Research Article

Atul A. Pawar#, Avinash A. Chaugule#, Hern Kim*

Greener synthesis of dimethyl carbonate from carbon dioxide and methanol using a tunable ionic liquid catalyst

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Abstract: Several types of ionic liquids (ILs) performance towards dimethyl carbonate (DMC) synthesis using cheap reactant (methanol) and waste CO\textsubscript{2} which is abundantly available in the environment are discussed. We synthesized ILs with cheap raw materials such as ethylene glycol. The main aim of this study is to synthesize efficient catalysts for the production of profitable fuel additives. ILs show high thermal stability, less viscosity, and low vapor pressure. In addition, some ILs have high CO\textsubscript{2} absorption capacity due to moderate acid-base properties. These ILs reversibly capture more CO\textsubscript{2} which is more efficient towards mass transport of methanol at optimum reaction conditions which enhance the DMC yield. This catalytic system is easily reusable for several reactions without decreased performance under the same reaction conditions. These reaction conditions had an effect on the synthesis of DMC. Temperature, pressure, IL loading, and IL/DMAP ratio were fine tuned. We propose a mechanism which the reaction may follow. The synthesized ILs required moderate reaction conditions and reduce waste gases (CO\textsubscript{2}) from the environments as they have high CO\textsubscript{2} absorption capacity compared to the metal oxide catalyst. Therefore, this catalytic system helps and gives new direction to synthesize new catalyst for other application.

Keywords: CO\textsubscript{2}; ILs; dehydrating agent; reaction mechanism.

1 Introduction

Carbon is one of the most abundant elements on earth and it is the key element in fuels and polymers. It is important for industry and transport, and thus the economy [1]. In recent decades, the conversion of carbon dioxide (CO\textsubscript{2}) into useful chemicals has attracted much attention because it is non-toxic and comes from a renewable source [2].

One of the most efficient ways to use CO\textsubscript{2} as a raw material is in the synthesis of linear carbonates such as dimethyl carbonate (DMC) and diethyl carbonate (DEC). Most researchers who have conducted experiments on CO\textsubscript{2} utilization have investigated hydrogenation of CO\textsubscript{2}, cycloaddition of CO\textsubscript{2} and epoxides, and reduction of CO\textsubscript{2} under photochemical or electrochemical conditions [3]. Traditionally, DMC is synthesized by phosgenation, the drawbacks of this process include the use of highly toxic and corrosive phosgene gas and the formation of large amounts of inorganic salts [4]. The four known processes used for DMC synthesis are: (i) oxidative carbonylation, (ii) a two-step process including carbon monoxide (CO) and nitric oxide (NO), (iii) transesterification of ethylene carbonate (EC) and propylene carbonate (PC) with methanol (MeOH), and (iv) direct synthesis of DMC from CO\textsubscript{2} and MeOH. The first two processes use toxic gases such as CO and NO which are harmful to nature. The transesterification of EC and PC with MeOH produces DMC and a useful byproduct (ethylene glycol). There are limitations to this route: harsh reaction conditions, expensive precursor, and there is no utilization of CO\textsubscript{2}. The direct synthesis of DMC from CO\textsubscript{2} and MeOH is a superior route from the viewpoint of green chemistry because of the relatively cheap raw material (MeOH) and water (H\textsubscript{2}O) is the main byproduct [5].

