

## Promotion of Ionic Liquid to Dimethyl Carbonate Synthesis from Methanol and Carbon Dioxide

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Promotion of ionic liquid, 1-ethyl-3-methylimidazolium bromide (emimBr), to the synthesis of dimethyl carbonate (DMC) from methanol and carbon dioxide in the presence of potassium carbonate and less amount of methyl iodide under mild conditions was investigated. The results showed that the high selectivity and raised yield of DMC was achieved due to the addition of emimBr in the reaction system. And effect of several reaction conditions such as temperature, pressure and amount of emimBr was discussed.

**Keywords**    promotion, ionic liquid, dimethyl carbonate, methanol and carbon dioxide

### Introduction

Dimethyl carbonate (DMC) is an important carbonylating and methylating agent substituting dimethyl sulfate and toxic phosgene, and an intermediate for higher carbonates and carbamates.<sup>1</sup> In addition, it is also a promising octane enhancer.<sup>2</sup> The widely used method of its preparation is the oxidative carbonylation of methanol by carbon monoxide with copper(II) or palladium(II) catalysts.<sup>3</sup> Recently, the utilization of carbon dioxide as the raw material for DMC synthesis has been attempted. The possible organotin-catalyzed formation of DMC from CO<sub>2</sub> was first proposed by Japanese group.<sup>4</sup> Kizlink *et al.*<sup>5</sup> have paid much attention to the improvement of the catalytic activities of this reaction, but a high turnover number (TON) is still not achieved. The utilization of zirconia and modified zirconia such as H<sub>3</sub>PO<sub>4</sub>/ZrO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub> to DMC formation from CO<sub>2</sub> and methanol was proposed by Tomishige's group.<sup>6-8</sup> Although the selectivity of DMC over these catalysts was very high (*ca.* 100%), unfortunately the methanol conversion is very low (less than 1%). Zhao *et al.*<sup>9</sup> reported that metal acetate effectively catalyzed the formation of DMC from carbon dioxide and methanol. Fujimoto and Arai *et al.*<sup>10,11</sup> reported the synthesis of DMC in the presence of base K<sub>2</sub>CO<sub>3</sub> and methyl iodide under milder conditions, although the methanol conversion was higher, the yield was still very low (less than or about 4%). In addition, Sakakura *et al.* applied an organotin catalyst to the synthesis of DMC from orthoester<sup>12</sup> and acetals,<sup>13</sup> the yield of DMC reported in these systems was high, however, these systems have disadvantages of the high cost of the starting materials and the difficulty in the catalyst-product separation due

to the homogeneous nature of the catalyst. So the direct synthesis of DMC from methanol and carbon dioxide is still far from satisfactory due to the difficulty in the activation of carbon dioxide, deactivation of the catalysts due to water formation in reaction process and the thermodynamic limitation. Under these circumstances, it would be valuable to study the reaction of DMC synthesis from methanol and carbon dioxide so as to raise the yield of DMC.

In our present investigation, we first report the promotion of ionic liquid, which has been the focus of much research in recent years, to the synthesis of dimethyl carbonate from methanol and carbon dioxide in the presence of potassium carbonate and less amount of methyl iodide under mild conditions. The results showed that high selectivity (*ca.* 100%) and raised yield (5.60%) of DMC was achieved due to the addition of 1-ethyl-3-methylimidazolium bromide (emimBr).

### Experimental

The ionic liquid emimBr was synthesized by the reported method.<sup>14</sup> All experiments were carried out in a stainless steel reactor with inner volume of 500 mL provided with a mechanical stirrer and an electric heater. A typical procedure is as follows: 75 mL (1.85 mol) of anhydrate methanol, 5 mL (0.08 mol) of CH<sub>3</sub>I, 4 g (0.029 mol) of K<sub>2</sub>CO<sub>3</sub> (their molar ratio: CH<sub>3</sub>OH : CH<sub>3</sub>I : K<sub>2</sub>CO<sub>3</sub> = 64 : 2.8 : 1) and a certain amount of ionic liquid were charged into the reactor. CO<sub>2</sub> was injected into the reactor to a low pressure, and then released, which was repeated for three times in order to remove the air from the reactor. Whereafter, CO<sub>2</sub> was injected to a desired pressure. The system was stirred

