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# Carbonylation of formaldehyde catalyzed by *p*-toluenesulfonic acid

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**Abstract**

A catalytic system consisting of *p*-toluenesulfonic acid, a transition metal complex such as $CF_3SO_3Ag$, and a solvent exhibits a high catalytic performance for the carbonylation of formaldehyde, followed by esterification with methanol, to produce methyl glycolate. The catalytic performance is significantly improved by using the ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, instead of organic solvents. This catalytic system shows higher yield of methyl glycolate at relatively low CO pressure in comparison to solid acid catalysts. The present system provides a potential process for synthesizing methyl glycolate via carbonylation of formaldehyde in much low corrosion in comparison to the previous system including strong inorganic liquid acids as solvents and catalysts.

*Keywords:* Formaldehyde; Carbonylation; Glycolic acid; Methyl glycolate; *p*-Toluenesulfonic acid; Catalysis

## 1. Introduction

Ethylene glycol has been widely used as a solvent for dyes and grease, freeze-proof liquids and a starting material for organic synthesis. Ethylene glycol is commercially produced by the partial oxidation of ethylene over silver catalysts to ethylene oxide which is then hydrated to ethylene glycol [1]. However, such a process has the drawback of low conversion yield of ethylene glycol. There have been a considerable number of efforts to synthesize ethylene glycol from syngas or its derivatives. Although direct production of ethylene glycol from syngas is simple, the very high pressure and the high cost of Rh based catalysts limit the development of this process [2]. Since formaldehyde is the intermediate of ethylene glycol production from syngas, there has been great interest in the synthesis of ethylene glycol by using formaldehyde as a starting material via the routes of hydroformylation of formaldehyde to glycolaldehyde or carbonylation of formaldehyde to glycolic acid [3,4]. The carbonylation of formaldehyde to ethylene glycol contains three steps: acid-catalyzed carbonylation under very high pressure to glycolic acid, esterification to methyl glycolate (MG) and hydrogenation to ethylene glycol. This process was once practiced commercially by the Du Pont Company and was discontinued in 1968 because of high corrosion rates in the presence of $H_2SO_4$ catalyst under 90 MPa. This process was improved by the use of concentrated $H_2SO_4$ and metal carbonyl cations, which enabled the carbonylation to proceed under mild conditions [5–7]. However, a strong inorganic liquid acid medium was also inevitably employed. The huge amount of strong inorganic liquid acids used for this reaction results in serious corrosion, difficulties in product separation and disposal problems. Although there have been several reports on the more environmentally friendly solid acid-catalyzed carbonylation of formaldehyde [8–10], the reaction could be only carried out at high CO pressures to produce acceptable yields. For example, the highest methyl glycolate yield of 80% could be obtained on Amberlyst 15 catalyst under a CO pressure as high as 24 MPa [10].

On the other hand, ionic liquids (ILs) are a new class of solvents which present interesting properties such as non-volatility, high stability and easy recyclability [11]. These green media have been successfully applied in a wide range of catalytic processes [12], including hydroesterification of *tert*-butyl alcohol with ethanol toward ethyl *tert*-valerate [13].

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In this work, we report a composite catalyst system consisting of *p*-toluenesulfonic acid (*p*-TsOH), a transition metal complex such as $CF_3SO_3Ag$ and a solvent, which shows high catalytic activities for the carbonylation of formaldehyde, followed by esterification with methanol, towards methyl glycolate. The catalytic activity is improved by using the ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, instead of organic solvents.

