

Synthesis of dimethyl carbonate from transesterification of ethylene carbonate with methanol using immobilized ionic liquid on commercial silica

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Abstract—Ionic liquid immobilized on commercial silica catalysts proved to be an effective heterogeneous catalyst for the synthesis of dimethyl carbonate (DMC) from transesterification of ethylene carbonate (EC) with methanol. The immobilized 1-*n*-alkyl imidazolium halide ionic liquid on commercial silica (RImX-CS) was characterized by EA, BET, FT-IR, ¹³C NMR and ²⁹Si NMR. It was found that RImX-CS with a longer alkyl chain length showed much better catalytic activity. RImX-CS with chloride (Cl[−]) as the counter anion showed the best catalytic activity. High temperature, high carbon dioxide pressure, and longer reaction time were favorable for the reactivity of BuImBr-CS. The catalyst can be reused for the reaction up to three consecutive runs without any considerable loss of its initial activity.

Key words: Dimethyl Carbonate, Ethylene Carbonate, Methanol, Immobilization, Ionic Liquid

INTRODUCTION

The synthesis of dimethyl carbonate (DMC) is one of the promising reactions for the utilization of naturally abundant carbon dioxide, which is one of greenhouse gases. DMC is achieving increasing importance in the chemical industry for its versatility as reagent and solvent, and its non-toxicity for human health and environment. It can be effectively used as an environmentally benign substitute for highly toxic phosgene and dimethyl sulfate in carbonylation and methylation reaction, as monomer for several types of polymers and intermediate in the synthesis of pharmaceutical and agricultural chemicals [1]. DMC can also be used as an octane booster due to its high oxygen content [2].

Conventionally, DMC has been synthesized by using phosgene and methanol. Therefore, a number of nontoxic DMC synthetic processes have been suggested: (1) oxidative carbonylation using CO, O₂ and methanol (2) direct synthesis of DMC from carbon dioxide and methanol (3) transesterification of methanol with cyclic carbonate. However, the oxidative carbonylation of methanol suffers from a low production rate, need for corrosion resistant reactors, and toxicity and potential explosion of CO.

For the transesterification method, many homogeneous and heterogeneous catalysts have been developed, such as tertiary amines [3], alkali metal or alkali metal compounds [4]. Knifton and Duranleau [5] used free organic phosphines supported on partially cross-linked polystyrene for the reaction. Heterogeneous catalysts such as alkali-treated zeolite [6,7], basic metal oxides [8,9], and hydrocalcite [10] were also reported. However, with some of these catalysts, activity or selectivity was not so high.

The use of ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted [11]. Ionic liquids have negligible vapor pres-

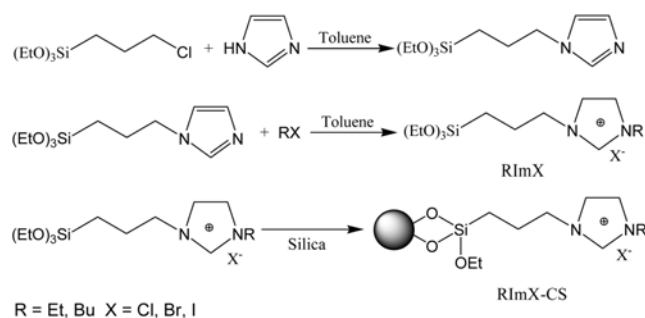
sure, excellent thermal stability and special characteristics in comparison with conventional organic and inorganic solvents. In the past decade, there has been increasing use of ionic liquids containing imidazolium and its counter anions in many research fields such as alternative reaction media, separation science and material synthesis [11]. Many reactions catalyzed with ionic liquids and showing high performance have been reported [12,13]. In particular, ionic liquids based on imidazolium cations and chloroaluminate anions, such as 1-butyl-3-methylimidazolium aluminium chloride ([BMIm] Cl/AlCl₃), have attracted growing interest [14,15].

