

Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide Catalyzed by Potassium Hydroxide under Mild Conditions

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Abstract: The synthesis of dimethyl carbonate (DMC) from methanol and carbon dioxide using potassium hydroxide as catalyst in the presence of CH₃I and the effect of ionic liquid on the reaction were investigated. The results showed that KOH is an effective catalyst; the high selectivity and raised yield of DMC formation under mild conditions were achieved. However, the addition of the ionic liquid, 1-ethyl-3-methylimidazolium bromide (emimBr), can evidently accelerate the conversion of methanol and yield of the product.

Keywords: Dimethyl carbonate, methanol, carbon dioxide, methyl iodide, ionic liquid, 1-ethyl-3-methylimidazolium bromide.

Dimethyl carbonate (DMC) is an important carbonylation and methylation agent, alternate of poisonous dimethyl sulfate and phosgene. Besides, DMC is also an intermediate for higher carbonates and carbamates¹ as well as a promising octane enhancer². The widely used method of its preparation is the oxidative carbonylation of methanol by carbon monoxide and oxygen with copper (II) and/or palladium (II) as catalyst³. Carbon monoxide is expensive and it may accompany a potential explosion hazard. Recently, the utilization of carbon dioxide, as a readily available, inexpensive and environmentally acceptable starting material for DMC synthesis has been attempted. The possible organotin-catalyzed formation of DMC from CO₂ was first proposed by Japanese groups^{4,5}. Kizlink *et al.* have paid much attention to improving the catalytic activities of this reaction, but a high turnover number (TON) is still not achieved⁶⁻⁸. The utilization of zirconia or modified zirconia, such as H₃PO₄/ZrO₂ or CeO₂-ZrO₂, to synthesis of DMC from CO₂ and methanol was investigated by Tomishige's group⁹⁻¹¹. 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.* reported that metal acetate effectively catalyzed the formation of DMC from carbon dioxide and methanol¹²; Fujimoto and Arai *et al.* reported the synthesis of DMC in the presence of base K₂CO₃ and methyl iodide under milder conditions^{13,14}, although the

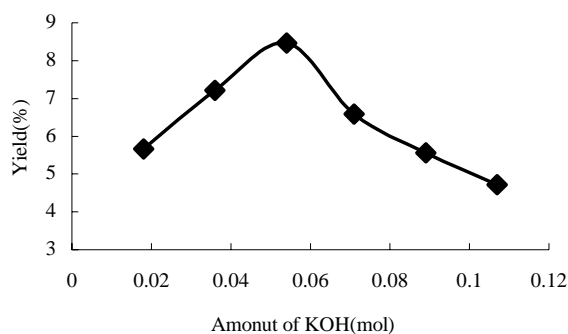
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methanol conversion was higher, the yield was still very low (less than or about 4%). Sakakura *et al.* applied an organotin catalyst to the synthesis of DMC from orthoester¹⁵ and acetals¹⁶, the yield of DMC reported in these systems was high, however, 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 is very important to investigate the reaction of DMC synthesis from methanol and carbon dioxide so as to raise the yield and selectivity of DMC. In our present investigation, we report the synthesis of dimethyl carbonate from methanol and carbon dioxide using KOH as catalyst and the effect of ionic liquid on the reaction under mild conditions. The results showed that the high selectivity (*ca.*100%) and raised yield (11.0%) of DMC was achieved in the presence of ionic liquid emimBr.

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. Potassium hydroxide (0.02-0.12 mol) was added in the reactor with a certain amount of anhydrate methanol, and then CH₃I (0.02-0.12 mol) was charged into it. After being purged three times with CO₂, the reactor was pressured to a certain pressure and heated to the desired temperature with stirring. After the required time, the liquid phase was cooled, sampled and analyzed by GC and GC-MS. The yield was calculated on the basis of methanol.

When the reaction of CO₂ and methanol was carried out in the presence of KOH and methyl iodide, DMC was formed. The yield of DMC increased in proportion with the amount of KOH up to the maximum 8.5%, and then it dropped down to minimum value 4.7% with continuous increase of KOH amount (**Figure 1**). This phenomenon may be ascribed to the fact that the rate of direct reaction of KOH with CH₃I rapidly increased when the molar ratio of KOH to CH₃OH was above 0.054/0.85, the catalyst KOH and CH₃I were greatly consumed¹⁷. In all the experiments, no by-product was detected by GC and GC-MS. The catalyst showed high activity and selectivity for the formation of DMC, the highest yield of DMC was 8.5% and the selectivity was 100%.