## 2. Experimental

The catalytic carbonylation of formaldehyde with CO was carried out in a 50 ml magnetically stirred stainless steel autoclave, sealed with a Teflon O-ring and equipped with a Teflon coated magnetic stirring bar, a 20 MPa manometer and an electric furnace. 1,3,5-Trioxane (98%, Kishida Chemicals) was used as a source of formaldehyde. Two types of ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIm[$PF_6$], $\geq$99%, Solvent Innovation) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm[$BF_4$], $\geq$97%, Fluka), were used without futher purification. In a typical experiment, 1,3,5-trioxane, water, an organic solvent or an ionic liquid, *p*-toluenesulfonic acid (monohydrate, >99%, Wako Chemicals) and a transition metal complex were charged into the autoclave. The reactor was flushed three times with CO (>99.95%) and then pressurized to a desired pressure. The initial CO pressure at room temperature was varied in the range of 2.5–15.0 MPa. The reactor was heated from room temperature to the desired temperature in ca. 30 min and held at this temperature for 2 h. After the reaction, the reactor was cooled to room temperature in an ice bath and depressurized over a period of ca. 10 min. For the esterification, excess methanol was added into the autoclave and continuously reacted at 135 °C for 2 h. After the reaction, the products were analyzed on a Hitachi G-3500 chromatograph equipped with a TC-Wax (0.25 μm, 0.25 mm i.d. × 30 m) capillary column, a split injector and an FID. A known quantity of toluene was added into the liquid products and served as the internal standard for quantitative analysis. Unconverted formaldehyde was detected as dimethoxymethane. In addition to desired MG, the reaction products contained methyl formate (MF), methyl acetate (MMAc) and some unidentified by-products of high molecular weights.

## 3. Results and discussion

### *3.1. Effects of solvent and transition-metal co-catalyst*

The strong organic acid, *p*-toluenesulfonic acid (*p*-TsOH) was used as the catalyst for the reaction of formaldehyde with CO in different solvents in the absence and presence of various transition metal complexes (Table 1). It can be seen that formaldehyde easily reacts with CO in the presence of the strong organic acid, *p*-TsOH. Nearly all the formaldehyde disappears using BMIm[$PF_6$] (entries 9–17) as the reaction medium, and only a small amount of formaldehyde remains unreacted in the case of BMIm[$BF_4$] (entry 8) or some organic solvents (entries 1–7). In the absence of transition metal complexes, higher yield of MG (71.7%) is obtained in BMIm[$PF_6$] (entry 9) than in methyl benzoate (59.8%) (entry 1) or in other organic solvents (entries 2–7). From Table 1, it can be seen that the addition of transition metal compounds has no any improving effect on the yield of MG in organic solvents (entries 2 and 3). Similar results have been obtained in the

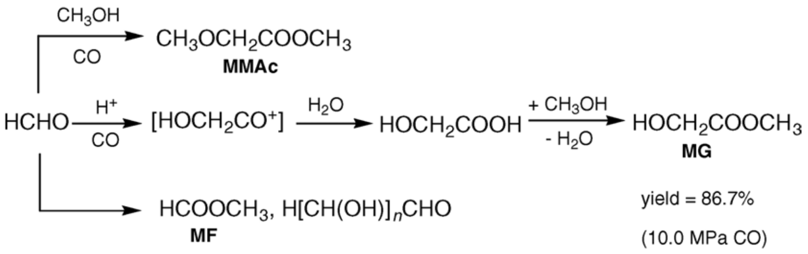
Table 1
Carbonylation of formaldehyde catalyzed by *p*-toluenesulfonic acid[a]

