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Effect of anion type of imidazolium based polymer supported ionic liquids on the solvent free synthesis of cycloaddition of CO_2 into epoxide

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ABSTRACT

Catalytic CO_2 fixation into value added products have attracted ample devotion due to the rapid increasing greenhouse gas effect. Especially, by using heterogeneous catalysts, particularly, the designer nature of organic functionality immobilized on polymer supports has driven significant attention. In this work, various tailor made imidazolium based ionic liquids (ILs) covalently immobilized on polymeric support were synthesized successfully (denoted as PSIL) and applied in the cycloaddition of CO_2 into epoxides. Imidazolium ($C_3H_5N_2^+$) and various counter anions such as Cl^-, Br^-, BF_4^-, PF_6^-, and NTf_2^-, were selected to construct less coordinated cations with anions in PSILs. In the fixation of CO_2 into epoxide, all the prepared PSILs showed efficient catalytic activity, among them 0.1 equiv. of PSIL-NTf_2^- composed of imidazolium cations and NTf_2^- anions was the most efficient, showing 100% conversion and 91% yield of the respective cyclic carbonate under 100 °C reaction temperature using 8 bar pressure in 8 h reaction time. This might be due to the least co-ordinated NTf_2^- anions with imidazolium cations played a vital role in the ring-opening of epoxide, enhancing the reaction rate and favourable for the worthy yield. In addition, the effects of various reaction parameters including amount of catalyst, temperature, and pressure were studied and numbers of substituted cyclic carbonates were prepared. It was found that PSILs were easily separated from the reaction mixture and reused several times without any significant loss of catalytic activity. The present solvent free catalytic system was found mild, kinetically fast, and naturally benign for the coupling of CO_2 into epoxide.

1. Introduction

The current existing transportations, power generations, and manufacturing industries are heavily dependent on fossil-based carbon sources including petroleum oils and natural gases and are responsible for the generation of anthropogenic carbon dioxide (CO_2) during its combustion and their consequences [1,2]. Therefore, many attempts have been considered to minimize the excessive CO_2 by Carbon Capture and Sequestration technologies [1–5]. In this regard, in last few decades many processes considered to minimize the additional CO_2 in the air [4]. Activation and consumption of CO_2 are still challenging due to its most thermochemically stable nature [5]. However, the catalytic installation of CO_2 into energy-rich substrates, such as epoxides to form cyclic carbonate or polycarbonates has attracted much attention. The production of five-membered cyclic carbonates through the 100% atom efficiency coupling of epoxides with CO_2 is one of the most promising way [6]. Cyclic carbonate products and derivatives are widely used as high-boiling polar and aprotic solvents, main precursors for synthesis of polymer materials as well as for the synthesis of fine chemicals intermediates [7–10].

Several homogeneous and heterogeneous catalysts including, metal oxides [11], metal organic frameworks (MOFs) [12], metal salts [13,14], transition metal complexes [15], ionic liquids (ILs) [16], and organic functionalized polymers [17] have been developed so far for this process. Among these catalysts, heterogeneous and homogenous ILs have shown predominant catalytic activity [16–24]. Considering the industrial applications of the coupling reaction of CO_2 with epoxide, efforts should be paid to develop heterogeneous ILs, which can be easily separable from the reaction and reuse in subsequent cycles [25,26]. In last decades, heterogeneous catalysts such as immobilized ILs on silica, MCM-41, cross-linked

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IL polymers, and polymer supported ILs with various functional groups have been evaluated [8–12].

Polymer supported ionic liquids (PSILs) are of growing interest as they combine the unique properties of ILs, such as good thermal stability, low volatility, and non-flammability, with enhanced mechanical stability, improved process ability. In last decades many attempts were carried out by utilizing PSILs as catalysts for the organic transformations [7,9,10,26]. In these cases, only selected halide anions such as Cl^-, Br^-, and I^-, which are strongly interconnected to bulky imidazolium cations have been utilized for the carbonate formation. It reports that, such kind of ILs fails to produce good leaving group in carbonate formation reaction. However, due to the strong interactions of cations and anions of PSILs in these reported methods need harsh reaction conditions to activate the leaving group [27–33]. Especially, the acidic proton of imidazolium ILs suffers from overcrowding and not available for opening of epoxide at the time of formation of carbonate [26,33]. Therefore, the activities of PSILs for the synthesis of cyclic carbonate are required to be enhanced in mild reaction condition [30]. Indeed, it is expected that selection of another anions, which can easily produce good leaving group to perform the reaction kinetically fast. To produce such kind of effect in this reaction various anions with increasing order of molecular size have to study. Therefore, in the present work Cl^-, Br^-, BF_4^-, PF_6^-, and NTf_2^- anions were selected. In the selected anions electrostatic interaction of anions with imidazolium cations varies with their molecular structures and atomic size. It is reported that the electrostatic interactions between cations and anions are important factor in determining catalytic performance of the cycloaddition of CO_2 into epoxide over PSILs [33–37].

In this work, we report effect of different anions of tailor made imidazolium based PSILs for the cycloaddition of CO_2 in epoxides to prepare cyclic carbonates. According to the cations and anions interactions of ILs, numbers of PSILs with different anions (Cl^-, Br^-, BF_4^-, PF_6^-, and NTf_2^-) were synthesized by exchanging the anions using metathesis reactions. The prime aim of this study is to develop the least interaction among cations and anions which help to conduct reaction in mild condition. Therefore, the growing orders of molecular structures were nominated in anions with imidazolium cations and established different PSILs to determine the effect of type of anion on coupling reaction of CO_2. The effects of catalyst amount, reaction temperature, CO_2 pressure were also determined. In addition, several cyclic carbonate were prepared in optimized reaction condition and recyclability of PSILs were determined.

2. Experimental

2.1. Materials

Merrifield resin (100–200 mesh), extent of labelling: 3.5–4.5 mmol/g Cl^- loading, 1.0% cross-linked (Aldrich), *N*-methyl imidazole (99.0%), potassium bromide (KBr) (IR grade) Potassium bromide (KBr) (99.0%), bis (trifluoromethane) sulfonimide lithium salt (99.0%) (Li (NTf_2)), sodium tetra fluoroborate salt ($NaBF_4$) (99.0%), sodium hexafluorophosphate salt ($NaPF_6$) (99.0%), acetonitrile (99.0%), ethyl acetate (HPLC grade), ethanol (reagent grade), carbon dioxide gas (99.999%) and all substrate for the synthesis of carbonate derivatives were purchased from Sigma Aldrich. Reagents were used as received without further purification. All solvents were purchased from commercial sources and were distilled from relevant agents prior to use. Whatman filter papers were used to separate PSILs catalyst from the reaction mixture. Ethanol and double distilled water was used throughout the experiments for washing the catalyst.

2.2. Catalyst characterization

FT-IR spectra of prepared catalyst were recorded on a Varian 2000 IR spectrometer (Scimitar series) by using the potassium bromide (KBr) disc method. Thermogravimetric analyses (TGA) were accomplished on Scinco TGA N-100 instrument with heating rate 5 °C/min in a nitrogen atmosphere. Elemental analysis and determination of elements (C, H, and N) was carried out using a Flash EA 1112 Elemental Analyser manufactured by Thermo Electron machine. The morphology and surface structure of Merrifield resin were monitored using the Sigma field emission scanning electron microscope (FE-SEM) (Carl Zeiss Sigma VP FE-SEM). The stability of polymeric backbone chain of Merrifield resin was confirmed by using X-ray diffraction patterns (XRD) obtained using an powder XRD patterns were recorded on a Rigaku Miniflex (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å) with a 2° min^{-1} scan speed and a scan range of 5–80° at 30 kV and 15 mA. All prepared derivatives of cyclic carbonate reactions were characterized by ^1H NMR and ^{13}C NMR spectroscopy on Bruker spectrometer 400 and 100 MHz, respectively using $CDCl_3$ as a solvent. The described chemical shifts were in contrast to TMS as reference for ^1H and ^{13}C NMR. All carbonate were also characterized by the FT-IR and GC–MS analysis.

