

## Selectivity Control of Carbonylation of Methanol to Dimethyl Oxalate and Dimethyl Carbonate over Gold Anode by Electrochemical Potential

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Carbonylation of methanol to dimethyl carbonate (DMC, **1**) and dimethyl oxalate (DMO, **2**) are currently very important key reactions. **1** is expected to be a safe carbonylation reagent to substitute for highly toxic phosgene for the synthesis of polycarbonate and isocyanates.<sup>1,2</sup> **2** is an intermediate for oxalic acid and is expected to reduce to ethylene glycol. Pd catalysis for the carbonylation of methanol is well-known.<sup>3</sup> UBE Industries developed the chemical processes for the production of **1** and alkyl oxalate with Pd-catalyst and alkyl nitrite.<sup>4</sup> The selectivities to **1** and **2** were drastically changed with additives and reaction conditions.<sup>5</sup> We have recently reported the selective electrochemical carbonylation to **1** over a Pd/carbon anode.<sup>6</sup> **2** was a minor product, and its selectivity could not be controlled over the Pd anode.<sup>6,7</sup> We have found new electrocatalysis of gold during the carbonylation studies. The selectivities to **2** and **1** could be controlled over the gold anode by an electrochemical potential.

The electrochemical carbonylation of methanol was studied under potentiostatic conditions by using an H-type conventional electrolysis cell. The electrolysis was carried out in MeOH with NaClO<sub>4</sub> electrolyte and bubbling CO (1 atm). Products, **2**, **1**, CO<sub>2</sub>, methylal (DMM), and methyl formate (MF), were analyzed by a gas chromatograph technique. Gold electrocatalyst was prepared by the impregnation method from HAuCl<sub>4</sub> solution and AC (active carbon). An Au anode was prepared from the HAuCl<sub>4</sub>/AC electrocatalyst, VGCF (vapor grown carbon fiber), and Teflon powder by the hot-press method.<sup>6</sup>

Table 1 shows electrochemical carbonylation activities over various anodes (metal compound/AC + VGCF). It was confirmed that **1** was selectively produced over the [PdCl<sub>2</sub>/AC + VGCF] anode (entry 1).<sup>6,7</sup> In entry 2, we have found that the [HAuCl<sub>4</sub>/AC + VGCF] anode was active for the carbonylation of methanol, and the major product was **2**, but **1** was minor. Other electrocatalysts did not show the carbonylation activity (entries 3–7).

To obtain information for a state of Au on the HAuCl<sub>4</sub>/AC electrocatalyst, XRD spectra were measured, and XRD patterns at 2θ = 38° and 44° were assigned to Au<sup>0</sup>(111) and Au<sup>0</sup>(200) from JCPDS data. HAuCl<sub>4</sub> on AC was reduced to Au<sup>0</sup> during the impregnation procedure. Therefore, the Au anode is indicated as [Au<sup>0</sup>/AC + VGCF], hereafter.

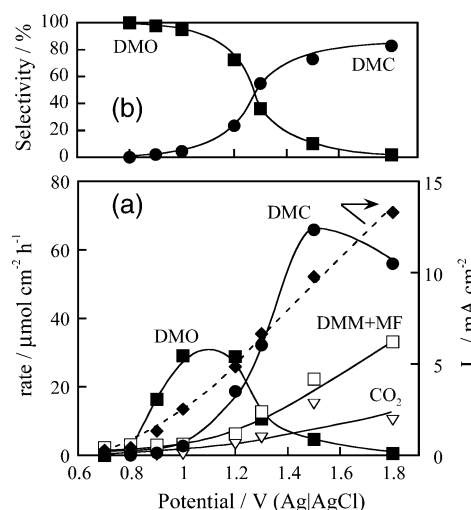
Figure 1a shows the effects of anode potentials on the electrochemical carbonylation of methanol over the [Au<sup>0</sup>/AC + VGCF] anode. **2** was produced at >+0.7 V. The formation rate of **2** attained to the maximum around +1.2 V. In contrast, **1** was produced at >+1.0 V and reached an upper limit at +1.5 V. The formation rate of the sum of DMM and MF increased with anode potentials >+1.0 V. On the other hand, the formation rate of CO<sub>2</sub> was suppressed even at higher anode potentials.

