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Polymer supported diol functionalized ionic liquids: An efficient, heterogeneous and recyclable catalyst for 5-aryl-2-oxazolidinones synthesis from CO_2 and aziridines under mild and solvent free condition

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ABSTRACT

Polymer supported diol functionalized ionic liquids (PS-DFILXs) were investigated as an efficient, heterogeneous and recyclable catalyst for coupling of carbon dioxide (CO_2) to aziridines providing high conversion with excellent regioselectivity towards 5-aryl-2-oxazolidinones under mild and solvent free conditions. The developed methodology was found to be applicable for wide variety of 1-alkyl-2-arylaziridines producing the corresponding 5-aryl-2-oxazolidinones with good yields and excellent regioselectivity. The hydroxyl groups present on vicinal carbon of PS-DFILX proved crucial for higher efficiency of catalyst. In addition, the catalyst could be reused for four consecutive recycles without significant loss in its catalytic activity and selectivity. Hence, the developed process represents environmentally benign chemical fixation pathway of CO_2 for synthesis of 5-aryl-2-oxazolidinones under mild condition.

1. Introduction

Entrapment of greenhouse gas CO_2 into valuable chemicals has received a great attention so as to limit the increasing concentration of atmospheric CO_2. In respect, exhaustive research has been made to understand the importance of utilization of CO_2 in organic synthesis [1–4]. One of the most attractive synthetic goals starting from CO_2 is synthesis of five-membered oxazolidinones possessing wide application as intermediates [5–8], chiral auxiliaries [9,10] and building blocks for biologically active pharmaceutical agents [11–13]. Therefore, the development of greener and efficient catalyst for synthesis of oxazolidinones under mild conditions has attracted much more attention.

From the prospective of green chemistry, synthesis of 2-oxazolidinones utilizing CO_2 as a feedstock is more attractive in comparison to other processes like carbonylation of 1,2-amino alcohols with phosgene or CO [14–17] and carboxylative cyclization of propargylamines or propargylic alcohols with CO_2 [18–21]. Several catalysts are been reported for synthesis of oxazolidinones from CO_2 and aziridines, using (salen)-Cr(III)/DMAP [22], phenol/DMAP [23], quaternary ammonium bromide functionalized polyethylene glycol [24], zirconyl chloride [25], polystyrene supported amino acid [26] and [C_4DABCO] Br [27]. However, most of the catalysts required harsh reaction conditions (8.0 MPa of CO_2 pressure, 100–140 °C temperature, longer reaction time and higher catalyst/substrate ratio) with tedious work up procedure. Hence, the development of environmental benign, thermo-stable, heterogeneous recyclable catalyst for efficient synthesis of oxazolidinones from CO_2 and aziridines under mild reaction condition is still desirable.

In recent years, ionic liquids (ILs) based heterogeneous catalysis has attracted a great attention as they permit mutual advantages of both homogeneous as well as heterogeneous catalysts [28–31]. In comparison to pure Lewis acidic ILs, IL-based heterogeneous catalyst offers additional advantage like decrease in the amount of ionic liquids used with ease of separation and efficient catalyst recovery [32–34]. In context, we envisage that the presence of vicinal hydroxyl groups on ionic liquid cation moiety have great potential to accelerate the reaction in forward direction. This is because of its strong chelating ability through hydrogen bonding with nitrogen atom of aziridines thus enabling the ring opening of aziridine. Han et al. made a similar observation wherein the activity of cellulose/KI was increased due to the presence of vicinal hydroxyl groups for ring opening reaction of epoxide to cyclic carbonate effectively [35]. This important observation encouraged us to develop an IL-based heterogeneous catalyst for cycloaddition of CO_2 and aziridines which would function at ambient temperature

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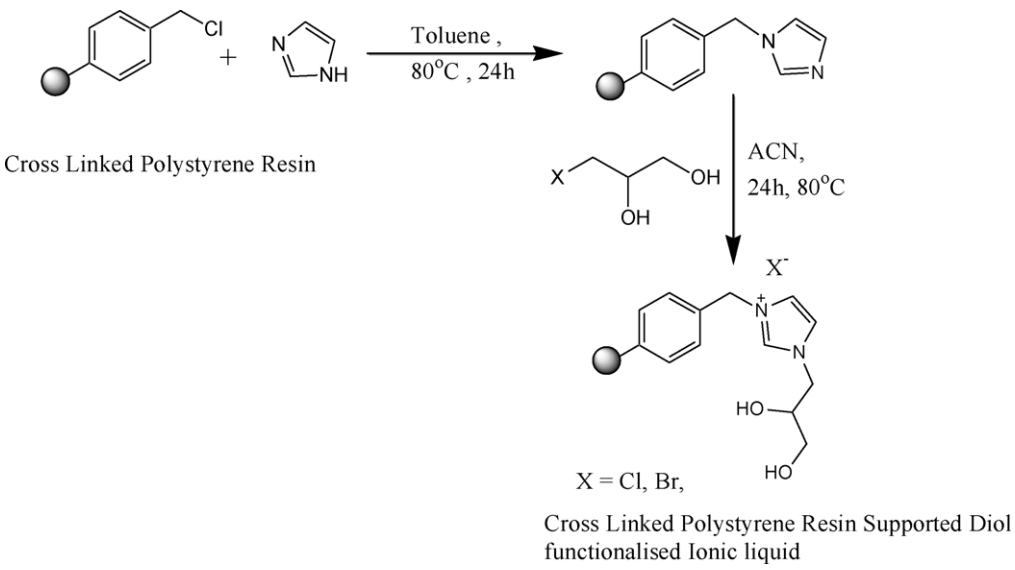


Scheme 1. Schematic representation for the preparation of polymer-supported diol functionalized ionic liquids as catalyst.

and pressure conditions. To best of our knowledge, this is the first report where an IL-based heterogeneous catalyst was efficiently employed to catalyze the reaction of aziridines with CO_2.