2.3. Preparation of polymer supported ionic liquids (PSILs)

In 100 mL round bottom flask Merrifield resin (3.5–4.5 mmol/g Cl^- loading % cross linked, 3.2 mmol Cl/g, Aldrich) 3 g, N-methyl imidazole (10 mmol) in dimethylformamide (DMF) (50 mL) was added and refluxed for 24 h. On completion, the reaction mixture was cooled to room temperature. It was then filtered and the obtained residue was washed with DMF, 0.1 mol/L HCl, water and methanol sequentially followed by drying under reduced pressure to afford imidazolium-loaded polymer supported IL which designated as PSIL-Cl^-. Further, to obtain various anions containing PSILs, metathesis reactions were carried out with metal salts such as KBr, Li (NTf_2), $NaBF_4$, and $NaPF_6$ and designated as PSIL-Br^-, PSIL-NTf_2^-, PSIL-BF_4^-, and PSIL-PF_6^-, in acetonitrile respectively. The samples were dried at 70 °C in a dry oven for 12 h. The resulting PSILs were obtained with good to efficient yield. These prepared catalysts were further characterized by solid NMR, FTIR and other modern analysis techniques to determine the anchored ILs with polymer support.

2.4. Procedure for cyclic carbonate preparation using PSILs

All cyclic carbonate preparation reactions were performed in a 50 mL batch reactor, equipped with pressure gauge, mechanical stirrer and temperature controllable heating mental. A stainless steel tubular reaction cell with an internal diameter 5.5 cm and height 7.5 cm was used to carry out the reaction. For a typical catalytic reaction procedure, the epoxide 5 mL, and PSIL (0.1 equiv.) were loaded into the autoclave without addition of any co-catalyst or solvent. After sealing the autoclave and purging it with nitrogen gas, autoclave was placed under constant pressure of carbon dioxide and then the reactor was heated to an appropriate temperature (12 °C/min). After completion of the reaction, reactor was cooled naturally and depressurized. When the reactor showed room temperature, seals have been removed and the reaction mixture was filtered using Whatman filter paper and liquid product was analyzed for further study. The product yields were determined by GC–MS, ^1H NMR, ^{13}C NMR, and FT-IR.

2.4.1. 4-(Chloromethyl)-1,3-dioxolan-2-one (Table 3, Entry 1)

Yield 91%; Thick oily liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 3.75 (m, 2H), 4.42 (m, H), 4.60 (t, H), 4.96 (m, H) ppm, ^{13}C NMR (100 MHz,

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$CDCl_3$): δ: 43.7, 68.1, 73.9, 155.4 ppm. IR range of C=O of carbonate: 1788 cm^{-1}.

2.4.2. 4-Butyl-1,3-dioxolan-2-one (Table 3, Entry 2)

Yield 82%; oily liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 4.19 (d, 2H), 4.21 (m, H), 1.59 (q, 2H), 1.31 (m, 2H), 1.39 (m, 2H), 0.96 (d, 2H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): δ: 14.6, 17.2, 22.3, 28.2, 35.9, 66.9, 71.2, 156.8 ppm. IR range of C=O of carbonate: 1796 cm^{-1}.

2.4.3. 4-(Hydroxymethyl)-1,3-dioxolan-2-one (Table 3, Entry 3)

Yield 91%; colourless liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 4.23 (d, 2H), 4.36 (m, H), 3.72 (d, 2H), 3.61 (s, H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ: 66.2, 68.1, 74.3, 157.3 ppm. IR range of C=O of carbonate: 1800 cm^{-1}.

2.4.4. 4-Phenyl-1,3-dioxolan-2-one (Table 3, Entry 4)

Yield 88%; White solid; ^1H NMR (400 MHz, $CDCl_3$): δ 4.39 (t, H), 4.78 (t, H), 5.63 (t, H), 7.37 (m, 2H); 7.45 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ: 77.2, 78.2, 126.3, 128.9, 129.2, 129.7, 136.1, 154.3 ppm. IR range of C=O of carbonate: 1804 cm^{-1}.

2.4.5. 4-(p-tolyl)-1,3-dioxolan-2-one (Table 3, Entry 5)

Yield 91%; White solid; ^1H NMR (400 MHz, $CDCl_3$): δ 4.41 (d, 2H), 5.59 (t, H), 7.28 (m, 2H); 7.92 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ: 64.8, 93.2, 122.6, 128.1, 129.2, 132.2, 154.7 ppm. IR range of C=O of carbonate: 1804 cm^{-1}.

2.4.6. 4,5-Dimethyl-1,3-dioxolan-2-one (Table 3, Entry 6)

Yield 90%; Thick oily liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 4.38 (m, 2H), 1.38 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ: 21.7, 74.8, 154.7 ppm. IR range of C=O of carbonate: 1791 cm^{-1}.

2.4.7. Hexahydrobenzo-1,3 dioxol-2-one (Table 3, Entry 7)

Yield 86%; white solid; ^1H NMR (400 MHz, $CDCl_3$): δ 1.41 (m, 2H), 1.59 (m, 2H), 1.92 (t, 4H), 4.68 (t, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ: 19.0, 26.6, 74.9, 155.6 ppm. IR range of C=O of carbonate: 1804 cm^{-1}.

2.4.8. Tetrahydro-3aH-cyclopenta-1,3-dioxol-2-one (Table 3, Entry 8)

Yield 78%; white solid; ^1H NMR (400 MHz, $CDCl_3$): δ 1.52 (m, 2H), 1.77 (m, 4H), 4.59 (t, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ: 24.3, 34.6, 76.4, 154.7 ppm. IR range of C=O of carbonate: 1798 cm^{-1}.

2.5. Catalyst (PSILs) separation and regeneration process

After completion of reaction, reaction mixture and catalyst was separated out by filtration method. The residue containing catalyst PSILs was washed three times by water and ethanol, correspondingly and dried at 70 °C in vacuum oven for 12 h. Consequently, dried catalyst was reutilized for next attempt of cyclic carbonate formation reaction of epoxide and CO_2.

3. Results and discussion

3.1. Synthesis of polymer supported ionic liquids (PSILs)

Scheme 1 demonstrates the synthetic route for the preparation of PSILs synthesized and characterized in this study. In brief, a known amount of polymer support (Merrifield resin) reacted with *N*-methyl imidazolium to produce PSIL-Cl^-, later on by using ion exchange metathesis reaction various other anions (Br^-, BF_4^-, PF_6^-, and NTf_2^-) were installed by reacting with various respective metal salts to prepare PSIL-Br^-, PSIL-BF_4^-, PSIL-PF_6^-, and PSIL-NTf_2^-, respectively. All reactions were takes places smoothly in mild and eco-friendly reaction conditions which produced high yield of synthesized PSILs. After successfully synthesis of PSILs were characterized by using fancy modern analytical and spectroscopic methods.

3.2. Characterization of PSILs

3.2.1. Fourier transform infrared spectroscopy (FT-IR) analysis of PSILs

To approve the immobilization of ILs on polymer support, FT-IR analysis of pure resin and prepared PSILs catalysts were performed and results are revealed in Fig. 1. All the prepared catalysts exhibited four typical infrared bands at 1606, 1566, 1154, and 1085 cm^{-1}, which correspond to the band adsorption of the heterocyclic imidazolium ring covalently anchored on polymer support [36,37]. On the other hand, in case of parent pure resin, these peaks were absent. A typical peak at 1265 cm^{-1} analogous to the stretching frequency of $-CH_2Cl$ functional group disappeared in all obtained PSILs, indicating complete modification of active sites present on polymer support by the anchoring of ILs. In addition, all peaks corresponding to the styrene backbone chains were present which means that polymeric backbone chain is stable throughout the synthesis process. In PSIL-NTf_2^-, PSIL-BF_4^-, and PSIL-PF_6^-, peaks corresponding to the NTf_2^- at 1054, 1139 and 1197 cm^{-1}, BF_4^- at 850, 750 cm^{-1}, and PF_6^- at 750, 740 cm^{-1} were observed [36–38]. The above results clearly revealed that, magnificently covalent immobilization of imidazolium based ILs on polymer support with preservation of parental backbone polymeric structure were successfully done.

