



Efficient synthesis of styrene carbonate from CO₂ and styrene oxide using zinc catalysts immobilized on soluble imidazolium–styrene copolymers

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ABSTRACT

Preparation of zinc catalysts (Zn/PS-IL[X], X = Br⁻, Cl⁻, BF₄⁻, and PF₆⁻) supported on imidazolium–styrene copolymers, as well as their catalytic use for the solvent-free synthesis of styrene carbonate from CO₂ and styrene oxide, are described. Among the catalysts examined, Zn/PS-IL[Br] was proved to be the most efficient. When used in a homogeneous system during the reaction process, Zn/PS-IL[Br] gave a 97.5% yield of product with a TOF value that can be up to about 3800 h⁻¹. Due to its immiscibility with ethanol, Zn/PS-IL[Br] can be separated like a heterogeneous catalyst through solvent precipitation, and reused at least three times for the reaction without significant loss of activity.

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1. Introduction

Development of an efficient process for chemical fixation of CO₂ has recently drawn much attention. CO₂ is not only a greenhouse gas but can also be used as an abundant and non-toxic building block for organic reactions. Direct fixation of CO₂ by coupling reaction with epoxide to synthesize cyclic carbonate is one of the most promising routes [1]. Despite extensive studies on this reaction, new investigations are still in progress [2].

Styrene oxide, in comparison with other epoxides such as propylene oxide and ethylene oxide, is more difficult to convert to styrene carbonate due to its less reactive β-carbon atom. This necessitates a long reaction time and high reaction temperature for CO₂ cycloaddition with styrene oxide. Homogeneous and heterogeneous catalyst systems have been reported for this reaction [3]. In general, heterogeneous catalyst systems such as MgO (Temp.: 150 °C, CO₂: 8 MPa, Time: 15 h, TOF: 0.02 h⁻¹) [3a], Bu₄NBr/SiO₂ (Temp.: 150 °C, CO₂: 8 MPa, Time: 8 h, TOF: 12 h⁻¹) [3b] and Et₄NBr/zeolite (Temp.: 120 °C, CO₂: 0.7 MPa, Time: 8 h, TOF: 10 h⁻¹) [3c] were favorable for product separation, but they suffered from a relatively low activity for the reaction. Very low turnover frequencies (TOFs) were observed for heterogeneous catalysts to achieve a satisfactory yield of product. Homogeneous catalyst systems such

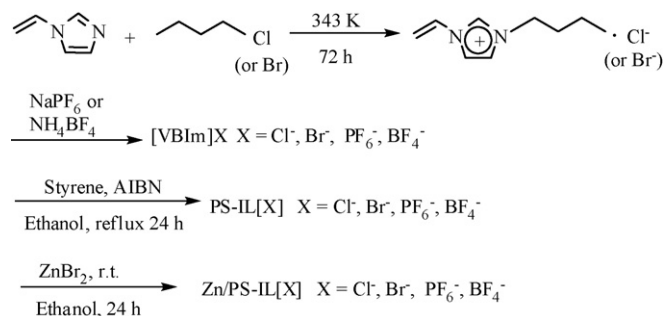
as Ni(PPh₃)Cl₂/PPh₃/Zn/Bu₄NBr (Temp.: 120 °C, CO₂: 2.5 MPa, Time: 1 h, TOF: 2066 h⁻¹) [3d] and ZnBr₂/Bu₄Ni (Temp.: 80 °C, CO₂: 8 MPa, Time: 0.5 h, TOF: 646 h⁻¹) [3e] can afford a much better performance for the reaction. However, one of the major weaknesses of homogeneous catalyst systems was that separating products from catalysts was difficult, particularly when the high boiling point of styrene carbonate is considered.

The use of soluble polymer-supported catalysts in chemical reactions has emerged as a promising and viable approach for synthetic chemistry due to the phase-selective solubility of polymer-supported catalysts, which can remarkably facilitate product separation and catalyst recovery [4]. We recently reported the synthesis of ionic liquid-based polymers by copolymerization of ionic liquid, i.e., 1-vinyl-3-butylimidazolium chloride, with styrene, and their use as novel polymer supports to immobilize noble metal catalysts such as Pd nanoparticles [5].