In present communication, we report the synthesis and catalytic activity of PS-DFILX as a highly efficient, heterogeneous and recyclable catalyst with mechanistic understanding of coupling reaction of CO_2 and aziridines under mild reaction condition. The catalyst exhibited significant catalytic activity providing good to excellent yield of the desired product with excellent chemo and regioselectivity at room temperature. Detailed studies revealed that the hydroxyl groups on the vicinal carbons of PS-DFILX plays a vital role for remarkable efficiency of the catalyst (Scheme 2).

2. Experimental

2.1. Materials

All chemicals and reagents were purchased from firms of repute with their highest purity available and used without further purification/pre-treatments. Polymer supported diol functionalized ionic liquid were prepared according to the procedure reported in literature [36] with slight modification.

2.2. Typical experimental procedure for the preparation of polymer-supported diol functionalized ionic liquids

2.2.1. Step-1: Preparation of imidazolium-loaded polymeric support (PS-IM)

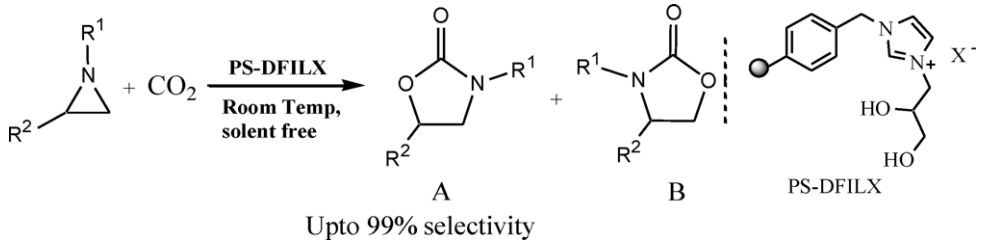
Merrifield peptide resin (2% cross linked, 2.3 mmol Cl/g, Aldrich) (10.0 g, 53.4 mmol), imidazole (53.5 mmol) and toluene (70 mL) were added to 100 mL round bottom flask and refluxed for 24 h. On completion, the reaction mixture was cooled to room temperature. It was then filtered and residue obtained was washed with toluene, 10% HCl, water and methanol sequentially, followed by drying under reduced pressure to afford the supported ionic liquid catalyst PS-IM (loading of ionic liquid was determined by elemental analysis). The catalyst was further characterized by FT-IR analysis to examine the attachment of ionic liquid.

2.2.2. Step-2: Preparation of polymer supported diol functionalized ionic liquids (PS-DFILXs)

Secondly, PS-DFILXs were prepared from PS-IM and corresponding halide substituted diol. In a typical preparation, 3-bromopropane-1,2-diol (54 mmol), PS-IM (10 g) and acetonitrile (70 mL) were added into a 125 mL three-necked flask equipped with a magnetic stirrer and was heated at 80 °C for 24 h with vigorous stirring. On completion of reaction, the reaction mixture was cooled to room temperature. The upper phase was decanted carefully and the solid residue was washed with ethyl acetate (3× 20 mL). Further, the solid was dried under vacuum at 60 °C for 12 h to provide the polymer supported 1-(2,3-dihydroxylpropyl)-imidazolium bromide (PS-DHPIMBr) (Scheme 1). Based on the similar procedure, the polymer supported 1-(2,3-dihydroxylpropyl)-imidazolium chloride (PS-DHPIMCl) was synthesized.

2.3. Characterization of polymer supported diol functionalized ionic liquids (PS-DFILXs)

To confirm the immobilization of DHPIMBr on a polymer, Fourier transform infrared (FT-IR) spectra were recorded on a



Scheme 2. Carboxylation of aziridine with CO_2.

PerkinElmer FT-IR spectrophotometer with anhydrous KBr as standard (Thermo Electron Co.). The amount of diol functionalized ILs attached on the (chloromethyl polystyrene resin) CMPS was determined by elemental analysis (Thermo finnigan) PS-DHPIMBr (loading, 3.2 mmol/g), PS-DHEIMCl (loading, 2.8 mmol/g). Solid-state NMR was carried out for ^{13}C nuclei. Thermo gravimetric analysis (TGA) was carried out using TGA-SDT (Q600 V8.2 Build 100) in a nitrogen atmosphere between 25 °C and 600 °C at a heating rate 5 °C/min.

