

Novel One-Step Synthesis to Cross-Linked Polymeric Nanoparticles as Highly Active and Selective Catalysts for Cycloaddition of CO₂ to Epoxides

Yubing Xiong, Yujiao Wang, Hong Wang, Rongmin Wang, Zipeng Cui

Key Laboratory of Eco-Environment-Related Polymer Materials Ministry of Education, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, People's Republic of China

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ABSTRACT: Highly cross-linked polymeric nanoparticles were prepared via novel one-step synthesis by copolymerizing ethylene glycol dimethacrylate (EGDMA) and the ionic liquid, 1-vinyl-3-(2-methoxy-2-oxyl ethyl) imidazolium chloride ([VMIm]Cl). The results indicated that nanoparticles with the average size of about 350 nm could be obtained conveniently through the cross-linking copolymerization. The nanoparticles were characterized using scanning electron microscopy, atomic force microscopy, Fourier transform Infrared, thermo gravimetric analysis, element analysis, and X-ray diffraction techniques. Moreover, the cross-linked polymeric nanoparticles were highly active and selective catalysts for the cycloaddition

reaction of carbon dioxide to epoxides. The influences of reaction time, reaction temperature, CO₂ pressure, and amount of catalyst on yield of the products were investigated. The results revealed that cyclic carbonates with high yield (98.4%) and selectivity (100%) could be produced on the condition of 0.1 g catalyst, 5 MPa CO₂, 160°C and 12 h. In addition, the nanocatalysts could be easily recovered by filtration, and reused several times with only slight loss of catalytic activity. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1486–1493, 2012

Key words: CO₂ fixation; cycloaddition; cross-linking copolymerization; polymeric nanoparticle; ionic liquid

INTRODUCTION

Carbon dioxide is a nontoxic, nonflammable, and naturally abundant C1 feedstock for organic reaction. The conversion of CO₂ to industrially useful compounds has therefore been a challenging pursuit for synthetic chemists, and has recently attracted great interest in view of the so-called sustainable society and environmental preservation.^{1,2} One of the most promising strategies in this field is the direct synthesis of cyclic carbonates via coupling of CO₂ with epoxides, which is an environmentally benign process with 100% atom efficiency.^{3–5} In particular, cyclic carbonates have been served as excellent aprotic polar solvents and extensively as intermediates in the production of pharmaceuticals and fine chemicals.^{6,7} Hitherto, a variety of organic and inorganic catalysts, including metal oxides,

alkali-metal halides, transition metal complexes, zeolite, titanosilicates, smectites, organic bases, and ionic liquids (ILs), have been explored to catalyze the cycloaddition of CO₂ to epoxides.^{8–11}

In recent years, ILs have attracted considerable attention due to their unique advantages, such as almost undetectable vapor pressure, wide liquid temperature range, excellent chemical stability, high thermal stability, and strong solvent power for a wide range of organic, inorganic and polymeric molecules.^{12–14} More recently, it was demonstrated that some ILs were active and selective catalysts for the cycloaddition of CO₂ to epoxides.^{15–19} Considering the separation and reusability of the catalysts, heterogeneous catalysts based on ILs were developed by supporting on silica, MCM-41 and cross-linked polymer.^{20–24} The solvent-free and metal-free reactions proceeded successfully under mild conditions, and the heterogeneous catalysts could be separated easily and reused. The combination of ILs as versatile reaction media with suitable catalyst, such as acid, base, nanostructures, or metal complex, may result in a more diverse and flexible platform to establish a highly effective and easily separable catalytic system.²⁵ Although the immobilization of ILs onto polymers has been studied,^{26–30} the design and preparation of highly effective heterogeneous catalysts are still desirable.^{31–33}

Correspondence to: Y. Xiong (yubing_xiong@163.com).

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We have demonstrated a novel one-step synthesis to cross-linked polymeric nanoparticles (CLPN) via conventional free radical copolymerization without the addition of any stabilizers or surfactants.³⁴ Herein, imidazole-based highly CLPN via free radical copolymerization of 1-vinyl-3-(2-methoxy-2-oxyl ethyl) imidazolium chloride ([VMIm]Cl) with the cross-linker ethylene glycol dimethacrylate (EGDMA) were prepared. Furthermore, the catalytic performance of CLPN for the cycloaddition of CO₂ to epoxides was examined. It was found that the nanocatalyst was highly active, selective and stable, and could be separated from the products easily. CLPN could be reused several times with only slight loss of the catalytic activity.

