



A novel strategy for conversion of methanol and CO₂ into dimethoxymethane in a basic ionic liquid



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ABSTRACT

The reaction of methanol with CO₂ to obtain dimethoxymethane (DMM) at 150 °C and initial pressure of 3.0 MPa CO₂ was realized in the presence of basic functionalized ionic liquid BmimOH. Although the conversion of methanol was low (2.4%), CO₂ as a soft oxidant was firstly introduced for selective oxidation of methanol into DMM. The effect of the functionalized group composed of ionic liquids on the reactivity and selectivity was explored and the activation and reaction mechanism of the ionic liquid for methanol and CO₂ was proposed. In addition, the reaction thermodynamics of methanol and CO₂ was discussed by calculating the thermodynamic functions of the reaction in order to explore the direction and limitation of the reaction.

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1. Introduction

The increasing emission of CO₂ from combustion of fossil fuels has become a global concern due to its resulting in green house effect and global warming [1]. Various approaches for the mitigation of CO₂ levels, ranging from capture, fixation and utilization, have been focused. Among them, the utilization of CO₂ as a feedstock for producing valuable chemicals is attractive as an integral part of the carbon cycle and also as a strategic part of recycling [2].

Dimethoxymethane (DMM) is an important intermediate [3] and has been widely used as diesel fuel additive with a high chemical stability, as reagent in organic synthesis and as an excellent solvent in pharmaceutical and perfume industries due to low toxicity [4]. Industrially, DMM is produced by the concentration of formaldehyde with methanol over acidic catalysts [5]. However, this approach is intricate and costly owing to the high reaction temperature and equipment corrosion caused by the acidic catalysts. This status renders investigations on one-step selective oxidation of methanol to DMM, a potential path considering economical and environmental advantages. A number of catalysts including supported rhenium oxide [6], SbRe₂O₆ [7], heteropoly acids [8], Cu-ZSM-5 [9], V₂O₅/TiO₂ [10] and VO_x/TS-1 [11] etc. have been used for this procedure, where three methanol molecules are incorporated

into one DMM molecule via oxidation of methanol to formaldehyde by O₂ gas and the concentration of formaldehyde with methanol. It is environmentally benign process as the only produced byproduct is water. The oxygen gas, widely utilized in the oxidation of organic compounds, sometimes leads to the burning of significant quantities of valuable hydrocarbons or alcohols and generates unwanted over oxidation products or carbon oxides due to its strong oxidizing power [12]. Hence, a soft oxidant CO₂ plays prominent role for selective oxidation of alkanes and alcohols, as well as oxidative dehydrogenation of various alkanes, alkyl aromatics and other hydrocarbons [13]. Recently, our group has reported the activation and conversion of CO₂ and methanol into dimethyl carbonate (DMC) by hydroxyl-functionalized ionic liquid, in which hydroxyl group plays a key role for the formation of DMC [14]. Unexpectedly, DMM as byproduct was found in the mixture products of some cases, implying that the reaction of methanol with CO₂ to synthesize DMM is possible in the presence of functionalized ionic liquids. Therefore, a novel pathway for utilizing CO₂ as a feedstock to produce DMM was tried in the catalysis of ionic liquids and the role of CO₂ in this process was explored. This route for synthesizing DMM from methanol and CO₂ catalyzed by ionic liquids has been not found in the reported literature so far.