2.4. General procedure for carboxylation of aziridines with CO_2

In a typical experimental procedure, coupling of aziridines with CO_2 was carried out in a 100 mL stainless steel autoclave reactor with a mechanical stirrer. Aziridine (1 mmol) and catalyst (1.5 mol %) were charged into the reactor at room temperature. CO_2 gas was introduced into the autoclave and then pressure was adjusted to desired pressure (5 MPa) and the mixture was stirred (550–600 rpm) continuously at room temperature for mentioned time period. On completion of reaction, the reactor was cooled in ice-water and CO_2 was ejected slowly. The reaction mixture was analyzed by GC (PerkinElmer, Clarus 400) equipped with a flame ionization detector (FID) and a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm). The residue was purified by column chromatography on silica gel (eluting with 10:1 to 1:1 petroleum ether/ethyl acetate) to afford the product. The products further analyzed by ^1H and ^{13}C spectra recorded on NMR spectrometer (Varian 300) using TMS as internal standard and by GC–MS (Shimadzu QP 2010) which are consistent with those reported in the literature [24–27].

2.5. Spectral data of selected products

2.5.1. Characterization of oxazolidinones

(i) 3-Ethyl-5-phenyloxazolidin-2-one (Table 1, entry 3)
^1H NMR (300 MHz, DMSO-d_6) δ = 7.34–7.65 (m, 5H), 5.51 (m, 1H), 3.93 (t, 1H), 3.43 (t, 1H), 3.15 (m, 2H), 1.15 (t, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) 157.57, 138.76, 131.83, 128, 126.9, 69.72, 51.15, 38.73, 12.41.
GC–MS (EI) *m/z* (%) = 191(55.0) $[M]^+$ 175(7.9), 146(39), 132(22), 105(22.2), 91(43.2), 77(22.1), 65(14), 57(100), 42(57.9).

(ii) 5-Phenyl-3-propyloxazolidin-2-one (Table 1, entry 4)
^1H NMR (300 MHz, DMSO-d_6) δ = 7.34–7.65 (m, 5H), 5.52 (m, 1H), 3.92 (m, 1H), 3.32 (m, 1H), 3.26 (m, 2H), 1.57 (m, 2H), 0.91 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) 158.10, 139.02, 132.09, 128, 125.59, 69.93, 52.23, 45.09, 20.75, 11.18.
GC–MS (EI) *m/z* (%) = 205(7.2) $[M]^+$, 204(51.0), 114(13), 132(100), 117(15), 105(41.0), 91(29.0), 70(38), 43(43), 42(33).

(iii) 3-Butyl-5-phenyloxazolidin-2-onen (Table 1, entry 6)
^1H NMR (300 MHz, DMSO-d_6) δ = 7.33–7.46 (m, 5H), 5.51 (m, 1H), 3.94 (t, *J* = 8.9 Hz, 1H), 3.41 (t, 1H), 3.19 (t, *J* = 7.0, 4.3 Hz, 2H), 1.40 (m, 2H), 1.29 (d, *J* = 7.6 Hz, 2H), 0.79–0.95 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) 158.03, 139.01, 128.99, 128.85, 125.60, 74.42, 52.25, 44, 29.49, 19.93, 13.79.
GC–MS (EI) *m/z* (%) = 219(55.7) $[M]^+$, 133(10.0), 134(100), 117(13.7), 105(37.4),103(30.0), 91(20.3), 84.5(25.7), 78(10).

(iv) 3-Hexyl-5-phenyloxazolidin-2-one (Table 1, entry 7)
^1H NMR (300 MHz, DMSO-d_6) δ = 7.33–7.45 (m, 5H), 5.55 (dd, *J* = 8.7, 7.2 Hz, 1H), 3.94 (t, *J* = 8.7 Hz, 1H), 3.41 (m, 1H), 3.18 (td, *J* = 7.1, 2.1 Hz, 2H), 1.47 (t, *J* = 6.8 Hz, 2H), 1.12–1.35 (m, 6H), 0.77–0.93 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) 158.06, 139.07, 129.03, 128.89, 125.63, 74.44, 52.30, 44.34, 31.53, 27.45, 26.6, 22.6, 14.12.
GC–MS (EI) *m/z* (%) = 247(42) $[M]^+$, 156(21.0), 132(100), 104(53.0), 43(36.0).

(v) 3-Cyclohexyl-5-phenyloxazolidin-2-one (Table 1, entry 10)
^1H NMR (300 MHz, DMSO-d_6) δ = 7.31–7.46 (m, 5H), 5.53 (dd, *J* = 8.7, 72 Hz, 1H), 3.92 (t, *J* = 8.9 Hz, 1H), 3.57 (m, 1H), 3.26 (m, 1H), 0.91–1.94 (m, 10H).
GC–MS (EI) *m/z* (%) = 245.90(12.7) $[M+1]^+$, 245(67) $[M]^+$, 201(18), 163(37), 157(35), 120(38), 104(100), 91(65.0), 55(80), 45(84), 41(57).

(vi) 3-Butyl-5-(4-(tert-butyl) phenyl) oxazolidin-2-one (Table 1, entry 12)
^1H NMR (300 MHz, DMSO-d_6) δ = 7.41–7.46 (m, 4H), 5.47 (m, 1H), 3.91 (t, *J* = 8.9 Hz, 1H), 3.39 (dd, *J* = 8.9, 7.4 Hz, 1H), 3.18 (t, *J* = 7.0 Hz, 2H), 1.39–1.53 (m, 4H), 1.17–1.35 (m, 9H), 0.93 (m, 3H).