We report herein that ZnBr₂ can also be efficiently immobilized on imidazolium–styrene copolymers that were prepared by copolymerization of 1-vinyl-3-butylimidazolium-based ionic liquids with styrene, and that the resulting supported zinc catalysts (Zn/PS-IL[X], X = Br⁻, Cl⁻, BF₄⁻, and PF₆⁻) were proved to be a type of novel soluble polymer-supported catalyst for the solvent-free synthesis of styrene carbonates from CO₂ and styrene oxide. That is, they can be used as a homogeneous catalyst during the reaction process, and can be separated like a heterogeneous catalyst through solvent precipitation. Among the catalysts investigated, Zn/PS-IL[Br] was the most efficient, which can offer a 97.5% product yield with a TOF value that can be up to about 3800 h⁻¹. Zn/PS-IL[Br] can be separated through solvent precipitation due to its immiscibility with

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Scheme 1. Preparation of IL-styrene copolymers and zinc catalysts supported thereon.

ethanol, and reused at least three times for the reaction without significant loss of activity.

2. Experimental

2.1. Synthesis of 1-vinyl-3-butyylimidazolium-based ionic liquids

Preparation of 1-vinyl-3-butyylimidazolium-based ionic liquid, imidazolium–styrene copolymers and the copolymer-supported zinc catalysts are shown in Scheme 1. According to the previously reported method [5], 1-vinyl-3-butyylimidazolium chloride (denoted as [VBIm]Cl) was first synthesized by the reaction of butyl chloride (1.2 mol equivalent) with 1-vinylimidazole at 70 °C for 48 h under an atmosphere of N₂. [VBIm]Cl was recovered as a pale yellow liquid after washing thrice with ethyl acetate and dried *in vacuo* at 70 °C. 1-Vinyl-3-butyylimidazolium bromide (denoted as [VBIm]Br) was synthesized in a similar way except that the reaction was carried out at room temperature for 72 h.

To prepare 1-vinyl-3-butyylimidazolium tetrafluoroborate (denoted as [VBIm]BF₄), NH₄BF₄ (1.2 mol equivalent) was added to a [VBIm]Cl aqueous solution, and the mixture was stirred at room temperature for 3 days. [VBIm]BF₄ was separated by CH₂Cl₂ extraction and washed thrice with distilled water. CH₂Cl₂ was removed under reduced pressure and the product was recovered as a yellow liquid after drying *in vacuo* at room temperature.

To prepare 1-vinyl-3-butyylimidazolium hexafluorophosphate (denoted as [VBIm]PF₆), NaPF₆ (1.2 mol equivalent) was added slowly to an aqueous solution of [VBIm]Cl at room temperature. Mixture was stirred for 1 day at room temperature. [VBIm]PF₆ was separated with a separating funnel and washed thrice with water. It was dried *in vacuo* at room temperature to offer the final product as a viscous yellow liquid.

2.2. Preparations of imidazolium–styrene copolymers

In a typical preparation of an imidazolium–styrene copolymer, styrene (1 mmol, purified by distillation before use) and ionic liquid (0.1 equiv.) were added to a 40-mL ethanol solution in a 100-mL round-bottom flask. After the reaction mixture was degassed using a thaw-and-melt method three times, AIBN (0.05 equiv. of double bond) was added. Reaction was allowed to proceed under reflux condition and an atmosphere of N₂ for 24 h. At the end of the reaction, the flask was cooled to room temperature. A white precipitate appeared at the bottom of the flask, which was separated by filtration and washed thrice with ethanol. After drying *in vacuo* at room temperature to remove solvent, the precipitate was ground with a mortar and pestle to afford the imidazolium–styrene copolymer denoted by PS-IL[X] (X = Cl[−], Br[−], BF₄[−], and PF₆[−]) in the form of white powder. This was further washed with ethanol to remove unbound ionic liquid, and dried *in vacuo* at room temperature.

2.3. Immobilization of ZnBr₂ on imidazolium–styrene copolymers

To immobilize ZnBr₂ on the imidazolium–styrene copolymer, ethanol (10 mL), the imidazolium–styrene copolymer (1.0 g) and ZnBr₂ (2 mmol) were added to a 50-mL round-bottom flask, and the mixture was stirred at room temperature for 24 h. The solid was recovered by filtration, washed with ethanol and methanol, and dried *in vacuo* at room temperature. The imidazolium–styrene copolymer-supported zinc catalysts were denoted by Zn/PS-IL[X] (X = Cl[−], Br[−], BF₄[−], and PF₆[−]).