EXPERIMENTAL

Materials

Carbon dioxide with a purity of 99.99% was provided from commercial source. 2,2'-Azobisisobutyronitrile (AIBN) was purchased from Shanghai Chemical Reagent Company and used as received. 1-Vinylimidazole (98%), epoxy cyclohexane, allyl glycidyl ether (99%), styrene oxide (98%), methyl chloroacetate (MCA), and EGDMA (98%) were purchased from Aladdin Reagent Co. Propylene oxide and epichlorohydrin (ECH) were chemical grade and analytical grade, respectively. All epoxides were distilled before use. Other reagents were analytical grade and were used as received.

Measurements

¹H nuclear magnetic resonance (¹H-NMR) spectra were measured using a Bruker AM 400MHz spectrometer at 25°C. Analytical GC was recorded on a Shimadzu GC-7A. N elements of the catalysts were measured using an Elementar Analysensysteme GmbH. Fourier transform Infrared (FT-IR) spectra were recorded on a DIGIL FTS3000 spectrophotometer using KBr tablets. X-ray diffraction (XRD) analysis was collected on a Philips X'Pert using Cu K α radiation at 40 kV. Thermogravimetric analyses (TGA) were measured on a Perkin-Elmer TG/TGA 6300 at a heating rate of 10°C min⁻¹ in a flowing nitrogen atmosphere. The morphology of CLPN was collected on a scanning electron microscope (SEM, JSM-6701F) and atomic force microscope (AFM, Nanoscope III microscope).

Preparation of 1-vinyl-3-(2-methoxy-2-oxyl ethyl) imidazolium chloride ([VMIm]Cl)

1-Vinyl-3-(2-methoxy-2-oxyl ethyl) imidazolium chloride ([VMIm]Cl) was prepared as follows: 1-vinylimidazole (1.99 g, 21.2 mmol) and MCA (2.38 g,

22.0 mmol) were added to a 100 mL round-bottom flask equipped with a magnetic stirrer. The mixture was stirred at 60°C for 48 h. [VMIm]Cl was obtained by washing three times with ethyl ether. The product was dried overnight under vacuum at room temperature and white powder was obtained. Yield: 65.6%. m.p. 71.7°C. [VMIm]X: ¹H-NMR (D₂O, 400 MHz, δ ppm): 8.9(s, 1H), 7.6 (s, 1H), 7.4 (s, 1H), 7.0 (s, 1H), 5.6–5.7 (m, 1H), 5.2–5.3 (d, 1H), 5.0 (d, 2H), 3.6 (s, 3H); ¹³C-NMR (D₂O, 100 MHz, δ ppm): 50.3, 54.0, 110.4, 119.5, 124.5, 128.2, 136.1, 168.4.

Preparation of cross-linked polymeric nanoparticles

Cross-linked polymeric nanoparticles were prepared directly by free radical copolymerization of [VMIm]Cl and EGDMA using AIBN as the initiator. In a typical experiment, EGDMA (2.57 g, 12.97 mmol), [VMIm]Cl (1.31 g, 6.48 mmol) and AIBN (0.07 g, 0.43 mmol) were dissolved in methanol (25 mL) in a round-bottom flask under nitrogen atmosphere. The mixture was stirred at 60°C for 24 h. CLPN was precipitated from the solvent and collected by filtration. The product was washed with acetone and dried under vacuum at 70°C for 12 h. Yield: 67.0%.

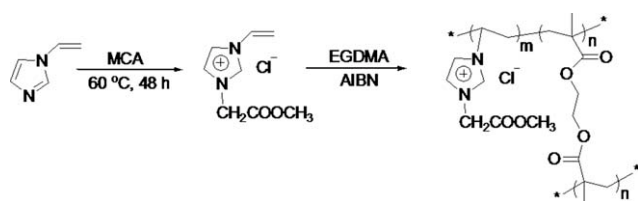
Cycloaddition reaction of CO₂ to epoxides

All the cycloaddition reactions were carried out in a 100 mL stainless steel reactor with magnetic stirrer and automatic temperature control system. After appropriate amounts of epoxide and catalyst were charged into, the reactor was heated to desired temperature. Then CO₂ was introduced into and the pressure was kept constantly till the reaction was completed. After the proper reaction time, the reactor was cooled to 0°C by immersing into iced water. Then CO₂ was released through a cold trap with *N,N*-dimethylformamide to capture the reactants and products entrained by CO₂. The mixture was filtrated after the catalyst was precipitated and the resulting filtrate together with the absorbent was analyzed by GC (GC2010AF). The retention time of the products were compared with available authentic standards. In the recyclability experiments of the CLPN catalyst, several parallel experiments in the first run were conducted to provide enough catalysts for the next run. The cyclic carbonates were analyzed at room temperature on a Bruker 400 MHz NMR spectrometer using CDCl₃ as the solvent.