(vii) 5-Phenyloxazolidin-2-one (Table 1, entry 1)
GC–MS (EI) *m/z* (%) = 162.96(16) $[M]^+$, 107(100), 91(13), 89(15), 45(31).

(viii) 3-Methyl-5-phenyloxazolidin-2-one (Table 1, entry 2)
GC–MS (EI) *m/z* (%) = 177(4) $[M]^+$, 176(29.40), 133(24.6), 132(55), 91(23), 85(10.7), 43(100).

2.5.2. Characterization of aziridines

(i) 1-Methyl-2-phenylaziridine (Table 1, entry 2)
^1H NMR (300 MHz, DMSO-d_6) δ = 7.07–7.39 (m, 5H), 2.37 (m, 3H), 2.24 (m, 1H), 1.72 (d, *J* = 3.4 Hz, 1H), 1.61 (d, *J* = 6.4 Hz, 1H).
GC–MS (EI) *m/z* (%) = 133(10) $[M]^+$, 132(100), 91(39), 42(12).

(ii) 1-Butyl-2-phenylaziridine (Table 1, entry 6)
^1H NMR (300 MHz, DMSO-d_6) δ = 7.31–7.40 (m, 2H), 7.23–7.30 (m, 3H), 2.31–2.54 (m, 3H), 1.88 (d, *J* = 2.3 Hz, 1H), 1.17 (d, *J* = 6.4 Hz, 1H), 1.31–1.61 (m, 4H), 0.99 (m, 3H).
GC–MS (EI) *m/z* (%) = 175.90(12) $[M]^+$, 174(72.8), 132(100), 133(30), 118(73.8), 98(45.5), 91(97.5), 65(14.1).

(iii) 1-Ethyl-2-phenylaziridine (Table 1, entry 3)
GC–MS (EI) *m/z* (%) = 147(12.5) $[M]^+$, 146(100), 118(25), 91(88), 77(11.3), 65(15.7).

(iv) 2-Phenyl-1-propylaziridine (Table 1, entry 4)
GC–MS (EI) *m/z* (%) = 161(8.6) $[M]^+$, 160(62.60), 118(47.7), 91(100), 65(10.7).

(v) 1-Tert-butyl-2-phenylaziridine (Table 1, entry 9)
GC–MS (EI) *m/z* (%) = 175(6.8) $[M]^+$, 174(34.1), 118(100), 91(94.5), 57(18.3), 41(15.0).

(vi) 1-Hexyl-2-phenylaziridine (Table 1, entry 7)
GC–MS (EI) *m/z* (%) = 203(21.8) $[M]^+$, 132(50.4), 126(26.6), 117(31.6), 114(19.6), 91(46.4), 86(23.7), 73(55.9), 72(66.9), 44(70.8), 43(100).

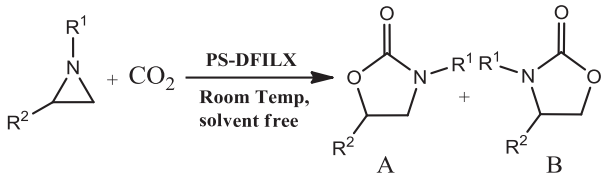
(vii) 1-Cyclohexyl-2-phenylaziridine (Table 1, entry 11)
GC–MS (EI) *m/z* (%) = 201(16.4) $[M]^+$, 200(68.4), 174(10), 119(14.6), 118(100), 91(96), 55(21.4), 41(18.3).

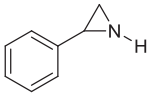
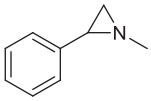
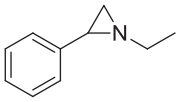
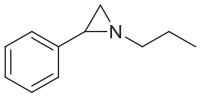
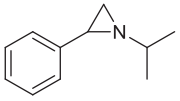
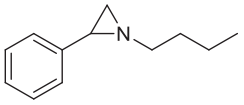
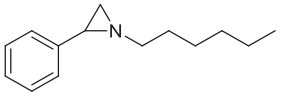
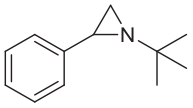
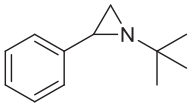
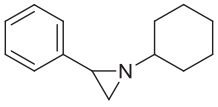
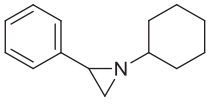
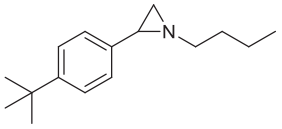
(viii) 1-Butyl-2-(4-(tert-butyl) phenyl) aziridine (Table 1, entry 12)
GC–MS (EI) *m/z* (%) = 231(3.8) $[M]^+$, 230(26.5), 229.95(94.7), 215(10), 187(94.7), 188(36.4), 160(41.5), 132(83.3), 118(53.0), 117(39.5), 98(56), 57(100), 41(50).

2.5.3. Catalyst reusability

The reaction was carried out as mentioned above in typical experimental procedure. After completion of reaction, the reaction mixture was cooled to room temperature and the insoluble catalyst was recovered by filtration technique. It was then thoroughly washed with acetone to remove all traces of product or reactant if present and was dried in oven at 80–85 °C for 1 h. It was then

Table 1
Carboxylative cyclization of various aziridines with CO_2 using PS-DHPIMBr as catalyst.[a].