In our previous work [16-20], we studied the performance of ionic liquid for the synthesis of cyclic carbonate from epoxide and carbon dioxide. Recently, ionic liquid-based heterogeneous catalysts have been developed to synthesize cyclic carbonate and they allow the combination of the advantages of both homogeneous ionic liquids and heterogeneous catalysts. Compared to pure Lewis acidic ionic liquids, such heterogeneous catalysts show additional advantages such as the reduction of the amount of ionic liquids employed and easy separation, as well as recovery of catalyst from the reaction mixture, which is desirable economically, environmentally and industrially. The immobilization of ionic liquids onto MCM-41 showed excellent activities for carbon dioxide insertion reactions; however, the use of expensive pore-directing agents and large amounts of organic solvents to remove the templates makes these catalysts impracticable for commercial scale-up [21]. Moreover, the ordering of the mesopores often decreases as a result. These problems could be avoided through the usage of low-cost and highly efficient catalysts by grafting ionic liquids onto commercial silica.

We have previously studied the synthesis of DMC using unsupported ionic liquids [22-25]. In the present work, immobilized imidazolium salt ionic liquids on commercial silica were prepared and examined for the esterification of EC and methanol. The effects of reaction time, carbon dioxide pressure, reaction temperature and amount of catalyst are discussed for better understanding of the reaction mechanism. A recycle test of the immobilized catalyst was also

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Scheme 1. Preparation step of RImX-CS.

carried out.

EXPERIMENTAL

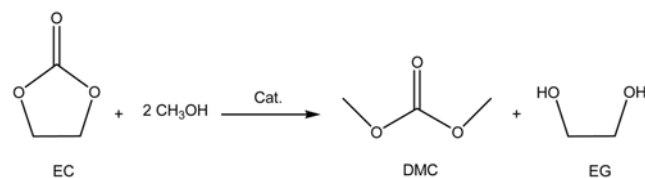
1. Material

Imidazole (Aldrich), 1-bromobutane (Aldrich), 1-chlorobutane (Aldrich), 1-bromopropane (Aldrich), bromoethane (Aldrich), 1-iodobutane (Aldrich), (3-chloropropyl) triethoxysilane (Sigma), toluene (Aldrich), acetonitrile (Dae Jung), zinc chloride (Sigma), dichloromethane (Dae Jung) and allyl glycidyl ether (Aldrich) were used as received. A commercial silica gel (surface area=500 m²/g, average pore size=60 Å) was purchased from Aldrich and purified using hot Piranha solution (H₂O₂ and H₂SO₄) before use.

2. Synthesis of RImX-CS

1-Alkyl-3-(3-triethoxysilylpropyl) imidazolium halide (RImX) was prepared using the procedure shown in Scheme 1. In a typical procedure, imidazole (3.4 g) was added in the flask containing 50 mL dry toluene, (3-chloropropyl) triethoxysilane (12 mL) was poured into the solution and the mixture was refluxed for 3 h under argon atmosphere. When the reaction was completed, 10 mL of 1-bromobutane was subsequently injected into the flask. The mixture was kept stirred for another 24 h; RImX can be obtained after removal of solvent. Following the similar procedures, RImX of different alkyl groups and counter anions were synthesized by using 1-chlorobutane, 1-bromopropane, bromoethane and 1-iodobutane to replace 1-bromobutane, respectively.

Synthesis of RImX grafted to commercial silica (RImX-CS) was carried out as shown in Scheme 1. Prior to immobilization, commercial silica was purified with hot Piranha solution (H₂O₂ and H₂SO₄) followed by rinsing in water and drying under a stream of nitrogen. The pretreated silica and ionic liquid were co-dispersed in anhydrous toluene in flask. The mixture was refluxed for 24 h under nitrogen atmosphere. The resultant product was filtered and washed with dichloromethane to remove excess ionic liquid. After evaporating the residual solvent in vacuum oven, RImX-CS was obtained.



Scheme 2. Synthesis of DMC from EC and methanol.