3.2.2. ^{13}C NMR spectroscopy analysis of PSILs

The structures of synthesized PSILs were also confirmed by solid-state ^{13}C NMR spectroscopy and results are summarized in Fig. 2. As shown in the ^{13}C NMR spectra of all PSILs, a sharp peak around 25–35 ppm is observed due to the terminal CH_3 protons of substituted imidazolium ring. The sharp peak at around 50 ppm corresponds to the CH_2 bridging moiety between imidazolium and benzene group present in the polymer support. The representative peaks of the carbon atoms of imidazolium rings are detected at range of 122–128, 137, and 142 ppm [39]. In case peaks which belong to the benzene ring of the backbone chain of polymer support (aromatic polystyrene skeleton) are probably overlapped with imidazolium peaks at around 120–140 ppm.

3.2.3. Thermogravimetric analysis (TGA) of synthesized PSILs

Thermal steadiness would also be significant character for the practical application of heterogeneous PSILs in various applications, since different reaction condition, vigorous shaking, drastic acid base treatment, and filtration may come across in different application processes. In this regard, the determination of thermal stability of synthesized PSILs is prime valuable [25]. In the present study, thermal stability of various PSILs including pure resin was determined by TGA and obtained results are accumulated in Fig. 3. In the TGA curves, especially in pure resin, it can clearly see that decomposition process occurred in single step. The main step of polystyrene degradation is from 350 to 450 °C, which is attributed to the main chain pyrolysis at about 400 °C with the evolution of aromatics from the degradation of the polystyrene.

All synthesized PSILs showed two step degradation patterns, however thermal stability varies depending on the molecular weight composition of grafted ILs on it. The first decomposition step is attributed to the grafted ILs and second major decomposition step is responsible for the polymer backbone chain. The PSIL-Cl^- and PSIL-Br^- are less stable compared to pure resin and other synthesized PSILs. In addition, due to its moisture sensitivity slight weight loss was observed at above 100 °C in PSIL-Cl^- and PSIL-Br^-. However, since they started to decompose at 195 °C and this weight

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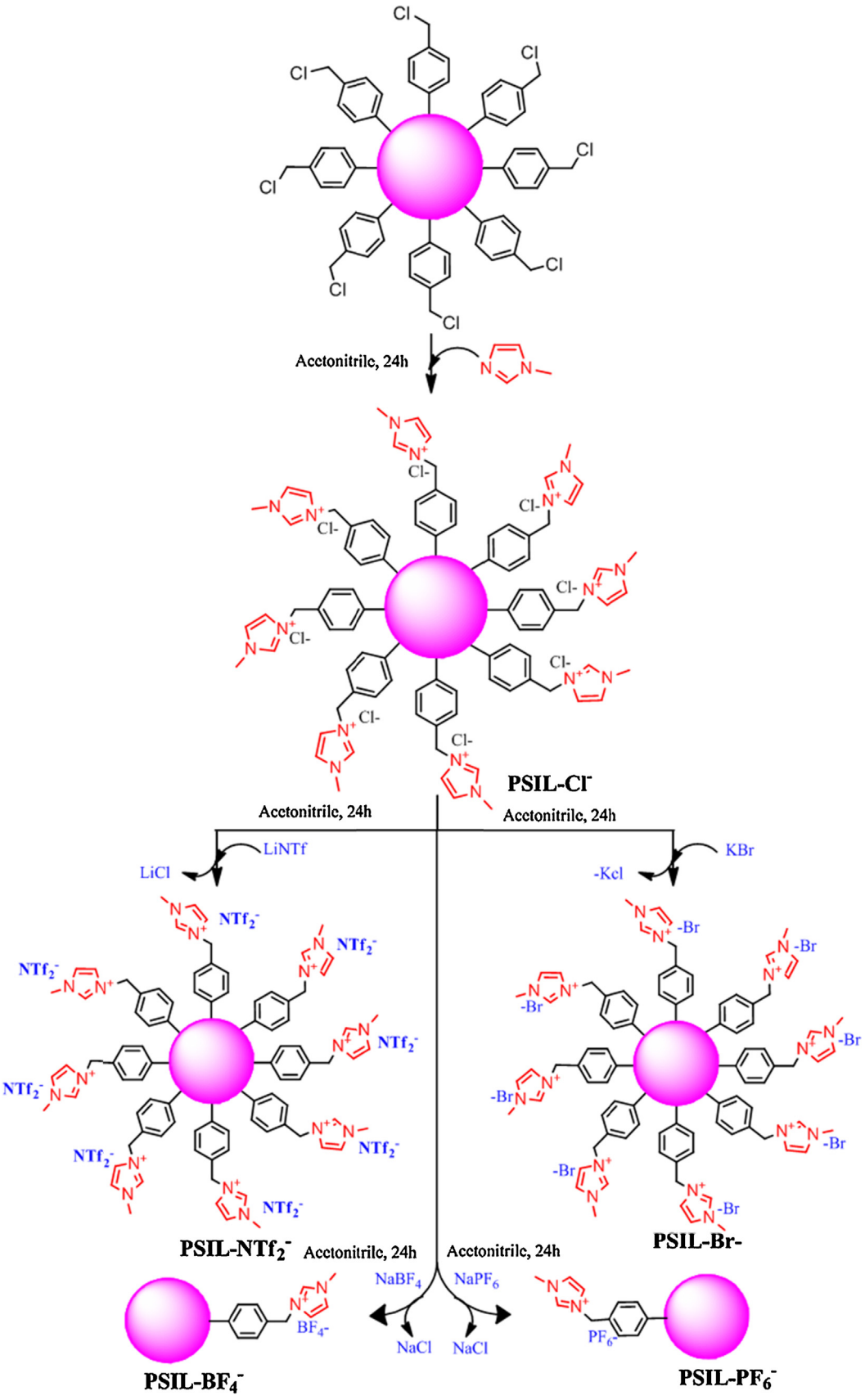

Scheme 1. Synthesis of various polymer supported ionic liquids containing different anions for the cyclic carbonate synthesis.

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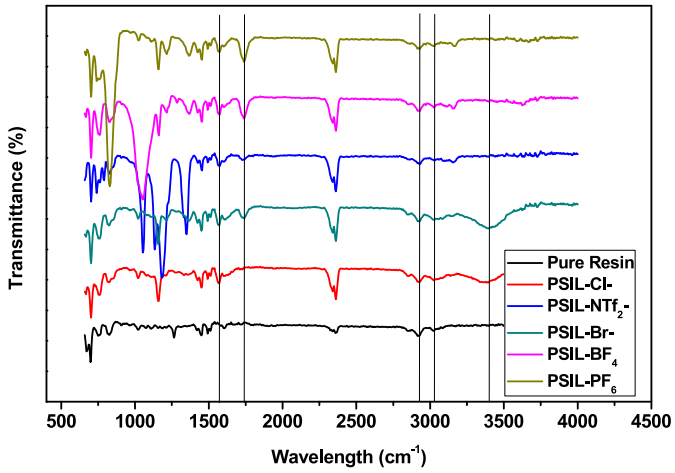

Fig. 1. FT-IR analysis of synthesized PSILs catalyst for the formation cyclic carbonate.

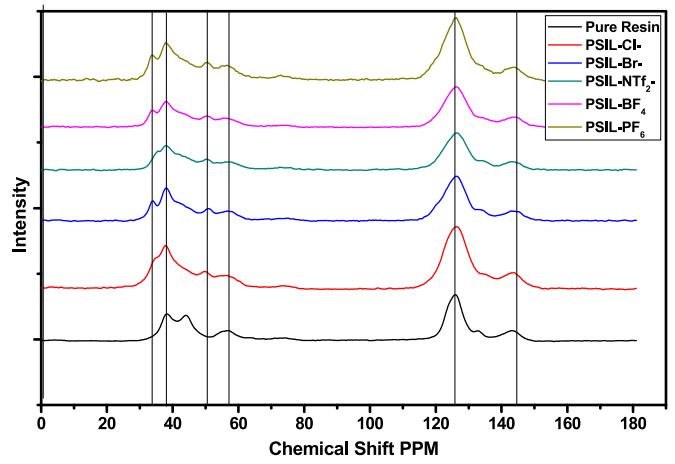

Fig. 2. ^{13}C NMR investigation of PSILs produced for the cycloaddition of CO_2 into epoxide.