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2. Experimental

2.1. Synthesis and characterization of ionic liquids

BmimOH (1-butyl-3-methylimidazolium hydroxide), EmimOH (1-ethyl-3-methyl imidazolium hydroxide), EtmimOH (1-hydroxyethyl-3-methylimidazolium hydroxide), BmimHCO₃ (1-butyl-3-methylimidazolium hydrocarbonate) and other ionic liquids were synthesized according to previous reported literatures [15]. A typical procedure for synthesis of BmimOH was as following: KOH (0.2 mol), pre-dehydrated BmimBr (0.2 mol) and CH₂Cl₂ (100 mL) were added to a three-necked flask fixed with a magnetic stirrer. The mixture solution was stirred at room temperature for 10 h. After the reaction completed, The mixture solution was filtered at reduced pressure to obtain a precipitate, followed by washing three times with ether. BmimOH was obtained after vacuum dried at 90 °C for 10 h. FT-IR spectrum was recorded on a Vertax-80 spectrometer in the KBr matrix in the range of 400–4000 cm⁻¹; ¹H NMR spectrum was recorded on AVANCE III NMR spectrophotometer (400 MHz, Bruker Company) using DMSO as solvent. ¹H NMR of BmimOH: δ 9.27 (s, 1H, N–CH–N), 7.82–7.83 (t, *J* = 1.7 Hz, 1H, N–CH–C), 7.75 (t, *J* = 1.7 Hz, 1H, N–CH–C), 4.17–4.20 (t, *J* = 7.2 Hz, 2H, N–CH₂), 3.86 (s, 3H, N–CH₃), 1.72–1.80 (m, *J* = 7.4 Hz, 2H, C–CH₂–C), 1.20–1.30 (m, *J* = 7.5 Hz, 2H, C–CH₂–C), 0.87–0.91 ppm (m, *J* = 7.2 Hz, 3H, C–CH₃); IR: 3434.0, 3079.0, 2963.9, 2872.8, 1659.2, 1534.4, 1460.1, 1378.5, 1172.3 cm⁻¹. ¹H NMR of EmimOH: δ 9.23 (s, 1H, N–CH–N), 7.79 (s, 1H, N–CH–C), 7.75 (d, *J* = 1.0 Hz, 1H, N–CH–C), 4.23–4.25 (t, *J* = 5.2 Hz, 2H, N–CH₂), 3.72 (s, 3H, N–CH₃), 3.66–3.71 ppm (m, *J* = 5.6 Hz, 3H, C–CH₃); IR: 3393.2, 2937.5, 2872.8, 1659.2, 1443.3, 1395.3, 1064.4 cm⁻¹. ¹H NMR of EtmimOH: δ 9.23 (s, 1H, N–CH–N), 7.77 (s, 2H, N–CH–C), 5.50 (s, 1H, –OH), 4.23–4.25 (t, *J* = 4.9 Hz, 4H, N–CH₂, C–CH₂), 3.71–3.73 ppm (t, *J* = 4.9 Hz, 3H, N–CH₃); IR: 3344.1, 3147.8, 2936.4, 2876.2, 1660.7, 1569.7, 1404.2, 1260.5, 1071.7 cm⁻¹. ¹H NMR of BmimHCO₃: δ 9.32 (s, 1H, N–CH–N), 7.85 (s, 1H, N–CH–C), 7.77 (s, 1H, N–CH–C), 4.17–4.21 (t, *J* = 7.4 Hz, 2H, N–CH₂), 3.87 (s, 3H, N–CH₃), 1.72–1.79 (m, *J* = 7.4 Hz, 2H, C–CH₂–C), 1.19–1.29 (m, *J* = 7.4 Hz, 2H, C–CH₂–C), 0.86–0.90 ppm (m, *J* = 7.4 Hz, 3H, C–CH₃); IR: 3434.0, 3143.8, 3079.0, 2963.9, 2872.8, 1632.8, 1575.2, 1469.7, 1172.3 cm⁻¹.

2.2. Catalytic tests

The catalytic reaction was carried out in a 0.25 L stainless steel autoclave with an electric heater and a mechanical stirrer. Methanol (25 mL, 0.625 mol) and BmimOH (38 mmol) were charged into the reactor. After being purged three times with CO₂, the reactor was pressured to an initial pressure of 3 MPa CO₂ and heated to 150 °C. The reaction was carried out at this temperature

for 6 h. At the end of the reaction, the mixture solution was distilled to separate the catalyst and the distillate was analyzed by GC (Agilent 7820) and GC–MS (Agilent 7890–5975). The conversion was calculated based on methanol.

