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Chemical conversion of CO₂: evaluation of different ionic liquids as catalysts in dimethyl carbonate synthesis

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Abstract

Dimethyl carbonate (DMC) synthesis from methanol and CO₂ was investigated using ionic liquids (ILs) as catalysts. ILs based on 1-alkyl-3-methyl imidazolium and N-alkylpyridine cations and [Cl⁻], [BF₄⁻], [PF₆⁻], [Tf₂N⁻] anions were used in this study. Selectivity in DMC increased in the anion order: [Tf₂N⁻] < [PF₆⁻] < [Cl⁻] < [BF₄⁻], following the same behavior for both cations. Methanol conversion was similar for all tested ILs. The best result for DMC selectivity (83%) was obtained when [emim][BF₄] was used as catalyst. After 5 recycling tests, a loss of 8.5% in the catalyst activity was observed for [bmim][BF₄].

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1. Introduction

In the recent years, global warming and environmental problems are frequently related to the high carbon dioxide (CO₂) concentration in the atmosphere. In this context, reducing the atmospheric concentration of CO₂ is a widely discussed imminent action [1-6]. Among the mitigation possibilities, there is the application of CO₂ capture and geological storage technologies. Another strategy is CO₂ capture and conversion to value-added products. CO₂ can be captured from various stationary sources and used as reactant and/or reaction medium for chemical syntheses [1,6]. Chemical transformation of CO₂ is one of the most interesting options for mitigation of environmental impacts, in which carbonate synthesis is a very efficient solution [3,6-9].

Dimethyl carbonate (DMC) is an important intermediate for different syntheses. DMC can be used to produce polycarbonates and polyurethanes (as carbonylating and alkylating agent), as well as fuel additives and solvents due to its versatile chemical reactivity and unique physical properties. Moreover, DMC is an environmentally benign mediator and a promising substitute for phosgene, dimethyl sulphate and methyl iodide in organic synthesis due to its low toxicity and rapid biodegradability [6,8,10-11].

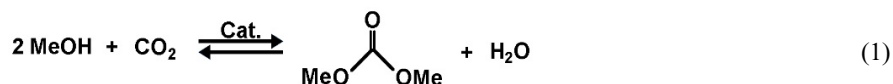
DMC is currently synthesized by oxidative carbonylation or phosgenation of methanol [12-15]. The processes for DMC production are efficient and the technology is well developed. However, the use of highly toxic or corrosive reagents and the waste generation are setbacks in these processes that do not follow Green Chemistry principles, demanding more environmentally friendly approaches and low energy requiring technical alternatives [7-8,10,12-13].

Implementation of synthetic methodologies based on CO₂ can contribute for reducing the concentration of this gas in the atmosphere. Even if these processes do not have a high impact on greenhouse gases mitigation, it provides a platform of options for CO₂ recycling [1,6,14].

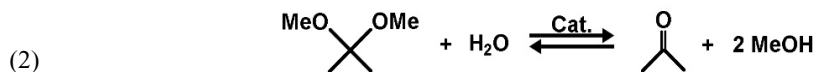
Synthesis of various carbonates using ionic liquids (ILs) are reported elsewhere [7-14,16-18]. Ionic liquids have demonstrated excellent performance as catalysts and reaction media. These compounds present particular properties (i.e. negligible vapor pressure and excellent thermal stability) and special characteristics compared with traditional organic or inorganic solvents [7-9].

The activity of the ionic liquid as catalyst depends on the nature of the cation and anion. The activity increases in the following order for the cations: [bmim⁺] > [bpy⁺] and anions: [BF₄⁻] > [Cl⁻] > [PF₆⁻] [9]. Studies on the influence of alkyl chain length (alkyl = C₂, C₄, C₆ and C₈) of the cation 1-alkyl-3-methylimidazolium evidenced that by increasing the alkyl chain the selectivity and conversion are decreased [7,19].