2.4. Immobilization of ZnBr₂ on ionic liquid-modified silica gel

For comparison, an analogous silica gel-supported zinc catalyst, denoted as Zn/SiO₂-IL[Cl], was also prepared by immobilization of ZnBr₂ on silica gel that was modified by a chloride-containing ionic liquid, i.e., *N*-3-(3-triethoxysilylpropyl)-3-methylimidazolium chloride, using a similar method reported previously [6].

2.5. Reaction and analysis

In a typical experiment, styrene oxide (2 mmol) and a certain amount of catalyst were charged successively into a 15-mL glass reactor (Fig. 4) to give a homogeneous solution. The glass reactor was mounted in a self-made autoclave equipped with a magnetic stirrer. CO₂ of the desired pressure was introduced through a plunger pump, and the reaction was allowed to proceed at 80–140 °C. At the end of the reaction, the reactor was cooled to room temperature. The reaction mixture in the glass reactor was a white solid. Ten milliliters of ethanol was added into the glass reactor, resulting in the formation of a suspension due to the immiscibility of Zn/PS-IL[X] (X = Cl[−], BF₄[−], and PF₆[−]) with ethanol. After centrifugation of the suspension at 12,000 rpm for 10 min, the catalyst was precipitated and a clear ethanol solution obtained. The ethanol phase was analyzed by a gas chromatograph equipped with a flame ionization detector using toluene as internal standard (Shimadzu DC-2014, ULBON HR-52 capillary column 25 mm × 0.32 mm). The recovered catalyst was dried *in vacuo* at room temperature and reused as described above.

3. Results and discussion

3.1. Characterization of imidazolium–styrene copolymers and their supported zinc catalysts

PS-IL[X] and Zn/PS-IL[X] (X = Cl[−], BF₄[−], and PF₆[−]) were characterized by inductively coupled plasma (ICP), gel permeation chromatography (GPC) and elemental analysis (Table 1). Depending on the ionic liquid used (particularly the anion part of the ionic liquid), the amounts of ionic liquid in the resulting copolymers PS-IL[Cl], PS-IL[Br], PS-IL[BF₄] and PS-IL[PF₆] were 0.46, 0.47, 0.59 and 0.76 mmol/g, respectively, approximately in the order Cl[−] = Br[−] < BF₄[−] < PF₆[−]. ICP analysis revealed a slightly different order regarding the loading amount of zinc on the imidazolium–styrene copolymers. PS-IL[Cl] gave a higher loading amount of zinc than PS-IL[Br] and PS-IL[BF₄], whereas PS-IL[PF₆]

Table 1
Characterization of supported zinc catalysts.

Catalyst	IL (mmol/g)	Zn (10 ³ mmol/g)	Mw	Mn
Zn/PS-IL[Br]	0.47	1.6	4138	3365
Zn/PS-IL[Cl]	0.46	6.5	4177	3424
Zn/PS-IL[BF ₄]	0.59	3.2	3688	3148
Zn/PS-IL[PF ₆]	0.76	21.7	4083	3786
Zn/SiO ₂ -IL[Cl]	0.81	260	–	–

Table 2
CO₂ cycloaddition with styrene oxide catalyzed by various zinc catalysts.^a

Run	Catalyst	Yield (%)	TOF (h ⁻¹)
1	Zn/PS-IL[Br]	97.5	3808
2	Zn/PS-IL[Cl]	35.0	1367
3	Zn/PS-IL[BF ₄]	19.5	761
4	Zn/PS-IL[PF ₆]	<1	–
5	Zn/[VMIm]Br	86.3	3363
6	Zn/[VBIm]Cl	27.1	846
7	Zn/SiO ₂ -IL[Cl]	10.6	413

^a Reaction conditions: CO₂: 3 MPa, styrene oxide: 2 mmol, temp.: 120 °C, time: 8 h. Zn: 6.4 × 10⁻⁵ mmol.

had the highest one. With regard to the molecular weight of imidazolium–styrene copolymers, GPC analysis revealed a relatively similar distribution of M_w and M_n . The former was about 4000, the latter about 3400. Dialkylimidazolium zinc tetrahalide complex can be formed from imidazolium halides and zinc halides, and therefore a much higher loading amount of zinc was observed in Zn/SiO₂-IL[Cl] [7].