RESULTS AND DISCUSSION

Preparation and characterization of CLPN catalyst

In our previous study,³⁴ a facile one-step to CLPN via conventional free radical copolymerization of



Scheme 1 Synthesis of imidazole-based cross-linked polymeric nanoparticles.

phosphorous ionic liquid (PIL), 4-vinylbenzyl-triphenylphosphorous chloride, and ethylene glycol dimethacrylate (EGDMA) in the selective solvent without any stabilizers or surfactants was exploited. Herein, imidazole-based CLPN were prepared conveniently via this one-step synthesis. The route to prepare CLPN is shown in Scheme 1. 1-vinyl-3-(2-methoxy-2-oxylethyl) imidazolium chloride ([VMIm]Cl) was firstly synthesized from 1-vinylimidazole and MCA. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra testified the desire structure of [VMIm]Cl. Then CLPN were synthesized directly by cross-linking copolymerization of [VMIm]Cl and EGDMA using AIBN as initiator in selective solvent.

Similarly, methanol was used as the selective solvent for this strategy to prepare CLPN. There was not opalescence after the polymerization, and the copolymer precipitated from the solvent. However, both SEM image [Fig. 1(a)] and AFM image [Fig.

1(c)] revealed that the copolymer particles were in the nanometer scale when the feed ratio of EGDMA and [VMIm]Cl was 2 : 1. SEM image also revealed that CLPN with the average size of 350 nm were obtained. The size was much larger than PIL-based CLPN (30–120 nm).³⁴ It may be because of the difference of the reactive activity of [VMIm]Cl and PIL when copolymerizing with EGDMA, in which [VMIm]Cl and PIL played the role of stabilizers or surfactants. PIL was more active monomer to copolymerize with EGDMA than [VMIm]Cl. Thus the nanoparticles with small size could be obtained due to more PIL chains in the copolymer. On the other side, there were more EGDMA chains in the copolymer when [VMIm]Cl was copolymerized with EGDMA. Therefore, the particles precipitated from the solvent because fewer [VMIm]Cl chains could not stabilize the polymeric nanoparticles. When the feed ratio of EGDMA and [VMIm]Cl were 1 : 2, 1 : 1, and 5 : 1, the nanoparticles could still be discerned although they were agglomerated [Fig. 1(d–f)]. Typically, the size of particles will decrease when the amount of surfactant increase in an emulsion polymerization. Therefore, the size of nanoparticles was the smallest when the feed ratio of EGDMA and [VMIm]Cl was 1 : 2.

The stability of CLPN was measured by TGA (Fig. 2). The results indicated that CLPN was stable below 230°C, which was much higher than the