The literature describes DMC synthesis by oxidative carbonylation of methanol (Eq. 1) at 493.15 K and 2.4 MPa using copper salts as catalysts and ILs as promoters, obtaining 17% of methanol conversion and 97.8% of selectivity for DMC [16]. Transesterification of propylene and ethylene carbonates at 413.15 K with [bmim][Cl] as catalyst resulted in 15% of conversion and 75% of selectivity [7,19].



Thermodynamic constraints related to the direct reaction of CO₂ and methanol, high CO₂ stability, DMC hydrolysis and catalyst deactivation are the key factors that contribute to the low DMC yield. Moreover, water withdrawal from reaction medium is extremely necessary to shift the equilibrium towards DMC formation direction [10,20]. Various additives, for example, 2,2-dimethoxypropane (Eq. 2) [21] and benzonitrile [22] can be used for water withdrawal in order to displace the yield towards the product, resulting in an increase up to 13 times of the synthesized DMC amount.



The aim of this study was to investigate the structure effect of ILs based on imidazolium and pyridine cations

combined with different anions ($[Cl^-]$, $[BF_4^-]$, $[PF_6^-]$ and $[Tf_2N^-]$) as catalysts. Temperature and reaction time for the direct synthesis of DMC from methanol and CO_2 , in presence of 2,2-dimethoxypropane as drying agent, were investigated. Recovery and recycling of an ionic liquid for the DMC synthesis were also described.

Nomenclature

[bmim][Cl]	1-butyl-3-methylimidazolium chloride
[bmim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborato
[bmim][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate
[bmim][Tf ₂ N]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[emim][BF ₄]	1-ethyl-3-methylimidazolium tetrafluoroborato
[emim][Tf ₂ N]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[mbmim][Tf ₂ N]	1-(3-methyl)butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[dmbmim][Tf ₂ N]	1-(3,3-dimethyl)butyl-3 methylimidazoliumbis(trifluoromethylsulfonyl)imide
[bpy][Cl]	N-butyl-pyridine chloride
[bpy][BF ₄]	N-butyl-pyridine tetrafluoroborato
[bpy][PF ₆]	N-butyl-pyridine hexafluorophosphate
[bpy][Tf ₂ N]	N-butyl-pyridinebis(trifluoromethylsulfonyl)imide
[epy][BF ₄]	N-ethyl-pyridinetetrafluoroborato
[epy][Tf ₂ N]	N-ethyl-pyridine bis(trifluoromethylsulfonyl)imide
[dmbpy][Tf ₂ N]	1-(3,3-dimethyl)butyl-pyridine bis(trifluoromethylsulfonyl)imide
ND	Not detected

2. Experimental

2.1. Synthesis and characterization of the ionic liquids

Ionic liquids based on imidazolium and pyridine cations combined with $[Cl^-]$, $[BF_4^-]$, $[PF_6^-]$ and $[Tf_2N^-]$ anions were synthesized following procedures well described elsewhere [23-25]. Figure 1 presents the synthesized ILs.

The synthesized ionic liquids were characterized by Fourier Transform Infrared Spectroscopy (FTIR) using a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer with attenuated total reflectance accessory (ATR) and by Proton Nuclear Magnetic Resonance (1H -NMR) on a Varian VNMRS 300 MHz spectrophotometer, using $DMSO-d_6$ as solvent and glass tubes of 5 mm in diameter. The residual chloride test was performed in a portable Vernier LabQuest system with a specific sensor.

[bmim][Cl]- 1H -NMR (300 MHz, $DMSO-d_6$) δ (ppm): 9.31 [s, 1H]; 7.86 [d, 1H, J = 1.8 Hz]; 7.80 [d, 1H, J = 1.6 Hz]; 4.25 [t, 2H, J = 7.2 Hz]; 3.94 [s, 3H]; 1.91-1.76 [m, 2H, J = 14.9; 7.5 Hz]; 1.33 [dt, 2H, J = 14.7; 7.3 Hz]; 0.97 [t, 3H, J = 7.3 Hz]. FTIR ν (cm^{-1}): 3137-3045 (C-H aromatic), 2957 (C-H of CH_2), 2871 (C-H of CH_3), 1634 (C=N aromatic), 1567-1463 (C=C aromatic), 1231 (C-N aromatic), 1169 (C-N aliphatic), 754 (Cl).

