Immobilized protic ionic liquids: Efficient catalysts for CO₂ fixation with epoxides

Xu Zhang¹, Dan Su¹, Linfei Xiao^{*1,2}, Wei Wu^{*1}

¹National Center for International Joint Research on Catalytic Technology, Key Laboratory of Chemical Engineering Process & Technology for High-efficiency Conversion, College of Heilongjiang Province, School of Chemistry and Material Sciences, Heilongjiang University, Harbin 150080, P. R. China

²State Key Laboratory of Chemical Resource Engineering; Beijing University of Chemical Technology, Beijing 100029, P. R. China

Abstract A series of immobilized protic ionic liquids were prepared and used as catalysts for chemical fixation of carbon dioxide with epoxide to form cyclic carbonate. The effects of reaction temperature, carbon dioxide pressure and the loading of immobilized ionic liquid on the synthesis of cyclic carbonate from carbon dioxide and epoxide were investigated. Under the optimized reaction conditions, PS-ImHI showed the highest catalytic activity, and propylene carbonate was yield to 98.1% with more than 99% of selectivity. In the coupling reaction of carbon dioxide and epoxide, the immobilized ionic liquids showed high stability and could be reused ten times and used in a continuous flow reaction with a fixed-bed reactor for more than 120 h without loss of catalytic activity.

Key words: Immobilized protic ionic liquids, Epoxides, Carbon dioxide, Cyclic carbonate

* Corresponding author: Tel./Fax.: +86(451)86609227; E-mail: xiaolf@hlju.edu.cn; wuwei@hlju.edu.cn

1 Introduction

Carbon dioxide is one of the most significant greenhouse gases which caused the global warming and climate change. Also, it is an easily available, naturally abundant, recyclable as well as a non-toxic, non-flammable and inexpensive C1 resource [1-6]. As a result, the efficient transformation of CO₂ into useful chemicals is an important contribution from the viewpoint of environmental protection and resource utilization [7-10]. The reaction of carbon dioxide with epoxide to form the five-membered cyclic carbonates has been extensively studied[11]. Cyclic carbonates can be used for various purposes [12,13], such as for aprotic polar solvents, electrolytes for batteries, precursors for producing polycarbonates, and intermediates in the synthesis of pharmaceuticals and fine chemicals.

In the past decades, the various homogeneous catalysts have been developed for chemical fixation of carbon dioxide to form cyclic carbonates [14-16], such as alkali metal salts [17,18], transition metal complexes [19-22], metal organic frameworks [23-26], organic bases[27,28], N-heterocyclic carbene [29], quaternary ammonium salts [30-33], quaternary phosphonium salts [34,35], organocatalyst [36,37], and ionic liquids [38-43]. Most of them are efficient for cycloaddition of carbon dioxide and epoxide, but the cost is high for product separation and/or catalyst fabrication. In terms of catalyst stability and separation of catalyst, heterogeneous catalysts are superior to the homogeneous ones[44]. Metal oxides[45], modified molecular sieves[46,47], ion-exchange resins[48,49], nanoparticles[50-52], Nitrogen-doped porous carbon monolith [53], poly(ionic liquid)[54,55], microporous organic polymers [56,57] and supported catalysts[58-64] were used to catalyzing synthesis of cyclic carbonate from epoxide and carbon

dioxide. However, their application is limited due to low activity, rigorous reaction conditions, unsatisfactory stability, and/or poor reusability.

Divinylbenzene cross-linked polystyrene (PS) was widely used as a heterogeneous catalyst support due to its compatibility with a wide range of reaction conditions, simple preparation, recyclability, environmental stability, low cost, and nonsolubility in commonly organic solvents and water. In the previous works, we found the basic ionic liquid supported on PS showed highly catalytic activity [65] in the hydrolysis of propylene carbonate to form 1,2-propylene glycol. In 2009, polystyrene resin-supported hydroxyl-functionalized ionic liquids were prepared by Sun et al. and used as catalysts in the cycloaddition of carbon dioxide and epoxide [66]. Park and co-workers described the application of a series of polystyrene-supported quaternized ammonium salts as catalysts in the synthesis of cyclic carbonates from epoxides and CO₂[67]. These catalysts showed the higher catalytic activity in the synthesis of cyclic carbonate from carbon dioxide and epoxide, but their reusability was not satisfactory.