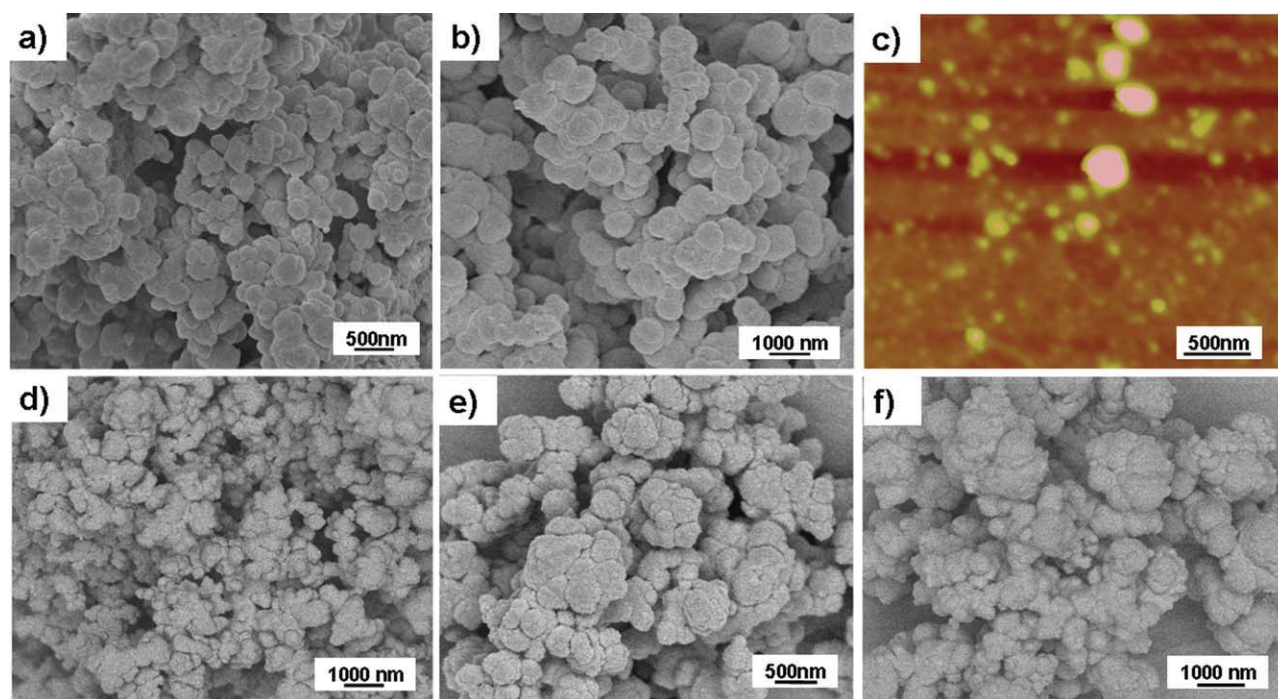


Figure 1 (a) SEM image of CLPN (EGDMA : [VMIm]Cl = 2 : 1, molar ratio); (b) SEM image of the reused nanoparticles; (c) AFM image of CLPN (EGDMA : [VMIm]Cl = 2 : 1, molar ratio); (d) SEM image of CLPN (EGDMA : [VMIm]Cl = 1 : 2, molar ratio); (e) SEM image of CLPN (EGDMA : [VMIm]Cl = 1 : 1, molar ratio); (f) SEM image of CLPN (EGDMA : [VMIm]Cl = 5 : 1, molar ratio). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

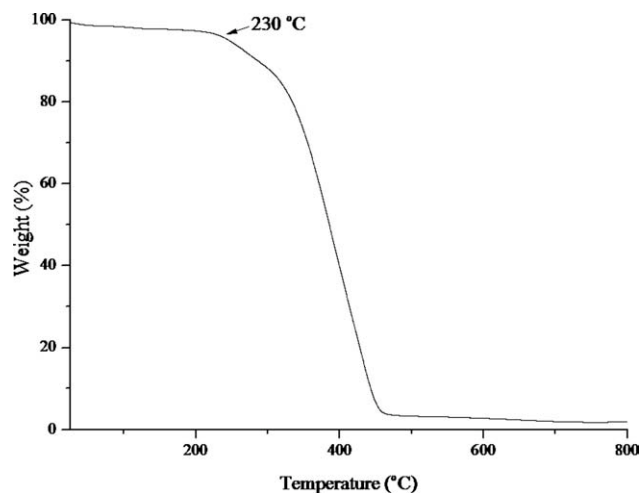


Figure 2 TGA curve of imidazole-based cross-linked polymeric nanoparticles.

cycloaddition reaction temperature. XRD measurement (Fig. 3) illustrated the amorphous structure of CLPN.

Coupling carbon dioxide with epichlorohydrin

The catalytic performances of various CLPN-based catalysts for the cycloaddition reaction of CO₂ to ECH were investigated. From Table I and Figure 1, it could be inferred that the morphology of catalysts as well as the N content played an important role in the cycloaddition reaction of CO₂ to ECH. Among of all these catalysts, the one with the highest N content (Entry 1 in Table I) presented the highest catalytic activity because N⁺ was the reactive center of the cycloaddition reaction catalyzed by imidazole-based ILs.³⁵ Although N content of CLPN with the molar ratio of EGDMA to [VMIm]Cl of 2 : 1 (entry 3