3.2. CO₂ coupling reaction with styrene oxide catalyzed by supported zinc catalysts

Catalytic performance of zinc catalysts for CO₂ cycloaddition with styrene oxide were investigated at 120 °C under a CO₂ pressure of 3 MPa (Table 2). Product yields largely depended on the catalyst type, particularly the anionic part of the ionic liquid in the copolymers, when polymer-supported zinc catalysts were used. The best result was achieved by using Zn/PS-IL[Br], which gave a TOF as high as about 3800 h⁻¹ with a product yield of 97.5% (run 1). Zn/PS-IL[Cl] showed a product yield of only 35.0%, which corresponded approximately to a TOF of 1300 h⁻¹ (run 2). The nucleophilicity of anion may play an important role in the reaction of CO₂ cycloaddition with epoxide in ionic liquids [8]. The observed better catalytic performance of Zn/PS-IL[Br] over Zn/PS-IL[Cl] could possibly be attributed to the stronger nucleophilicity of Br⁻ than that of Cl⁻ under the reaction condition.

Ionic liquids containing BF₄⁻ and PF₆⁻ are known for their inferior performances when used as reaction medium in the ZnBr₂-catalyzed CO₂ cycloaddition with styrene oxide [8]. When Zn/PS-IL[BF₄] was employed, lower yield of product (19.5%) and TOF (about 700 h⁻¹) were observed as expected (run 3). Zn/PS-IL[PF₆] gave a product yield of <1% (run 4).

For comparison, CO₂ cycloaddition with styrene oxide was also carried out by using the homogeneous catalysts ZnBr₂/[VMIm]Br and ZnBr₂/[VBIm]Cl as well as the heterogeneous catalyst Zn/SiO₂-IL[Cl]. Zn/SiO₂-IL[Cl] could be roughly viewed as a silica gel analog of Zn/PS-IL[Cl]. As can be seen, ZnBr₂/[VMIm]Br gave a product yield of 86.3% and a TOF of about 3300 h⁻¹, which was in the same performance range as other homogeneous catalysts for the reaction, such as ZnCl₂/[BMIm]Br (run 5) [3g]. Again, a lower yield of product of 27.1% was obtained in the Cl⁻-containing ionic liquid [VBIm]Cl due to the weaker nucleophilicity of Cl⁻ than that of Br⁻ (run 6). A product yield of 10.6% was observed for Zn/SiO₂-IL[Cl] (run 7). On the basis of the above results, it can be concluded that the use of imidazolium–styrene copolymer as organic support to immobilize ZnBr₂ can greatly enhance the catalytic performance of the ZnBr₂/ionic liquid system for the CO₂ cycloaddition with styrene oxide, offering much higher activity than the silica gel-supported analog (and even the homogeneous counterpart). This may result from the increase in the interfacial area between the catalyst and the substrate. Similar results were observed in our previous study when an imidazolium–styrene copolymer-supported Pd catalyst was used for hydroesterification and hydrogenation reactions [5].

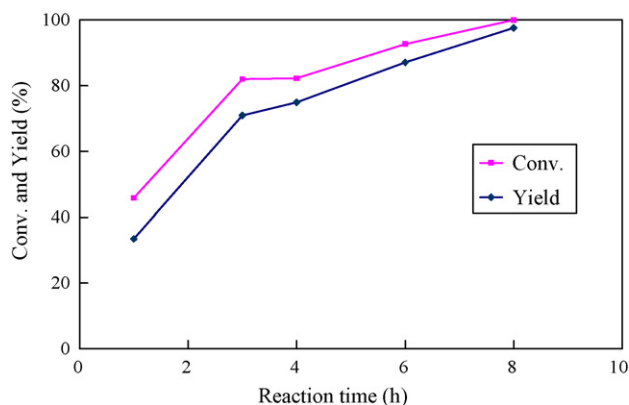


Fig. 1. Effect of reaction time on CO₂ cycloaddition with styrene oxide (Cat.: Zn/PS-IL[Br], Zn: 6.4 × 10⁻⁵ mmol, CO₂: 3 MPa, styrene oxide: 2 mmol, temp.: 120 °C).