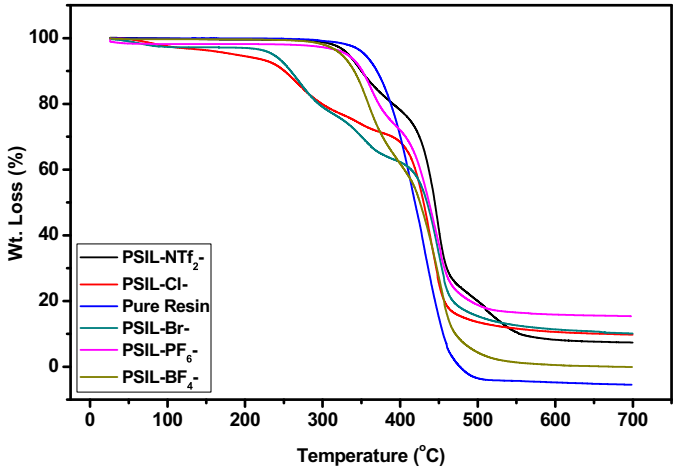

Fig. 3. TGA analysis of prepared various PSILs for the fixation of CO_2 into epoxide.

loss is attributed to the weight gained by ILs anchored on polymer support. The second largest weight loss was initiated at 350 °C where the decomposition of polymer backbone chain occurred. Furthermore, PSIL-BF_4^- and PSIL-PF_6^- showed decomposition in two steps. The first loss (340 °C and 352 °C) is attributed to the loss of grafted ILs and second loss appeared at 430 °C is due to the degradation of polymer support. These PSIL-BF_4^- and PSIL-PF_6^- are moisture stable and could not show any weight loss due to the moisture. Among all the synthesized supported ILs, PSIL-NTf_2^- was found to be the most thermally stable PSILs. The initial decomposition phase obtained at 381 °C. Whereas, decomposition belongs to the polymer backbone chain obtained at above 430 °C. This decomposition pattern of PSIL-NTf_2^- is good agreement with TGA pattern of pure ILs which has NTf_2^- moiety as anions [8,25]. It is reported that ILs having NTf_2^- moiety as anions are thermally stable above 400 °C [25]. However, the obtained thermograms of PISLs manifested that synthesized PSILs have sufficient thermal stability for the various catalytic applications.

3.2.4. FE-SEM analysis of PSILs

An effort was made to examine the morphology of synthesized PSILs catalyst using FE-SEM. The covalent grafting of ILs bulky unit on polymeric resin had a noticeable effect on its morphology. Fig. 4 shows that pure resin (a, b) is sphere with highly smooth surface, whereas the PSIL-Cl^- catalyst (c, d) has coarse surface in nature. However, the polymeric resin in the other PSILs [PSIL-Br^- (e, f), PSIL-NTf_2^- (g, h) PSIL-BF_4^- (i, j) PSIL-PF_6^- (k, l)] did not appear spherical in shape because of some degradation. These kinds of degradations were already experienced in previous study [36], and this might be due to large amount of covalently anchored IL unit make surface tension beyond the critical limit, leading to a fragmentation of spherical particles. However, the fragmented polymeric beads might enhance catalytic activity because reactants are accessible to surface active sites. It is expected that fragmentation of polymeric beads can improve the catalytic activity in the fixation of CO_2.

3.2.5. Elemental and XRD analysis of PSILs

To determine the elemental composition of prepared PSILs, elemental analysis was carried out and results are listed in Table 1. The amount of attached IL was calculated from elemental analysis and it found in the range of catalytic amount and the amount was ILs 2.0–2.5 mmol/g. In addition to that the amount of nitrogen in synthesized PSILs is drastically increased compared to pure resin, indicating that the imidazole was effectively immobilized through the covalent bonding. The amount of the attached IL varies according to the composition of cation and anions present in the ILs.

Fig. S1 in supporting information shows the X-ray diffraction patterns of synthesized PSILs in the present study. The XRD patterns of PSILs have strong diffraction peaks in the range of $2\theta = 15–25°$, rather than this there is no any another peaks which give some information regarding the supported ILs. The present broad peak at $2\theta = 19$ indicates that there is no any harm to the parental polystyrene backbone chain throughout the ILs covalent grafting process and preserved crystalline nature [40].

3.3. Catalytic activity in fixation of CO_2 into epoxide

The catalytic activity of prepared PSILs in the fixation of CO_2 into epoxides was initially investigated using styrene oxide (1) as prototypical substrate in order to prepare final cyclic carbonate product (2), and results are summarized in Table 2. First, we have conducted the reaction in the presence of 0.5 equiv. of pure resin which is used as support in this study, and it fails to give desired product even after prolonged reaction period (48 h) at 100 °C (Entries 1, 2). Later on successively, we determined effect of catalyst by conducting the several reactions in the presence of synthesized different PSILs as catalysts at 100 °C and results are displayed in Fig. 5 as well as accumulated in Table 2. PSIL-Cl^- which has combination of imidazolium cations and Cl^- anions was able to obtained 100% conversion but fails to give desired yield of cyclic

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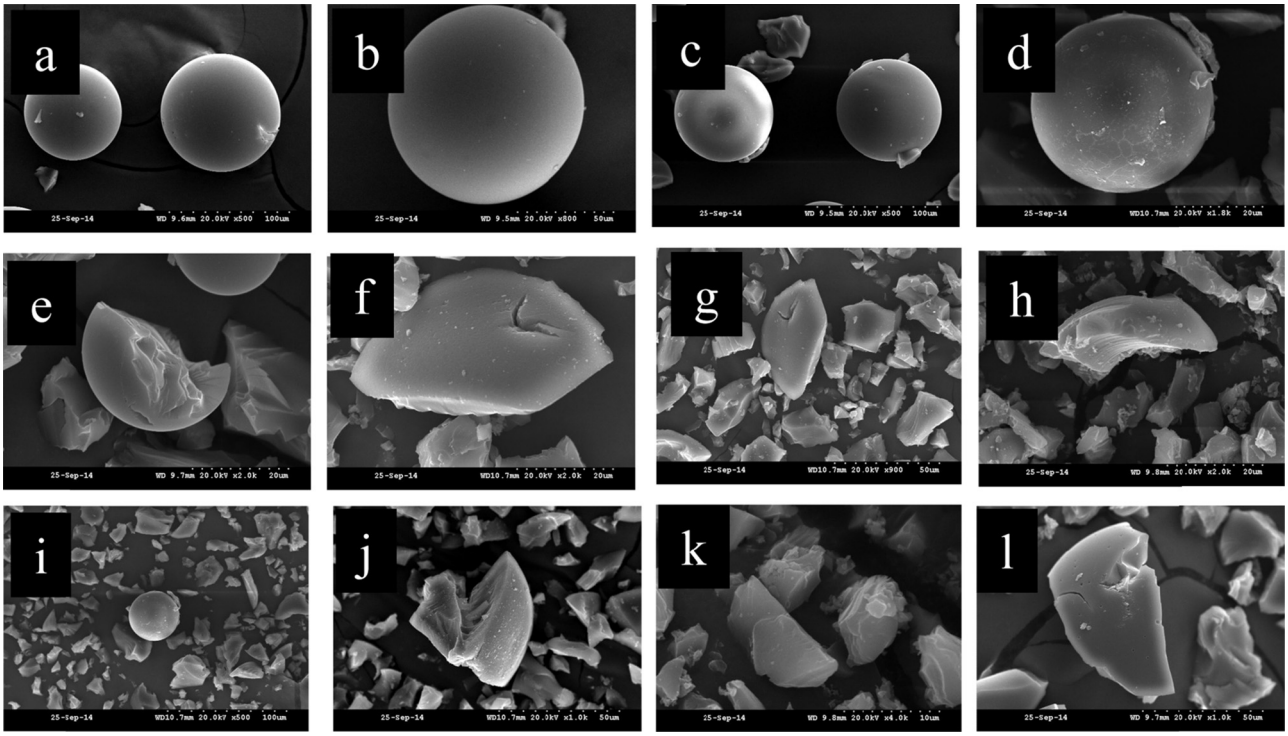

Fig. 4. Morphology and surface analysis of PSILs.

Table 1
Elemental analysis data of prepared various PSILs for the cycloaddition of CO_2 into epoxide.

