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Heterogeneous catalytic conversion of CO_2 and epoxides to cyclic carbonates over multi-functional tri-*s*-triazine terminal-linked ionic liquids

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Abstract: Novel metal-free tri-*s*-triazine terminal-linked ionic liquids have been developed from various precursors of urea derivative-based ionic liquid/urea by co-condensation method. These were successfully used for the chemical fixation of CO_2 to epoxides producing cyclic carbonates under mild and green conditions in which no co-catalyst and solvent were needed. The tri-*s*-triazine terminal-linked ionic liquids so prepared possess multi-functionalities of hydrogen bond donor (HBD) ability, nucleophilicity, and Lewis base property, which are vital to the ring-opening of epoxide and the activation of CO_2. Reaction parameters (temperature, CO_2 pressure, catalyst loading, time, water content) on cycloaddition of CO_2 with propylene oxide (PO) to propylene carbonate (PC) over tri-*s*-triazine terminal-linked ionic liquids were optimized. It has been shown that, under the optimal conditions, the catalyst is also

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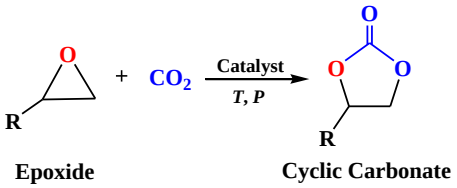
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versatile to CO_2 cycloaddition with other epoxides, can be reused up to five consecutive recycles without significant loss of activity, and can still remain active in the existence of moderate amount of water. Possible reaction mechanism has been proposed. The single-component, metal-free, multi-functional and easily recyclable tri-*s*-triazine terminal-linked ionic liquids reported herein can be an effective and eco-friendly catalyst for highly efficient CO_2 fixation.

***Keywords*:** Tri-*s*-triazine; Ionic liquid; Carbon dioxide; Epoxide; Cyclic carbonate

1. Introduction

Concerns about climate change caused by carbon dioxide (CO_2) emissions through human activities as well as fossil fuel consumption have increased in recent years, and the Intergovernmental Panel on Climate Change (IPCC) predicts 1.9 ^{o}C rise in temperature by the year 2100 [1]. Therefore, reduction in CO_2 production is of great importance in viewpoint of "sustainable society" and "green chemistry" concepts. Meantime, the catalytic transformation of CO_2, as an abundant, cheap and renewable C1 building block, into useful organic compounds has attracted much attention from the viewpoint of better utilization of carbon resources and prevention of global warming [2,3]. However, due to its inherent thermodynamic stability and kinetic inertness, the development of efficient catalytic process for chemical fixation CO_2 still remains a challenge [4]. One of the most promising endeavors in this area is the cycloaddition of CO_2 with epoxides to yield cyclic carbonates (Scheme 1), as the cyclic carbonates have found numerous potential applications ranging from polar and aprotic solvents to chemical intermediates [5,6].

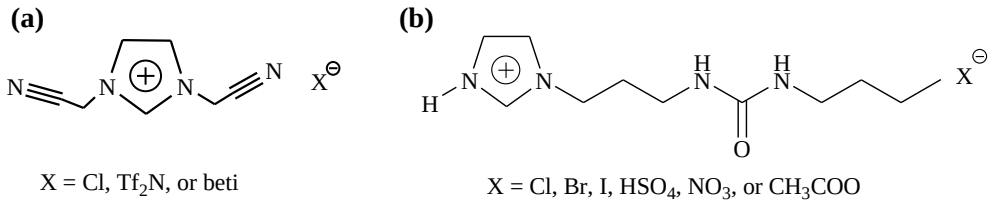


Scheme 1. Cycloaddition of CO_2 to epoxide.

A broad variety of catalysts for the synthesis of cyclic carbonates have been developed so far, including metal oxides [7], metal-salen complexes [5,8], metal organic frameworks (MOFs) [9,10], ionic liquids (ILs) [11-13] and organic functionalized polymers [14]. Among these catalysts, transition metal-based materials accounted for a large proportion, but their uses were limited due to the unsafety to ecology and humanity in the long term. Besides, tailor-made ILs with various active groups were reported and showed predominant catalytic activities due to unique characteristics such as Lewis acid-base bi-functionalities, thermal and chemical stabilities, negligible vapor pressure, and selective solubility towards organic and inorganic materials [15]. High viscosity of these ILs makes them difficult for practical application and the separation of ILs from the products always needs distillation or extraction by volatile organic solvents, which also does not meet the concepts of "sustainable society" and "green chemistry". Considering the industrial applications of the CO_2 coupling reaction with epoxide, efforts have been paid to develop heterogeneous ILs, such as immobilized ILs on silica [16], MCM-41 [17], zeolitic imidazolate framework-90 (ZIF-90) [18], cross-linked polymer [19], carbon nanotube [20] and mesoporous carbon nitride [21], which can be easily separable from the reaction mixture and reused in the subsequent cycles. The key drawbacks associated with immobilized ILs are the tedious preparation process, involvement of toxic transition metals, and the leaching problem of active sites during the reaction [22]. Hence, it is still a hot topic for development of simple, eco-friendly, metal-free, reusable heterogeneous catalysts that are capable of promoting the CO_2 fixation with high yield and selectivity under mild conditions.

Recently, Lee et al. reported an approach to obtain cation cross-linked ionic liquids using task-specific ionic liquid (TSIL) monomers with easily cross-linked nitrile groups (Scheme 2a) through ionothermal cyclotrimerization reactions at a lower temperature of 400 ^{o}C without any catalyst, the cations were co-condensed, simultaneously, a significant fraction of anions were remained [23]. The key structural

feature of TSIL monomers for synthesis of cross-linked ILs is the presence of certain functional groups that can undergo cross-linking reactions at elevated temperature. Inspired by this, we anticipate that multi-functional tri-*s*-triazine terminal-linked ionic liquids with hydrogen bond donor groups (N-H), nucleophilicity (I^-) and Lewis base property (NH/NH_2), which are responsible for the activation of epoxide and CO_2 in the CO_2 coupling reaction, could be prepared by choosing suitable TSILs at appropriate temperature. Herein, the urea derivative-based ionic liquids (UDILs) with different anions (Scheme 2b) were developed and used as the precursors, which were facilely synthesized at room temperature with high nitrogen contents. The functional urea-based group in UDILs coordinated with additional urea can go through the co-condensation at lower calcination temperatures ($\leq$ 500 ^oC) and, under these conditions, the imidazole ring and partial nucleophilic anion can remain, yielding the multi-functional integrated tri-*s*-triazine terminal-linked ionic liquids. To the best of our knowledge, there is no report on the novel tri-*s*-triazine terminal-linked ionic liquids as heterogeneous catalysts for the synthesis of cyclic carbonates. Thus, such functionalized ionic liquids were prepared using various UDILs precursors in different additional urea contents at different calcination temperatures and the materials obtained were tested for the chemical fixation of CO_2 to epoxides yielding cyclic carbonates. The effects of reaction parameters including reaction temperature, CO_2 pressure, and catalyst concentration on catalytic activities were also investigated. Additionally, the reusability of tri-*s*-triazine terminal-linked ionic liquids was examined and plausible reaction mechanism was discussed. The newly developed metal-free tri-*s*-triazine terminal-linked ionic liquids have been shown to overcome such drawbacks as difficulty in separation, high viscosity, and moisture sensitivity of homogeneous TSILs, as well as those of immobilized ILs mentioned above. The catalysts developed in the present work would be promising for the effective chemical transformation of CO_2 under mild and green conditions.