Entry	Substrates	Time (h)	Conversion (%)[b]	Selectivity A:B (%)	TOF (h^{-1})[c]
1		3	99	95:5	21.9
2		3	100	92:8	22.2
3		3	100	97:3	22.2
4		3	100	99:1	22.2
5		3	99	99:1	22.2
6		3	100	99:1	22.2
7		3	99	97:3	22.0
8		8	15	99:1	1.2
9[d]		12	65	97:3	3.6
10		12	20	95:5	1.1
11[d]		8	67	95:5	5.6
12		3	99	98:2	22.0

[a] *Reaction condition*: aziridines (1 mmol), catalyst (PS-DHPIMBr) (1.5 mol%), CO_2 pressure (5 MPa), temperature (room temperature, 25 °C).
[b] Conversion based on GC analysis.
[c] Turnover frequency (TOF): sum of moles of A and B produced per mole of catalyst per hour.
[d] Temperature (110 °C).

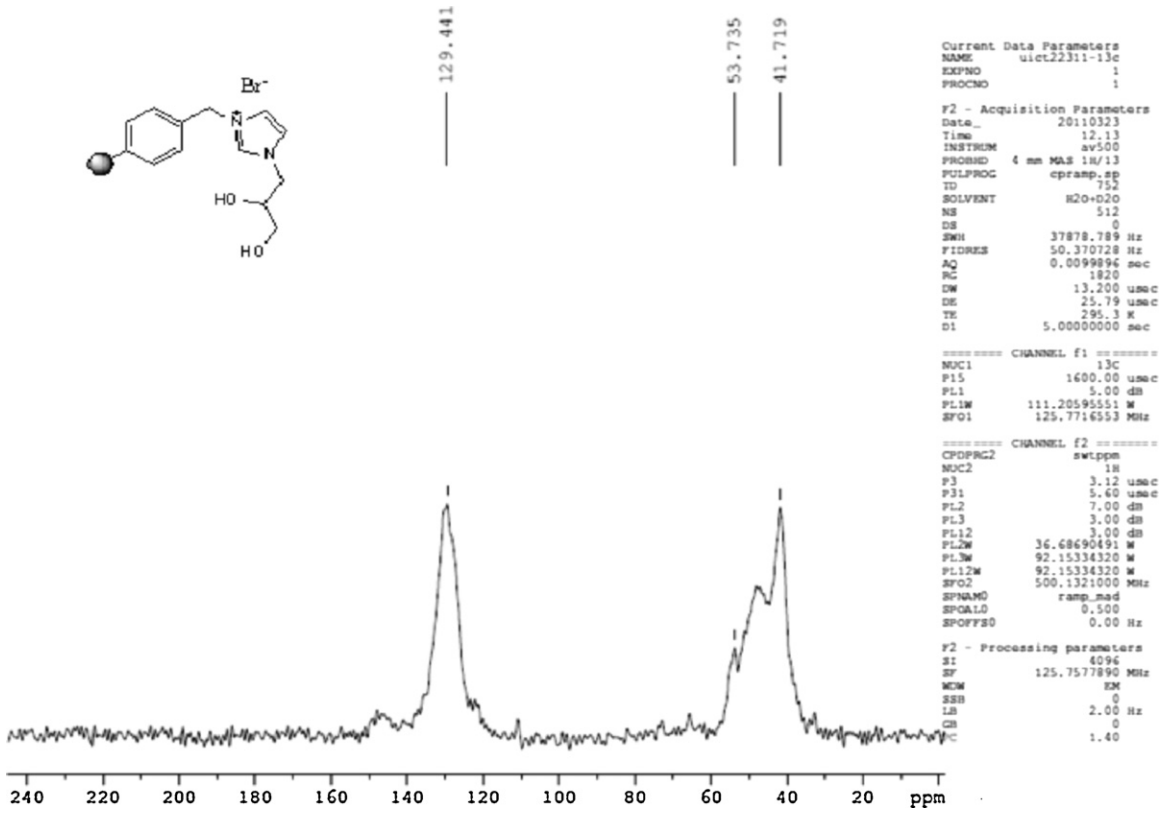


Fig. 1. Solid state ^{13}C NMR of PS-DHPIMBr catalyst.

further used for recyclability study. The same procedure was followed for consecutive recycling.

3. Results and discussion

3.1. Characterization of polymer supported diol functionalized ionic liquids (PS-DFILXs)

The novel imidazolium-based ionic liquids with diol functionality possessing different anions were chemically immobilized using the commercial available polystyrene resin via covalent bonds. The resulting heterogeneous catalysts (PS-DHPIMX) and polystyrene resin were characterized by FT-IR analysis. As shown in supplementary data (Fig. S1, 1b and 1c), the PS-DHPIMX displays a typical strong peak corresponding to O–H stretching frequency centred at about 3302 cm^{-1}. In comparison with polystyrene resin, newly appeared C–H stretching (2923.57 and 2846 cm^{-1}) and imidazolium ring stretching bands (1618 and 1454.07 cm^{-1}) are the characteristic features for presence of IL components in the heterogeneous catalysts. In supplementary information (Fig. S1, 1a) the typical peak centred at 1265 cm^{-1} corresponding to the stretching frequency of the functional group CH_2Cl which disappears in the spectra of PS-DHPIMBr (Fig. S1, 1b) and PS-DHPIMCl (Fig. S1, 1c) suggesting the complete modification of CMPS. This fact provides an evidence for chemical immobilization of the active catalyst on the CMPS support.