3. Synthesis of DMC

The transesterification reaction was carried out in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical reaction, RImX-CS catalyst (0.2 g), EC (25 mmol) and excess methanol (200 mmol) were charged into the reactor, and the CO₂ was introduced at room temperature to a preset pressure. The reaction was started by stirring when the desired temperature and pressure were attained. The reaction was performed in a batch operation mode. The analysis of the products and reactants was performed by using a gas chromatograph (HP 6890N) equipped with an FID and a capillary column (HP-5, 5% phenyl methyl siloxane). Selectivities to DMC and EG are calculated on the basis of EC as a limited reactant.

4. Characterization

The elemental analysis (EA) was operated using Vario EL III. 2 mg of the samples was subjected to 1,100 °C and sulfanilic acid was used as a standard. Solid-state NMR was carried out with ²⁹Si and ¹³C frequencies of 79.5, 100.6 MHz, respectively, on INOVA-400 WB MAS probe. ²⁹Si MAS spectra were measured at room temperature with the following conditions: magic-angle spinning at 5 kHz; $\pi/2$ pulse, 6.5 μ s and a repetition delay of 60 s; 3928 scans which referenced to tetramethylsilane. ¹³C cross-polarization spectra were measured with a recycle delay of 5 s, 1024 scans with the following conditions: magic-angle spinning at 5 kHz; $\pi/2$ pulse, 7 μ s. The spectra were referenced to tetramethylsilane.

RESULTS AND DISCUSSION

1. Characterization of Catalysts

1-1. Elemental Analysis (EA) Results

The amount of grafted RImX was determined by means of EA. To get maximum grafting amount of RImX, an effective alternative is to control the employed amount of RImX in the grafting reaction process. According to our previous work [26] on the optimization of the amount of employed, 5 mmol of RImX per gram silica was used. The corresponding grafted amounts of RImX determined by EA are summarized in Table 1.

1-2. ²⁹Si and ¹³C MAS-NMR Characterization

To investigate the efficiency of grafting reaction, a solid-state ²⁹Si MAS-NMR analysis of BuImBr-CS was carried out. As shown in Fig. 1, two peaks are centered at -93 and -103 ppm corresponding to Q₃ (Si (OSi)₃ (OH)) and Q₄ (Si (OSi)₄) silicon atoms, respectively. The peaks situated at -61.9, -50.3 and -42.2 ppm are assigned to the T₃ (Si (OSi)₃ R), T₂ (Si (OSi)₂ R (OH)) and T₁ (Si (OSi) R (OH)₂) organosiloxane, which indicates the presence of organic functionalization moieties as the part of the silica.

Fig. 2 shows the ¹³C MAS-NMR spectrum of BuImBr-CS. The chemical shifts at 135 and 150 ppm correspond to the three imida-

Table 1. EA and grafting amount of RImX in different RImX-CSs

Run	Catalyst	N (wt%)	H (wt%)	C (wt%)	Amount of RImX (mmol/g-cat)
1	BuImCl-CS	2.60	3.49	8.21	0.93
2	BuImBr-CS	4.71	3.96	11.41	1.68
3	BuImI-CS	4.74	3.84	11.77	1.69
4	EtImBr-CS	5.33	3.51	11.30	1.90

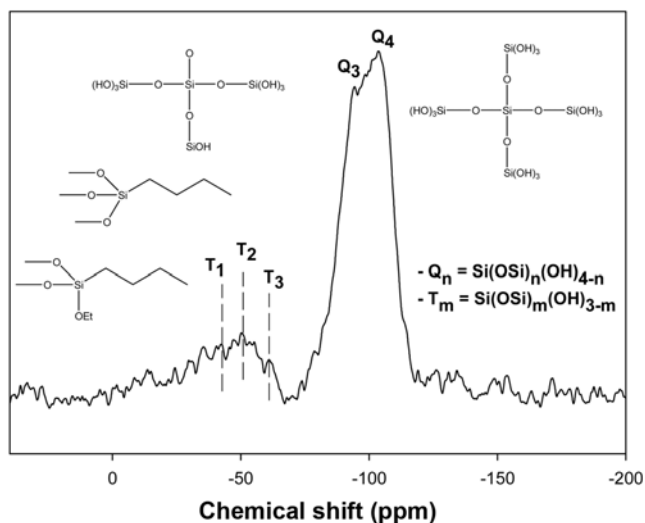


Fig. 1. Solid-state ^{29}Si MAS-NMR spectra of BuImBr-CS.