Scheme 2. Chemical structures of (a) nitrile-functionalized ILs and (b) UDIL precursors used in this work.

2. Experimental

2.1. General information

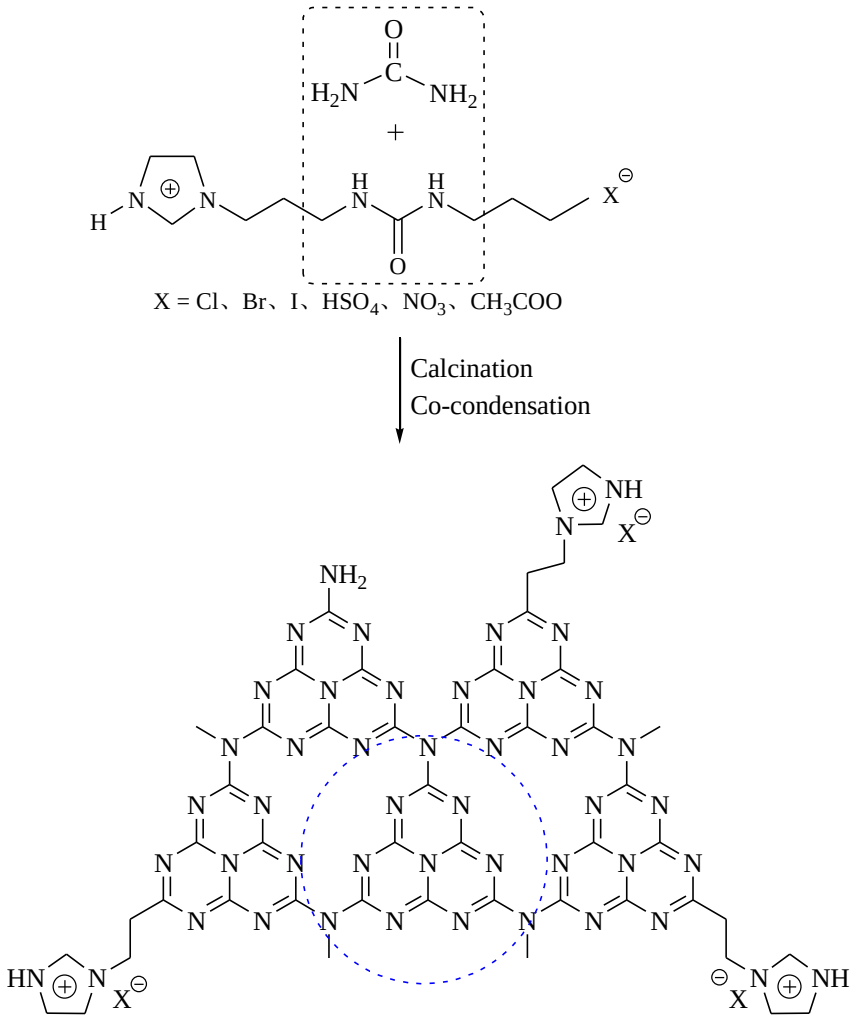
Isocyanic acid butyl ester (98%) was purchased from Adamas Reagent Co. Ltd. and 1-(3′-aminopropyl) imidazole (98%) from Alfa Aesar Chemical Co. Ltd. Hydrochloric acid (36-38%), hydrobromic acid (40%), and hydroiodic acid (45%) were obtained from Sinopharm Chemical Reagent Co. Ltd. Carbon dioxide of 99.99% purity was purchased from Harbin Qinghua Industrial Gases Co. Ltd. and propylene oxide (99%) from Beijing InnoChem Science & Technology Co. Ltd. Other epoxides and chemicals of analytical purity were commercially available and used as received.

2.2. Preparation of tri-s-triazine terminal-linked ionic liquids

The UDIL precursors were prepared as follows. Briefly, 1-(3′-aminopropyl) imidazole (6.0 g, 47.9 mmol) was dissolved in 20 mL acetonitrile under dry N_2 atmosphere. To this solution equimolar isocyanic acid butyl ester pre-dissolved in 10 mL acetonitrile was dropwise mixed under stirring. The solution obtained was further stirred overnight followed by removing the solvent and drying at 60 ^{o}C under vacuum. The compound synthesized was then protonated with the corresponding protonic acid (e.g. HCl, HBr, HI) to obtain the UDIL precursors with different anions. The UDIL/urea precursors were prepared by mixing UDIL (1.5 g) with different amounts of urea in 10 mL deionized water and stirred to mix well at room temperature and then removing water at 80 ^{o}C.

Typically, the tri-s-triazine terminal-linked ionic liquids with different nucleophilic anions (Scheme 3) were prepared by heating the UDIL/urea precursors in

an alumina crucible with a cover in a tube furnace. The precursors were heated at a heating rate of 5 ^{o}C/min up to 500 ^{o}C under N_2 flow for 2 h. After cooling to room temperature, the black samples obtained were ground into powder. Those so prepared will be denoted as UDIL-X-φU (500) and the samples obtained from UDIL precursors (without urea addition) as UDIL-X (500), where X represents the different anion of UDIL precursor, φ represents the relative mass of urea added to UDIL. Similarly, UDIL-X sample via calcination at 600 ^{o}C will be UDIL-X (600) and so on.



Scheme 3. Proposed structure of tri-*s*-triazine terminal-linked ionic liquids and tri-*s*-triazine structure marked in blue.

2.3. Catalyst characterization

FT-IR spectra were measured on PerkinElmer Spectrum 100 FT-IR Spectrometer

using KBr pellets. The morphology of samples was examined by scanning electron microscopy (SEM) using a Hitachi S-4300. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Thermo Fisher Scientific Escalab 250Xi. X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Advance X-ray powder diffractometer with Cu Kα radiation (40 kV, 40 mA) for phase identification. Solid state ^{13}C MAS NMR measurements were performed on a Varian Infinity Plus 400 NMR spectrometer.

2.4. Catalytic activity test

The cycloaddition of CO_2 with epoxide was performed in a 50 mL high pressure stainless-steel reactor. In a typical run, the air in the reactor was replaced with CO_2, 0.1 g of UDIL-I-60%U (500) catalyst and 2.0 g (34.5 mmol) of propylene oxide (PO) were added into the reactor, and it was heated using an oil bath to preset temperature. At the desired reaction temperature, CO_2 was introduced into the reactor to a certain pressure and the reaction was run while stirring. After the completion of the reaction, the reactor was cooled in an ice-water bath and excess CO_2 was released slowly. The liquid product was separated from UDIL-I-60%U (500) catalyst by centrifugation, diluted with ethyl acetate, and then analyzed on GC (Agilent GC-7890A, Agilent 19091J-413 capillary column and FID detector). As PO is highly volatile, quantitative analysis of the product is inaccurate by internal standard method. Hence, the GC quantitative analysis of the product is performed by external standard method. The catalyst was washed with ethyl acetate (5 mL) three times, dried under vacuum, and then reused directly for the next run. The same cycloaddition procedures apply for other catalysts.