[bmim][BF₄] - 1H -NMR (300 MHz, $DMSO-d_6$) δ (ppm): 9.17 [s, 1H]; 7.85 [d, 1H, J = 1.7 Hz]; 7.79 [d, 1H, J = 1.6 Hz]; 4.26 [t, 2H, J = 7.2 Hz]; 3.94 [s, 3H]; 1.95-1.76 [m, 2H, J = 14.9; 7.5 Hz]; 1.36 [dt, 2H, J = 14.6; 7.3 Hz]; 1.00 [t, 3H, J = 7.3 Hz]. FTIR ν (cm^{-1}): 3164-3121 (C-H aromatic), 2964 (C-H of CH_2), 2877 (C-H of CH_3), 1628 (C=N aromatic), 1575-1466 (C=C aromatic), 1285 (C-N aromatic), 1169 (C-N aliphatic), 1030-843 (B-F). Cl^- (0.36 %).

[bmim][PF₆]- 1H -NMR (300 MHz, $DMSO-d_6$) δ (ppm): 9.06 [s, 1H]; 7.73 [d, 1H, J = 1.6 Hz]; 7.66 [d, 1H, J = 1.6 Hz]; 4.14 [t, 2H, J = 7.2 Hz]; 3.86 [s, 3H]; 1.83-1.67 [m, 2H, J = 14.8; 7.4 Hz]; 1.25 [dt, 2H, J = 14.8; 7.3 Hz]; 0.89 [t, 3H, J = 7.3 Hz]. FTIR ν (cm^{-1}): 3170-3125 (C-H aromatic), 2966 (C-H of CH_2), 2878 (C-H of CH_3), 1611 (C=N

aromatic), 1572-1466 (C=C aromatic), 1252 (C-N aromatic), 1168 (C-N aliphatic), 816-749 (P-F). Cl⁻ (0.24 %).



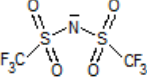
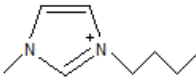
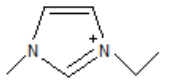
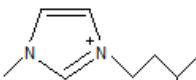
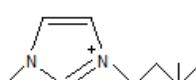
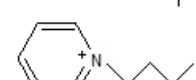
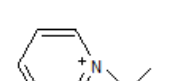
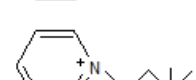
Cation X Anion	Cl ⁻			
	[bmim][Cl]	[bmim][BF ₄]	[bmim][PF ₆]	[bmim][Tf ₂ N]
	—	[emim][BF ₄]	—	[emim][Tf ₂ N]
	—	—	—	[mbmim][Tf ₂ N]
	—	—	—	[dmbmim][Tf ₂ N]
	[bpy][Cl]	[bpy][BF ₄]	[bpy][PF ₆]	[bpy][Tf ₂ N]
	—	[epy][BF ₄]	—	[epy][Tf ₂ N]
	—	—	—	[dmbpy][Tf ₂ N]

Fig. 1: ILs used as catalysts for DMC synthesis.

[bmim][Tf₂N] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.11 [s, 1H]; 7.78 [d, 1H, J = 1.7 Hz]; 7.86 [d, 1H, J = 1.6 Hz]; 4.22 [t, 2H, J = 7.2 Hz]; 3.91 [s, 3H]; 1.87-1.68 [m, 2H, J = 14.9; 7.4 Hz]; 1.29 [dt, 2H, J = 14.7; 7.3 Hz]; 0.90 [t, 3H, J = 7.3 Hz]. FTIR ν (cm⁻¹): 3158-3121 (C-H aromatic), 2967 (C-H of CH₂), 2879 (C-H of CH₃), 1618 (C=N aromatic), 1571-1466 (C=C aromatic), 1212 (C-N aromatic), 1179 (C-N aliphatic), 1052 (S=O), 842 (N-S), 789 (C-S), 740-652 (C-F). Cl⁻ (0.06 %).