With this in mind we pursued the direct synthesis of DMC from CO\textsubscript{2} and MeOH. Different types of catalysts have been reported in DMC synthesis such as: organotin [6], copper-based catalysts [7], homogeneous and heterogeneous catalysts [8,9], organometallic complexes.
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[10], phosphines [11], organic bases [12], metal oxides [13–15], acid-base bifunctional systems [2], zeolite-smectite catalysts [12], and supported organic base catalysts [16]. However, many of these catalytic systems require extreme reaction conditions and produce low yields. Low catalyst stability and/or reactivity and low methanol conversions are also common due to the inertness of CO₂ and deactivation of the catalyst. DMC on the other hand has low toxicity, is non-corrosive, and is biodegradable [17]. DMC can be used as a precursor for polycarbonate synthesis, in the polyurethane manufacturing industry, as an electrolyte in lithium-ion batteries, as an alkylating and carbonylating agent, and as a polar aprotic solvent [18–20]. According to the literature several types of ionic liquids (ILs) have been used for the synthesis of DMC instead of metal oxide catalysts as ILs possess high CO₂ absorption capacity at moderate reaction conditions, they are ionic compounds (organic salt) and are liquids below 100°C or even at room temperature. ILs can be used in different organic synthesis reactions due to their chemical and thermal stability, negligible vapor pressure, recyclability, high solubility in polar and non-polar solvents [21], non-flammability, mechanical and electrochemical backbone, and high electrical conductivity. Moreover, ILs are useful in electrochemical applications, extraction reactions, gas separations, carbohydrate dissolution, polymer chemistry, as anti-microbial and anti-electrostatic agents, in activation and stabilization of biomolecules, and nanoscience technology [22,23,32,24–31]. The main drawbacks of DMC production are the formation of significant amounts of H₂O in the reaction mixture and low DMC yield. There are two practical solutions to these issues: an equilibrium shift towards products by increasing the CO₂ pressure and developing adequate dehydrating agents or synthesized active catalysts. According to this literature review more novel active materials need to be developed which are easy to prepare and are low cost. Binary and ternary catalysts are used in the DMC synthesis which are more toxic to the environment due to their degradation and therefore there is a need to develop a single component catalytic system for DMC synthesis.

Various kinds of imidazolium-based monocationic and dicaticionic ILs are reported for DMC synthesis. Their main limitations are low yield, low CO₂ solubility, toxicity and their expensive precursors. Thus, in this study we focused on improving the precursor and the DMC yield. The ILs were synthesized using cheap, easily available, biodegradable materials (ethylene glycol). The cation was vinyl-imidazole because of availability, moderate acidic properties, and easy polymerization capability. The anion was Bis (trifluoromethane) sulfonimide [NTf₂], as it has high CO₂ absorption capacity, it reacts with CO₂ forming [NTf₂...CO₂], a new anionic intermediate which is more basic than the original anion. The interaction between [NTf₂] and MeOH is much greater than with the bulky and charge- delocalized anions BF₄⁻ and PF₆⁻ [33,34]. The cationic and anionic parts form a synergistic link and capture more CO₂ [35]. The synthesized ILs are considerably reactive in DMC synthesis. We tested the CO₂ solubility in reaction mixture with and without ILs and concluded that ILs can dissolve more CO₂ in the reaction mixture [36].

The dehydrating agent, 4-dimethyl amino pyridine (4-DMAP), is effective in absorbing H₂O from the reaction mixture. There are various amine containing moieties similar to DMAP such as 4-(pyrrolidin-1-yl) pyridine (4-PYP) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) (pKa 13.5). The disadvantage of using these different bases is that they form a large amount of polycarbonate (byproduct of DMC). Therefore the yield of dimethyl carbonate (DMC) decreases due to high basicity [37]. In the case of 4-DMAP, which is less basic (pKa 9.6) than the aforementioned different bases, 4-DMAP is planar and an ideal Lewis base [38]. Chiral DMAP was recently employed for a number of enantioselective organic reactions due to its steric bulk, electron donating nature, and ability to attract moisture [39]. Herein, we report new di-cationic ILs for the synthesis of DMC which have the ability to adsorb large amounts of CO₂ and thus results in better yield and higher selectivity as compared to the metal oxide and monocationic ILs catalytic systems.

The single component catalytic system reveals a remarkable performance and good thermal strength and therefore we were able to easily synthesize DMC at adequate reaction conditions. Moreover, the ILs need an easy synthesis method, no addition of metal oxide complexes and at ordinary reaction conditions the yield of DMC was higher. Therefore, here we report the three classes of Lewis acidic ILs for the synthesis of DMC. To the best of our knowledge, there is no report available based on the EG[Vim][NTf₂] ILs.

2 Experimental section

2.1 Materials

1-Vinyl imidazole, Mesyl chloride (MsCl), acetonitrile (CH₃CN), dichloroethane (DCE), dichloromethane (DCM), methanol (MeOH), bis(trifluoromethanesulfonfyl) imide lithium salt, potassium hexafluorophosphate,
2-cyanopyridine, 4-dimethyl aminopyridine (DMAP), 1,8-diazabicyclo [2.2.2] undec-7 -ene (DBU), triethylamine, ethylene glycol, potassium bromide (KBr), sodium dicyanamide, sodium sulphate, and carbon dioxide gas (99.999%) were purchased from Alfa Aesar. All chemicals were purchased at 99% purity and used as received without further purification.