| Entry | Metal complex | Solvent | HCHO conversion (%) | Yield (%) | | | Selectivity (%) |
|---|---|---|---|---|---|---|---|
| | | | | MG[b] | MF[b] | MMAc[b] | |
| 1 | – | MB[c] | 93.8 | 59.8 | 6.3 | 5.2 | 63.8 |
| 2 | $CF_3SO_3Ag$ | MB | 93.6 | 59.3 | 1.7 | 4.2 | 63.4 |
| 3 | $(CF_3SO_3)_2Cu$ | MB | 95.9 | 59.2 | 5.9 | 6.6 | 61.7 |
| 4 | $AgBF_4$ | MB | 96.0 | 55.3 | 4.8 | 2.7 | 57.6 |
| 5 | $AgBF_4$ | Methanol | – | 3.6 | – | 0.7 | – |
| 6 | $AgBF_4$ | Hexane | 95.2 | 34.7 | 3.0 | 1.8 | 36.4 |
| 7 | $AgBF_4$ | MA[c] | 95.9 | 59.7 | 6.5 | 5.5 | 62.3 |
| 8 | $CF_3SO_3Ag$ | BMIm[$BF_4$][c] | 93.2 | 49.7 | 4.8 | 1.5 | 53.3 |
| 9 | – | BMIm[$PF_6$] | 99.0 | 71.7 | 1.4 | 0.6 | 72.4 |
| 10 | $CF_3SO_3Ag$ | BMIm[$PF_6$][c] | 99.5 | 86.7 | 1.8 | 0.7 | 87.1 |
| 11 | $AgBF_4$ | BMIm[$PF_6$] | 99.6 | 83.3 | 0.6 | 1.3 | 83.6 |
| 12 | $Ag_2SO_4$ | BMIm[$PF_6$] | 99.4 | 81.0 | 1.7 | 1.0 | 81.5 |
| 13 | $CH_3COOAg$ | BMIm[$PF_6$] | 99.3 | 79.3 | 1.8 | 1.2 | 79.9 |
| 14 | $(CH_3COO)_2Pd$ | BMIm[$PF_6$] | 99.7 | 75.2 | 3.3 | 2.9 | 75.4 |
| 15 | $(CF_3SO_3)_2Cu$ | BMIm[$PF_6$] | 97.8 | 80.8 | 2.5 | 0.5 | 82.6 |
| 16 | $CuSO_4$ | BMIm[$PF_6$] | 99.7 | 75.4 | 2.6 | 1.6 | 75.6 |
| 17 | $CuCl_2$ | BMIm[$PF_6$] | 99.8 | 74.7 | 1.9 | 0.5 | 74.8 |

[a] *Reaction conditions of carbonylation*: formaldehyde = 34 mmol, *p*-TsOH = 16.8 mmol, metal ion/*p*-TsOH (molar ratio) = 0.01, water = 34 mmol, solvent = 4.0 ml, CO pressure (initial pressure at room temperature) = 10.0 MPa, 135 °C, 2 h. *Reaction conditions of esterification*: methanol = 0.68 mol, 135 °C, 2 h.

[b] MG, methyl glycolate; MF, methyl formate; MMAc, methyl methoxy acetate.

[c] MB, methyl benzoate; MA, methyl acetate; BMIm[$BF_4$], 1-butyl-3-methylimidazolium tetrafluoroborate; BMIm[$PF_6$], 1-butyl-3-methylimidazolium hexafluorophosphate.



Scheme 1.

methyl benzoate and methyl acetate solvents (entries 4 and 7). Much lower yield of MG has been obtained in the hexane solvent (entry 6), probably due to its low polarity. Reaction almost does not proceed with methanol as a solvent (3.6% MG yield) (entry 5). BMIm[$BF_4$] gives a yield of MG even lower than in some organic solvents (entry 8). The addition of transition metal compounds as co-catalysts into BMIm[$PF_6$] results in improvements of the MG yield (entries 10–17). $CF_3SO_3Ag$ gives the highest yield of MG as high as 86.7% at 10.0 MPa of CO (Scheme 1) (entry 10), which is much higher than the MG yield (about 54%) on the solid acid catalyst, Amberlyst 15, at the same CO pressure [10]. In comparison with the organic solvents, the good yield of MG using BMIm[$PF_6$] as reaction medium is probably due to the stabilization effect of the acylium ion intermediate, $HOCH_2CO^+$, in BMIm[$PF_6$] (Scheme 1). Ionic liquids are ionic solvents that consist entirely of ions and possess a strong static field. This strong static field can probably stabilize the acylium cation, leading to the formation of glycolic acid in ionic liquids more easily.

### 3.2. Effect of $H_2O$ addition

From the reaction mechanism shown in Scheme 1, it seems that the addition of $H_2O$ facilitates the conversion of the acylium ion intermediate, $HOCH_2CO^+$, to glycolic acid. The effect of water addition on the carbonylation of formaldehyde using the room temperature ionic liquid BMIm[$PF_6$] as the reaction medium is presented in Table 2. In the absence of water, nearly all the formaldehyde disappears, but the yield of MG is as low as 38.1% and a large amount of polyglycolide forms. The addition of $H_2O$ into the reaction mixture causes the yield of MG to increase until reaching the highest value at $H_2O$/HCHO (molar ratio) = 1.0. The yield of MG begins to decrease with further $H_2O$ addition, and at the same time, a small amount of unreacted formaldehyde appears. Obviously, water appears to stabilize the carbonylated formaldehyde as glycolic acid and depresses the formation of polyglycolide. On the other hand, the addition of excess $H_2O$ moderates the acidity of the reaction mixture, and therefore, results in the lowering of catalytic activity.