[emim][BF₄] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.10 [s, 1H]; 7.78 [d, 1H, J = 1.8 Hz]; 7.73 [d, 1H, J = 1.6 Hz]; 4.19 [m, 2H, J = 7.3 Hz]; 3.85 [s, 3H]; 1.42 [t, 3H, J = 7.3 Hz]. FTIR ν (cm⁻¹): 3162-3121 (C-H aromatic), 2988 (C-H of CH₂), 2883 (C-H of CH₃), 1630 (C=N aromatic), 1575-1455 (C=C aromatic), 1235 (C-N aromatic), 1170 (C-N aliphatic), 1030-843 (B-F). Cl⁻ (ND).

[emim][Tf₂N] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.15 [s, 1H]; 7.78 [d, 1H, J = 1.8 Hz]; 7.70 [d, 1H, J = 1.6 Hz]; 4.19 [m, 2H, J = 7.3 Hz]; 3.85 [s, 3H]; 1.35 [t, 3H, J = 7.3 Hz]. FTIR ν (cm⁻¹): 3159-3123 (C-H aromatic), 2992 (C-H of CH₂), 2893 (C-H of CH₃), 1632 (C=N aromatic), 1574-1471 (C=C aromatic), 1226 (C-N aromatic), 1186 (C-N aliphatic), 1055 (S=O), 841 (N-S), 789 (C-S), 740-650 (C-F). Cl⁻ (ND).

[mbmim][Tf₂N] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.13 [s, 1H]; 7.79 [d, 1H, J = 1.7 Hz]; 7.70 [d, 1H, J = 1.8 Hz]; 4.24 [t, 2H]; 3.85 [s, 3H]; 1.69 [m, 2H, J = 7.2 Hz]; 1.51 [m, 1H, J = 13.4; 6.5 Hz]; 0.92 [s, 6H]. FTIR ν (cm⁻¹): 3157-3121 (C-H aromatic), 2964 (C-H of CH₂), 2877 (C-H of CH₃), 1628 (C=N aromatic), 1573-1471 (C=C aromatic), 1226 (C-N aromatic), 1180 (C-N aliphatic), 1048 (S=O), 846 (N-S), 789 (C-S), 739-653 (C-F). Cl⁻ (ND).

[dmbmim][Tf₂N] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.15 [s, 1H]; 7.80 [d, 1H, J = 1.8 Hz]; 7.69 [d, 1H, J = 1.8 Hz]; 4.24 [t, 2H]; 3.84 [s, 3H]; 1.92 [t, 2H]; 1.01 [s, 9H]. FTIR ν (cm⁻¹): 3154-3122 (C-H aromatic), 2962 (C-H of CH₂), 2873 (C-H of CH₃), 1645 (C=N aromatic), 1573-1470 (C=C aromatic), 1224 (C-N aromatic), 1179 (C-N aliphatic), 1051 (S=O), 840 (N-S), 790 (C-S), 740-653 (C-F). Cl⁻ (0.04 %).

[bpy][Cl] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.36 – 9.26 [m, 2H]; 8.64 [t, 1H, J = 7.8 Hz]; 8.25 [t, 2H]; 4.71 [t, 2H, J = 7.4 Hz]; 1.90 [m, 2H, J = 9.3 Hz]; 1.38 [dt, 2H]; 0.90 [t, 3H, J = 7.4 Hz]. FTIR ν (cm⁻¹): 3145-3080 (C-H aromatic), 2961 (C-H of CH₂), 2873 (C-H of CH₃), 1633 (C=N aromatic), 1561-1463 (C=C aromatic), 1229 (C-N aromatic), 1167 (C-N aliphatic), 755 (Cl).