2.2 Characterization and measurements

The synthesized ILs were characterized by a different spectroscopic techniques such as $^1$H NMR, $^{13}$C NMR, and FT-IR analysis. NMR spectra were recorded in DMSO-d$_6$ on 400 MHz and 100 MHz spectrometers using TMS as an internal standard. The FT-IR spectra of samples were recorded using a Varian 2000 (scimitar series) spectrophotometer. A spectrum was recorded from 4000 to 500 cm$^{-1}$ maintaining a resolution of 4 cm$^{-1}$ with 32 scans in transmittance mode. Thermogravimetric analysis (TGA, model SCINCO, N-1000) was used for thermal study of ILs from 25 to 600°C, with a heating rate of 10°C/min under inert gas (N$_2$) (50 mL/min). The crystallization temperature of ILs was studied using differential scanning calorimetry (DSC) Mettler DSC 822 instrument in a sealed platinum pan with 10°C/min heating and cooling rate, under N$_2$ gas (50 mL/min). The viscosity of ILs was calculated using Brookfield model DV-II+ programmable viscometer connected with water jacket and temperature measuring device.

2.3 Synthesis of new ILs

2.3.1 Preparation of ethylene glycol dimesylate (EG[OMs]$_2$) precursor

In brief, in a round bottom flask containing 1.0 mmol of ethylene glycol and 2.1 mmol of tri-ethylamine was mixed with 20 mL dichloromethane (DCM) with vigorous stirring. The reaction mixture was then cooled to 0°C for 30 minutes in an ice bath. Mesyl chloride was added dropwise with constant stirring over a period of 15-20 minutes under an inert gas atmosphere. The reaction mixture was then warmed to 30°C for 12 hours. The reaction progress was monitored by thin layer chromatography (TLC) using mobile phase ethyl acetate: hexane (70:30) ratio. After 12 hours the reaction was quenched with H$_2$O followed by extraction using 50:50 H$_2$O and DCM, the synthesized ionic liquids were dried with inorganic salt (sodium sulphate). The organic layer was concentrated under reduced pressure. The resulting product, ethylene glycol dimesylate (EG[OMs]$_2$), was isolated as a white crystalline solid then dried under vacuum at 30°C for 24 hours (Yield 89.4%) (Scheme 1).

$^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 2.97 (6H, s), 4.34 (4H, t). FT-IR (500-4000 cm$^{-1}$): 793 cm$^{-1}$ (S-O), $\sim$1166-1326 cm$^{-1}$ (S=O), 2945 cm$^{-1}$ (C-H).

$^{13}$C NMR (100 MHz): 37.37, 67.40.

2.3.2 Synthesis of ethylene glycol (EG)-di (1-vinyl imidazolium) dimesylate IL EG[Vim]$_2$[OMs]$_2$

1.0 mmol dimesylate precursor and 2.1 mmol 1-vinyl-imidazole were added to a round-bottom flask containing 20 mL acetonitrile. The reaction mixture was refluxed under inert gas atmosphere at 80°C for 72 hours and then was slowly cooled to room temperature. The solvent was removed under vacuum followed by ethyl acetate washing to remove unreacted starting material and the product was dried under vacuum at 30°C for 12 hours. The obtained product is EG-di (1-vinyl imidazolium) di-mesylate IL in Quasi-solid (solid-liquid mixture) form (Yield 90.4%) (Scheme 1). $^1$H NMR (400 MHz, DMSO-d$_4$): $\delta$ 2.97 (6H, s), 4.34 (4H, t), FT-IR (500-4000 cm$^{-1}$): 793 cm$^{-1}$ (S-O), 1166-1326 cm$^{-1}$ (S=O), 2945 cm$^{-1}$ (C-H). $^{13}$C NMR (100 MHz): 37.37, 67.40.
2.3.3 Synthesis of ethylene glycol (EG)-di (1-vinyl imidazolium) bis (difluoromethanesulfonyl) imide IL EG[Vim]₂[NTf₂]₂

To a round-bottom flask 0.17 mol glycol-di (1-vinyl-imidazolium) di-mesy late, 0.34 mol bis (trifluoromethanesulfonyl) imide lithium salt was added to 20 mL acetone. The reaction mixture was stirred at room temperature for 72 hours under N₂ gas, after which it was washed with acetone to remove any unreacted salt. The resulting quasi-solid product was dried under vacuum at 60°C for 6 hours (Yield 89.2%) (Scheme 2).