Recently, we found protic ionic liquid demonstrated high activity and excellent selectivity in the cycloaddition of CO₂ to epoxides [68]. In contrast to other ionic liquids, protic ionic liquids have a number of unique properties, just as low cost, easy preparation and a variable proton activity. To overcome the problem of separating protic ionic liquid from the reaction mixture, we highlight the use of PS as a support and develop the polymer-supported protic ionic liquid for the synthesis of cyclic carbonate (Scheme 1). In this manuscript, various immobilized protic ionic liquids on the PS were synthesized and their catalytic performances in cycloaddition of CO₂ to epoxides were investigated in detail. In addition, the effects of reaction parameters and the reusability of polymer-supported protic ionic liquid were also studied.

Scheme 1 Synthesis of cyclic carbonate from epoxide and carbon dioxide

2 Experimental

2.1 Preparation of immobilized protic ionic liquids

The immobilized protic ionic liquid can be easily synthesized by the following method: a mixture of highly cross-linked chloromethylated polystyrene (PS-Cl) (6 g, chlorine content 30 mmol) and imidazole (2.037 g, 30 mmol) in toluene were added into a 100 mL round-bottomed flask. The mixture was refluxed under stirring for overnight. After cooled down to room temperature, the solid residue was collected by filtration and washed separately with anhydrous ethanol and water. Then, the solid was dried under vacuum at 60 °C for 12 h to give polystyrene immobilized imidazole (PS-Im). Next, the immobilized imidazole (PS-Im) was put into the mixture of deionized water and excessive amounts of hydrochloric acid. The mixture was performed at room temperature and stirred for 12 h. After the reaction, the mixture was filtered and washed until the pH value was 7. Then, the residue was dried under vacuum at 30 °C for 10 h, the immobilized imidazolium hydrochloride on PS (PS-ImHCl) was obtained (Scheme 2).

Scheme 2 Synthesis of protic ionic liquids on the PS

A series of other immobilized protic ionic liquids, such as immobilized imidazolium hydrobromide (PS-ImHBr), immobilized imidazolium hydroiodide (PS-ImHI) and immobilized imidazolium tetrafluoroborate (PS-ImHBF₄) were prepared following the same method (Scheme 2).

2.2 Characterization of immobilized protic ionic liquids

The loading of protic ionic liquids on the PS was determined by elemental analysis. The FT-IR spectrum was recorded using a PerkinElmer spectrum 100 spectrometer in KBr pellet form. Scanning electron microscopic (SEM) observations were carried out over an S-4800 scanning electron microscope. NMR measurements were performed at room temperature on a Bruker Avance III 400 MHz spectrometer. For solid-state NMR for the observation of ^{13}C resonances, cross-polarization magic angle spinning (CPMAS) at 10 kHz was selected to record carbon spectra.

2.3 Procedure for the synthesis of propylene carbonate

The synthesis of propylene carbonate through the cycloaddition of CO_2 to propylene oxide was chosen as a model reaction to evaluate the catalytic activity of the immobilized protic ionic liquids.

The cycloaddition reactions were carried out in a 50 mL stainless steel autoclave with an electric heater and a magnetic stirrer. For a typical process: the reactor vessel was charged with propylene oxide (5.0 mL, 71.5 mmol) and supported protic ionic liquid (0.5 mmol). The reactor was placed under a desired pressure of carbon dioxide and heated to a designated temperature for a designated period of time. The reactor was cooled in an ice-water bath and released the remaining CO_2 . The resulting mixture was analyzed using a GC (Agilent 7820) that was equipped with a flame ionization detector (FID) and the products were identified by GC-MS (Agilent 6890-5973N).