Table 2
Influence of $H_2O$ addition on the carbonylation of formaldehyde[a]

| $H_2O$/HCHO (molar ratio) | HCHO conversion (%) | Yield (%) | | | Selectivity (%) |
|---|---|---|---|---|---|
| | | MG | MF | MMAc | |
| 0 | 99.7 | 38.1 | 0.5 | 1.2 | 38.2 |
| 0.5 | 99.9 | 57.4 | 0.9 | 1.0 | 57.5 |
| 1.0 | 99.5 | 86.7 | 1.8 | 0.7 | 87.1 |
| 5.0 | 85.4 | 54.9 | 5.2 | 0.4 | 64.3 |
| 10.0 | 49.5 | 3.8 | 2.9 | 0.1 | 7.7 |

[a] *Reaction conditions of carbonylation*: *p*-TsOH = 16.8 mmol, $CF_3SO_3Ag$ = 0.168 mmol, formaldehyde = 34 mmol, BMIm[$PF_6$] = 4.0 ml, CO pressure (initial pressure at room temperature) = 10.0 MPa, 135 °C, 2 h. *Reaction conditions of esterification*: methanol = 0.68 mol, 135 °C, 2 h.

Table 3
Effect of CO pressure on the carbonylation of formaldehyde[a]

| CO pressure[b](MPa) | HCHO conversion (%) | Yield (%) | | | Selectivity (%) |
|---|---|---|---|---|---|
| | | MG | MF | MMAc | |
| 2.5 | 98.7 | 28.6 | 0.7 | 0.8 | 29.0 |
| 5.0 | 99.5 | 60.7 | 1.3 | 1.0 | 61.0 |
| 7.5 | 99.6 | 79.1 | 1.2 | 0.8 | 79.4 |
| 10.0 | 99.5 | 86.7 | 1.8 | 0.7 | 87.1 |
| 15.0 | 100.0 | 90.7 | 1.4 | 0.7 | 90.7 |

[a] *Reaction conditions of carbonylation*: *p*-TsOH = 16.8 mmol, $CF_3SO_3Ag$ = 0.168 mmol, formaldehyde = 34 mmol, BMIm[$PF_6$] = 4.0 ml, water = 34 mmol, 135 °C, 2 h. *Reaction conditions of esterification*: methanol = 0.68 mol, 135 °C, 2 h.

[b] Initial pressure at room temperature.

### 3.3. Effect of CO pressure

A high CO pressure is also advantageous for the carbonylation of formaldehyde. Table 3 shows the effect of reaction pressure on the carbonylation of formaldehyde in the presence of $CF_3SO_3Ag$ and *p*-TsOH. At 2.5 MPa of CO, only a small amount of MG is formed. By raising the CO pressure to 10.0 MPa, the yield of MG dramatically increases to a value as high as 86.7%, which is much higher than the MG yield (about 54%) on the Amberlyst 15 catalyst at the same CO pressure [10]. The yield of MG increases only a little to 90.7% by further increasing the CO pressure to 15.0 MPa.

## 4. Conclusions

In summary, we have successfully demonstrated that a catalytic system consisting of *p*-toluenesulfonic acid, a transition metal complex such as $CF_3SO_3Ag$, and a solvent exhibits a high catalytic performance for the carbonylation of formaldehyde, followed by esterification with methanol, to produce methyl glycolate. Especially, the catalytic performance is significantly improved by using the ionic liquid BMIm[$PF_6$] instead of organic solvents. This catalytic system is more efficient and shows excellent yield of MG at relatively low CO pressure in comparison to solid acid catalysts. The present system provides a potential process for synthesizing methyl glycolate via carbonylation of formaldehyde in much low corrosion in comparison to the previous system including strong inorganic liquid acids as solvents and catalysts.

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