To investigate the efficiency of grafting reaction, a solid-state ^{13}C NMR analysis of PS-DHPIMBr was carried out. As shown in Fig. 1, the chemical shifts at 124 and 140 ppm corresponds to the three imidazole ring carbon atoms. The signal at 53 ppm is attributed to the carbon atoms connecting on imidazole ring and other carbon atoms gave peaks from 25 to 47 ppm.

In addition, the thermal stability of catalyst was investigated using a TGA analysis under nitrogen atmosphere between 25 and 400 °C at a heating rate 5 °C/min. The results revealed that PS-DHPIMBr could tolerate about 304.9 °C with little loss in weight (Please refer to supplementary information, Fig. S2).

3.2. Application of (PS-DFILX) catalyst for 5-aryl-2-oxazolidinones synthesis

To investigate the effects of molecular composition (diol functionality and halide anion) on cycloaddition reaction, the polymer-supported 1-(2-3-di-hydroxyl-propyl)-imidazolium-bromide (PS-DHPIMBr) and polymer-supported 1-(2-3-di-hydroxyl-propyl)-imidazolium chloride (PS-DHPIMCl) were screened for the oxazolidinones synthesis (Scheme 2). We observed that PS-DHPIMBr provided 98% yield with high selectivity of 97% for 'A' whereas PS-DHPIMCl provided 96% yield with appreciable selectivity of 95% for 'A'. These slight variations observed in catalytic activity of PS-DHPIMBr and polymer-supported 1-(2-3-di-hydroxyl-propyl)-imidazolium chloride (PS-DHPIMCl) might be due to differences in nucleophilicity of the anions. The control experiments were carried out in absence of catalyst keeping other reaction parameters constant, however no yield of desired product was obtained signifying that PS-DFILX was responsible for the respective transformation and it was observed that the typical TOF of the catalyst PS-DHPIMBr is 22 h^{-1}. The catalytic activity of PS-DHPIMBr was comparatively higher and hence was selected for further study.

In order to optimize the reaction conditions, initial studies were conducted using PS-DHPIMBr as a choice of catalyst for synthesis of 5-aryl-2-oxazolidinones from 1-butyl-2-phenylaziridine

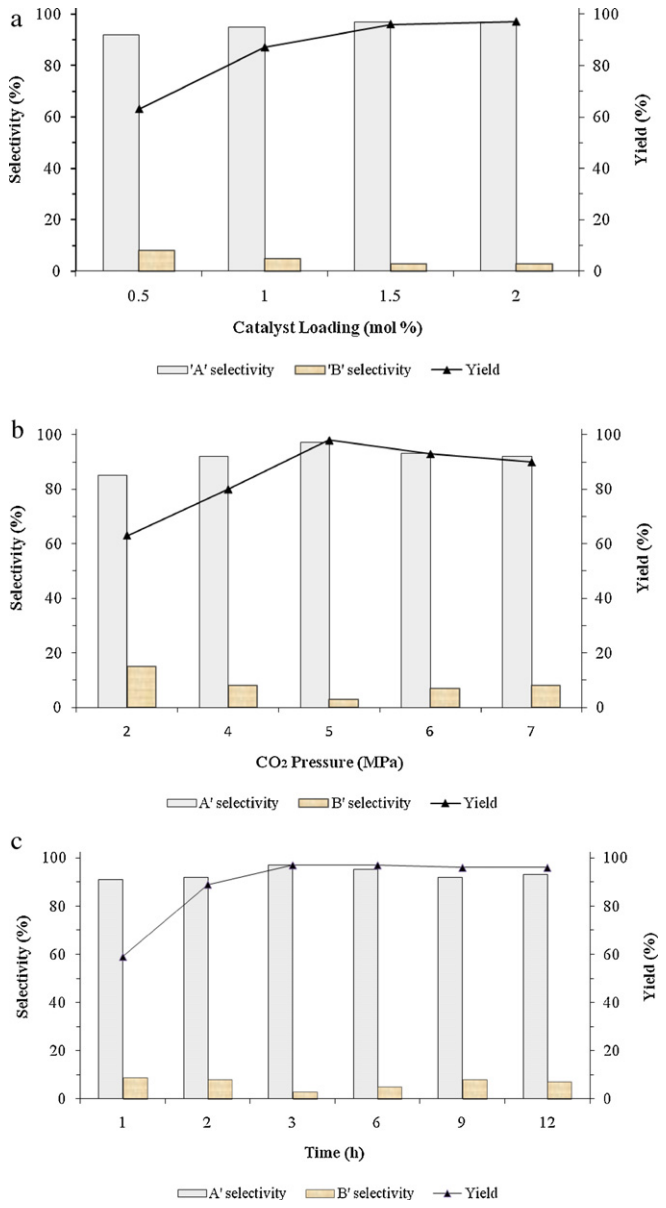


Fig. 2. Optimization of reaction parameters for oxazolidinones synthesis.

and CO_2 as a model reaction. Various reaction parameters such as catalyst screening, catalyst loading, reaction temperature and time were studied and the results obtained are summarized (Fig. 2).