1H NMR (400 MHz, DMSO-d₆): 4.70 (4H, s), 5.40-5.42 (2H, d), 5.88-5.92 (2H, d), 7.25-7.30 (2H, m), 7.72 (2H, s), 8.15 (2H, s), 9.36 (2H, s). FT-IR (500-4000 cm⁻¹): 1132-1340 cm⁻¹ (S=O), 1457 cm⁻¹ (-CH₂ bend), 1561 cm⁻¹ (N-H), 1664 cm⁻¹ (C=N), 3101 cm⁻¹ (Ar-H), 3149 cm⁻¹ (=CH₂ stretch vibration).

13C NMR (100 MHz): 39.85, 49.13, 109.29, 119.65, 123.75, 129.26, 136.61.

2.3.5 Synthesis of ethylene glycol EG -di (1-vinyl imidazolium) dicyanamide IL EG[Vim]₂[N(CN)₂]₂

Quasi-solid (Yield 92.6%) (Scheme 2). 1H NMR (400 MHz, DMSO-d₆): 4.69 (4H, s), 5.41-5.43 (2H, d), 5.88-5.91 (2H, d), 7.26-7.28 (2H, m), 7.72 (2H, s), 8.15 (2H, s), 9.33 (2H, s). FT-IR (500-4000 cm⁻¹): 1184-1310 cm⁻¹ (S=O), 1450 cm⁻¹ (-CH₂ bend), 1550 cm⁻¹ (N-H), 1649 cm⁻¹ (C=N), 2196-2240 cm⁻¹, (C=N) 3079 cm⁻¹ (Ar-H), 3149 cm⁻¹ (=CH₂ stretch vibration).

13C NMR (100 MHz): 39.89, 49.12, 109.42, 119.67, 123.74, 129.32, 136.63.

2.4 Linear carbonate production

2.4.1 DMC production from CO₂ and MeOH

Dimethyl carbonate (DMC) production from methanol (MeOH) and carbon dioxide (CO₂) (Scheme 3) was performed in a batch reactor connected to a stainless steel (SS) reaction vessel (100 mL) with a heating coil and mechanical stirrer. The reaction vessel contained 20 g (625 mmol) of MeOH, EG[Vim]₂[NTf₂]₂ IL 1.28 mmol, DMAP 4.10 mmol under 6.5 MPa CO₂ pressure and at 130°C. The reaction mixture was constantly stirred at 850 rpm for 6 hours after which it was cooled in an ice cold water and slowly depressurized to remove the unreacted CO₂. The IL/DMAP was separated under reduced pressure. The liquid phase of product (DMC) was analyzed by gas chromatography (GC-17A, SHIMADZU) using capillary
column (STABILWAX, 30 m length, 0.53 mm ID, 1 mm film thickness) and a flame ionization detector (FID). Furthermore, the product was identified using FT-IR (supporting information Figure 3).

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Thermal properties of ILs

The thermal degradation pattern of the ILs was examined by thermal gravimetric analysis (TGA) and the crystallization temperature was studied by differential scanning calorimetry (DSC) under N₂ gas from 25 to 600 °C at a heating rate of 10 °C/min. A slower heating rate results in a more accurate thermal degradation pattern [40,41] and in TGA if the heating rate is higher than 10 °C/min the decomposition temperature will not be accurate [42]. The decomposition pattern depends on a number of factors such as the viscosity of ILs, heat capacity, the nature of the cation and anion, IL geometry, and total molar mass of the ILs [43]. The thermal pattern of room temperature ionic liquids (RTILs) is shown in Figure 1 and demonstrates that the synthesized ILs are stable up to 300 °C. Thermogram of EG[Vim]₂[PF₆]₂ IL shows weight degradation from 70 to 170 °C which is attributed to the hydrophilic nature of ILs. When the temperature is increase above 170 °C the decomposition of the imidazole compounds occurs. The EG[Vim]₂[PF₆]₂ IL is stable up to 230 °C due to its hydrophobicity, intramolecular interactions, high molecular mass, more density, and high viscosity. Similarly, for EG[Vim]₂[N(CN)₂]₂ IL thermal degradation starts at a low temperature because, polymerization of the dicyanamide anion takes place [44]. The thermal degradation of EG[Vim]₂[NTf₂]₂ IL shows 10% weight loss at 70 °C due to the decomposition of mesylate anions. A 90% weight loss was evident between 250 and 350 °C as a result of the decomposition of the vinyl-imidazole cation. The [NTf₂]⁻ anion containing RTILs have a wider liquid range and higher thermal stability than other anionic compounds [45]. The geometrical dicationic ILs are thermally stable above 300 °C unlike most traditional monocationic ILs [46]. Figure 2 illustrates the DSC curve of dicationic ILs from 25 to 200 °C. The EG[Vim]₂[NTf₂]₂ IL is in a quasi-solid state at room temperature with the glass transition temperature observed at 100 °C and the crystallization temperature observed at 125 °C. Further heating did not result in the observation of further changes because of the stable nature of IL and the presence of the [NTf₂]⁻ anion which conveys high thermal stability. The [NTf₂]⁻ anion is water repellent (insoluble in water). Therefore, ILs absorb minimal amounts of water from the atmosphere and therefore the ionic liquids is insoluble in water. Therefore, the interaction between cation and anion is less. This is the main reason for the high thermal stability of ionic liquids at higher temperature. Therefore, according to the DSC results the ionic liquids is in Quasi-solid state [47].