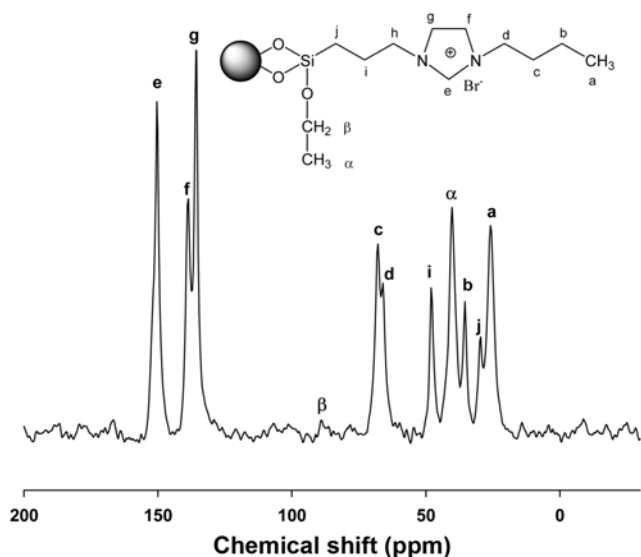


Fig. 2. ^{13}C CP MAS NMR spectra of the BuImBr-CS.

zole ring carbon atoms. The signal at 65 ppm is attributed to the carbon atoms connecting on imidazole ring and other carbon atoms give peaks from 25 to 47 ppm.

2. Reactivity Test in the Synthesis of DMC from EC and Methanol

The synthesis of DMC from the transesterification of EC and methanol was carried out in a high-pressure batch reactor using the heterogeneous RImX-CS catalysts.

DMC and EG were main products of the transesterification reaction. Dimethyl ether and glycol monoethyl ether were byproducts, and small peaks of ethylene oxide from the decomposition of EC could be detected at longer reaction time and at high temperature.

Fig. 3 shows time variant conversion of EC and yield of DMC and EG at 160 °C with BuImBr-CS catalyst under initial CO_2 pressure of 1.34 MPa. As the reaction time proceeded, the conversion of EC increased up to 6 h, and then it remained nearly constant. It was reported that the reaction time needed to arrive at equilibrium de-

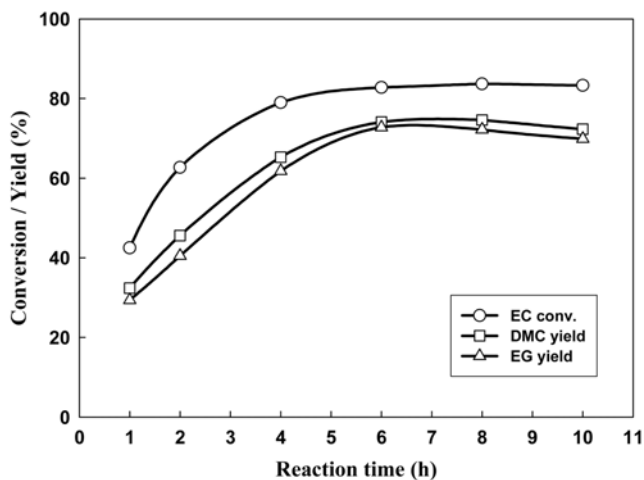


Fig. 3. Effect of reaction time on the synthesis of DMC from EC and methanol (Reaction conditions: EC=25 mmol, MeOH=200 mmol, $T=160\text{ }^{\circ}\text{C}$, $P_{\text{CO}_2}=1.34\text{ MPa}$).