In an effort to determine the optimum concentration of the catalyst, we studied the catalyst loading ranging from 0.5 to 2 mol% where increase in initial catalyst concentration up to 1.5 mol% has increased the yield of product while further increase catalyst loading had no profound effect on the yield of the desired product (Fig. 2a). The effect of the CO_2 pressure on the catalytic activity of PS-DHPIMBr was studied at room temperature in a pressure range of 2-8 MPa and the results are shown in Fig. 2b. We observed that increasing the pressure from 2 MPa to 5 MPa increased the selectivity for 'A' and yield of the reaction while further increase in pressure led to slight decrease in the selectivity for 'A' and yield of the reaction. The effect of reaction time on the yield of 5-aryl-2-oxazolidinones was also investigated (Fig. 2c). The reaction was performed at room temperature and 5 MPa pressure. The result demonstrates that the reaction proceeded rapidly within 2 h while the yield exceeded up to 97% after completion of 3 h. It is noteworthy to mention that the time required to achieve the remarkable yield of desired product with appreciable selectivity was very less in comparison to other reported heterogeneous catalysts such as polystyrene-supported amino acids [26] indicating that the developed catalytic protocol was very efficient for above transformation. Hence, the final optimized reaction parameters for the synthesis of 5-aryl-2-oxazolidinones were aziridine (1 mmol), catalyst loading (1.5 mol%), CO_2 pressure (5 MPa), temperature (room temperature, 25 °C) and reaction time (3 h).

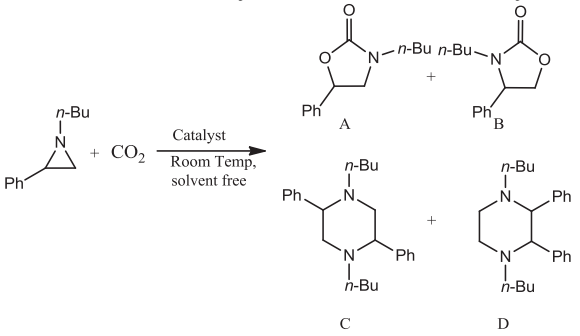
Further to demonstrate the utility and general applicability of developed protocol, the cycloaddition reactions of CO_2 with a variety of aziridines were studied under optimized reaction conditions (Table 1, entries 1–12). The catalyst was found to be enormously active providing corresponding 5-aryl-2-oxazolidinones with good to excellent yields with excellent regioselectivity. Especially, with increase in the alkyl chain on nitrogen of aziridine excellent yield of expected product with appreciable regioselectivity were obtained (Table 1, entries 2–7) while increasing steric hindrance of R^1 group led to a lower yield of desired product (Table 1, entries 8 and 10). The problem of steric hindrance could be overcome with increasing the temperature of reaction to obtain appreciable yields of expected products (Table 1, entries 9 and 11). The above results indicated that PS-DHPIMBr was an effective catalyst for the cycloaddition reaction of aziridines and CO_2 under mild and solvent free conditions.

3.3. Reaction mechanism

Several research groups reported that hydrogen bonding can activate the ring-opening reaction of oxygen analogue of aziridines [37,38]. In present study, PS-ILs with diol functional groups demonstrated better catalytic activity and selectivity for ring opening of aziridines. It was interesting to study the reasons for high efficiency of catalyst for cycloaddition reactions (Table 2, entries 1–8). We wondered that hydroxyl groups might play a key role in promoting the reaction. To investigate the effect of hydroxyl groups on cycloaddition reaction, the experiments of coupling reaction of CO_2 and aziridines were conducted using KI as catalyst in presence of several compounds bearing hydroxyl groups (Table 2, entries 2–6). It was observed that the diols with two hydroxyl groups on the vicinal carbons were more capable to promote the reaction in forward direction rather than water, monohydroxyl alcohols and other diols (Table 2, entries 3–4). Similar results were obtained using KBr as a co-catalyst for present study (Table 2, entry 7). This strongly signifies that the vicinal hydroxy group is favourable for the cycloaddition reaction. In addition, it is well known that the two hydroxyl groups in 1,2-diol can form ring species with nitrogen atoms by hydrogen bonding where 6-membered or 7-membered ring species are most stable [39–42].

On the basis of these findings and previous reports [24–27] we proposed a plausible mechanism for the chemical fixation of CO_2 reaction (Scheme 2). The coupling reaction is initiated by polarisation of C-N bond of aziridines through hydrogen bonding of hydroxyl groups of ILs which acts as a Lewis acidic site (Fig. 3). This activates the aziridine ring (I) and further leads to the ring opening via two different pathways (path 'a' and 'b'). It mainly depends on the nature of R^1 group present on N-atom of aziridines (step II) followed by cyclization leading to oxazolidinones and regeneration of the catalyst. The main product A could originate from ring-opening of the aziridine at the most hindered carbon, as in general three

Table 2
The effect of various co-catalysts and diol functional IL on the synthesis oxazolidinones synthesis.[a].