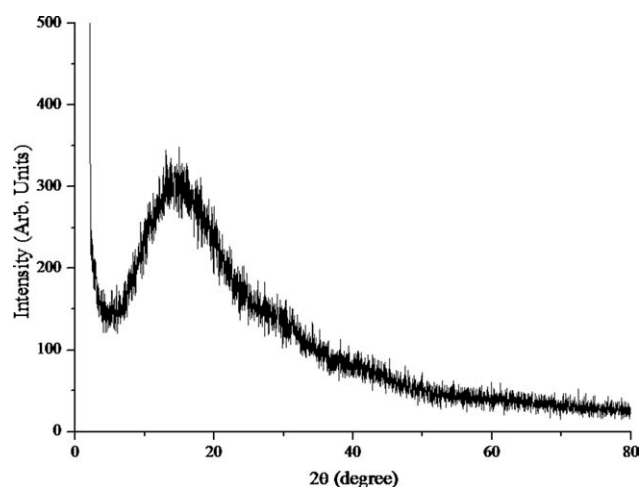


Figure 3 XRD curve of imidazole-based cross-linked polymeric nanoparticles.

TABLE I
Effects of Different CLPN on the Carbonate Synthesis^a

Entry	Catalyst	N content (%)	Yield (%)	Selectivity (%)
1	1 : 2 ^b	1.99	99.1	100
2	1 : 1	1.50	82.5	100
3	2 : 1	1.33	98.4	100
4	5 : 1	0.60	75.2	100
5	poly([VMIm]Cl) ^c	13.8 ^d	94.8	100

^a Reaction conditions: ECH: 3 mL, catalyst: 0.1 g, CO₂ pressure: 5 MPa, reaction temperature: 160°C, reaction time: 12 h.

^b The molar ratio of EGDMA to [VMIm]Cl.

^c Homopolymer of [VMIm]Cl.

^d N content was calculated on the monomeric unit base.

in Table I) was lower than the one of entry 2 in Table I, it still exhibited much higher catalytic activity, which was presumably because the nanoparticles were separated [Fig. 1(a)] and could be dispersed easily in ECH. N content of Poly([VMIm]Cl) was the highest, but it presented lower catalytic activity. It was probably because the larger density of the active sites in poly([VMIm]Cl) would result in insufficient use of the active sites.²⁹ Furthermore, it should be noted that poly([VMIm]Cl) was soluble in the product which was disadvantage for the separation of catalyst and cyclic carbonate. Entry 4 (Table I) presented the lowest catalytic activity because of its lowest N content and larger size. In addition, all these CLPN catalysts exhibited very high selectivity for the coupling of CO₂ and ECH under the condition used.

The influence of reaction time on cyclic carbonate yield and selectivity in the addition of CO₂ to ECH is depicted in Figure 4. The reactions were performed in the presence of 0.1 g CLPN at 160°C under 5 MPa CO₂. The results indicated that the

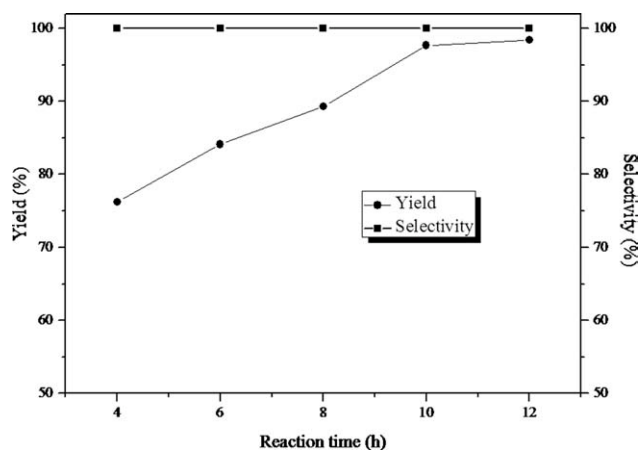


Figure 4 Influence of reaction time on the cyclic carbonate yield and selectivity. Reaction conditions: ECH: 3 mL, catalyst (entry 3 in Table I): 0.1 g, CO₂ pressure: 5 MPa, reaction temperature: 160°C.

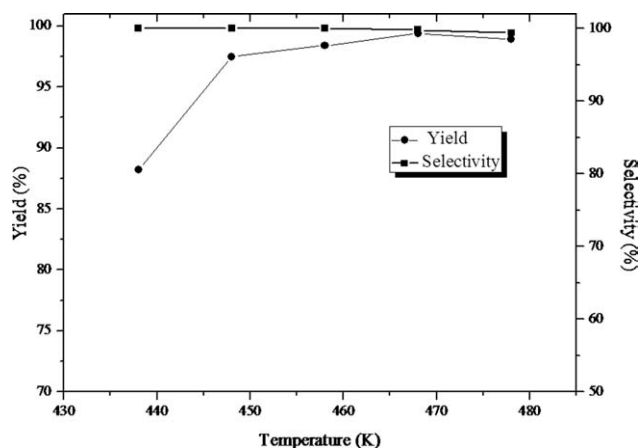


Figure 5 Temperature dependence of the cyclic carbonate yield and selectivity. Reaction conditions: ECH: 3 mL, catalyst (entry 3 in Table I): 0.1 g, CO₂ pressure: 5 MPa, reaction time: 12 h.