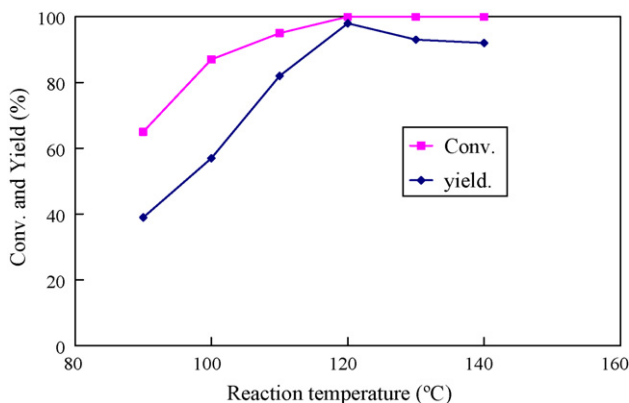


Fig. 2. Effect of reaction temperature on CO₂ cycloaddition with styrene oxide (Cat.: Zn/PS-IL[Br], Zn: 6.4 × 10⁻⁵ mmol, CO₂: 3 MPa, styrene oxide: 2 mmol, time: 8 h).

3.3. Effects of reaction time and temperature on CO₂ cycloaddition with styrene oxide catalyzed by Zn/PS-IL[Br]

The effects of time and temperature on the reaction were then investigated in view of the fact that Zn/PS-IL[Br] could offer a high yield of product for the CO₂ cycloaddition with styrene oxide (Figs. 1 and 2).

A relatively long reaction time was needed to achieve a high yield of styrene carbonate (Fig. 1). When the reaction was carried out at 120 °C at a CO₂ pressure of 3 MPa using 2 mmol styrene oxide and 6.4 × 10⁻⁵ mmol Zn/PS-IL[Br], it took 8 h to complete the reaction, resulting in a product yield of 98%. Increasing reaction temperature

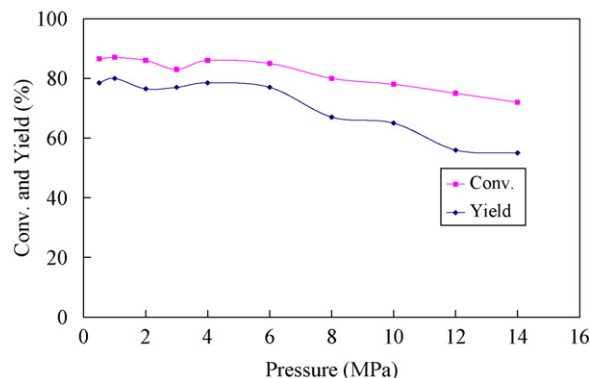


Fig. 3. Effect of CO₂ pressure on CO₂ cycloaddition with styrene oxide (Cat.: Zn/PS-IL[Br], Zn: 6.4 × 10⁻⁵ mmol, time: 4 h, styrene oxide: 2 mmol, temp.: 120 °C).

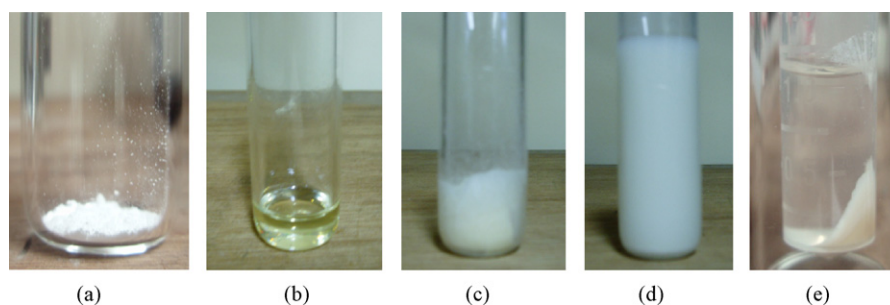


Fig. 4. Phase changes of reaction system at different reaction stages (a: Zn/PS-IL[Br], b: before reaction, c: after reaction, d: addition of ethanol, e: after centrifugation).

greatly enhanced the product selectivity, and the highest yield of product was achieved at 120 °C (Fig. 2). Further increase in the reaction temperature to 130 °C or 140 °C led to a slight decrease in product yield. Because the β -carbon atom of styrene oxide is less reactive than that of other epoxides (e.g., propylene oxide, ethylene oxide), styrene oxide is usually more difficult to convert to styrene carbonate, so a relatively long reaction time and high reaction temperature are needed.