Sr. No	Components	N (wt.%)	C (wt.%)	H (wt.%)	ILs grafted (mmol/g)
1	Pure resin	0.0582	80.61	6.31	–
2	PSIL-Cl^-	7.09	71.12	6.70	2.54
3	PSIL-Br^-	7.00	51.35	3.88	2.50
4	PSIL-NTf_2^-	6.69	65.01	5.02	2.19
5	PSIL-BF_4^-	7.01	66.42	5.34	2.22
6	PSIL-PF_6^-	6.51	59.87	4.68	2.06
7[a]	PSIL-NTf_2^-	6.32	64.56	4.89	1.92

[a] Elemental analysis performed after 8th reuse.

carbonate in a short reaction period at 100 °C (Entry 3). There is some report which showed the efficient yield of cyclic carbonate with Cl^- anion containing ILs [7,9,10,26]. These reported reactions are conducted at high temperature (>150 °C) and high pressure. Its specifies that, strong interaction of cations and anions are present between Cl^- anion and imidazolium cations which cannot easily produced nucleophile at the time of epoxide ring opening and need harsh reaction condition [17,31,33,40,41]. However, PSIL-Br^- was showed only 61% yield with 100% conversion of reactant, here the effect of anion (Br^-) showed major effect on the yield of cyclic carbonate (Entry 4).

The obtained results of PSIL-Cl^- and PSIL-Br^- showed major variations in yield of cyclic carbonate because of atomic radius and bond dissociation energy of imidazolium cations with respective anions which plays a crucial role while performing the CO_2 coupling reaction with epoxide [17,26,33]. It is reported that, the atomic size increases, the interactions of anions and cations decreases. We believed that, due to this reason, the high molecular size containing anion Br^- anion with imidazolium cation obtained high yield compared with Cl^- anions. Furthermore, to decrease interactions of cations and anions we have selected BF_4^- and PF_6^- PSILs and conducted reactions with PSIL-BF_4^- and PSIL-PF_6^-. These reactions showed 72% and 79% yield of respective carbonate with 88% and 91% conversion of reactants, respectively (Entries 5, 6). The obtained results of these PSILs also proved that the least coordinated cations and anions are highly beneficial for the protocol. In case of 0.5 equiv. of PSIL-NTf_2^-, 100% conversion with 91% yield for cyclic carbonate was obtained (Entry 7). This outstanding result of PSIL-NTf_2^- was obtained in a 6 h reaction time under 8 bar CO_2 pressure at 100 °C. According to the reported literature, ILs or PSILs, which consist of Cl^- and Br^- anions have smaller molecular size and strong interactions with the imidazolium cations, which needs harsh reaction condition and longer reaction time for high catalytic activity [17,31,33,40,41]. It is also reveals that, anions BF_4^- and PF_6^- are also strongly intermingled with the imidazolium cations, which showed restricted yield of respective carbonated product compared with PSIL-NTf_2^- [33,40,41,43] On the other hand, It is also stated that, NTf_2^- anions have the least interaction with imidazolium cations, which enhanced the catalytic activity under mild reaction condition via developing the nucleophile easily in mild condition [17,33,41]. The obtained activity results of these PSILs are in good agreement with reported literature interaction energies between cations and anions, exhibited in the decreasing order of $NTf_2^- > PF_6^- > BF_4^- > Br^- > Cl^-$. From these activity results, it is revealed that least coordinated PSIL-NTf_2^- is highly suitable for the cycloaddition of CO_2 in to epoxide which showed heights yield in mild condition in this report (Fig. 6) [17,41–43].

From the obtained catalytic activity trend, it exposed that, nucleophile leaving ability of ILs plays a crucial role in the yield of cyclic carbonate. It can be seen, from the above series of anions used in the present study, NTf_2^- anion has best leaving ability and less interaction with cations in PSILs [17]. In addition, it is also reported that NTf_2^- anions are basic in nature which can strongly interact with the acidic CO_2 molecules which can help for fast collision of reactants and obtained respective product in mild reaction condition [17,41]. From these obtained results and collected information of reported literature methods, we can say that, instead of

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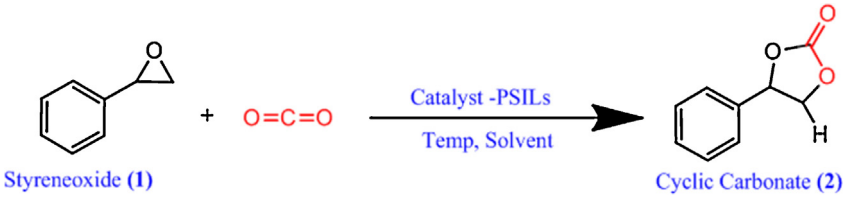
Table 2
Optimization of reaction condition for fixation of CO_2 into epoxide to produce cyclic carbonate over PSILs[a].



Styreneoxide **(1)** Cyclic Carbonate **(2)**

Sr. No.	Catalyst	Catalyst amount (equiv.)	Solvent	Time (h)	Temp. (°C)	Conv. (%)[b]	Yield[c] (%)
1	–	–	–	48	100	0	0
2	Pure Resin	0.5	–	48	100	0	0
3	PSIL-Cl^-	0.5	–	20	100	100	52
4	PSIL-Br^-	0.5	–	12	100	82	61
5	PSIL-BF_4^-	0.5	–	12	100	91	72
6	PSIL-PF_6^-	0.5	–	14	100	88	79
7	PSIL-NTf_2^-	0.5	–	6	100	100	91
8	PSIL-NTf_2^-	0.4	–	6	100	100	94
9	PSIL-NTf_2^-	0.2	–	8	100	100	92
10	PSIL-NTf_2^-	0.1	–	8	100	100	88
11	PSIL-NTf_2^-	0.1	–	8	80	48	21
12	PSIL-NTf_2^-	0.1	–	8	120	100	87
13	PSIL-NTf_2^-	0.1	–	8	140	100	68
14	(bmIm)(NTf_2)	0.1	–	8	100	100	78
15	PSIL-NTf_2^-	0.1	DCM	8	100	100	58
16	PSIL-NTf_2^-	0.1	Acetonitrile	8	100	100	76
17	PSIL-NTf_2^-	0.1	1,4 Dioxane	8	100	62	41
18	PSIL-NTf_2^-	0.1	DMF	8	100	76	36
19	PSIL-NTf_2^-	0.1	2-Propanol	8	100	85	81

[a] All reactions were carried out on 5 g of styrene oxide with catalyst and 8 bar CO_2 pressure.
[b] Conversion were determined by GC.
[c] Yield refers to the isolated product, characterized by GC–MS, ^1H and ^{13}C NMR, and FT-IR.

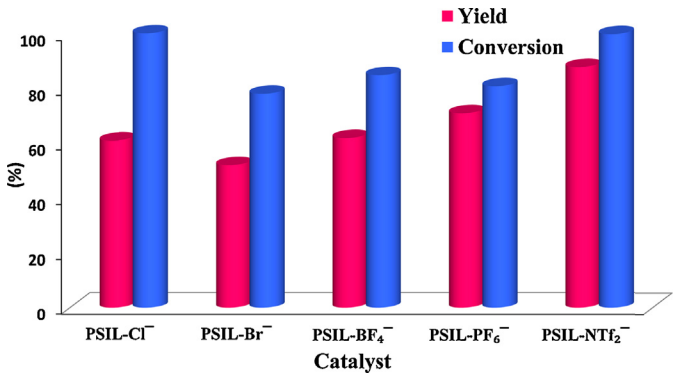


Fig. 5. Determination of catalytic activity of prepared various PSILs for the cyclic carbonate formation.

modifying the cations by substitution of bulky groups, if we used strong nucleophile as anion with methyl imidazolium cation, then there is no any additional functional group substation required on cation for the opining of epoxide. Sterically less hindered acidic proton of imidazolium ring can form interaction with epoxide which can help to open the epoxide ring by strong nucleophile [26,33]. Therefore, in the present study obtained reaction results of carbonate synthesis support the above hypothesis. From all these results of catalytic fixation of CO_2 in epoxide, PSILs-NTf_2^- catalyst has the outstanding catalytic ability due to the strong nucleophilic nature of anion for the preparation of cyclic carbonate among the rest of PSILs. Thus, for further study, PSIL-NTf_2^- catalyst was elected to determine the effect of mole economy, temperature, solvent, and CO_2 pressure effect.