3. Results and discussion

3.1. Catalyst characterization

The FT-IR spectra of various samples prepared with different precursors were depicted in Fig. 1. All the samples contained heteroaromatic functional groups, as stretching absorption of N-H groups in the aromatic ring was seen in the region of

3550-3300 cm^{-1} [24]. The band at 3189 cm^{-1} was owing to the free -NH_2 stretching vibration attached to the sp^2 hybridized carbon in the aromatic ring [25]. Its relative intensity gradually weakened with increasing calcination temperature. At 700 ^oC, the band at 3189 cm^{-1} was almost invisible. When 60 wt% urea was added to the precursors, the -NH_2 absorption peak shifted to 3169 cm^{-1}. The bands that appeared at 1617-1650 cm^{-1} were assigned to C=C and C=N in aromatic skeletal stretching vibrations [26]. The peak at 1603 cm^{-1} was assigned to N-H bending vibration [27]. The band centered at ca. 1312 cm^{-1} was attributed to aromatic C-N stretching vibration and the peak at adjacent 995 cm^{-1} was for the -C=CH groups [28]. These FT-IR results demonstrated the existence of the typical functional groups in the samples obtained. The morphology of UDIL-I-60%U (500) sample was examined by SEM and it was observed to have block-like structure (later in Fig. 5C). The features of this structure in the target reaction will be discussed later.

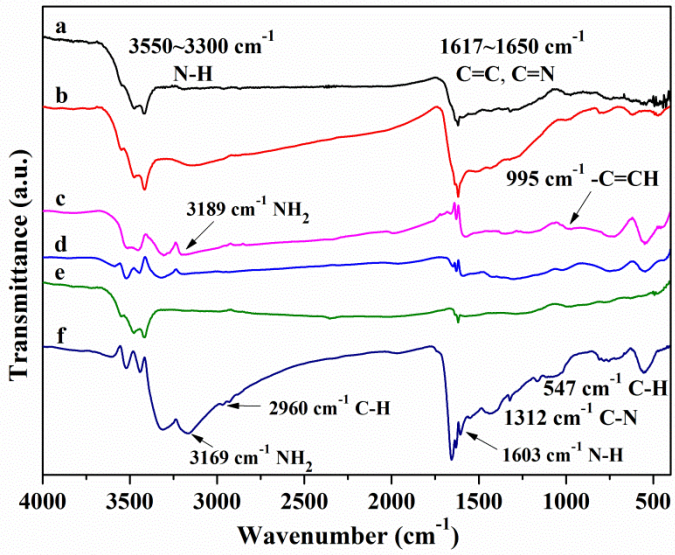


Fig. 1. FT-IR spectra of (a) UDIL-Cl (500), (b) UDIL-Br (500), (c) UDIL-I (500), (d) UDIL-I (600), (e) UDIL-I (700) and (f) UDIL-I-60%U (500).

To further investigate the structure of the samples prepared, the solid state ^{13}C MAS NMR analysis was conducted (Fig. 2). For the samples obtained by calcining UDIL-I precursor at different temperatures, there appeared characteristic signals at 124-132 ppm and 15-22 ppm, respectively, corresponding to the carbon atoms of the

imidazolium ring and alkyl groups of the side chains [29,30], due to the carbonization of partial alkyl side chains. With an increase in calcination temperature, the peak of the imidazolium ring became sharper and the alkyl group peak became weaker, indicating that the carbonization occurred to more extent in the side chains (Fig. 2A). When 60% urea was added in the precursors, two additional peaks located at 157.4 and 164.2 ppm were observed for UDIL-I-60% (500), which could be ascribed to the C(i)N_3 and C(e)N_3 groups in tri-*s*-triazine unit (Fig. 2B) [31,32]. Also the peaks became stronger with increasing urea content, while the characteristic signals of the imidazolium ring and the side chain groups became weaker. All these results suggested that the additional urea co-condensed with the urea derivative groups in the side chain of UDIL-I, forming the tri-*s*-triazine terminal-linked ionic liquids under the calcination conditions.

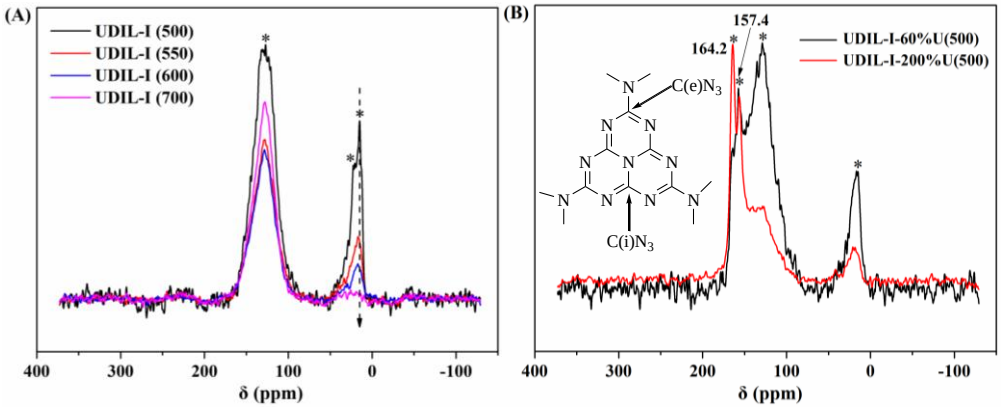


Fig. 2. ^{13}C MAS NMR spectra of (A) UDIL-I samples calcined at different temperatures and (B) UDIL-I-φU (500) samples.

The XRD patterns of the samples obtained are shown in Fig. 3. The UDIL-I (500) had a low intensity (002) diffraction peak centered at 25.8^o, characteristic of graphitic C structure due to the partial carbonization of alkyl side chains in UDIL-I [33]. On the addition of 60 wt% urea into UDIL precursor, the resultant UDIL-I-60%U (500) showed multiple new diffraction peaks of melam, melem or melon constituents formed by *s*-triazine units [32,34], which were demonstrated to activate CO_2 favorably [35]. With increasing urea content to 200 wt%, a fresh diffraction peak

appeared at 26.2°, which was ascribed to carbon nitride analogues derived from tri-*s*-triazine units [32].

