation (eq 1 and 4) and the oxidation (eq 2 and 3) was produced at the cathode. We must continuously study to clarify the reaction mechanism for the formation of DMC and DMO over the $PdCl_2$/VGCF anode.

$$3CH_3OH \rightarrow (CH_3O)_2CH_2 + H_2O + 2H^+ + 2e^- \quad (2)$$

$$2CH_3OH + H_2O \rightarrow HCO_2CH_3 + 4H^+ + 4e^- \quad (3)$$

$$2CH_3OH + 2CO \rightarrow (CO_2CH_3)_2 + 2H^+ + 2e^- \quad (4)$$

As described so far, the three-phase boundary electrolysis was effective for the carbonylation of MeOH to DMC under mild conditions. A good performance of the DMC production ($40\,TON\,h^{-1}$, 67% current efficiency, 82% CO-selectivity) over the $PdCl_2$ ($2.1\,\mu mol\,cm^{-2}$)/VGCF anode was obtained at 1.8 V (Ag|AgCl) by using the neutral electrolyte ($NaClO_4$ $0.1\,mol\,l^{-1}$).

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