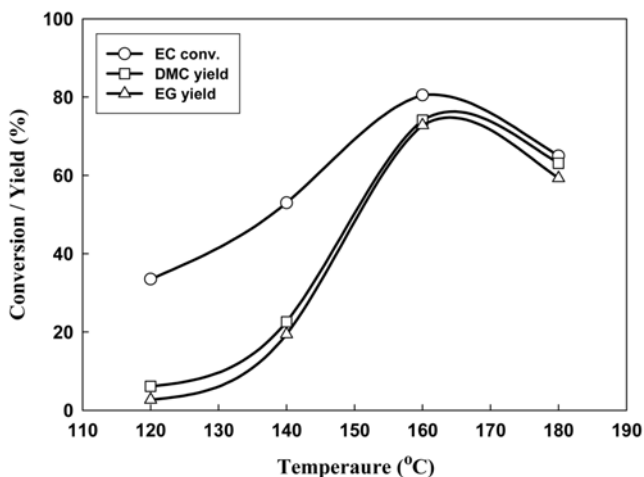


Fig. 4. Effect of reaction temperature on the synthesis of DMC from EC and methanol (Reaction conditions: EC=25 mmol, MeOH=200 mmol, reaction time=6 h, $P_{\text{CO}_2}=1.34\text{ MPa}$).

pended highly on the type of catalysts [27]. LiOH, KOH and K_2CO_3 catalysts reached equilibrium in less than 1 h; however, KBr and KI arrived at equilibrium after more than 6 h. The yield of DMC and EG also increased up to 6 h, but the yield of DMC was higher than that of EG. According to a mechanism proposed by Fang and Xiao [28], DMC was produced via several reaction steps involving the formation of CH_3O^- and its reaction with EC. Ethylene glycol (EG) was suggested to form by the reaction of methanol and the by-product intermediate produced in the step of DMC synthesis. Therefore, the lower selectivity of EG can be explained by a lower reaction rate of this consecutive reaction.

The transesterification of EC and methanol was performed at different temperatures in the range of 120–180 °C and the results are shown in Fig. 4. The conversion of EC and product yield increased as temperature increased from 120 °C to 160 °C. However, EC conversion decreased at 180 °C probably due to the partial decomposition of the DMC to EC for the long reaction time at high temperature.

Table 2. Effect of pressure on the synthesis of DMC from EC and methanol

Run	I.P. (MPa)	EC conv. (%)	DMC yield (%)	EG yield (%)
1	0.11	81.1	67.0	29.3
2	0.79	80.6	71.7	69.5
3	1.34	80.5	74.1	72.8

Reaction conditions: EC=25 mmol, MeOH=200 mmol, catalyst=BuImBr-CS, T=160 °C, time=6 h

Table 3. EC conversion and DMC selectivity for different amount of catalysts

Run	Catalysts	Amount	EC conv. (%)	DMC yield (%)	EG yield (%)
1	BuImBr-CS	0.10 g	72.9	61.3	57.9
2	BuImBr-CS	0.20 g	80.5	74.1	72.8
3	BMIImBr ^a	0.336 mmol	77.6	72.9	73.0

Reaction conditions: EC=25 mmol, MeOH=200 mmol, T=160 °C, time=6 h, P_{CO₂}=1.34 MPa

^aHomogeneous BMIImBr with the same amount of ionic liquid as that in 0.2 g of BuImBr-CS

Table 2 shows the effect of CO₂ pressure on the reactivity of the BuImBr-CS catalyst. The yield of DMC and EG at 160 °C increased as the initial CO₂ pressure increased from 0.11 to 1.34 MPa. CO₂ is not a reactant for the transesterification of EC and methanol. However, high CO₂ pressure could inhibit the decomposition of EC to ethylene oxide and CO₂. Earlier studies reported that pressure has a positive role in the synthesis of cyclic carbonates from CO₂ and epoxides [8,29,30].