[bpy][BF₄] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.13-9.04 [m, 2H]; 8.61 [t, 1H, J = 7.9 Hz]; 8.17 [t, 2H]; 4.60 [t, 2H, J = 7.4 Hz]; 1.99 [m, 2H, J = 9.3 Hz]; 1.39 [dt, 2H]; 0.92 [t, 3H, J = 7.3 Hz]. FTIR ν (cm⁻¹): 3140-3097 (C-H aromatic), 2965 (C-H of CH₂), 2877 (C-H of CH₃), 1636 (C=N aromatic), 1496-1467 (C=C aromatic), 1221 (C-N aromatic), 1173 (C-N aliphatic), 1022-873 (B-F). Cl⁻ (0.44 %).

[bpy][PF₆] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.13-9.04 [m, 2H]; 8.61 [t, 1H, J = 7.8 Hz]; 8.22 [t, 2H]; 4.60 [t, 2H, J = 7.4 Hz]; 1.91 [m, 2H, J = 9.2 Hz]; 1.39 [dt, 2H]; 0.92 [t, 3H, J = 7.4 Hz]. FTIR ν (cm⁻¹): 3150-3104 (C-H aromatic), 2966 (C-H of CH₂), 2877 (C-H of CH₃), 1618 (C=N aromatic), 1559-1465 (C=C aromatic), 1219 (C-N aromatic), 1168 (C-N aliphatic), 816-747 (P-F). Cl⁻ (0.05 %).

[bpy][Tf₂N] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.11-9.04 [m, 2H]; 8.59 [t, 1H, J = 7.8 Hz]; 8.15 [t, 2H]; 4.59 [t, 2H, J = 7.4 Hz]; 1.89 [m, 2H, J = 9.2 Hz]; 1.35 [dt, 2H]; 0.91 [t, 3H, J = 7.4 Hz]. FTIR ν (cm⁻¹): 3142-3094 (C-H aromatic), 2969 (C-H of CH₂), 2879 (C-H of CH₃), 1636 (C=N aromatic), 1500-1467 (C=C aromatic), 1231 (C-N aromatic), 1176 (C-N aliphatic), 1052 (S=O), 850 (N-S), 786 (C-S), 739-653 (C-F). Cl⁻ (0.10).

[epy][BF₄] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.14-9.05 [m, 2H]; 8.60 [t, 1H, J = 7.8 Hz]; 8.22 [t, 2H]; 4.63 [m, 2H, J = 7.3]; 1.55 [t, 6H, J = 7.3 Hz]. FTIR ν (cm⁻¹): 3162-3120 (C-H aromatic), 3000 (C-H of CH₂), 2889 (C-H of CH₃), 1630 (C=N aromatic), 1575-1458 (C=C aromatic), 1226 (C-N aromatic), 1170 (C-N aliphatic), 1031-848 (B-F). Cl⁻ (ND).

[epy][Tf₂N] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.15-9.04 [m, 2H]; 8.63 [t, 1H, J = 7.8 Hz]; 8.30 [t, 2H]; 4.60 [m, 2H, J = 7.3]; 1.51 [t, 6H, J = 7.3 Hz]. FTIR ν (cm⁻¹): 3159-3122 (C-H aromatic), 2989 (C-H of CH₂), 2890 (C-H of CH₃), 1630 (C=N aromatic), 1575-1468 (C=C aromatic), 1225 (C-N aromatic), 1177 (C-N aliphatic), 1050 (S=O), 845 (N-S), 790 (C-S), 740-652 (C-F). Cl⁻ (ND).

[dmbpy][Tf₂N] - ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm): 9.10 -9.05 [m, 2H]; 8.62 [t, 1H, J = 7.8 Hz]; 8.12 [t, 2H]; 4.65 [t, 2H, J = 7.4 Hz]; 1.83 [t, 2H]; 0.97 [s, 9H]. FTIR ν (cm⁻¹): 3155-3122 (C-H aromatic), 2963 (C-H of CH₂), 2874 (C-H of CH₃), 1640 (C=N aromatic), 1579-1472 (C=C aromatic), 1219 (C-N aromatic), 1178 (C-N aliphatic), 1050 (S=O), 839 (N-S), 791 (C-S), 740-652 (C-F). Cl⁻ (0.09 %).