yield of cyclic carbonate increased rapidly with reaction time and higher yield (above 95%) could be achieved within 10 h. In addition, the selectivity of cyclic carbonate was 100% during the reaction course, which illustrated the high selectivity of CLPN catalysts.

The dependence of cycloaddition reaction on temperature is summarized in Figure 5. It was found that the reaction temperature affected significantly on the yield of cyclic carbonate. The yield of cyclic carbonate increased rapidly with the increase of temperature at lower temperature range (below 150°C). When the reaction temperature increased further, there was no notable increase in the yield of cyclic carbonate. Both the yield and selectivity of the product decreased slightly when the cycloaddition reaction was conducted at 180°C. It was due to the side reaction occurred at higher temperature. It has been reported that there were some side reactions in the cycloaddition reaction, such as ECH polymerization, the isomerization to acetone and the ring opening by water to propylene glycol.^{36,37} The GC study showed that the by-products in the present cycloaddition reaction of ECH was 3-chloro-1,2-propylene glycol. Therefore, the main side reaction was the ring opening of cyclic carbonate caused by the residual water on the surface of CLPN nanoparticles at higher temperature. The reaction temperature was higher than many other catalysts, which was presumably due to the steric hindrance from the catalysts.

Figure 6 depicts the influence of CO₂ pressure on the cyclic carbonate yield at 160°C. It can be seen clearly that the increase in CO₂ pressure benefited to enhance the cyclic carbonate yield greatly at lower CO₂ pressure (below 2 MPa). CO₂ pressure exhibited little influence on the cyclic carbonate yield in the range of 2–5 MPa. Both the yield and selectivity of cyclic carbonate decreased greatly when CO₂ pres-

sure was above 5 MPa. One possible explanation for this can be ascribed to the high solubility of CO₂ and high diffusion rate owing to the EGDMA's affinity towards CO₂.³⁸ Simultaneously, it was demonstrated that there were two phases in the system under all the experimental conditions.³⁹ The top phase was a CO₂-rich phase and the bottom phase was an ECH-rich phase. The concentration of CO₂ in the bottom phase increased with the increase of pressure. This favored the reaction, considering that CO₂ was a reactant. On the other hand, the concentration of ECH in the bottom phase decreased as the pressure was increased, which was not favorable to the reaction because ECH was also a reactant. In addition, more ECH was extracted into the CO₂-rich phase at higher pressures which reduced the reaction rate. The competition of these opposite factors resulted in a maximum in the pressure versus yield curve.²⁹ It was also reported that too high CO₂ pressure may retard the interaction between epoxides and the catalyst.³⁶ Therefore, higher CO₂ pressure did not benefit the cycloaddition reaction catalyzed by CLPN.

Figure 7 shows the effect of the amount of catalyst on the formation of cyclic carbonate. The carbonate yield increased when the amount of CLPN was increased from 0.02 to 0.1 g. When it was further increased, however, both the yield and selectivity of cyclic carbonate decreased. The reactive sites for the cycloaddition reaction increased when the catalyst amounts were increased. Thus, the yield of cyclic carbonate was enhanced when the amounts of CLPN were increased. The yield of cyclic carbonate decreased slightly when the amount of CLPN is 0.12 g. One possible explanation for this could be ascribed to the strong polar surface of CLPN catalysts. Over many catalysts would be liable to conglomerate in ECH due to the weak polarity of ECH.