The dependence of the reaction on the amount of catalyst used was investigated. As shown in Table 3, the EC conversion and the yield of DMC and EG increased when the amount of BuImBr-CS catalyst increased from 0.10 to 0.20 g. BuImBr-CS catalyst having the same amount of immobilized BuImBr showed higher reactivity than the soluble BuImBr catalyst since the immobilized catalyst has more favorable micro environment inside the pores.

To investigate the effect of ionic liquid structure in the transesterification of EC and methanol, RImX-CS of different alkyl groups and counter anions were examined and the results are shown in Table 4. From runs 2 and 4, it is observed that EC conversions and TON of DMC increased with increasing alkyl chain length of the grafted RImXs. These results are in agreement with the previous reports

Table 4. Effect of ionic liquid structure on the synthesis of DMC from EC and methanol

Run	Catalysts	EC conv. (%)	DMC yield (%)	EG yield (%)	TON of DMC ^a
1	BuImCl-CS	57.8	53.2	53.4	143.0
2	BuImBr-CS	68.4	60.0	63.0	89.3
3	BuImI-CS	68.0	59.5	57.5	87.8
4	EtImBr-CS	68.1	56.4	53.8	74.1

Reaction conditions: EC=25 mmol, MeOH=200 mmol, T=160 °C, reaction time=4 h, P_{CO₂}=1.34 MPa

^aTON=(mole of DMC)/(mole of RImX)

Table 5. EC conversion and yield of DMC and EG for recycle test using BuImCl-CS

Run	EC conv. (%)	DMC yield (%)	EG yield (%)	TON of DMC ^a
Fresh (0.2 g)	78.4	71.1	70.6	95.6
1st (0.18 g)	76.0	67.7	68.2	101.1
2nd (0.168 g)	75.1	67.5	67.9	108.0
3rd (0.155 g)	71.6	63.5	63.2	110.1

Reaction conditions: EC=25 mmol, MeOH=200 mmol, T=160 °C, reaction time=6 h, P_{CO₂}=1.34 MPa

^aTON=(mole of DMC)/(mole of RImX)

on the effects of alkyl chain length [31,32]. It could be explained that increasing the bulkiness of the alkyl chain, which forces the halide ions away from the cation easier, results in less electrostatic interaction between anion and cation and consequently increases the availability of the anion.

It is generally known that the type of anion of ionic liquid has significant effects on the catalytic performance of ionic liquids [33,34]. RImXs with different halide anions, Cl⁻ (BuImCl-CS), Br⁻ (BuImBr-CS) and I⁻ (BuImI-CS) were used to catalyze the transesterification reaction between EC and methanol. As shown in runs 1, 2, and 3, the TON of DMC decreased in the order of BuImCl-CS (143.0)>BuImBr-CS (89.3)>BuImI-CS (87.8). Nucleophilicity and steric hindrance are both in the order I⁻>Br⁻>Cl⁻ [14]. These two conflicting factors may influence the interaction of the anion with carbon atom of CO₂. In this reaction, the effect of steric hindrance seems to be dominant to that of nucleophilicity of the anions.

Recycling experiments were carried out to investigate the stability of the immobilized ionic liquid catalyst. In each cycle, the catalyst was separated by filtration and then used directly for the next run without regeneration or addition of BuImBr-CS catalyst. Table 5 shows the activity of the reused BuImBr-CS catalyst. The weight of recovered catalyst decreased a little due to the filtration step. The conversion of EC and the yield of DMC also decreased slightly after three consecutive runs. However, the TON of DMC even increased during the recycle experiments. It means that the catalyst can be reused at least up to three consecutive times without any considerable loss of its initial activity.

CONCLUSION

In the synthesis of DMC from EC and methanol, the immobilized ionic liquid on commercial silica (RImX-CS) showed good catalytic activity without using any solvent. It was found that RImX-CS with a longer alkyl chain length showed much better catalytic activity. RImX-CS with chloride (Cl⁻) as the counter anion showed the best catalytic activity among RImX-CS catalysts with different counter anions. High temperature, long reaction time, and high CO₂ pressure also increased the catalytic activity. The BuImBr-CS can be easily recovered and reused without any considerable loss of its initial activity.

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