Figure 1b shows the selectivities to **2** and **1** based on CO. The selective carbonylation to **2** was performed at lower potentials. In contrast, the selectivity to **1** was fairly high at higher potentials. This fact clearly proves that the electrochemical carbonylation

**Table 1.** Electrochemical Carbonylation<sup>a</sup> over Various Anodes

| entry | anode              | formation rate / μmol cm <sup>-2</sup> h <sup>-1</sup><br>(current efficiency/%) |               | I <sub>d</sub> / mA cm <sup>-2</sup> |
|-------|--------------------|--|---------------|--------------------------------------|
|       |                    | DMC, <b>1</b>  | DMO, <b>2</b> |                                      |
| 1     | PdCl <sub>2</sub>  | 58.6 (67.7)  | 0.2 (0.2)     | 4.6                                  |
| 2     | HAuCl <sub>4</sub> | 2.3 (5.1)  | 29.6 (65.1)   | 2.4                                  |
| 3     | RhCl <sub>3</sub>  | 0 (0)  | 0 (0)         | 1.2                                  |
| 4     | RuCl <sub>3</sub>  | 0 (0)  | 0 (0)         | 5.0                                  |
| 5     | IrCl <sub>3</sub>  | trace  | trace         | 1.5                                  |
| 6     | CuCl <sub>2</sub>  | 0 (0)  | 0 (0)         | 1.1                                  |
| 7     | AC+VGCF            | 0 (0)  | 0 (0)         | 1.5                                  |

<sup>a</sup> T = 298 K, anode potential = 1.0 V (Ag|AgCl), anodes: [metal compound/AC + VGCF], NaClO<sub>4</sub> (0.1 mol l<sup>-1</sup>)/MeOH.

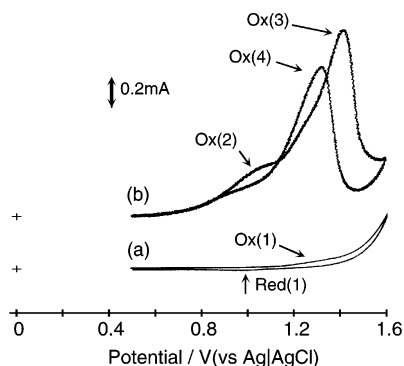


**Figure 1.** Effects of anode potential on the carbonylation of methanol over the [Au<sup>0</sup>/AC + VGCF]. T = 298 K, Au loading 6 wt %, CO (101 kPa), NaClO<sub>4</sub> electrolyte 0.1 mol l<sup>-1</sup>.

selectivities can be controlled over the [Au<sup>0</sup>/AC + VGCF] anode by potentials.

To obtain information for electrocatalysis of the [Au<sup>0</sup>/AC + VGCF] anode, cyclic voltammogram (CV) studies were carried out. However, no significant CV spectra were obtained because of large double-layer capacity of the [Au<sup>0</sup>/AC + VGCF] electrode. Therefore, CV studies for the Au wire electrode were carried out under the same conditions as those for electrochemical carbonylation (Figure 2). CV(a) shows a spectra of Au wire swept between +0.5 V and +1.6 V in He. Small oxidation current, Ox(1) at +1.2 V, and small reduction current, Red(1) at +1.0 V, were observed. This redox couple was assigned to Au<sup>3+</sup>/Au<sup>0</sup> from standard redox potentials.

Large oxidation current above +1.5 V was due to oxidation of methanol to DMM and MF. In CO, large oxidation current was observed at lower potentials >+0.6 V in CV(b). When the potential was swept to the positive side, two oxidation peaks, Ox(2) at +1.0



**Figure 2.** Cyclic voltammograms over the Au electrode. Scan rate 50 mV/s, NaClO<sub>4</sub> electrolyte 0.1 mol l<sup>-1</sup>, (a) He, CH<sub>3</sub>OH, (b) CO, CH<sub>3</sub>OH.

V and Ox(3) at +1.4 V, were observed in CV(b). When the potential was returned and swept to the negative side, there were no reduction peaks corresponding to the Ox(2) and Ox(3), but an oxidation peak, Ox(4), was observed. No redox couple in CV(b) proposed that the Ox(2), Ox(3), and Ox(4) peaks were electrochemically irreversible reactions. The Ox(2) peak potential was more negative than that of Au<sup>0</sup>/Au<sup>3+</sup>. Therefore, the oxidation current in the Ox(2) should be due to oxidation of CO or the carbonylation over Au<sup>0</sup>. The Ox(3) peak potential overlapped that of the Au<sup>0</sup>/Au<sup>3+</sup>, Ox(1), which proposed that the large oxidation current was due to the CO oxidation or the carbonylation over Au<sup>3+</sup>. The Ox(4) peak may correspond to that of the Ox(3). On the basis of potentiostatic electrolysis results (Figure 1), the Ox(2) over Au-wire anode may be corresponding to the formation of **2**, and the Ox(3) and the Ox(4) may be corresponding to the formation of **1**.