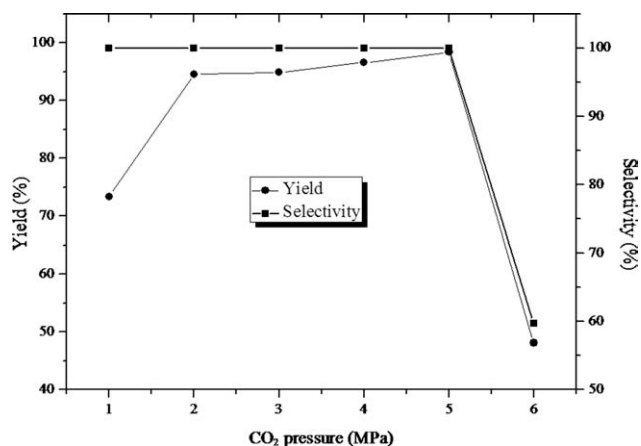


Figure 6 Dependence of the cyclic carbonate yield and selectivity on CO₂ pressure. Reaction conditions: ECH: 3 mL, catalyst (entry 3 in Table I): 0.1 g, reaction temperature: 160°C, reaction time: 12 h.

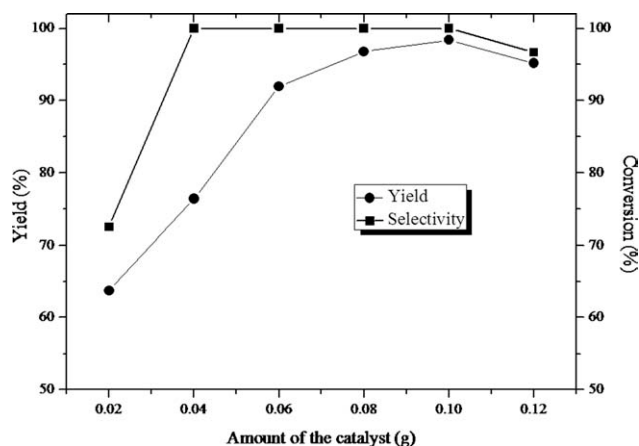


Figure 7 Effect of the amount of catalyst on the cyclic carbonate synthesis. Reaction conditions: ECH: 3 mL, CO₂ pressure: 5 MPa, reaction temperature: 160°C, reaction time: 12 h.

Catalyst recovery and reuse

Experiments were also conducted to investigate the recyclability of CLPN catalyst. In each run, CLPN as a solid were recovered by filtration directly. After rinsed with acetone and dried, the catalysts were reused in the next run. As shown in Figure 8, CLPN catalyst could be reused for five runs only with slight loss of its catalytic activity, and the selectivity still remains 100%. The loss of catalytic activity may be due to the residual cyclic carbonate in CLPN and the enlargement of the nanoparticles size than before use. As shown in Figure 1(b), the average size of reused CLPN was about 500 nm which was much larger than the one before use. As a result, the yield of cyclic carbonate decreased because the reused

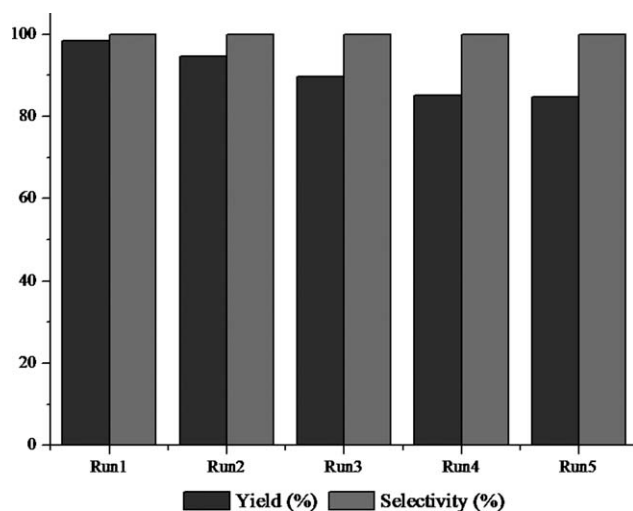


Figure 8 Stability and reusability of CLPN catalyst. Reaction condition: ECH: 3 mL, catalyst (entry 3 in Table I): 0.1 g, CO₂ pressure: 5 MPa, reaction temperature: 160°C, reaction time: 12 h.

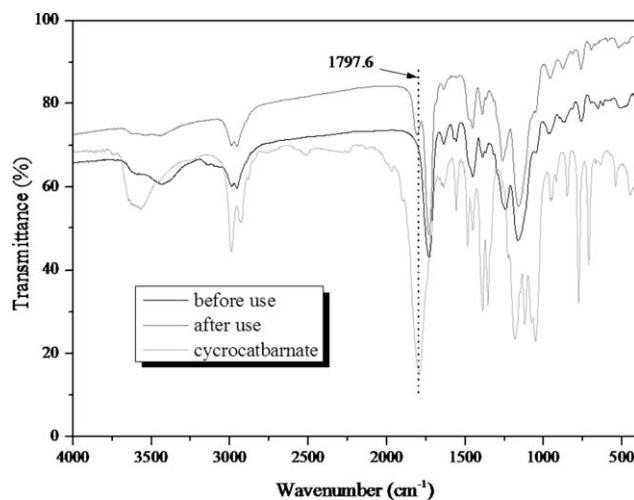


Figure 9 FT-IR spectra of CLPN (before and after the cycloaddition reaction) and cyclic carbonate.