Entry	Catalyst	Conversion (%)[b]	Regioselectivity (%)			
			A	B	C	D
1	None	≤10	≤1	–	–	–
2[c]	CH_3OH	67	77	10	6	7
3[c]	$HOCH_2CH_2OH$	100	97	3		
4[c]	Propane-1,2-diol	100	98	2	–	–
5[c]	$HO(CH_2)_3OH$	99	89	6	2	3
6[c]	$HO(CH_2)_4OH$	99	86	7	4	3
7[d]	$HOCH_2CH_2OH$	100	97	3	–	–
8[e]	$HOCH_2CH_2OH$	≤10	–	–	–	–

[a] *Reaction conditions*: aziridine (1 mmol), CO_2 (5 MPa), room temperature (25 °C), time (3 h).
[b] Conversion based on GC analysis.
[c] Co-catalyst used like KI (15 mg).
[d] Co-catalyst used like KBr (15 mg).
[e] Without using co-catalyst.

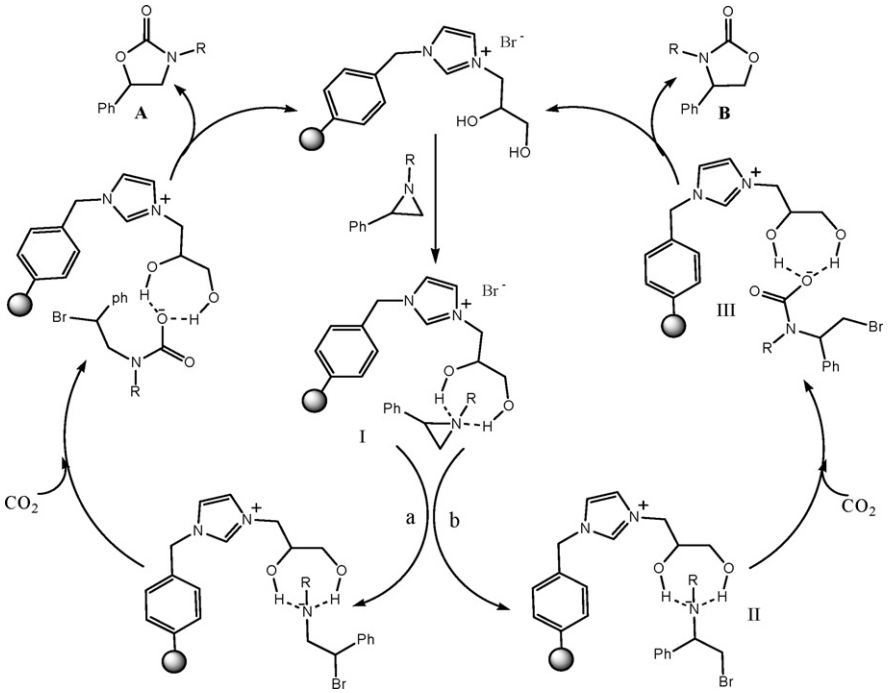


Fig. 3. The proposed reaction mechanism for cycloaddition of aziridines and CO_2 catalyzed by PS-DHPIMBr.

member heterocyclic rings opens by this route [43]. Overall the role of the hydroxyl groups on vicinal carbon atom was proposed to involve initial activation of the aziridine and stabilization of the ring-opened (II) and carbamate intermediates formed (III) during the reaction which reduced the time as well as temperature of reaction.

3.4. Catalyst reusability

Stability and reusability of the catalysts are the two key issues that identify their potential and practical application for industrial scale. From economical point of view catalyst reusability was investigated for four consecutive recycles (Fig. 4). During the

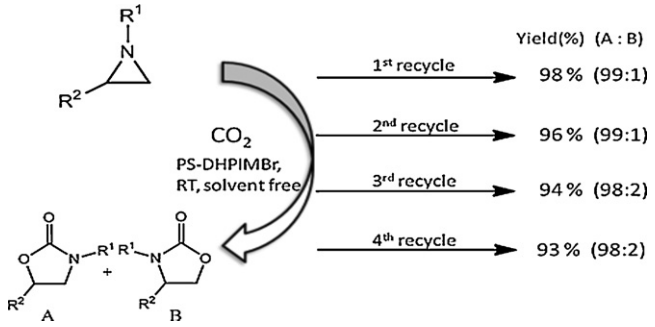


Fig. 4. Catalyst reusability.

study, it was observed that PS-DHPIMBr as a catalyst was effectively recycled without any significant loss in catalytic activity thus emphasizing its high activity and stability for 5-aryl-2-oxazolidinones synthesis.

4. Conclusion

In conclusion, we developed a facile, highly selective and recyclable catalytic protocol for synthesis of 5-aryl-2-oxazolidinones using PS-DHPIMBr as a catalyst. The catalyst revealed remarkable activity as the vicinal hydroxyl groups played a vital role in promoting the reaction in forward direction. To the best of our knowledge, PS-DFILX is the first heterogeneous catalysts to display catalytic activity under such mild conditions. One of the salient features of this protocol is that the catalyst can be readily recovered by simple filtration and reused with retention of catalytic activity. The obtained exciting results appeals for the further development of the methodology for large scale applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.10.007.

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