3 Results and discussion

3.1. Characterization of the catalysts

The PS grafted by protic ionic liquids with different anions (Cl^- , Br^- , I^- and BF_4^-) were

prepared and their loading were determined by elemental analysis (EA), and the results were shown in Table S1. The result of PS-ImHI indicated that there were 4.0 mmol/g of N element in the catalyst, demonstrating 2.0 mmol/g of ionic liquid were immobilized on the PS. And the fixing amount of PS-ImHBF₄, PS-ImHCl and PS-ImHBr were 1.7 mmol/g, 1.9 mmol/g and 2.0 mmol/g, respectively.

To make sure immobilizing the protic ionic liquids on polystyrene resin successfully, PS, PS-Im and PS-ImHX (X=Cl, Br, I) were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and the results were shown in Fig. 1. For the PS, the distinguishing band at 1265 and 670 cm⁻¹ was owing to the C-Cl bonds on which the catalyst was supported. When the imidazole was supported on the PS, these peaks were disappeared and the characteristic peaks of imidazole around 1624 and 1556 cm⁻¹ could be clearly observed, which were ascribed to C=C and C=N stretching vibrations of the imidazole ring. Furthermore, compared to the immobilized imidazole, absorption peak of C=C and C=N of imidazolium ring in supported imidazolium hydrohalide exhibit blue shift. All of the above mentioned IR bands were found in the process for synthesis of supported ionic liquids, confirming the immobilization of the ionic liquid on the surface of the PS.

Fig. 1 FT-IR spectrum of PS-Cl, PS-Im and PS-ImHX (X=Cl, Br, I)

The structures of PS-ImHI were well represented by ¹³C solid-state NMR spectra, as shown in Fig. S1. PS-ImHI: δ /ppm = 38.4 (aliphatic polystyrene skeleton), 51.6 (C3), 121.6 (C2, C2'), 127.0 (aromatic polystyrene skeleton), 133.7 (C1), 143.8 (aromatic poly-styrene skeleton). According to the literature [69,70], all the peaks of ¹³C MAS NMR were assigned. And ¹³C MAS

NMR was coincide with the results of FT-IR and elemental analysis and in fair agreement with the structures of the target product as shown in Scheme 2.

SEM reflected the morphology and surface shape of PS-Im and PS-ImHI, and SEM images of PS and PS-ImHI were studied. As shown in Fig. 2 a and b, the surface of PS-Im is smooth. With the grafting of ionic liquid on the material, there is clear roughening of surface (Fig. 2 c and d), and it suggested ionic liquid was immobilized on the PS [71].

Fig. 2 SEM images of (a, b) PS-Im and (c, d) PS-ImHI

3.2 Catalytic performance of immobilized protic ionic liquids

The various of immobilized protic ionic liquids on PS was evaluated as catalysts for the synthesis of cyclic carbonates *via* the reaction of epoxides with carbon dioxide under solvent-free and metal-free conditions.

From the results in Table 1, it can be seen that the support PS-Cl shows no catalytic activity for the synthesis of propylene carbonate from propylene oxide and carbon dioxide (Table 1, entry 1). The catalytic activity of the immobilized protic ionic liquids depends strongly on its anion. When PS-ImHCl was used as a catalyst, the propylene carbonate was yield to 62.1% (Table 1, entry 3). But, nearly no product was detected over the PS-ImBF₄ (Table 1, entry 2), it was due to the very weak nucleophilicity of BF₄⁻ in this process. When using the Br⁻ and I⁻ with stronger nucleophilicity [40,43], the yield of propylene was increased, and the propylene carbonate was yield to 77.1% in the presence of PS-ImHI (Table 1, entry 5). These results were corresponded to the increasing nucleophilicity and leaving ability of the halide anion: Cl⁻ < Br⁻ < I⁻. According to the mechanism proposed in previous works [66,67], the nucleophilic attack of the halide anion on the