CLPN provided less specific surface area. Cyclic carbonate was often used as aprotic polar solvents and it was very difficult to remove it from the catalyst completely because of its high boiling point (above 473 K). The residual cyclic carbonate in reused CLPN could be confirmed by FT-IR and TGA measurements. As shown in Figure 9, the peak at 1797.6 cm⁻¹ in the curve of reused catalysts was ascribed to the stretch vibration of C=O of cyclic carbonate. Moreover, TGA curves (Fig. 10) indicated that the weight loss of the catalyst after use emerged earlier which was due to the residual cyclic carbonate. Both of the results illustrated that there was residual cyclic carbonate which would result in enlargement of the nanoparticles size.

Coupling carbon dioxide with other epoxides

To demonstrate the catalytic activity of CLPN, cycloaddition reactions of CO₂ to different epoxides were

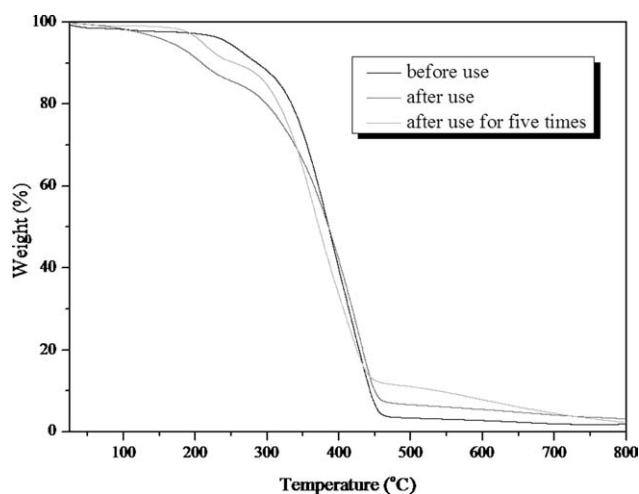
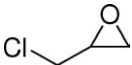
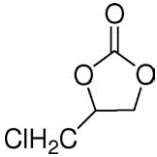

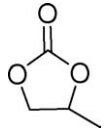
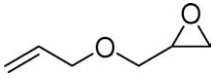
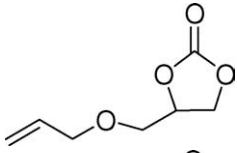
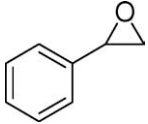
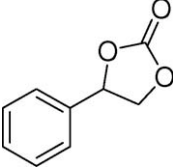


Figure 10 TGA curves of CLPN and reused CLPN.

TABLE II
Synthesis of Various Cyclic Carbonates Using CLPN

Entry	Epoxide	Product	Yield (%)	Selectivity (%)
1			98.4	100
2			98.4	99.3
3			91.3	97.8
4			86.6	99.6

Epoxide: 3 mL, catalyst (entry 3 in Table 1): 0.1 g, CO₂ pressure: 5 MPa, reaction temperature: 160°C, reaction time: 12 h.

also conducted at 160°C and 5 MPa CO₂ (as shown in Table II). The results indicated that the catalytic system was applicable to coupling CO₂ with a variety of terminal epoxides with high yield and selectivity. In all these epoxides, the activity of styrene oxide was the lowest, which may be due to the steric hindrance and electronic effects. In addition, double bond in allyl glycidyl ether was stable in the process which illustrated that the reaction was a good method to prepare functional monomer with double bond.

CONCLUSIONS

In summary, imidazole-based heterogeneous nanocatalyst was prepared conveniently through a novel one-step synthesis. The results indicated that solvent and the molar ratio of EGDMA to [VMIm]Cl played a very important role in the formation of CLPN in this strategy. Moreover, CLPN exhibited excellent stability, activity and selectivity in the cycloaddition reaction of CO₂ to epoxides, and CLPN could be easily separated from the products and reused. It is expected that the highly active and selective nanocatalyst provides a feasible strategy for CO₂ fixation.

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