3.1.1 The viscosity and miscibility of ILs

Viscosity is an important parameter in the study of the nature of ILs. The highly viscous nature of ILs directly
affects the mass transfer of the reaction and vice versa [48]. Figure 3 shows the viscosity of ILs from room temperature to 65°C. ILs were completely dried under high vacuum for up to 3 hours below this temperature. The viscosity of ILs varies according to temperature. Initially, at 25°C, the viscosity of all ILs was observed at 605, 910, 470, and 420 cP for [OMs]-, [PF$_6$]-, [N(CN)$_2$]-, and [NTf$_2$]- anions respectively. Of all ILs, the viscosities of [PF$_6$]- and [OMs]- anions with the vinyl-imidazole cation were higher than for other anions with the same cation. The reasons for this are the strong electrostatic force between cation and anion. Increasing the temperature further resulted in a decrease in the viscosity of the ILs. At higher temperatures all ILs melt and their viscosity decreased due to the decreased interaction between cation and anion.

From the above results it was concluded that, the synthesized ILs with [PF$_6$]-, and [OMs]- anions have higher viscosity than ILs with other anions due to intra and intermolecular hydrogen bonding and van der Waals forces. The [OMs]- anion is completely miscible with water (polar) and completely insoluble in benzene (non-polar) due to the weak interaction between solvents and [OMs]- anion. In the case of [NTf$_2$]- and [PF$_6$]- anions they are miscible with benzene and immiscible with water.

3.1.2 Determination of acidity for di-cationic ILs

In dimethyl carbonate (DMC) synthesis acidic sites activate the methanol and basic sites activate the carbon dioxide (CO$_2$), thus catalytic activity mainly depends on the Lewis acidic-basic nature of the catalyst [49]. The Lewis acidity-basicity of ILs is measured by Fourier transform-infrared (FT-IR) and UV-visible spectroscopy [50] using pyridine as an intermediate molecule. Figure 4 shows the shift of the position of the pyridine mixed EG[Vim]$_2$[NTf$_2$]$_2$ ILs bands from 1434 to 1439 cm$^{-1}$ and 1573 to 1580 cm$^{-1}$, clearly demonstrating that the IL is a Lewis acid which forms pyridinium ions [PyH]$^+$ [51]. Hence, highly fluorinated anion salts have low basicity, and the imidazolium cation has lower basicity than the phosphonium cation with the same anions [42].

3.2 Catalytic performance of ILs

The catalytic performance of ILs was analyzed for DMC synthesis from CO$_2$ and MeOH. There are several types of drying agents (moisture sensitive agents) reported for organic carbonate synthesis such as 4-dimethylaminopyridine (DMAP), 1,4-diazabicyclo [2.2.2] octane (DABCO), 1,8-diazabicyclo [2.2.2] undec-7-ene (DBU), 1,5,7-triaza-bicyclo [4.4.0]dec-5-ene (TBD), and hexamethylene tetramine (HMTA). Their efficacy is probably due to their Lewis basicity and ability to attract moisture [52]. In this study DMC was formed from CO$_2$ and MeOH using an IL/DMAP catalyst. No product yield was detected without the catalyst (Table 1, entry 1). When DMAP was used without ILs, no reaction occurred (Table 1, entry 2) due to the lack of an active site to adsorb CO$_2$. Employing EG[Vim]$_2$[PF$_6$]$_2$ IL as a catalyst without DMAP yielded DMC (Table 1,
Table 1: Catalytic performance of ILs on dimethyl carbonate production.