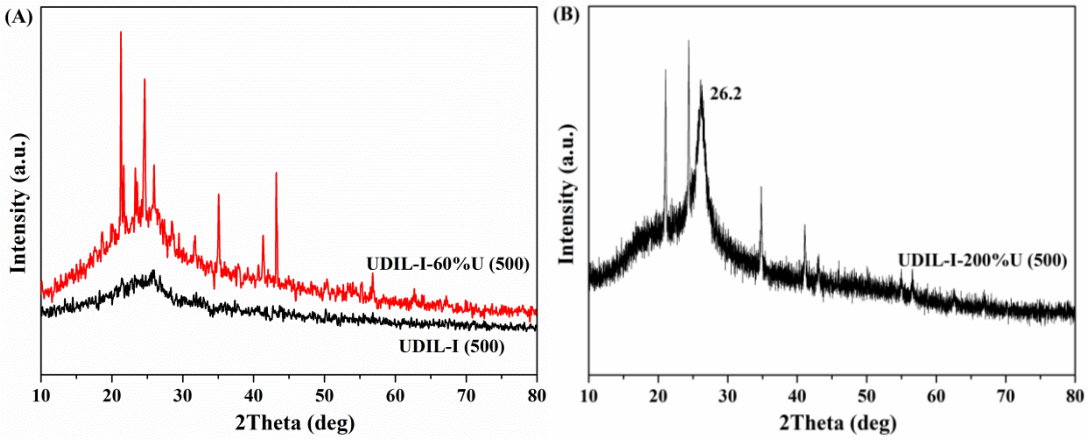


Fig. 3. XRD patterns of (A) UDIL-I (500) and UDIL-I-60%U (500) and (B) UDIL-I-200%U (500).

Fig. 4 shows the XPS spectra of UDIL-I (500) and UDIL-I-60%U (500) samples. For the former sample, the C 1s peak could be fitted with two peaks at binding energies of 283.9 and 285.8 eV (Fig. 4A), the peak at 283.9 eV was assigned to C=C/C-C groups [36] and the peak at 285.8 eV was identified as sp^3 C bonded with N or O (C-N or C-O) [37]. The N 1s spectrum could be separated into two peaks at binding energies of 399.9 and 401.5 eV (Fig. 4B), attributed to O-C-N and C-N-H groups, respectively [38]. After the introduction of urea into the UDIL-I precursor, the UDIL-I-60%U (500) sample showed quite different surface chemical states from UDIL-I (500), and C, N, I and O species were detected in survey spectra (Fig. 4F). The C 1s spectrum of UDIL-I-60%U (500) was deconvoluted into three peaks at 284.5, 286.4, and 288.2 eV (Fig. 4C). The peak at 284.5 eV was assigned to the graphitic carbon (C-C bond), the peak of 286.4 eV was assigned to C-O-C or C-N (amine) [39], and the peak at 288.2 eV indicated the existence of C-N-C coordination between tri-*s*-triazine units [40]. The N 1s spectrum could be divided into three peaks centered at 398.3, 399.3 and 400.0 eV (Fig. 4D). The peak at 398.3 eV corresponded to the C-N-C group and those at 399.3 and 400.0 eV were attributed to the binding

energies of nitrogen atoms for C-NH_2 and -NH- groups, respectively [38, 39]. These N assignments were quite consistent with the results obtained for the C 1s spectrum. Thus, nitrogen atoms were successfully integrated to tri-*s*-triazine units in the form of N bonding to C atoms. Additionally, the peaks located at 617.8 and 629.3 eV corresponded to I $3d_{5/2}$ and I $3d_{3/2}$ (Fig. 4E), which confirmed the presence of elemental iodine in UDIL-I-60%U (500) sample. All these XPS results were essentially consistent with the FT-IR analysis.

The relative amounts of elements in the different samples were estimated from the XPS results obtained. As shown in Table 1, the total amounts of N and I species in UDIL-I decreased with increasing precursor calcination temperature from 500 to 700 ^{o}C, while that of C species increased, also indicating that more alkyl side chains were carbonized. When UDIL-I (500) and UDIL-I-U (500) are compared, the amount of N species is larger for the latter and increases with increasing urea content in the precursor, while that of I species is smaller for the latter due to the formation of tri-*s*-triazine units by co-condensation (Scheme 3). The results were consistent with the ^{13}C NMR analysis ones. As discussed later, the presence of Lewis base and nucleophilic I^- in the UDIL-I-φU catalyst is significant for the CO_2 fixation to epoxide.

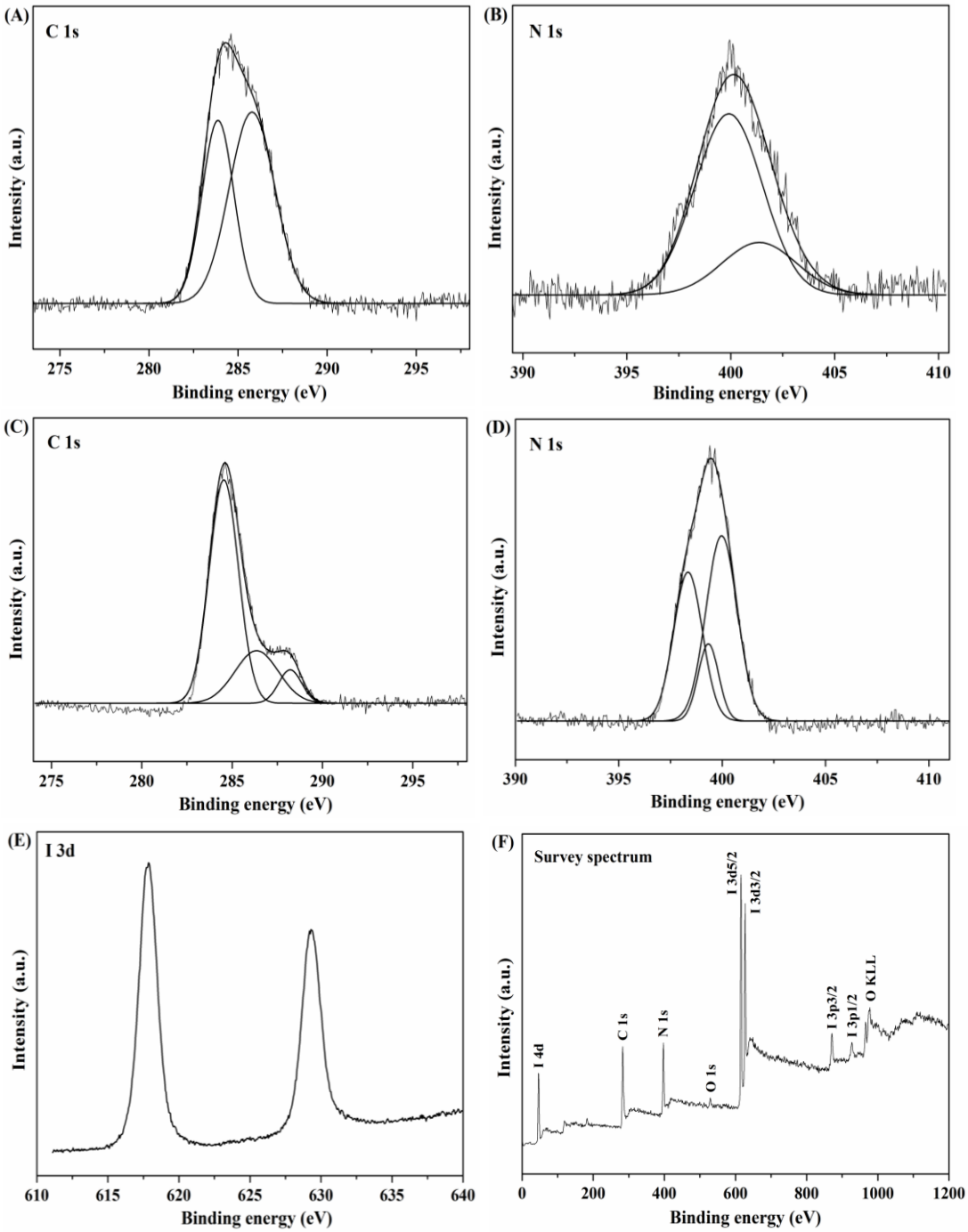


Fig. 4. XPS spectra of UDIL-I (500) (A, B) and UDIL-I-60% (500) (C, D, E, F).