To identify a correlation between oxidation currents of Ox(2), Ox(3), Ox(4), and product formations, quantitative analysis of product yields during the CV cycle were examined by repeating CV cycles more than 200 times. A very good reproducibility of CV spectra was observed. Yields of **2** and **1** normalized at 100 cycles between +0.5 and +1.2 V were 0.5 μmol (26% CE) and 0.4 μmol (24% CE), respectively. Significant yields of **2** and **1** were obtained, which proved that the electrochemical carbonylation of methanol was completed during the CV cycle. When the CV scan extended from +0.5 to +1.6 V, the **2** and **1** yields (100 CV) were 0.8 μmol (13% CE) and 2.1 μmol (33% CE), respectively. A large increase in the **1** yield was observed by the extension of the potential from +1.2 to +1.6 V but a little increase in the **2** yield. These results strongly proposed that the oxidation current of the Ox(3) and Ox(4) was corresponding to the formation of **1**. On the other hand, the oxidation current of Ox(2) was mainly corresponding to the formation of **2**.

If the Ox(3) and Ox(4) were strongly involved in the formation of **1**, Au<sup>3+</sup> would promote the formation of **1**. Therefore, stoichiometric reactions of Au<sup>3+</sup>, MeOH, and/or CO in the presence of NaClO<sub>4</sub> were studied (Table 2). Entry 1 shows the stoichiometric reaction among HAuCl<sub>4</sub>, MeOH, and CO. **1** and CO<sub>2</sub> were produced, but there were no formations of **2**, DMM, and MF (eq 1).

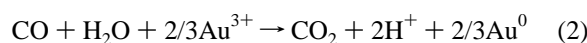
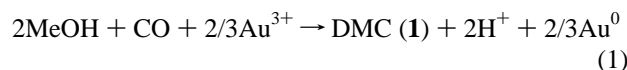
When CO was absent (entry 2), no products were observed. On the other hand, when MeOH was replaced by H<sub>2</sub>O (entry 3), almost perfect stoichiometric oxidation of CO to CO<sub>2</sub> with H<sub>2</sub>O by Au<sup>3+</sup> proceeded (eq 2). Purple-black powder (Au<sup>0</sup>) was deposited after the experiments of entries 1 and 3. Of course, no products formed

**Table 2.** Stoichiometric Reaction<sup>a</sup> of HAuCl<sub>4</sub> with CO and MeOH

| entry |  | amount of products/μmol |       |        |                 |
|-------|--|-------------------------|-------|--------|-----------------|
|       |  | DMC 1                   | DMO 2 | DMM+MF | CO <sub>2</sub> |
| 1     | HAuCl <sub>4</sub> , CO, CH <sub>3</sub> OH              | 15.3                    | 0     | trace  | 4.2             |
| 2     | HAuCl <sub>4</sub> , He, CH <sub>3</sub> OH              | 0                       | 0     | 0      | 0               |
| 3     | HAuCl <sub>4</sub> , CO, H <sub>2</sub> O                | 0                       | 0     | 0      | 43.5            |
| 4     | Au/AC, CO, CH <sub>3</sub> OH                            | 0                       | 0     | trace  | 0               |
| 5     | HAuCl <sub>4</sub> , CO, CH <sub>3</sub> OH <sup>b</sup> | 3.4                     | 0     | trace  | trace           |

<sup>a</sup> T = 298 K, reaction time = 60 min, Au compounds 30 μmol, CO 101 kPa, NaClO<sub>4</sub> (0.1 mol l<sup>-1</sup>)/MeOH (30 mL). <sup>b</sup> Without NaClO<sub>4</sub>.

with the Au<sup>0</sup>/AC (entry 4). It is to be noted that the yields of **1** and CO<sub>2</sub> remarkably decreased (entry 5) when NaClO<sub>4</sub> was removed from the reaction conditions of entry 1. This result proposed that NaClO<sub>4</sub> in methanol should enhance the carbonylation.



In conclusion, **1** was produced through the indirect electrochemical carbonylation of MeOH and CO, mediated by Au<sup>3+</sup>/Au<sup>0</sup> (or Au<sup>+</sup>) redox reaction. On the other hand, **2** was produced by the direct electrochemical carbonylation of methanol with CO over Au<sup>0</sup>, because the oxidation current of Ox(2) was corresponding to the formation of **2** and **2** was not formed in the stoichiometric reactions (Table 2). Detailed reaction mechanisms for the formation of **2** over Au<sup>0</sup> and for **1** over Au<sup>3+</sup> have not yet been clarified. The carbonylation selectivities to **2** and **1** over the [Au<sup>0</sup>/AC + VGCF] anode could be controlled by changing the oxidation state of gold with anode potentials. This unique function of Au electrocatalysis should be the first report.<sup>8</sup>

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