epoxide ring is the rate-determining step, and its leaving ability in the ring-closing step is very important for the five-membered cyclic carbonate synthesis. In 2009, Sun et al. found PS supported 1-(2-hydroxyl-ethyl)-imidazolium-based ionic liquids showed the high catalytic activity in the synthesis of propylene carbonate from carbon dioxide and propylene oxide [66], and the propylene carbonate was yield to 98% with using 1.6 mmol% PS supported 1-(2-hydroxyl-ethyl)-imidazolium iodide as a catalyst when the reaction was carried out for 4h under 120 °C and 2.5MPa. He et al. reported the 99.2% propylene carbonate was given when the 5 mmol% Insoluble Ion Exchange Resin D201 was used as a catalyst under the 8.0 MPa pressure for 24h [72]. More recently, Yin et al. found that the about 95% yield of propylene carbonate was obtained over 1.2 mmol% polymer-supported quaternary ammonium salts under 150 °C for 5h [73]. Compare to these above method, the propylene carbonated was yield to 98.2% with employing PS-ImHI as a catalyst (Table 1, entry 6) under the relatively mild reaction conditions.

Table 1 Catalytic performances of supported protic ionic liquid

3.3 Influence of reaction parameters

Firstly, the effects of the catalyst concentration on the cycloaddition of carbon dioxide and propylene were investigated in the presence of PS-ImHI at 140°C and 2.0 MPa of total pressure and the results were shown in Fig.3. The results in Fig.3 were indicated that the yield of propylene carbonate was increased with increasing the concentration of immobilized protic ionic liquid. When the 0.4 mmol PS-ImHI was used as a catalyst, the propylene carbonate was yield to 65.7%; and the loading of PS-ImHI was increased to 1.0 mmol, the yield of propylene carbonate was achieved 95.5%, and further improve the amount of catalyst to 1.6 mmol, the yield of propylene

carbonate was approached 97.7%. As a consequence, using 1.0 mmol PS-ImHI as a catalyst was optimal in the synthesis of propylene carbonate from carbon dioxide and propylene oxide.

Fig. 3 the effect of amount of catalyst on the synthesis of propylene carbonate

The influence of reaction temperature was then investigated when the 1.0 mmol PS-IMHI was used as a catalyst, and the results were shown in Fig.4. From Fig. 4, it was observed that the yield of propylene carbonate was increased with increasing the reaction temperature. When the reaction temperature was 110°C, the propylene carbonate was yield to 78.7%, and the yield of propylene carbonate was increased to 95.5% with increasing the reaction temperature to 140°C. Further rising reaction temperature to 150°C would cause only a slight increase of propylene carbonate's yield. Therefore, the optimal reaction temperature was 140 °C in the presence of PS-ImHI.

Fig. 4 the effect of reaction temperature on the synthesis of propylene carbonate

The effect of CO₂ pressure was also studied for the reaction and the results showed that the pressure had a great impact on the yield of cyclic carbonate (Fig. 5). The yield of propylene carbonate was increased with increasing the reaction pressure in the ranking up to 2.5 MPa and further increase of the pressure causes a decline in the yield of propylene carbonate. Such an effect of pressure on the reaction has also been observed in other catalytic systems [39,65,66]. Based on these reports, it could be explained that propylene carbonate was in its liquid form under the adopted reaction conditions. A high pressure mainly caused by CO₂ would reduce propylene oxide conversion because a lowered propylene oxide concentration in the vicinity of the catalyst was not

favorable to the reaction since propylene oxide was also a reactant [39].