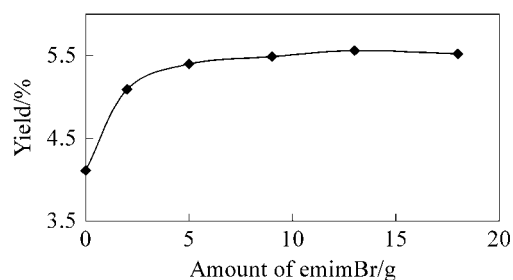
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and heated to a desired temperature. After cooling to room temperature, the resulting gas and solution were analyzed by GC and GC-MS. The yield was calculated on the basis of methanol.

## Results and discussion

The promotion of ionic liquid emimBr to DMC synthesis is shown in Figure 1. When no emimBr was added in the reaction system, the yield of DMC was 4.11% at pressure of 7.3 MPa and temperature of 80 °C, which is consistent with the literature (4.04%).<sup>10</sup> The yield increased to 5.09% when 2 g (0.01 mol) of emimBr was added and raised to 5.58% when 13 g (0.07 mol) added, indicating that the addition of the ionic liquid emimBr to the system of direct DMC synthesis from CO<sub>2</sub> and CH<sub>3</sub>OH in the presence of K<sub>2</sub>CO<sub>3</sub> and CH<sub>3</sub>I is effective for the increase of the conversion. And it probably approaches thermodynamic equilibrium state because the yield is basically constant with the amount of emimBr rising from 5 to 18 g. In addition, it was known from GC and GC-MS analysis that the reaction is an atom-economical one with the DMC selectivity of about 100% and no other byproducts were detected, even though the reaction was performed at higher temperature such as 100 and 120 °C.

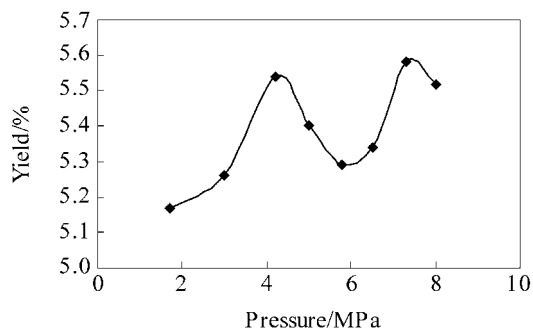


**Figure 1** Effect of emimBr on DMC formation. *T*: 80 °C, *p*(CO<sub>2</sub>): 7.3 MPa, time: 8 h, K<sub>2</sub>CO<sub>3</sub>: 4 g, CH<sub>3</sub>I: 5 mL.

It is known that the DMC formation from CO<sub>2</sub> and CH<sub>3</sub>OH in the presence of CH<sub>3</sub>I is catalytic with respect to K<sub>2</sub>CO<sub>3</sub>,<sup>11</sup> and CH<sub>3</sub>I acts as a reactant; at the same time, it is also involved in the catalytic cycle, at least partly in the reaction process.<sup>10</sup> The addition of emimBr in the system authentically increases the yield and selectivity of DMC; the latter is more significant for catalytic reaction. Therefore, the emimBr is an effective promoter for the DMC formation.

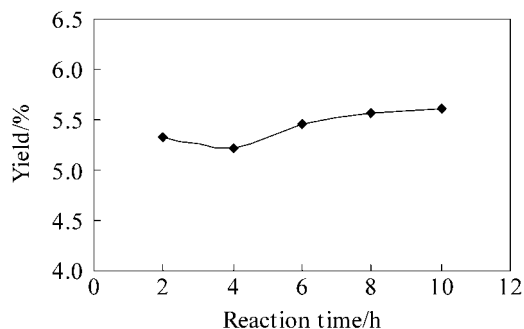
The effect of CO<sub>2</sub> pressure on the reaction is little (Figure 2) due to addition of emimBr, and the yield changed from 5.17% to 5.52% in the range of pressure from 1.7 to 8 MPa. The two maxima of yield were also observed at about 4.2 MPa and 7.3 MPa, although there is a little difference between the yield values of the product at different pressures. It has been reported that, when CO<sub>2</sub> is used as a solvent or a reactant, reaction rates are maximal near the critical pressure of CO<sub>2</sub> (7.3 MPa).<sup>9,10,12</sup> And at low pressures of CO<sub>2</sub>, liquid and gaseous CO<sub>2</sub> coexist in the reactor. With increasing the