Table 1 Amount of elements (atomic %) in various samples prepared.[a]

Sample	C	N	O	I
UDIL-I (500)	69.9	16.9	4.6	8.7
UDIL-I (600)	78.8	13.4	6.3	1.5
UDIL-I (700)	81.7	11.0	6.6	0.7

UDIL-I-20%U (500)	72.4	20.4	3.9	3.3
UDIL-I-60%U (500)	61.6	30.3	0.8	7.2
UDIL-I-200%U (500)	43.1	55.5	0.3	1.1

[a] Hydrogen content is not taken into account for the calculation.

3.2. Catalyst screening

Initially, the cycloaddition of propylene oxide with CO_2 to produce propylene carbonate was selected to test the catalytic activity of different catalysts derived from various UDIL precursors and the results obtained were summarized in Table 2. No product was detected in the absence of catalyst (entry 1) and the high-viscous precursor UDIL-I afforded the cycloaddition reaction with 70% yield and 99% selectivity under conditions employed (entry 2). After calcination at 500 ^{o}C, the UDIL-I (500) gave a slightly increased PC yield of 77% with the satisfied selectivity (entry 5). The UDIL-X (500) with different halide anions indicated markedly different catalytic activities (entries 3-8). The UDIL-X (500) samples with the anions of NO_3^-, CH_3COO^- and HSO_4^- showed unsatisfactory catalytic activities, which were ascribed to the weak nucleophilicity or the decomposition of the anions when UDIL precursors were polymerized at 500 ^{o}C, thus resulting in the difficulty of epoxy-ring opening [41]. Meantime, the activity of UDIL-X (500) with halide anions decreased in the order of $I^- > Br^- > Cl^-$, due to the integrated effects of nucleophilicity and the presence of intramolecular hydrogen bond. The stronger hydrogen bond interaction was formed for Cl^- and Br^- than I^-, which endowed I^- with the enhanced leaving ability as compared with Cl^- and Br^-, and I^- was more likely to go through nucleophilic attack for epoxy-ring opening, which is an important step for the coupling reaction. Similar results were also reported by Han [42], Park [43] and Hirose et al. [44] using polyaniline salts, carboxymethyl cellulose supported ILs, and dual 2-pyridinemethanol/TBAI system as catalysts, respectively. Additionally, the influence of precursor calcination temperature on catalyst activities (entries 5 and 9-12) revealed that the catalyst exhibited an increased catalytic performance with

increasing calcination temperature from 450 ^{o}C to 500 ^{o}C. However, further increasing calcination temperature to 700 ^{o}C resulted in a dramatic decrease of the catalytic performance, because of the almost complete carbonization of alkyl side chains and the concomitant loss of active sites (such as NH/NH_2 and I species) at higher temperature, which have been demonstrated by FTIR, ^{13}C MAS NMR and XPS analyses, prevented the activation of substrates and the ring-opening step. It was observed that when UDIL-I was mixed with an appropriate amount of urea as co-precursors, urea species co-condensed with the urea-derivative groups in the side chain of UDIL-I and formed the tri-*s*-triazine terminal-linked ionic liquids after calcination. This sample could have a larger N content of Lewis base and the enhanced HBD capability to some extent, in which I^- anion could almost remain, as revealed by XPS results (Table 1). The UDIL-I-U samples showed higher activities compared to UDIL-I one (entries 5, 13, 14). The highest 94% PC yield was achieved with the UDIL-I-60%U (500) under metal-, co-catalyst- and solvent-free conditions while remaining the selectivity (entry 14). Further increase of urea amount decreased the product yield (entries 15 and 16), possibly attributed to the further co-condensation of additional urea and tri-*s*-triazine units to carbon nitride analogues, which resulted in the decrease of I^- concentration in catalyst, as shown in Table 1. Hence, further investigation has been made with the most active catalyst of UDIL-I-60%U (500).

Table 2 Catalyst screening for CO_2 cycloaddition to PO.[a]

Entry	Catalyst	Reaction results[b]	
		Y_{PC} (%)	S_{PC} (%)
1	none	—	—
2[c]	UDIL-I	70	99
3	UDIL-Cl (500)	13	99
4	UDIL-Br (500)	29	99
5	UDIL-I (500)	77	99

6	UDIL-NO_3 (500)	trace	—
7	UDIL-CH_3COO (500)	trace	—
8	UDIL-HSO_4 (500)	10	99
9	UDIL-I (450)	65	99
10	UDIL-I (550)	58	99
11	UDIL-I (600)	5	99
12	UDIL-I (700)	4	99
13	UDIL-I-20%U (500)	79	99
14	UDIL-I-60%U (500)	94	99
15	UDIL-I-100%U (500)	22	99
16	UDIL-I-200%U (500)	16	99

[a] Reaction conditions: PO 34.5 mmol (2.0 g), catalyst 5 wt%, 120 ℃, 1.5 MPa CO_2, 2.5 h.

[b] Y_{PC}: PC yield; S_{PC}: PC selectivity; all based on GC analyses.

[c] The precursor without calcination.

Besides the excellent catalyst activity, the sustainability and recycling are also decisive criteria for the possible large-scale application. After each run, the solid UDIL-I-60%U (500) catalyst was separated from reaction system by centrifugation, washed, dried, and then reused in the next batch under the same reaction conditions (120 ℃, 1.5 MPa, 5 wt% catalyst, 3.0 h). The catalyst presented an excellent recyclability up to five cycles with only a slight loss of its original catalytic activity and the satisfied selectivity to PC did not change (Fig. 5A). The recovered UDIL-I-60%U (500) catalyst was analyzed by FT-IR and SEM (Fig. 5B-D). The structure of UDIL-I-60%U (500) was essentially similar to its pristine form, but the C=C and C=N stretching vibrations (1617-1650 cm^{-1}) in aromatic skeleton became weakened. This could be due to some damage of the skeletal structure by the recycled runs under vigorous stirring. SEM pictures (Fig. 5C-D) showed that the block-like structure became fractured. Such a structural change should not be significant and so the catalyst could indicate the good recyclability.