Figure 1 The effect of KOH amount on the reaction



The experiment was also carried out with respect to methyl iodide. Without methyl iodide in the reaction system, the formation of DMC was almost to zero. The yield of DMC increased with increase of the amount of CH_3I added in the reaction system, the yield reached maximum of 8.5%, while the amount of CH_3I was 0.048 mol, and then the yield of DMC basically become constant, when the amount of CH_3I increased further. This implies that the addition of CH_3I plays very vital role in the synthesis of DMC catalyzed by basic catalysts. It was also obtained from the experimental results that the maximum formation of DMC was 0.036 mol, when the amount of CH_3I was 0.048 mol, its surplus quantity in the reaction mixture was determined to be about 0.02 mol. This finding showed that the consumed amount of CH_3I was about 0.028 mol, which is less than the amount of DMC formation. Therefore, CH_3I acts as a promoter in the reaction process.

Figure 2 the effect of CO_2 pressure on the reaction

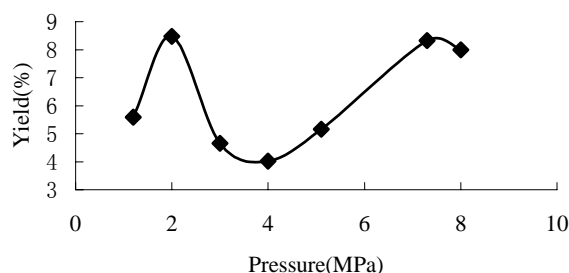


Figure 3 the effect of ionic liquid emimBr on the reaction

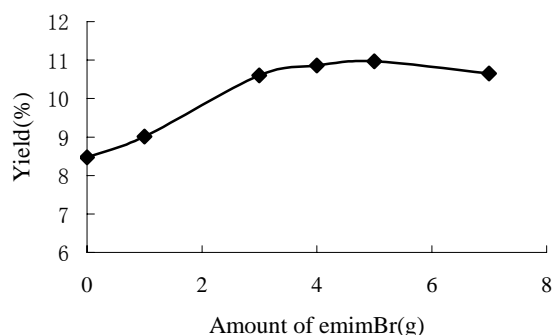


Figure 2 illustrates the effect of CO_2 pressure upon the yields of DMC in the presence of KOH . As the pressure of CO_2 is raised, the DMC formation shows two maxima near 2.0 MPa and 7.3 MPa. It is a very similar to Arai's work, two maxima near 4.5 and 8.0 MPa with K_2CO_3 as catalyst. **Figure 2** also indicates that high CO_2 pressures are not required for the DMC formation and supercritical conditions are detrimental for the reaction. The high yield (8.5%) of DMC formation was achieved at about 2.0 MPa. It has been reported that when CO_2 is used as a solvent or a reactant,

the reaction rates are maximal near the critical pressure of CO₂ (7.3 MPa)¹²⁻¹⁴. And at low pressure of CO₂, liquid and gaseous CO₂ coexists in the reactor. With the increase of the CO₂ pressure, the volume of liquid phase increased gradually. Probably, the increase in the liquid volume should arise from absorption of CO₂ into the liquid. So the increase in the yield of DMC observed up to 2.0 MPa should be ascribed to the absorption of CO₂. However, the volume increased slightly with increasing the pressure up to 6.0 MPa. The decrease of the yield of DMC observed between 2.0 MPa and 7.3 MPa might result from the dilution effect¹⁴.

When ionic liquid emimBr was added in the reaction system, the conversion of methanol and yield of DMC evidently increased (**Figure 3**). The maximum value of DMC yield reached at 11%, when 4 g of emimBr was added. Subsequently, the yield of DMC formation basically kept constant with the continuous increase of emimBr amount. The reason was that the higher yield obtained in the presence of ionic liquid may be ascribed to the strong polarity and electrostatic field of the ionic liquid, which may stabilize the charged intermediate^{18,19}. However, its promotion mechanism needs to be further investigated.

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