2.2. Synthesis of the dimethyl carbonate

The synthesis of dimethyl carbonate from methanol and CO₂ was carried out with 2,2-dimethoxypropane as drying agent and with the different synthesized ILs as catalysts. In order to evaluate the influence of reaction time and temperature on the DMC synthesis, experiments at 413.15 K and 443.15 K were performed during 12, 24 and 48 hours. All experiments were conducted under 4.0 MPa of CO₂ pressure in a stainless steel autoclave of 120 cm³ equipped with magnetic stirring. For all syntheses, it was used 250 mmol of methanol, 25 mmol of 2,2-dimethoxypropane and 2.5 mmol of ionic liquid. No additional solvent was used in the synthesis. The autoclave was pressurized with CO₂ and heated until the working temperature. After reaction completion, the reactor was cooled and slowly depressurized. Recycling of the catalyst system was also evaluated in the best reaction condition.

The separation of the catalyst from reaction products was performed by vacuum distillation. The resulting liquid mixtures were analysed using a Shimadzu GC-14B gas-chromatograph equipped with a flame ionization detector

(FID) and a DB-5HT column (15 m x 0.32 mm x 0.10 μ m), using amyl alcohol as internal standard and dimethyl ether as solvent.

3. Results and discussion

3.1. Effect of reaction time and temperature

The effect of reaction time and temperature on DMC formation by oxidative carbonylation of methanol with CO₂ was investigated and the results are presented in Table 1.

Aiming to evaluate the influence of the reaction time on DMC synthesis, [bmim][Cl] (Entries 1,3-4) and [bmim][BF₄] (Entries 5,7-8) were tested as catalysts. By increasing the reaction time from 12 h to 24 h, the conversion of methanol and DMC selectivity are significantly enhanced. The same behavior was described in the literature [20] for reaction times up to 24 h. When the reaction time was increased to 48 h, a slight decrease on these parameters was observed due to the formation of other products than DMC. Thus, according to these results, it could be defined the optimum reaction time of 24 h for the investigated experimental conditions (4.0 MPa and 443.15 K).

Table 1. Effect of temperature and time in DMC synthesis using IL as catalysts.

Entry	Ionic Liquid	Temperature (K)	Time (h)	Methanol Conversion (%)	Selectivity of DMC (%)
1	[bmim][Cl]	443.15	12	1.39	24.58
2	[bmim][Cl]	413.15	24	3.74	58.39
3	[bmim][Cl]	443.15	24	7.46	53.02
4	[bmim][Cl]	443.15	48	6.35	39.42
5	[bmim][BF ₄]	443.15	12	3.15	52.56
6	[bmim][BF ₄]	413.15	24	4.31	81.54
7	[bmim][BF ₄]	443.15	24	7.43	81.31
8	[bmim][BF ₄]	443.15	48	6.03	68.47

Reaction conditions: methanol (250 mmol), 2,2-dimethoxypropane (25 mmol), catalyst (2.5 mmol), initial CO₂ pressure of 4.0 MPa.

Having established the reaction time of 24 h for DMC synthesis, the influence of temperature was evaluated with [bmim][Cl] (Entries 2,3) and [bmim][BF₄] (Entries 6,7) as catalysts. By varying the temperature from 413.15 K to 443.15 K, the conversion of methanol in DMC was considerably higher. However, a slight loss of selectivity for both ILs was observed which is related to a greater kinetic energy of the molecules that favors formation of other structures. For [bmim][Cl] the conversion increased from 3.74% to 7.46% and for [bmim][BF₄] from 4.31% to 7.43%. These results evidenced that the higher the reaction temperature, the higher the kinetic energy supplied to the molecules.