Fig. 5 the effects of reaction pressure on the synthesis of propylene carbonate

The influence of reaction time on the synthesis of propylene carbonate was given in Fig. 6. From Fig. 6, it can be seen that the yield of propylene carbonate was increased rapidly within the first 3.0 h, and almost quantitative yield could be achieved with >99 % selectivity. When another two hours were employed to synthesize of propylene carbonate, only a slight rising on the yield of propylene carbonate was observed. It was to say that PS-ImHI could be an effective catalyst for converting CO₂ into cyclic carbonate in 3.0 h.

Fig. 6 the effect of reaction time on the synthesis of propylene carbonate

3.4 Cycloaddition reactions with various epoxides

In order to study the efficiency and general applicability of the catalyst PS-ImHI, the cycloaddition of CO₂ with various epoxides under optimized reaction conditions was carried out and the results were listed in Table 2. It can be seen that this catalyst was efficient for the mono-substituted terminal epoxides and all reactions preceded smoothly providing appreciable yield of desired product (Table 2, entries 1-3). In general, the styrene oxide **1d** was a phenyl-substituted epoxide and its conversion to styrene carbonate **2d** was low compared with that of **1a**, and it was because a planar conformation allows the aromatic ring to stabilize the charge in the coordinated alkoxide and the inductive effect of the phenyl group is responsible for stabilization of the charge in the transition state describing the ring-closing step [20,37] (Table 2, entry 4). Additionally, we also examined the cyclohexene oxide **1e** was used as substrate in this

coupling process. Because the higher hindrance created from the two rings of **1e**, which obstructed the nucleophilic attack of I^- and caused the decrease of ring-opening rate, the corresponding cyclic carbonate **2e** was yield to 66.0% when the reaction time was prolonged to 24 h (Table 2, entry 5).

Table 2 Cycloaddition reactions with various epoxides

3.5 Catalyst recycling

In addition to the catalytic activity, recyclability is also a very important criterion to evaluate a heterogeneous catalyst. Regarding this issue, a set of reusing experiments were carried out under the optimal conditions and the corresponding catalytic results were listed in Fig. S2. Herein, the catalyst was separated from the reaction mixture by filtration and then used for the next run directly without any disposed. In each run, the propylene carbonate selectivity remained constant (>99%), and propylene carbonate yield changed only slightly after ten runs. The results indicate that PS-ImHI exhibits excellent reusability and stability for repetitive use in the cycloaddition reaction of carbon dioxide and epoxide.

Moreover, we characterized the recovered catalyst by FT-IR (Fig. S3). Compared to the fresh one, the similar FT-IR spectra was obtain when the recovered catalyst was characterized by FT-IR. And it can be deduced that this catalyst has excellent reusability and stability for the cycloaddition reaction of carbon dioxide and propylene oxide.

In order to further evaluate the catalytic stability of PS-ImHI, the cycloaddition of carbon dioxide and epichlorohydrin was performed in a high-pressure fixed-bed continuous-flow reactor, which was operated in the up-flow mode. The reactor consisted of stainless steel tubes, which were loaded with catalyst PS-ImHI. A mixture of epichlorohydrin and CO_2 , which was continuously introduced into the reactor with a pump, passed through the catalyst bed and the

backpressure regulator. The liquid products were collected and analyzed by GC with FID detector.

TOF was calculated as the moles of propylene carbonate per molar imidazolium-halide moieties

per hour. The reaction conditions were 1.5 g of catalyst, the flow rate of epichlorohydrin was 0.02

mL/min (WHSV=0.95h⁻¹), while the CO₂ had a flow rate of 50 mL/min, and the temperature was

gradually increased and maintained at 140 °C at the total pressure of 2.5 MPa. Due to the

instability of instrument, the catalyst showed low activity between 20 h and 40 h, but when the

reaction was continuous after 40h, the catalyst showed stability activity in the reaction. From Fig.7,

it can be seen that the yield of epichlorohydrin carbonate was greater than 90% for more than 120

h, and this results indicated PS-ImHI shown excellent stability in the coupling reaction of carbon

dioxide and epoxide.