3. Results and discussion

3.1. Catalytic activities of various catalysts

Table 1 depicted the preliminary catalytic performance for the methanol conversion obtained in the presence of CO₂ and ionic liquids as catalysts at 150 °C. The blank experiment showed that the direct reaction of methanol and CO₂ in the absence of any catalyst could not be carried out due to no any product generated. However, BmimOH exhibited higher activity for the conversion of methanol and CO₂ into DMM with 2.4% conversion and 85.0% selectivity. A small amount of dimethoxyethane (DEM), dimethoxypropane (DPM), trioxane (13.1%) and trace of methyl formate (MF) were detected in the mixture products (entry 2). The byproduct trioxane possibly resulted from oligomerization of formaldehyde converted from the reaction of methanol with CO₂. Its formation had a remarkable impact on the reactivity of methanol and distribution of the obtained products. As shown in the table, the addition of trioxane as a reactant to the methanol–CO₂ system caused low conversion of methanol and selectivity to DMM. Except for the by-products DEM + DPM, a mixture of carboxylic acid esters such as butyl formate, methyl propionate and butyl propionate etc were relatively increased as compared with the entry 1 in this case (entry 3).

Apparently, the addition of the trioxane restrained the reactivity of CO₂ with methanol to generate DMM, but it promoted side reaction to produce by-products. Although a higher conversion of methanol was observed when O₂ was used instead of CO₂ (entry 4), the selectivity to DMM was low (31.7%) with 68.3% selectivity to the byproducts such as DMC, DEM + DPM and eaters. This was also very different from the reported work on selective oxidation of methanol catalyzed by difunctionalized catalyst over which DMM was achieved with high selectivity, as well as high conversion of methanol [16]. These findings implied that basic ionic liquid catalysts are more favorable for activating CO₂ molecule to produce DMM.

It is well known that CO₂ can act as both an electron acceptor and donor [17,18]. When CO₂ is activated by electron transfer from a catalyst to the CO₂ molecule, the formed CO₂⁻ is a bent anion in its equilibrium geometry. If the charge transfer moves from the CO₂ to the catalyst, a CO₂⁺ cation would be formed with its linear geometry. Moreover, an energetically favored reaction will involve the anionic species because the ground state of CO₂ molecule is found to be linear system with an enthalpy of 1650.6 KJ/mol [13]; whereas, the double-well ground state of CO₂ represents a bent

Table 1
the catalytic activity of various ionic liquids.

En	Catalysts	reactants	Con (%)	S _{DMM} (%)	S _{DMC} (%)	S _{DXM} (%)	S _{ester} (%)
1	blank	Me + CO ₂	–	–	–	–	–
2	BmimOH	Me + CO ₂	2.4	85.0	–	1.9	trace
3	BmimOH	Me + CO ₂ + Tr	0.4	46.4	–	3.1	50.5
4	BmimOH	Me + O ₂	1.3	31.7	8.2	10.9	49.2
5	EmimOH	Me + CO ₂	0.8	76.2	–	–	23.8
6	BmimBF ₄	Me + CO ₂	–	–	–	–	–
7	BmimBr	Me + CO ₂	–	–	–	–	–
8	BmimHCO ₃	Me + CO ₂	–	–	–	–	–
9	CH ^a	Me + CO ₂	0.6	3.6	95.2	–	–
10	EtmimOH ^a	Me + CO ₂	0.2	–	77.6	21.7	–
11	BmimOH/MgO–Al ₂ O ₃	Me + CO ₂	0.7	46.3	11.1	29.7	8.3

Reaction conditions: reaction time 6 h; temperature 150 °C; initial CO₂ pressure 3.0 MPa; methanol 0.625 mol; ionic liquid 38 mmol. Conv- conversion; S- selectivity; Tr- trioxane, DXM-DEM + DPM, En- entry, Me-CH₃OH, CH- choline hydroxide.

^a Reaction temperature 140 °C, catalyst 66 mmol.

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