| Entry | Catalyst                  | Yield of DMC (mmol) | Selectivity of DMC (%) |
|-------|---------------------------|----------------------|------------------------|
| 1     | Without ionic liquid      | -                    | -                      |
| 2     | Only DMAP                 | -                    | -                      |
| 3     | EG[Vim]2[PF6]2            | 32.5                 | 16.7                   |
| 4     | EG[Vim]2[N(CN)2]2        | 45.5                 | 25.5                   |
| 5     | EG[Vim]2[NTf2]2          | 53.7                 | 37.8                   |
| 6     | EG[Vim]2[PF6]2/DMAP      | 32.6                 | 20.3                   |
| 7     | EG[Vim]2[N(CN)2]2/DMAP   | 35.9                 | 35.1                   |
| 8     | EG[Vim]2[NTf2]2/DMAP     | 41.9                 | 91.8                   |

Reaction conditions: MeOH: 625 mmol, IL: 1.28 mmol, DMAP: 4.1 mmol, CO₂ pressure, 6.5 MPa at 130 °C, 6 h.

A plausible reason for this is that the [PF₆]⁻ anion binds more strongly with the cation. Using different ILs such as EG[Vim]2[N(CN)2] and EG[Vim]2[OMs] resulted in increased DMC yield. The CO₂ solubility depends on various factors such as mole fraction, viscosity, dipole moment, polarizability, quadrupole moments, Lewis acidity-basicity, and nonspecific dispersion forces between the CO₂ and IL [53,54]. EG[Vim]2[NTf2]₂ IL resulted in the highest DMC yield due to the anion’s ability to capture CO₂. The main byproduct is water so a low amount of water would indicate that the DMC formation should be higher. Therefore, formation of water during the reaction had an effect on the DMC yield.

To overcome this problem, we used a moisture sensitive agent, 4-dimethyl amino pyridine (DMAP) which acts as a water trapping agent and a Lewis base in the synthesis of ILs. The binary EG[Vim]2[NTf2]₂/DMAP catalytic system gives a higher yield of DMC than remaining ILs within a 6 hour reaction time because the combination of DMAP and IL provides the moderately Lewis acidic and basic sites required for DMC synthesis. They reversibly capture more CO₂ and shift the equilibrium towards products [55]. EG[Vim]2[NTf2]₂/DMAP displays the highest activity with the greater DMC yield (Table 1, entry 8) than the other prepared IL/DMAP catalytic systems (Table 1, entry 6-7). This is mostly likely due to EG[Vim]2[NTf2]₂ ILs having a higher solubility of CO₂. Moreover, organic base (DMAP) provides synergistic combination of cation and anion therefore it has an enormous potential to enhance the reaction in the forward direction. This reaction of CO₂ and MeOH with IL/DMAP catalytic system can easily capture and convert CO₂ into a valuable product. Increasing the concentration of CO₂ in the reaction mixture with MeOH resulted in CO₂ changing from gas to liquid phase and methanol changing from liquid to gas at equilibrium. The liquid phase of CO₂ is much more reactive than the gas phase and the conversion to product is much higher [48]. Therefore, EG[Vim]2[NTf2]₂/DMAP catalytic system was deliberated for further studies.

3.2.1 Effect of reaction temperature, pressure, and time on DMC production

The effect of temperature was studied on the basis of yield and selectivity of DMC. The reaction was carried out in a stainless-steel autoclave containing 20 g of MeOH (625 mmol), 1.28 mmol of IL, 4.1 mmol of DMAP under 6.5 MPa CO₂ pressure for 6 hours. For comparison, the DMC synthesis was initially carried out at room temperature resulting in negligible DMC yield. Increasing the temperature to 70 °C resulted in a gradual increase in yield to 13 mmol of DMC. Further temperature increases increased the DMC yield steadily. The highest yield was obtained at 130 °C when the IL, MeOH, and CO₂ were in single liquid phase. A further increase in temperature resulted in a gradual decrease in yield. This might be due to the formation of the byproduct dimethoxymethane (DMM) and subsequently degradation of DMC [56] as shown in Figure 6.
Optimal CO$_2$ pressure results in high conversion and selectivity. Without CO$_2$ pressure the DMC yield is low because of stable nature of CO$_2$ caused by the great bond strength between carbon and oxygen. The high pressure must be necessary for CO$_2$ activation. An increase in reaction pressure increased the yield and selectivity. DMC yield and selectivity were greatest at 6.5 MPa. From these results it is apparent that the CO$_2$ pressure is directly proportional to the MeOH conversion, as shown in Figure 7.