Fig. 7 Epichlorohydrin carbonate yield during a continuous flow reaction with a fixed-bed reactor

3.6 Possible mechanism

Based on previous literatures [11,20,37,66,67] and the results of this study, a reasonable catalytic cycle was supposed for the coupling reaction from CO₂ and propylene oxide over the PS-ImHI catalyst (Scheme 3). First, through hydrogen bond, the coordination of proton with oxygen atom of propylene oxide resulted in polarization of the epoxide C-O bonds and forming an active epoxide (I), and then, nucleophilic attack of I⁻ on the less hindered β-carbon atom of the coordinated propylene oxide furnished the ring-opened intermediate (II). Then, the oxygen anion of (II) interacted with the CO₂ that lead to the insertion of CO₂ into the halohydrin, and an alkyl carbonate anion (III) was formed. Finally, the intermediate (III) further converted to the corresponding cyclic carbonate through intramolecular ring closing. In meantime, the catalyst was

regenerated. During the entire process of reaction, the proton on the supported protic ionic liquids was proposed to involve initial activation of propylene oxide and stabilization of the intermediate (II) and (III) formed during the reaction.

Scheme 3 A possible mechanisms for the synthesis of cyclic carbonate over the PS-ImHI

4 Conclusions

The immobilized protic ionic liquids on the PS were prepared and characterized by FT-IR, element analysis, SEM and solid-state NMR. In the cycloaddition reaction of carbon dioxide and epoxide to form cyclic carbonate, the immobilized protic ionic liquid showed highly catalytic activity and stability. Investigations of the effects of the supported protic ionic liquid revealed that supported protic ionic liquid bearing a more nucleophilic anion exhibited higher activity. It was also found that reaction parameters play important roles in determining the catalytic performance of PS-supported protic ionic liquid catalysts. The synergistic effects of cation and anion in supported protic ionic liquids were the key factors in the synthesis of cyclic carbonate from carbon dioxide and epoxides. When the PS-ImHI was employed as a catalyst, the propylene was yield to 98.1% with >99% selectivity under the optimal reaction conditions and its catalytic activity didn't have an obvious decrease after cycle using for 10 times. When the coupling reaction was performed in a high-pressure fixed-bed continuous-flow reactor, the yield of epichlorohydrin carbonate was greater than 90% for more than 120 h.

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Table 1 Catalytic performances of supported protic ionic liquid ^a

Entry	ILs	Selectivity (%)	Yield ^c (%)	TON ^d
1	PS-Cl	-	-	-
2	PS-ImHBF ₄	>99	9.3	13
3	PS-ImHCl	>99	62.1	89
4	PS-ImHBr	>99	64.0	92
5	PS-ImHI	>99	77.1	110
6 ^b	PS-ImHI	>99	98.1	70

^a Reaction conditions : propylene oxide 71.5 mmol, catalyst 0.50 mmol, reaction temperature 140 °C, CO₂ pressure 2.0 MPa, reaction time 2.0 h;

^b Catalyst 1.0 mmol, reaction temperature 140 °C, CO₂ pressure 2.5 MPa, reaction time 3.0 h;

^c Isolated yield;

^d TON is calculated as the molar ratio of product to the supported imidazolium site.

Table 2 Cycloaddition reactions with various epoxides ^a

Entry	Substrate	Product	Selectivity %	Yield %	TON ^c
1	1a	2a	>99	98.1	70
2	1b	2b	>99	89.6	64
3	1c	2c	>99	94.4	67
4	1d	2d	>99	70.6	50
5 ^b	1e	2e	>99	66.0	47

^a Reaction conditions: epoxide 71.5 mmol, **PS-ImHI** 1.00 mmol g, reaction pressure 2.5 MPa, reaction temperature 140 °C, reaction time 3.0 h;

^b Reaction time 24.0 h;

^c TON is calculated as the molar ratio of product to the supported imidazolium site.