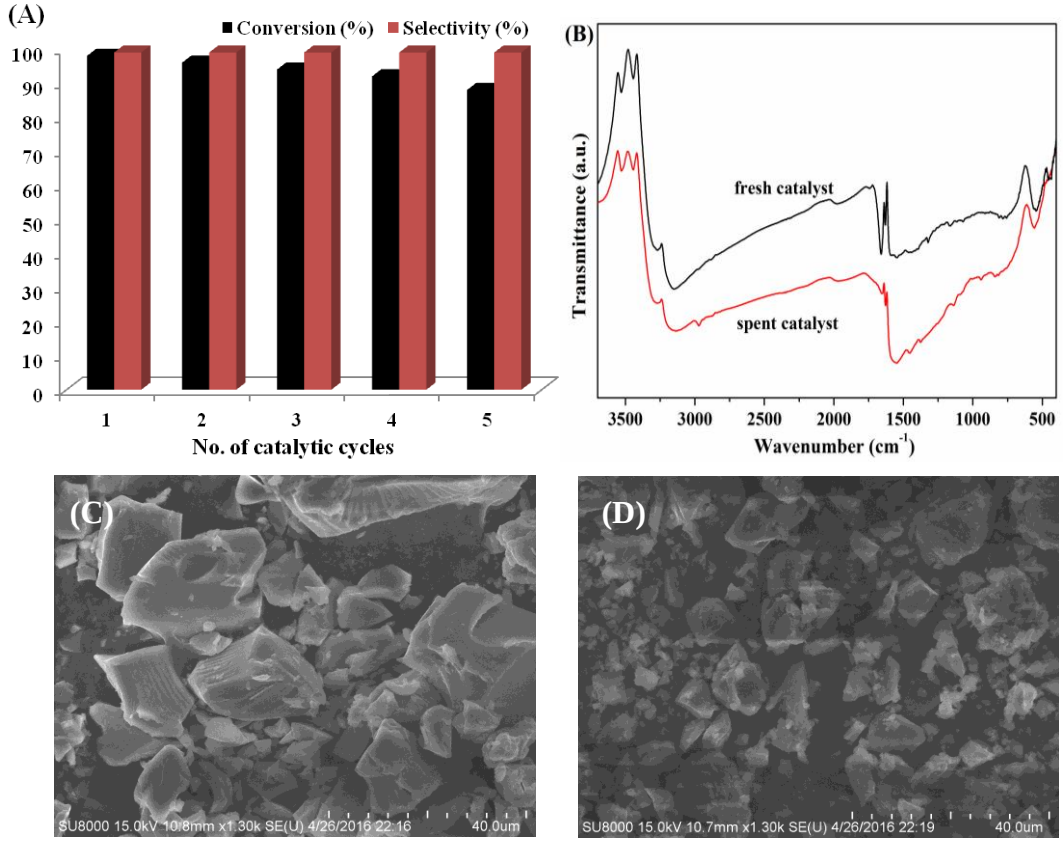


Fig. 5. (A) Recyclability of UDIL-I-60%U (500) catalyst, (B) FT-IR spectra of fresh and spent UDIL-I-60%U (500) after five cycles, and SEM images of (C) fresh UDIL-I-60%U (500) and (D) spent UDIL-I-60%U (500) catalyst.

3.3. Effects of reaction parameters

With the most active tri-*s*-triazine terminal-linked ionic liquid of UDIL-I-60%U (500) catalyst, the effects of different reaction parameters such as temperature, CO_2 pressure, and catalyst concentration on PC synthesis were investigated. As shown in Fig. 6A, the temperature displayed a significant impact on the coupling reaction. Only 40% PC yield was obtained at 90 ^{o}C but, with increasing temperature to 120 ^{o}C, the PC yield was sharply enhanced to 94%. The high PC yield was also achieved at temperatures of 90-140 ^{o}C and the satisfied selectivity to the desired product was obtained at any temperatures examined. From a practical standpoint of energy-saving and effective removal of reaction heat as steam, the optimal reaction temperature was 120 ^{o}C.

Fig. 6B depicts the effect of CO_2 pressure on PC synthesis. It was clearly seen that a dramatic rise of PC yield to 77% was observed by using 0.5 MPa CO_2 pressure. With further increase of CO_2 pressure from 1.0 MPa to 1.5 MPa, the PC yield was moderately increased from 88% and 94%. This trend was caused by the variation in CO_2 concentration. When CO_2 pressure was raised, CO_2 molecules were dissolved into the substrate PO phase, and the increased CO_2 concentration as reactant was a positive factor at low CO_2 pressure. Further increase of CO_2 pressure, a dilution effect occurred and CO_2 pressure no longer markedly promoted the reaction. Hence, a mild CO_2 pressure of 1.5 MPa was sufficient for the satisfactory synthesis of PC.

Fig. 6C shows the effect of catalyst concentration on the PC yield and selectivity. The catalyst concentration had significant impact on the reaction, and PC yield was remarkably enhanced from 25% to 94% with the catalyst concentration increasing from 0.5 wt% to 5 wt%. While, no obvious change in the PC yield was observed with further increase of catalyst loading. The dependence of reaction time was also examined (Fig. 6D). The cycloaddition of CO_2 and PO gradually proceeded with reaction time, and 94% PC yield was obtained in the first 2.5 h. With prolonging reaction time to 3 h, PO was almost quantitatively converted with the satisfied selectivity to PC.