CO<sub>2</sub> pressure, the volume of liquid phase increases. Probably, the increase in the liquid volume should arise from absorption of CO<sub>2</sub> into the liquid. So the increase in the yield of DMC observed up to 4.2 MPa should be ascribed to the absorption of CO<sub>2</sub>. However, the volume increases slightly with increasing the pressure up to 6 MPa. The decrease in the DMC yield observed from 4.2 to 7.3 MPa would result from the dilution effect.<sup>11</sup>



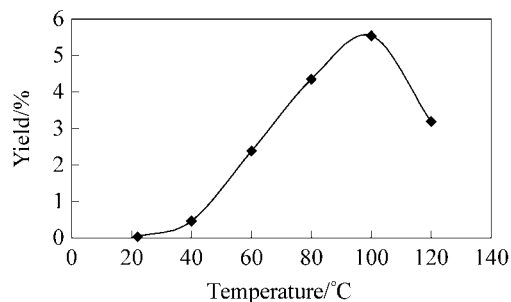
**Figure 2** Effect of pressure on DMC formation. *T*: 80 °C, emimBr: 13 g, time: 8 h, K<sub>2</sub>CO<sub>3</sub>: 4 g, CH<sub>3</sub>I: 5 mL.

Figure 3 showed the effect of the reaction time on the yield of DMC. It is known from the figure that the yield reached to 5.33% at reaction time of 2 h, 5.58% at 8 h and 5.55% at 10 h, and this finding suggested that the equilibrium state of the reaction was almost achieved at reaction time of 2 h. As the raise of temperature, the yield increased rapidly and reached to the maximum of 5.54% at 100 °C with the addition of 2 g of emimBr at the pressure of 2 MPa (Figure 4), then fell to 3.19% at 120 °C. The fall of the yield is maybe attributed to the reduction of CO<sub>2</sub> amount in order to maintain the constant pressure at higher temperature.

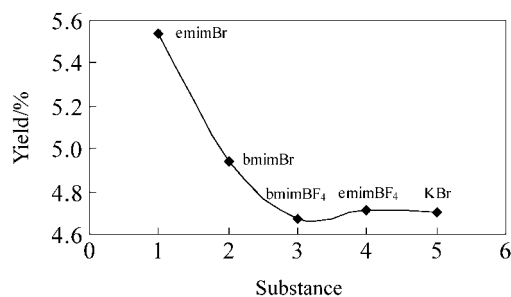


**Figure 3** Effect of reaction time on DMC formation. *T*: 80 °C, emimBr: 13 g, *p*(CO<sub>2</sub>): 7.3 MPa, K<sub>2</sub>CO<sub>3</sub>: 4 g, CH<sub>3</sub>I: 5 mL.

The promotion of other compounds containing different cations and anions such as emimBF<sub>4</sub>, bmimBr, bmimBF<sub>4</sub> (bmim=1-butyl-3-methylimidazolium) and KBr to the DMC synthesis was also investigated. The results are shown in Figure 5. bmimBr is also an effective promoter even though its activity is lower than emimBr. However, the promotion of ionic liquids emimBF<sub>4</sub> and bmimBF<sub>4</sub> was low in comparison with emimBr. The yield of DMC is 4.71% and 4.67% respectively, and the yield is 4.70% in the presence of



**Figure 4** Effect of temperature on DMC formation. Time: 8 h, emimBr: 13 g,  $p(\text{CO}_2)$ : 7.3 MPa,  $\text{K}_2\text{CO}_3$ : 4 g,  $\text{CH}_3\text{I}$ : 5 mL.



**Figure 5** Effect of different substances on DMC formation.  $T$ : 80 °C,  $p(\text{CO}_2)$ : 7.3 MPa, time: 8 h.

KBr after substituting the cation emim<sup>+</sup> with K<sup>+</sup>, indicating that the promotion of the emimBr and bmimBr may be attributed to the mutual action of the cation emim<sup>+</sup> or bmim<sup>+</sup> and anion Br<sup>-</sup> to the formation

process of DMC from carbon dioxide. Its promotion mechanism needs to be further investigated.

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