3.2. Comparing ionic liquids as catalysts for DMC synthesis

The catalytic performance of the different ILs based on imidazolium and pyridinium cations for DMC synthesis is shown in Table 2. It is known that DMC synthesis from methanol by oxidative carbonylation route is thermodynamically unfavorable [15,26], consequently in absence of catalyst (Entry 9) only traces of DMC was detected.

The influence of the ionic liquid anion is comparable for [bmim⁺] (Entries 3,7,10-11) and [bpy⁺] cations (Entries 16-19), showing no significant variation on methanol conversion but in DMC selectivity. The selectivity in DMC increases in the anion order: [Tf₂N⁻] < [PF₆⁻] < [Cl⁻] < [BF₄⁻], same trend observed for both cations. Chloride, the most nucleophilic anion, does not show the best DMC selectivity (53.02% for [bmim][Cl] and 53.44% for [bpy][Cl], Entries 3,16 respectively) when compared with the anion [BF₄⁻] (81.31% for [bmim][BF₄] and 60.72% for [bpy][BF₄], Entries 7,17 respectively), probably due to the greater acidity of the chloride anion [9,16]. Moreover, the

catalyst efficiency can be related to the water affinity of the studied ILs. The anions $[Cl^-]$ and $[BF_4^-]$ are hydrophilic and they probably interact with the water phase formed during the reaction, thus preventing DMC hydrolysis. The anion size can also influence the DMC selectivity, which decreases by increasing the anion size (except for $[Cl^-]$). It is noteworthy that in the absence of the drying agent (2,2-dimethoxypropane), methanol conversion was not detected.

Table 2. Comparing different ILs as catalysts for DMC synthesis.

Entry	Ionic Liquid	Methanol Conversion (%)	Selectivity of DMC (%)
9	-	Trace	-
10	[bmim][PF ₆]	7.19	46.99
11	[bmim][Tf ₂ N]	6.89	39.30
12	[emim][BF ₄]	9.22	83.30
13	[emim][Tf ₂ N]	8.98	43.01
14	[mbmim][Tf ₂ N]	6.81	35.13
15	[dmbmim][Tf ₂ N]	6.65	33.63
16	[bpy][Cl]	7.73	53.44
17	[bpy][BF ₄]	7.52	60.72
18	[bpy][PF ₆]	7.57	41.40
19	[bpy][Tf ₂ N]	7.43	34.54
20	[epy][BF ₄]	7.65	63.72
21	[epy][Tf ₂ N]	9.35	38.49
22	[dmbpy][Tf ₂ N]	6.78	28.81

Reaction conditions: methanol (250 mmol), 2,2-dimethoxypropane (25 mmol), catalyst (2.5 mmol), initial CO₂ pressure of 4.0 MPa, T = 443.15 K, t = 24 h.

Comparing the imidazolium (Entries 1-15) and pyridine (Entries 16-22) cations, methanol conversion is quite similar for both cations (imidazolium around 7.57%; pyridine around 7.71%). Regarding the DMC selectivity, the imidazolium cation is more promising, reaching 83.30% for the [emim][BF₄] and 81.31% for [bmim][BF₄]. The imidazolium cation is 12% more selective than pyridine cation possibly due to its higher basicity. Imidazole ring has two nitrogen atoms in its structure, one participates in the ring resonance and leaves the electronic pair of the other free, resulting in an increase in the basicity and therefore in the reactivity with CO₂ for DMC formation [9].

The size of the alkyl side-chain of the ILs cations was also evaluated for DMC selectivity and methanol conversion. The imidazolium (Entries 7,11-13) and pyridine (Entries 17,19-21) cations were studied by varying the carbon chain from C₄ to C₂. It can be highlighted from Table 2 that decreasing the size of the side-chain, an improvement in methanol conversion and DMC selectivity is achieved (pyridine cation: 14% and 8% respectively; imidazolium cation: 27% and 5% respectively). This result is probably due to the hydrophilicity of the cation, which decreases as the chain increases. In addition, the reactivity and solubility of ILs in methanol decreased with increasing carbon side-chain of the cation [7,19].