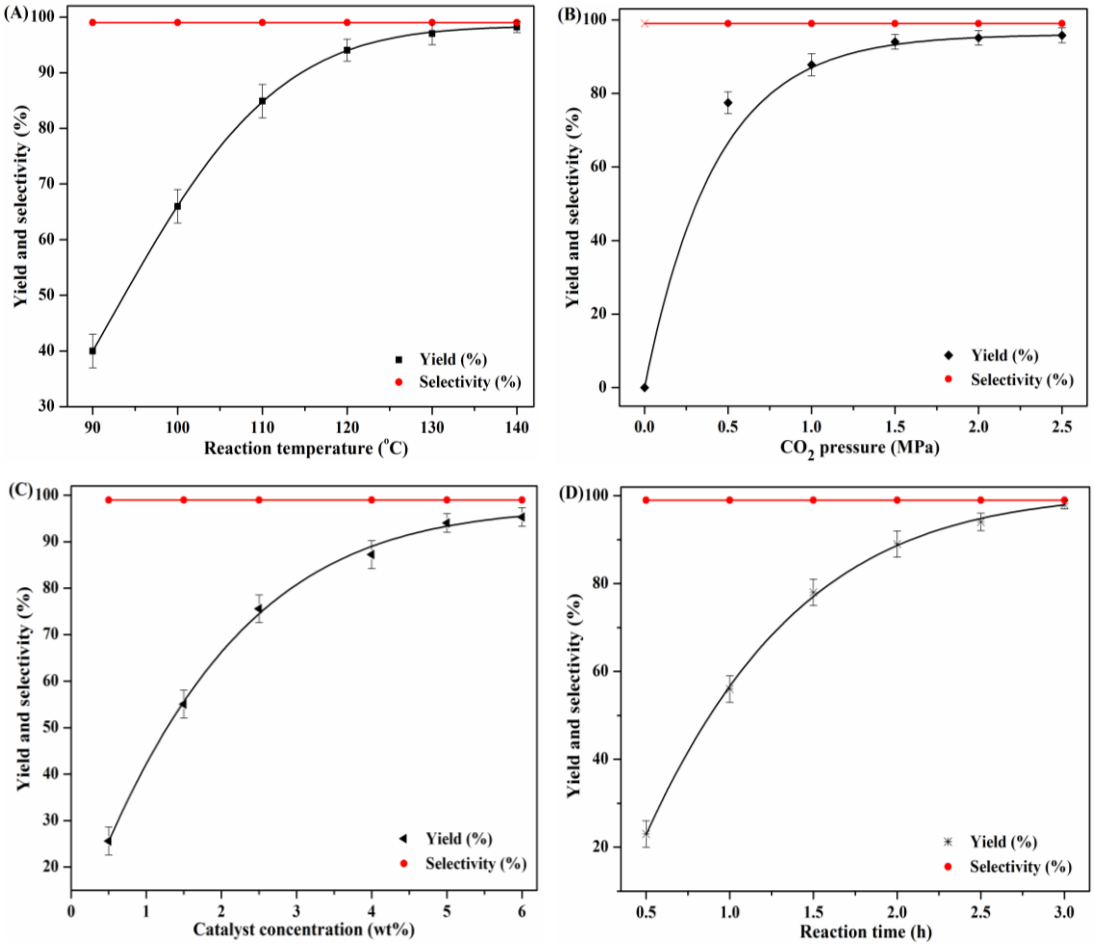


Fig. 6. Influence of reaction parameters of (A) temperature, (B) CO_2 pressure, (C) catalyst concentration, and (D) reaction time using UDIL-I-60%U (500) catalyst. Standard reaction conditions: PO 34.5 mmol (2.0 g), 5 wt% catalyst, 120 ℃, CO_2 1.5 MPa, 2.5 h.

Considering that water is inevitable in real post-combustion flue gases, the influence of coexisting water has additionally been examined under the same conditions. The UDIL-I-60%U (500) was not suitable for this purpose because it showed almost completely PO conversion (Table 2, entry 14). Hence, UDIL-I-20%U (500) with a moderate catalytic activity (Table 2, entry 13) was selected. The reaction results in the presence of water are given in Fig. 7. Surprisingly, there was no significant influence on PC yield by changing H_2O/catalyst mass ratio from 0 to 25 wt%, which was not consistent with the previously reported results that water acted as hydrogen bond donor and could to some extent promote the CO_2 cycloaddition to epoxides over homogeneous butyl-triphenylphosphonium iodide (PPh_3BuI) and

1-(2-hydroxyl-ethyl)-3-buthylimidazolium bromide ([HEBim]Br) catalysts [45,46]. As illustrated in Scheme 4, in the present reaction system, there were two phases including the top PO-CO_2-H_2O gas phase and the bottom PO-CO_2-catalyst solid-liquid mixed phase where the reaction mainly took place. The UDIL-I-20%U (500) catalyst is immiscible with H_2O and H_2O should exist in the top gas phase at a reaction temperature of 120 ℃. When the reaction proceeds at the expense of PO in the bottom phase, reactant PO molecules may be supplied from the top phase but H_2O is unlikely to move to the bottom phase. The first step of the ring-opening of epoxide occurs in the bottom phase in which the nucleophilic attacking agent of I^- anion exists (but it is absent in the top phase) and the following steps occur in the same phase in which CO_2 and the catalyst coexist. The presence of H_2O in the bottom reaction phase should be insignificant and so it has no effect on the reaction in the present reaction system as observed (Fig. 7). When further increase H_2O/catalyst mass ratio to a larger scale, such as 50%-100%, the PC yield was enhanced duo to a certain increase in the H_2O concentration in the bottom reaction phase. The H_2O molecules should then be likely to assist the ring-opening of epoxide by forming hydrogen bond with the oxygen atom of epoxide.

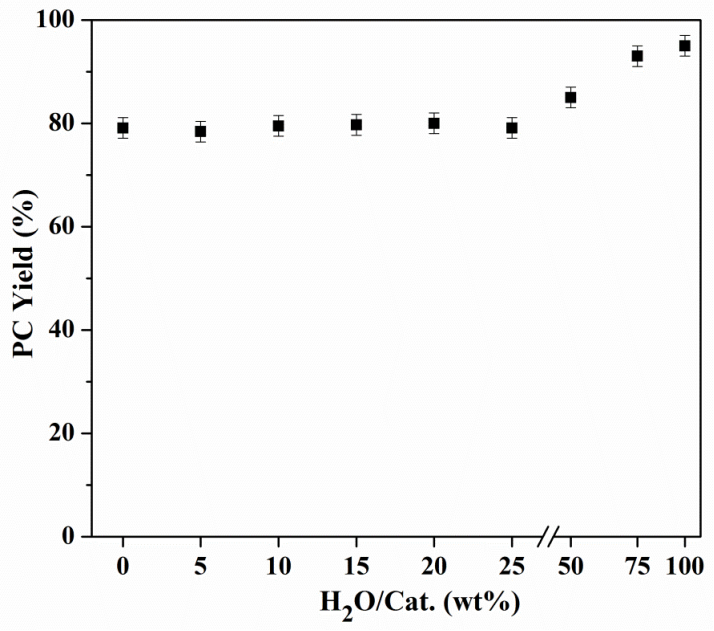
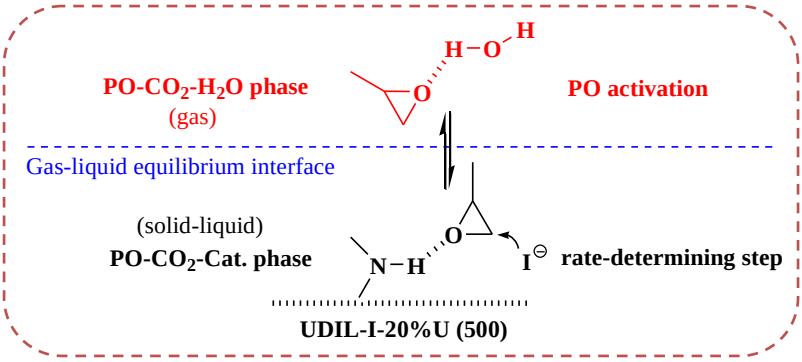


Fig. 7. Effect of water on PC synthesis over UDIL-I-20%U (500) catalyst. Conditions: PO 34.5

mmol (2.0 g), 5 wt% catalyst, 120 ℃, 1.5 MPa, 2.5 h.