According to our results 6 hours was the optimal reaction time at which the highest DMC yield of 41.9 mmol was obtained. Longer reaction times resulted in a decrease in DMC yield probably due to hydrolysis [57] as shown in Figure 8.

### 3.2.2 Effect of different moisture sensitive agents and IL loading on DMC production

The DMC yield was increased from 22.2 to 41.9 mmol at constant loading of ILs (1.28 mmol) when different moisture sensitive agents were used. Initially when 1,8-diazabicyc[2.2.2]undec-7-ene (DBU) was used the DMC yield was negligible. In the case of 2-cyanopyridine...
the DMC yield was higher as this agent provides more basic sites which can easily trap the H\textsubscript{2}O molecules. The disadvantage of using 2-cyanopyridine is that it forms 2-picoliamide upon reaction with H\textsubscript{2}O and is not stable at elevated temperatures resulting in low DMC yield. On the other hand, 4-dimethyl aminopyridine (DMAP) possesses an amino group and is mildly basic allowing it to trap water molecules resulting in a high DMC yield.

In Figure 9 we studied the ILs loading. Firstly, the reaction was performed without IL resulting in no DMC formation. When 0.5 g of IL was used, the selectivity and yield increased gradually. Based on this result we increased the amount of IL to 1 g resulting in a higher yield and selectivity. The higher concentration of IL in the reaction mixture provides more active sites and higher surface area on which CO\textsubscript{2} can be captured. Upon increased amount of ILs to 1.5 g the DMC yield and selectivity were decreased.
drastically because of the higher loading probably lower down the acidic or electrophilic sites of the ILs, therefore, decrease the DMC yield.

### 3.3 Proposed reaction mechanism

The synthesized ILs are active towards organic carbonate (DMC) synthesis. The reaction mechanism we proposed based on the reaction progression is shown in Scheme 4. In the first step, the DMAP abstracts the acidic hydrogen of vinyl-imidazole cation and then nucleophilic attack of the vinyl-imidazole ring anion on the carbonyl carbon of CO₂ takes place, resulting to form anionic carbamate intermediate. The electron rich nucleophilic oxygen species of the carbamate group attacks the hydrogen atom of the MeOH, leading to the formation of methoxide anion. The methoxide anion attacks the electrophilic carbon atom of the CO₂ followed by removal of water. Subsequently, another methoxide anion attacks the carbonyl group of the CO₂ and finally DMC is formed and at the same time the ILs regeneration take place.

### 3.4 Recyclability of catalyst

Reusability of a catalyst is important from an industrial point of view. The synthesized IL/DMAP catalytic system can be reused for the production of DMC as shown in Figure 10. For the second recycle reaction the IL was removed by vacuum distillation from the reaction mixture and further reused beneath the identical reaction conditions. The recycled IL can be reused under the same reaction conditions (130°C, 6.5 MPa CO₂, and 6 hours) for five cycles with maintaining the same yield and selectivity of DMC. Furthermore, the ILs stability is confirmed by the TGA (Figure 11) shows good stability of the ILs with high yield of DMC and the FT-IR spectroscopy (Figure 12)
which shows that the structure of ILs changes after fifth time reused. From these results we determine that the ILs catalyst is stable and effective for DMC synthesis.

4 Conclusion

In summary, a chain of ILs with different anions and the same cation were synthesized for the production of DMC from CO$_2$ and MeOH. The performance of the ILs was much better than that reported for dicationic ILs. This may be because the new system is a Lewis acid, an important parameter in DMC synthesis. Moreover, the DMAP absorbed more water from the reaction mixture improving the DMC yield. The ILs were synthesized using ethylene glycol. The EG[Vim]$_2$[NTf$_2$]$_2$/DMAP (1:3 ratio) catalytic system was the most efficient with 91.8% selectivity and 41.9 mmol DMC yield. The steric bulk and electronic properties of the Lewis base can play a dual role in determining the selectivity and activity of the catalyst [39]. The given catalyst could be easily recycled up to five runs. These environmentally friendly ILs can be used as substitutes for metal oxides and also minimize waste gases (CO$_2$) from the environment, key factors from the green chemistry point of view.

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