To determine the effect of catalyst amount, numbers of reactions were conducted with gradual reduction of amount of catalyst. When 0.4 equiv. amount of catalyst was used for same reaction at uniform condition, catalyst does not showed any noticeable effect on yield and conversion (Entry 8). Furthermore, again reduced the amount of catalyst from 0.4 to 0.2 equiv., catalyst did not produced efficient yield in same reaction time and this reaction need slight more reaction time (8 h) for the 100% conversion which display steady effect in the yield of cyclic carbonate (Entry 9). 0.1 equiv. of catalyst (PSIL-NTf_2^-) showed 100% conversion and obtained 88% yield in 8 h reaction time in the same reaction condition (Entry 10). From these obtained outcomes, it can conclude that, according to the lowering of amount of catalyst reaction need longer reaction time. However, it did not showed any negative impact of the yield of cyclic carbonate and epoxide conversion. Therefore, considering the mole economy of catalyst 0.1 equiv. of catalyst amount was nominated for further study.

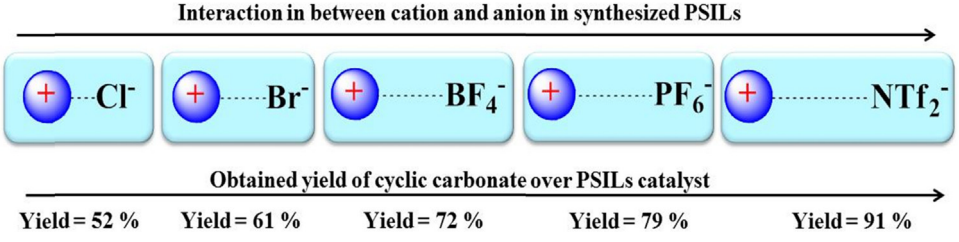


Fig. 6. Effect of interaction in between cation and anion in synthesized PSILs on yield of cyclic carbonate formation.

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On the other side, we have determined effect of reaction temperature with this protocol for the same reaction. Temperature showed major effect on the yield and conversion, when we reduced reaction temperature from 100 °C to 80 °C reaction could not complete within same reaction time, and reaction showed only 48% conversion and 21% yield of respective carbonate (Entry 11). In this case, only small amount of side products together with cyclic carbonate were found. They are the isomers of styrene oxide, such as respective ketone and aldehyde. Isomerization of styrene oxide is very communal phenomenon while performing the reaction in pressurized condition, in good agreement with reported literatures [8,9,24]. Higher than 100 °C reaction temperature showed negative effect on selectivity, at 120 °C and 140 °C, 100% conversion was obtained but the yield of cyclic carbonate was reduced. Results showed 87% and 68% cyclic carbonate was obtained at higher temperature respectively with this catalyst (Entries 12, 13). The obtained lower yield of cyclic carbonate with 100% conversion at higher temperature was responsible for the partial decomposition of the cyclic carbonate and negligible side products are found such as polymerized product of cyclic carbonate [24]. From the literature, it is found that, the selectivity of the reaction decreases as the reaction temperature was raised beyond 100–110 °C [24,34].

In addition, in order to study the effect of supported phase of ILs and pure ILs, we have conducted reactions at 100 °C using 8 bar CO_2 pressure in 8 h reaction time, where 0.1 equiv. of pure IL (without polymer support) in homogenous phase was used as catalyst. This reaction was very sluggish and did not give efficient yield of carbonate even if it needs tedious work-up procedure for separation (Entry 14). We believed that active sites in the covalently immobilized ILs on polymer support are highly responsible for high yield of carbonate with supported ILs phase as catalyst which makes process easier and greener.

Moreover, to determine the effect of solvent on the present reaction using PSIL-NTf_2^- as catalyst, numbers of reactions were carried out for fixation of CO_2 in to epoxide in various solvents such as aprotic polar solvents and protic polar solvents in optimized reaction condition. Initially, we performed reactions in aprotic polar solvents which have low boiling points such as dichloromethane (DCM) and acetonitrile as well as later on performed reactions in aprotic solvents with high boiling points such as 1,4-dioxane and dimethylformamide (DMF). Solvents DCM and acetonitrile were observed slight active for this protocol and obtained 58% and 76% yield of cyclic carbonate (Entries 15, 16) due to the high mass flow addition of CO_2 at optimized reaction condition. Whereas solvents 1,4-dioxane and dimethylformamide (DMF) were found very sluggish and provide only 41 and 36% yield of respective carbonate product (Entries 17, 18). The reaction in polar protic solvent such as 2-propenol resulted highly effective for this protocol and obtained highest yield of cyclic carbonate in solvent mediated reactions (81%) (Entry 19). These results suggested that, the protic polar solvents are quite favourable for the cyclic carbonate formation by fixation of CO_2 in to epoxide, because protic solvents can activate the epoxide ring via hydrogen bond formation between the hydroxyl and epoxy groups, this hypothesis suggested by many researchers in their reports [9,24,34].

Subsequently, the effect of CO_2 pressure on the yield of carbonate by using prepared PSIL-NTf_2^- catalyst was also determined on optimized reaction condition. As shown in Fig. 7, the pressure had very noteworthy effect on the yield and conversion upon the deviation of CO_2 pressure. At 100 °C reaction temperature, slight change in CO_2 pressure showed major effect. This could be described by the pressure effect on the concentration of CO_2 and epoxide, since epoxides are in liquid state under the given reaction condition, and when the reaction was carried out at lower pressure (4 and 6 bar) the lower concentration of CO_2 showed the less yield of

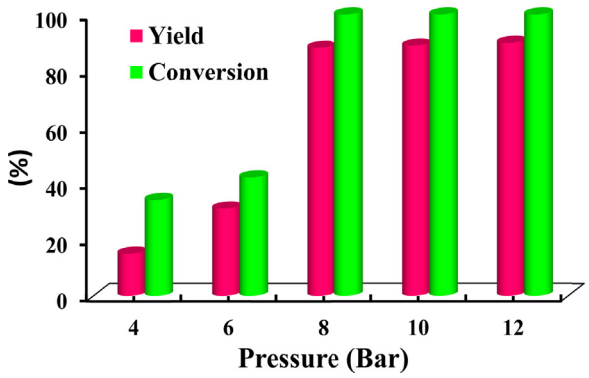

Fig. 7. Determination of effect of pressure on catalytic activity of PSIL-NTf_2^- for the formation of cyclic carbonate.

carbonate [32–35], whereas 8 bar reaction pressure showed tremendous results in which 100% conversion and 88% yield was obtained. However, higher than 8 bar CO_2 pressure did not showed any impact with PSIL-NTf_2^- on the yield and selectivity of main cyclic carbonate product at 100 °C reaction temperature.

Finally to understand the specific role of tailor-made combination of imidazolium cations with NTf_2 anionic moiety, the plausible reaction mechanism was proposed and shown in Scheme 2. Initially, the acidic proton of imidazolium ring which is placed in between two nitrogen atom is less sterically hindered due to the substation of methyl group is interact towards the oxygen atom of the epoxide ring [24,29,44,45]. However, based on the obtained results of PSIL-NTf_2^-, the cations and anions showed major influence on the cycloaddition of epoxide with CO_2. In case of imidazolium cations ILs maximum chances is to produce hydrogen bonding interaction of the IL with epoxide [17,42–45]. In order to evaluate and determine the presence of hydrogen bonding between an acidic proton of PSIL-NTf_2^- and epoxide (styrene oxide), a FTIR analysis were performed (Fig. 8). The FT-IR spectrum of pure PSIL-NTf_2^-, demonstrate a vibration band at 3035 and 2966 cm^{-1}, which alters broader and less instance and shifted to 3015 and 2922 cm^{-1} respectively, upon accumulation of an excess of epoxide at room temperature. These strong bands are assigned to the C—H (acidic proton and carbon) stretching modes of the imidazolium ring [17,42–45]. These exhibited frequency shifts of imidazolium ring can be ascribed to the intermolecular interaction of acidic proton of imidazolium present in PSIL-NTf_2^- and epoxide by hydrogen bonding. Furthermore, some out-of-plane deformation bands in the finger print region also shift as a significance of the interaction with epoxide. However, the strongest interaction and large shifting of peak was observed between the acidic protons of imidazolium ring with oxygen atom of epoxide.