3.4. Effect of pressure on CO₂ cycloaddition with styrene oxide catalyzed by Zn/PS-IL[Br]

CO₂ pressure has been known as one of the most important factors affecting the CO₂ cycloaddition reaction with epoxide. Depending on the catalyst used and the gas–liquid phase behavior of the reaction system, the optimal yield of cyclic carbonates could be achieved at different pressure ranges, e.g., mild pressure for ZnBr₂/[Bmim]Br (1.5 MPa) [3g], medium pressure for ZnBr₂/*n*-Bu₄NI (8 MPa) [3c] and supercritical pressure for [C₈-mim]Br (14 MPa) [9]. The effect of CO₂ pressure on the CO₂ cycloaddition with styrene oxide catalyzed by Zn/PS-IL[Br] is illustrated in Fig. 3. As can be seen, when the reaction was carried out at 120 °C under varied CO₂ pressures, a CO₂ pressure lower than 6 MPa was found to be favorable for the reaction, under which yields of product and conversions of styrene fluctuated only in a small scale. This may be attributed to the homogeneous nature of the reaction system that can allow the reaction to proceed smoothly in the liquid phase. Further increasing the CO₂ pressure had a negative effect on the reaction. Both yields of product and conversions of styrene decreased correspondingly with the increase in the CO₂ pressure. This may result from the phase change of CO₂ from a gas to a supercritical fluid, because a part of styrene oxide can dissolve in the supercritical CO₂. This would inevitably decrease the amount of the reaction substrate in the liquid phase where the reaction occurs.

3.5. Separation of styrene carbonate and recycling of Zn/PS-IL[Br]

Separation of styrene carbonate from homogeneous catalysts when the reaction was carried out in a homogeneous system is difficult because styrene carbonate is solid with a high boiling point, even though a higher catalytic activity can be achieved. The heterogeneous system was favorable for styrene carbonate separation, but suffered from lower activity. The use of Zn/PS-IL[Br] as a soluble polymer catalyst for the CO₂ cycloaddition with styrene oxide can simultaneously provide high activity and easy separation of product. Phase changes of the reaction system at different reaction stages are illustrated in Fig. 4. When the white powder Zn/PS-IL[Br] was mixed with styrene oxide, a homogeneous solution was obtained (a and b). After the termination of the reaction, the reaction mixture was a white solid

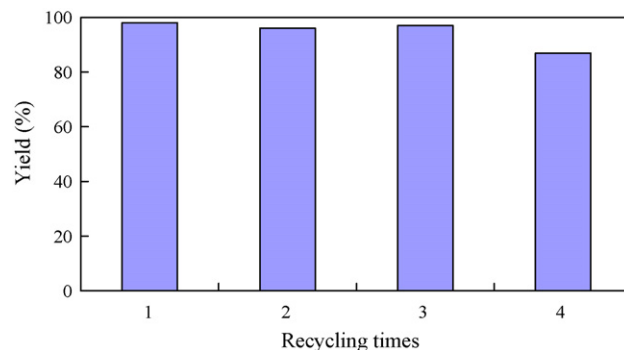


Fig. 5. Recycling of Zn/PS-IL[Br] for CO₂ cycloaddition with styrene oxide (Cat.: Zn/PS-IL[Br], Zn: 6.4×10^{-5} mmol, CO₂: 3 MPa, styrene oxide: 2 mmol, temp.: 120 °C, time: 8 h).

(c). Addition of ethanol to the post-reaction mixture resulted in the formation of a suspension due to the precipitation of Zn/PS-IL[Br] (d). Zn/PS-IL[Br] was recovered after centrifugation of the suspension at 12,000 rpm for 10 min (e). Gas chromatographic analysis revealed that styrene carbonate was obtained in high purity from ethanol solution because other by-products were not detected.

The reusability of Zn/PS-IL[Br] was also investigated (Fig. 5). Zn/PS-IL[Br] exhibited a relatively good performance in the recycling of the reaction, which can be used at least three times without much loss of activity.

4. Conclusions

We demonstrated the use of a type of novel zinc catalyst supported on soluble polymers for the solvent-free synthesis of styrene carbonate from CO₂ and styrene oxide. The catalysts were prepared by immobilization of ZnB₂ on imidazolium–styrene copolymers. When Zn/PS-IL[Br] was used for the reaction, high activity and easy separation of product could be achieved simultaneously. Zn/PS-IL[Br] was reusable for the reaction, suggesting that this kind of catalyst supported on imidazolium–styrene copolymers may have great potential in synthetic chemistry.

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