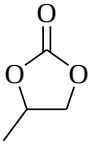


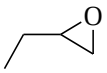
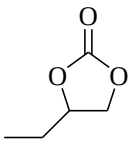
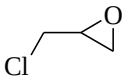
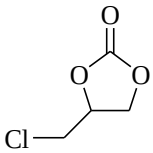
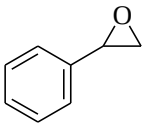
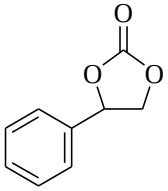
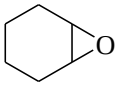
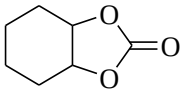
Scheme 4. Possible phase behavior of the reaction mixture in the presence of H_2O.

3.5. Catalytic activity towards CO_2 cycloaddition to various epoxides

To determine the adaptability of UDIL-I-60%U (500) catalyst, the substrate scope of coupling reaction involving a series of substituted epoxides was examined (Table 3). The coupling reaction of terminal epoxides attached with either electron-withdrawing or electron-donating groups could smoothly proceed to yield the corresponding cyclic carbonates with satisfactory yields and selectivities (entries 1-4). While the internal epoxide of cyclohexene oxide with crowded cyclohexene ring exhibited relatively low conversion even under the harsh reaction conditions of 130 ^{o}C, 3.0 MPa CO_2, and 9.0 h although the selectivity to the desired product was also good (entry 5). The results revealed that the steric hindrance played a major role in catalytic activity than the electronic effect.

Table 3 Cycloaddition of CO_2 to various epoxides over UDIL-I-60%U (500) catalyst.[a]

Entry	Epoxide	Product	*T* (℃)	*t* (h)	Reaction results[b]	
					Y (%)	S (%)
1			120	3.0	98	99

2			120	3.0	94	99
3			120	3.0	99	99
4			120	3.0	83	99
5[c]			130	9.0	45	98

[a] Reaction conditions: epoxide 34.5 mmol (2.0 g), 5 wt% catalyst, 1.5 MPa CO_2.

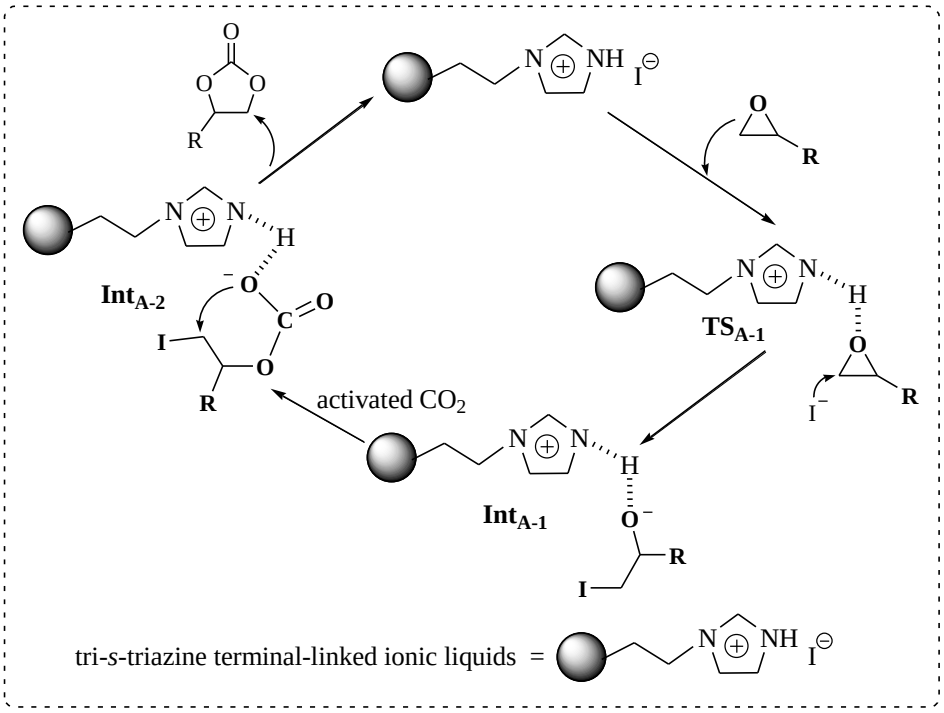
[b] Y: product yield; S: product selectivity; all based on GC analyses.

[c] *P* = 3.0 MPa.

3.6. Plausible reaction mechanism

The presence of N-H, NH_2 and nucleophilic I^- groups in tri-*s*-triazine terminal-linked ionic liquid can give UDIL-I-60%U (500) catalyst the multi-functionalities of the hydrogen bond donor ability, basicity, and nucleophilicity, which are vital to the activation of epoxide and CO_2 together with the ring-opening of epoxide. Feasible reaction mechanism for tri-*s*-triazine terminal-linked ionic liquid catalyzed reaction is proposed in Scheme 5. Initially, the N-H or NH_2 groups in the catalyst act as hydrogen bond donor to form the hydrogen bond with the oxygen atom of epoxide, resulting in the polarization of C-O bond, which makes ring-opening of epoxide easy (TS_{A-1}). The nucleophilic I^- group subsequently attacks on the less hindered β-carbon atom of epoxide and opens the epoxy ring to generate oxygen anion intermediate (Int_{A-1}). Experimental and theoretical evidences have demonstrated that the ring-opening is the rate-determining step for the coupling reaction [47], thus explaining the importance of N-H (or NH_2) and I^- present in the catalyst. Subsequently, the NH_2 groups linked in terminal of tri-*s*-triazine units (Scheme 3)

could act as Lewis base to activate CO_2 species by forming the carbamate, which has been verified in the literature [35]. Then, the oxygen anion intermediate (Int_{A-1}) interacts with the activated CO_2 to form the new intermediate (Int_{A-2}). Finally, the intermediate Int_{A-2} is converted into the final product of cyclic carbonate and regenerates the catalyst by the subsequent intramolecular ring-closure step. The synergistic actions of multi-functional groups provided by tri-*s*-triazine terminal-linked ionic liquid can facilitate the CO_2 coupling reaction effectively.



Scheme 5. Reaction mechanism proposed for cycloaddition of CO_2 and epoxide over tri-*s*-triazine terminal-linked ionic liquids.

4. Conclusions

A series of novel tri-*s*-triazine terminal-linked ionic liquids were prepared via co-condensation of UDIL and additional urea precursors. The catalyst preparation and reaction conditions were optimized and UDIL-I-60%U (500) was observed to show an excellent performance in the cycloaddition of CO_2 to various epoxies yielding the corresponding cyclic carbonates under mild solvent-free conditions. For propylene oxide, for example, a high propylene carbonate yield of 98% was achieved at 120 ℃

and at 1.5 MPa CO_2 in 3 h. In addition, the catalyst was recyclable for five repeated runs and tolerant to the presence of water. The excellent catalytic activity of UDIL-I-60%U (500) was attributed to the multi-functionalities involving the hydrogen bond donor, Lewis basicity, and nucleophilicity, which were vital to the activation of epoxide and CO_2 together with the ring-opening of epoxide. Compared with the reported TSILs, the present heterogeneous catalyst overcomes the difficulty of separation due to their high viscosity and will be promising for the design of environment-friendly and effective processes for the chemical transformation of CO_2 including the addition to epoxides and other reactions.

Acknowledgements

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