The coordination of the acidic proton with the oxygen atom of epoxide resulted in the polarization of C—O bond, which make opening of epoxide easy [29,44,45], while the nucleophilic NTf_2^- attack from the less hindered β-carbon atom of the epoxide followed at the same time and opening of epoxide occurred [44,45]. This is the rate-determining step for this coupling reaction. However, the results acquired in this study designate that both cation and anion play a significant role. Later on, the oxygen anion intermingled with carbon atom of the CO_2 molecule to form the new intermediate acyclic carbonate. Lastly, the intermediate would be converted into a cyclic carbonate by the elimination of PSIL-NTf_2^- in the original form. The imidazolium cation with least coordinated with NTf_2 anion plays a vital role in the ring-opening of epoxide. Furthermore it fascinates the strong interaction of acidic proton with oxygen which produced rapid opening of epoxide and attach of the NTf_2 nucleophile. These obtained results with this protocol

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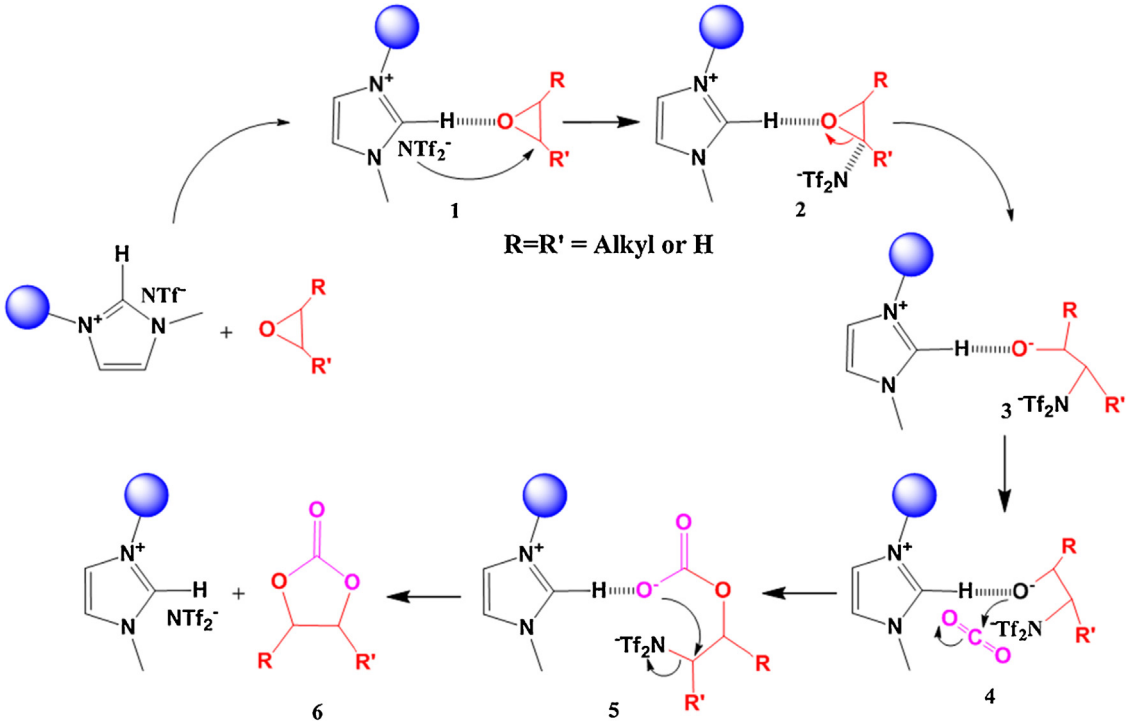

Scheme 2. Proposed reaction mechanism of fixation of CO_2 in to epoxide over heterogeneous PSILs catalyst for cyclic carbonate formation.

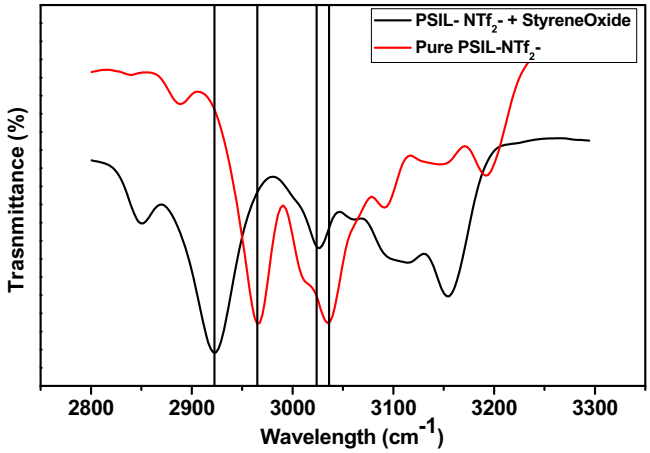

Fig. 8. Determination of hydrogen boding in catalyst PSIL-NTf_2^- with epoxide by FT-IR spectroscopy.

designate a synergistic effect on assistant with the cycloaddition reactions of epoxides into cyclic carbonate [42–45].

Later on, to determine the adoptability of synthesized PSIL-NTf_2^- catalyst tested for the preparation of various cyclic carbonate by using number of different substituted epoxides and obtained results are summarized in Table 3. Both types of epoxide substrates (internal and terminal) were reacted respectively in the presence of PSIL-NTf_2^-. The selectivity and conversion towards the cyclic carbonate products were admirable with all substrates in the optimized reaction condition. In comparison with internal epoxide, terminal epoxide such as aliphatic and aromatic epoxide showed higher carbonate yields (Table 3, Entries 1–5). Whereas, internal epoxide are usually difficult to transform to cyclic carbonates due to the higher steric overcrowding nearby the epoxide ring, which can hinder the nucleophilic attack by the anion. Therefore, in case butane oxide obtained lowest yield (Table 3, Entry 6). Moreover, cyclic carbonates from cyclohexane and cyclopentene oxide was also showed restricted yield compared with terminal epoxides (Table 3, Entries 7, 8).

3.4. Recyclability of PSILs catalyst

To conclude the reusability of the catalyst, PSIL-NTf_2^- catalyst was separated and regenerated by using process as mentioned in Section 2. Reusability of PSIL-NTf_2^- catalyst was considered up-to eight cycles for the synthesis of 2 (Fig. 9(a)). There is no major damage in the yield and conversion of 2 was determined up-to six successive cycles and the yield of 2 was maintained almost consistence during these recycling tests. After six cycles there is negligible loss in yield and conversion was observed in 7th and 8th cycle with PSIL-NTf_2^- (Fig. 9(b)). Furthermore, after completion of recyclability, we also performed FE-SEM and FT-IR analysis of recovered PSIL-NTf_2^- catalyst after eight cycles (Fig. 9(c)) and compared physicochemical property with fresh PSIL-NTf_2^- catalyst (Fig. 9(d)). FE-SEM results reveals that, there is no any morphological damage was observed in PSIL-NTf_2^- catalyst even after eight successive cycles. In addition to that, catalyst could not show any chemical alteration in covalent immobilized ILs on Merrifield resin. A FT-IR spectrum of recycled PSIL-NTf_2^- was almost identical with the FT-IR spectra obtained from fresh PSIL-NTf_2^- catalyst (Fig. 9(e)).