The effect of the branching of the cation alkyl side-chain in imidazolium (Entries 14-15) and pyridine (Entry 22) was evaluated. One methyl ([mbmim⁺]) and two methyl ([dmbmim⁺] and [dmbpy⁺]) ramifications were introduced. All results were inferior to those achieved without addition of ramification in the cation alkyl side-chain. A gradual loss of catalytic activity was observed with the imidazolium cation (Entry 11). The [bmim][Tf₂N] ionic liquid gives 6.89% of methanol conversion and 39.30% of selectivity to DMC, while adding ramification the conversion was similar (6.81% and 6.65%, Entries 14-15) but the selectivity decreased to 35.13% and 33.63% for one and two-methyl ramifications, respectively. It represents a selectivity loss of 15% when adding the two-methyl ramification in the imidazolium cation and a loss of 18% for pyridine cation. The addition of ramification in the alkyl side-chain typically increases the free volume for entrapping gas and consequently the CO₂ solubility [17], which could result in a higher catalytic activity. As depicted in Table 2, a decrease in selectivity and activity was not observed experimentally with addition of methyl ramification in the cation alkyl side-chain. This behavior is probably due to the steric hindrance caused by the ramification, which hinders the interaction of the substrate with the catalyst.

3.3. Recycling of the IL used as catalyst for DMC synthesis

The recycling of the [bmim][BF₄] ionic liquid as catalyst in the oxidative carbonylation of methanol was investigated (Figure 2). For catalyst recovery, the reaction products and unreacted methanol were separated from the IL after the reaction by distillation under reduced pressure.

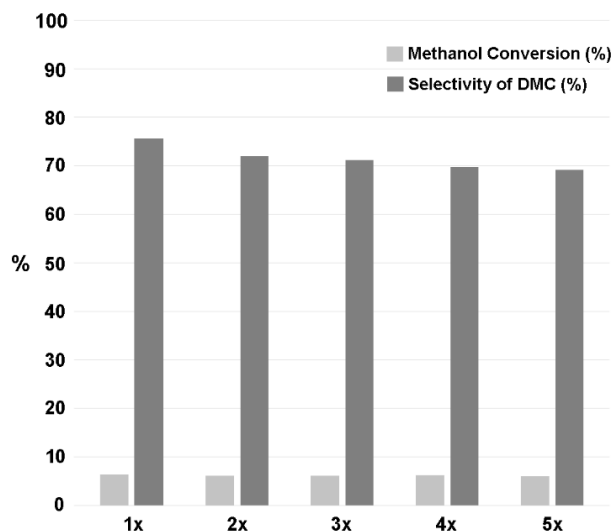


Fig. 2. Recycling of [bmim][BF₄] as catalyst in DMC synthesis.

The catalytic activity of the [bmim][BF₄] is maintained constant for methanol conversion up to five times with slight loss of selectivity for DMC. This decrease in selectivity is possibly due to a loss of IL during handling and transferring from reaction media. FTIR analysis of [bmim][BF₄] after five recycles showed no changes when compared with the original IL, indicating that there is no catalyst degradation.

4. Conclusions

We have proposed a strategy to enhance the conversion of a thermodynamically unfavorable chemical reaction using different ILs as catalysts. Our results indicate an optimum condition for temperature and reaction time for DMC synthesis, which are 443.15 K and 24 h under 4.0 MPa of CO₂ pressure. The comparison between the imidazolium and pyridine cations confirmed a better selectivity for imidazolium based cation in all tests. Comparing different anions, the tetrafluoroborate was more selective in DMC synthesis. A decrease in the size of the cation alkyl side-chain slightly increases the catalytic activity of the ionic liquid, improving methanol conversion and DMC selectivity. The steric hindrance caused by the addition of branching in the cation alkyl side-chain significantly decreases the catalytic activity. This decrease was observed as increases the number of ramifications. The reuse of an ionic liquid as catalyst for DMC synthesis is possible as evidenced in our results. DMC selectivity and methanol conversion were almost constant up to five cycles.

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