Furthermore, to investigate the reason of activity loss, we have determined the amount of ILs remaining on the recovered catalyst after 8 cycles by TGA and elemental analysis experiments as shown in Fig. 10. The TGA curve of recycled catalyst showed almost similar decomposition pattern with that of fresh catalyst. The fresh catalyst showed 27.4 wt.% loss in the first step attributed to decomposition of grafted ILs, whereas the recycled catalyst showed 22.6 wt.% loss of catalyst after 8 cycles. Accordingly, the amount of grafted IL decreases from 2.19 mmol to 1.92 after 8 cycles (Table 1). This means that decrease of catalytic activity from 6th cycle in recyclability tests of PSIL-NTf_2^- might be due to the petite leaching of

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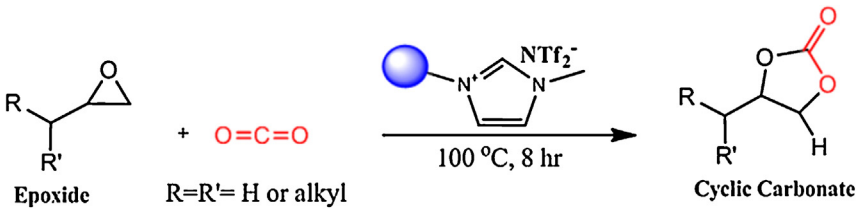
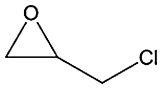
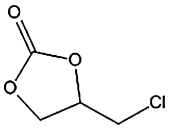
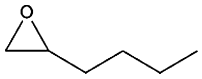
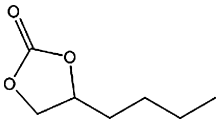
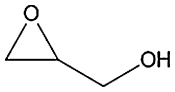
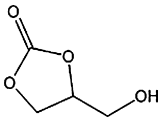
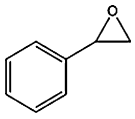
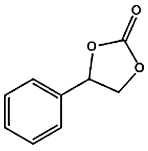
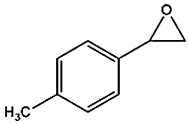
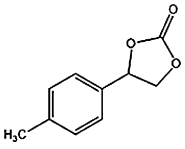
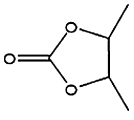
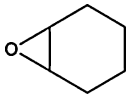
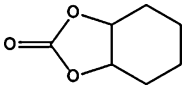
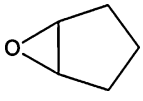
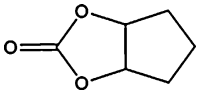
Table 3
Synthesis of various cyclic carbonate using CO_2 and epoxide over PSILs[a].



Sr. No	Epoxide substrate	Time (h)	Product	Yield[b] (%)	Conv. (%)	IR range (cm^{-1})
1		6.0		91	100	1788
2		6.0		82	100	1796
3		7.0		91	100	1800
4		8		88	100	1804
5		8		85	100	1804
6		8.0		78	100	1791
7		10.0		82	100	1798
8		12.0		78	100	1798

[a] All reactions were carried out on 5 g of substrate with PSIL-NTf_2^- catalyst without any solvent.
[b] Yield refers to the isolated product. Products were characterized by ^1H, ^{13}C NMR, IR spectroscopy and GC–MS.

ILs from support material. However the amount of leaching is very negligible even after eight successive cycles. Therefore, from above results, it can be conclude that, synthesized PSILs could be recycled up to several cycles without losing texture property and covalently immobilized ILs structural alteration. Currently, progressive future modifications are going on in ILs structures as well as support material in our laboratory to improve selective adsorption of CO_2 and conversion into subsequent catalytic organic transformations.

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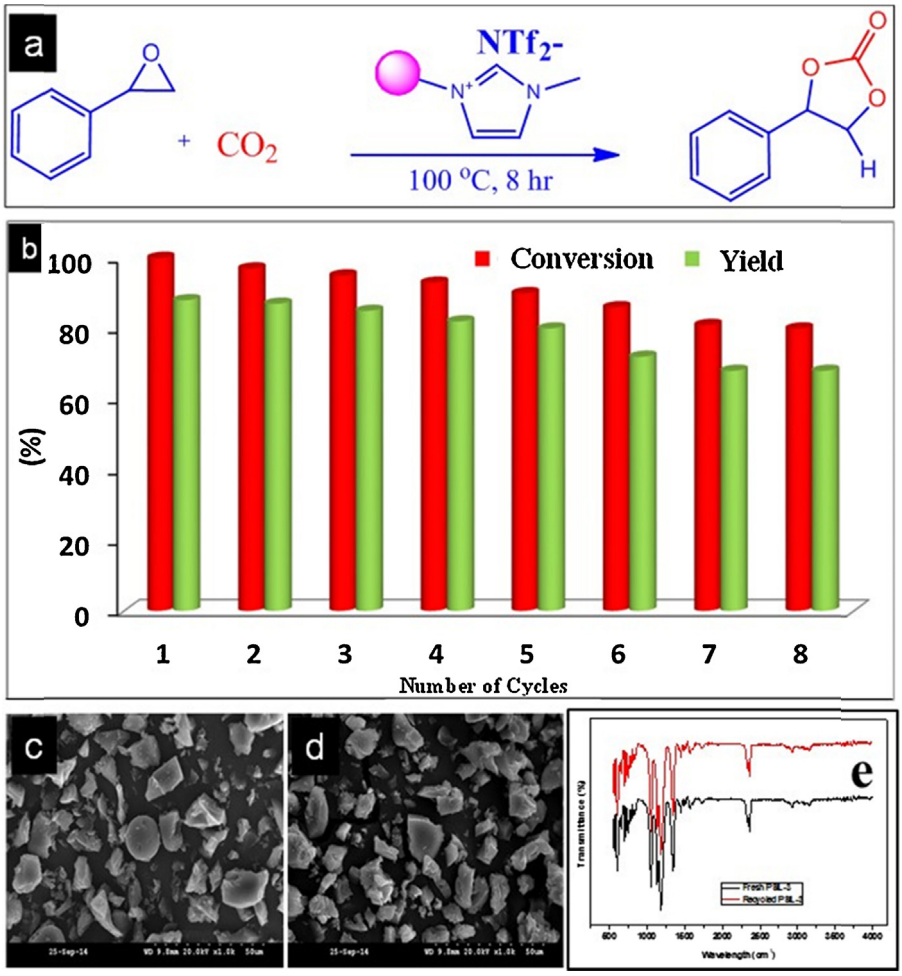

Fig. 9. Recyclability test of PSIL-NTf_2^- in coupling reaction of CO_2 and epoxide.

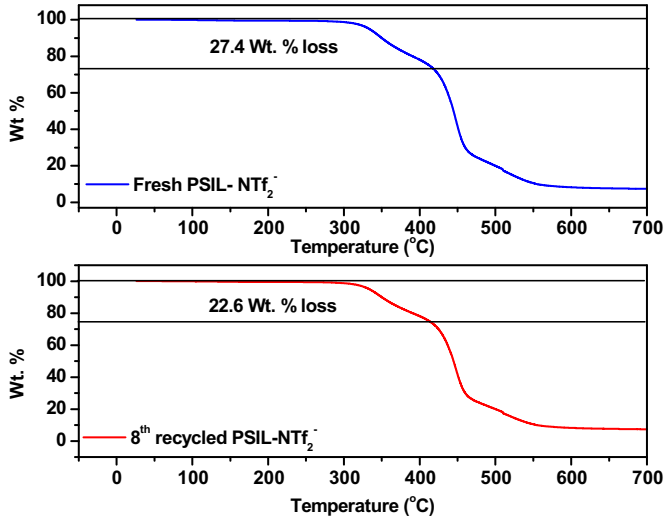

Fig. 10. TGA Analysis of fresh catalyst and 8th recycled catalyst from carbonate formation reaction.

4. Conclusions

In summary, we have constructed tailor-made polymer supported imidazolium based ILs that acts as highly efficient catalysts for the cycloaddition of CO_2 into epoxide to produce selective cyclic carbonate in solvent free condition. Various PSILs were developed by keeping constant imidazolium ring and exchanging the anions with metal salts and determined their anion effect with imidazolium cation on cycloaddition of CO_2 in to epoxide. From the obtained results, and reported data of interactions energies between these cations and anions studied in this study showed a trend $NTf_2^- > PF_6^- > BF_4^- > Br^- > Cl^-$, which is also replicated from their catalytic activity. Especially, least coordinated PSIL-NTf_2^- (imidazolium cation and NTf_2 anion) was found the highly efficient catalyst for this protocol. The selected catalyst converted various substituted alkyl and aromatic epoxide in to corresponding cyclic carbonate in efficient yields with good conversion than the free IL in mild reaction condition. As a fruitful result, 100% conversion and 88% cyclic carbonate was obtained using 8 bar CO_2 pressure at 100 °C reaction temperature in 8 h reaction time. These synthesized PSILs have many practical advantages such as easy product separation and purification by simple procedure catalyst recovery and number of time reuse. In addition, no noticeable changes in catalytic performance were found after being used in 8th cycles. These aspects are technically striking for considering the use of these catalysts for the eco-friendly fixation of CO_2 into epoxide to obtained cyclic carbonate in high yield.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2015.09.048.

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