ORIGINAL PAPER

Novel and Highly Efficient Conversion of Carbon Dioxide to Cyclic Carbonates Using Benzotriazolium Ionic Liquid-Modified Periodic Mesoporous Organosilica as a Heterogeneous and Recyclable Nanocatalyst

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Abstract

In the present study, we demonstrated the synthesis of copper oxychloride anionic benzotriazolium ionic liquid-modified periodic mesoporous organosilica PMO@ILCu$_2$(OH)$_3$Cl$_2$(x) as efficient and green retrievable heterogeneous nanocatalysts for the synthesis of cyclic carbonates via cycloaddition of CO$_2$ with epoxides. Compared to other nanocatalysts, a superior catalytic activity was observed with PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0), giving excellent yields and selectivities *under solvent-* and cocatalyst-free conditions. We also found that the existence of intensification synergistic effects from the hydroxyl groups sites of periodic mesoporous organosilica and the active sites of the functionalized ionic liquid, resulting in the enhanced catalytic *activity*. The catalytic process displayed ease of recovery, excellent stability and recyclability for at least five runs without significant loss of its catalytic activity. The developed catalytic system is proven to be a powerful tool for the chemical fixation of CO$_2$ with epoxides to produce the cyclic carbonates.

Keywords Immobilized ionic liquid · Periodic mesoporous organosilica · Synergistic catalysis · Cycloaddition · Cyclic carbonates

1 Introduction

Chemical fixation of carbon dioxide (CO$_2$) into value-added chemicals has attracted widespread attention recently, as CO$_2$ is an abundant, inexpensive, nontoxic C1 source as well as being the primary greenhouse gas [1–6]. Among possible processes, the transformation of CO$_2$ with epoxides into cyclic carbonates has 100% atom efficiency and is one of the most valuable and sustainable strategies. Cyclic carbonates have been widely used as raw materials in pharmaceuticals, fuel additives, electrolytes and fine chemicals [7–9]. Therefore, there has been a growing interest in the synthesis of cyclic carbonates, and a number of catalytic systems have been developed for the synthesis of cyclic carbonates, including metal complexes [10–12], organocatalysts [13, 14], Lignin/KI [15], B$_2$O$_3$/nBu$_4$NBr [16], MOFs [17–19], NH$_3$I-Zn/SBA-15 [20], WP-KI [21], Cu$_6$ cluster/nBu$_4$NBr [22], CoPc/TiO$_2$ [23], and others [24–26]. However, most of these catalyst systems suffer from drawbacks associated with the use of expensive reagents, harsh reaction conditions, relatively rare availability and catalyst reusability problems. Therefore, the development of catalytic systems that are both efficient and environmentally benign for the synthesis of cyclic carbonates still poses a considerable challenge.

Ionic liquids (ILs) have been of much interest as they have a wide range of applications in the areas of separation, catalysis and industrial chemistry [27–30]. Especially, metal-containing ionic liquids have been successfully used as catalysts in catalytic synthesis, which combine the advantages of both ionic liquid and transition metal catalysis and often leading to improved catalytic performance comparing to the classical ionic liquids [31, 32]. In this respect, many ILs including metal-containing ILs have been synthesized and they exhibited good catalytic performance in the transformation of CO$_2$ into cyclic carbonates [33–37]. Despite these advances, these catalytic systems often suffer from some disadvantages such
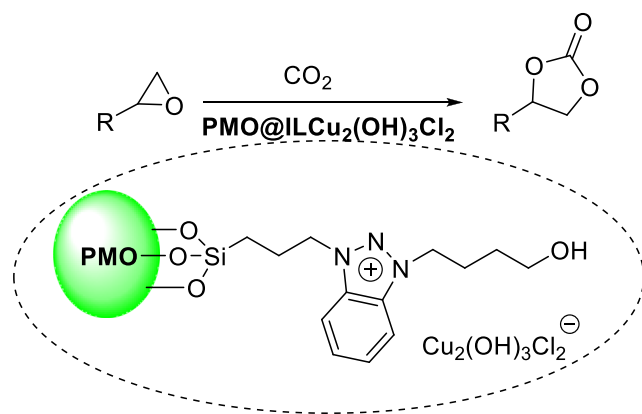
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as ILs separation and recyclability. To facilitate easy separation and recycling of catalyst, heterogeneous catalysis offer an alternative strategy for improving recyclability [38–47]. Thus, the development of highly efficient and easily recyclable heterogeneous catalysts in combination with the characteristics of homogeneous ILs is highly desirable. The immobilization of ionic liquids on silica supports materials have been explored as develop novel and promising heterogeneous supported ionic liquids [48–53], which is a versatile way to keep ionic liquid and support tightly together and *simplify* separation, improve their catalytic activity and *reusability.* Among silica-based materials, periodic mesoporous organosilicas (PMOs) have attracted significant research interests because of their uniform and tunable pore sizes, highly ordered mesostructure, large surface areas and heterogeneous functional moieties distribution properties [54–57]. Especially, the introduction of active sites into PMOs for the synthesis of functionalized PMOs towards specific application demands in the fields of separation and catalysis has attracted a lot of attention [58–64]. Likewise, the immobilization of functionalized ILs on periodic mesoporous organosilicas and led to the formation of ionic liquid-functionalized PMOs, which were expected to afford highly useful catalytic materials retaining properties of the both moieties.

In the light of these considerations, the present work would to introduce the immobilization of novel benzotriazolium ionic liquid onto periodic mesoporous organosilica to fabricate multifunctional ionic liquid-based PMOs nanomaterials. These resulting new modified mesoporous nanomaterials with different *loading* levels of IL have been evaluated as recoverable catalysts for chemical fixation of CO_2 with epoxides in the absence of nucleophilic cocatalyst and solvent (Scheme 1). We were delighted to find that these as-synthesized nanocatalysts exhibit an enhancement in the catalytic activity for conversion of CO_2 to cyclic carbonates, by which high yields and selectivities could be obtained under relatively moderate conditions. Additionally, we also found that the nanocatalyst acts as an excellent synergic catalyst in which the catalytic activity could be boosted by the immobilized functional groups of IL and hydroxyl active sites on the PMO framework. The proposed multifunctional nanocatalyst is found to be highly effective for the homogeneous catalytic cycloaddition and easily heterogeneous reusable for several consecutive cycles, which offers a new solution for green and recyclable catalytic synthesis of cyclic carbonates with high performance and sustainable efficiency.

2 Experimental

2.1 General

All reagents are analytical grade and used without further purification. Pluronic 123 ($EO_{20}PO_{70}EO_{20}$) and 1,2-bis(triethoxysilyl)ethane were obtained from Sigma-Aldrich. The crystallinity of the samples was analyzed by powder X-ray diffraction (XRD) using a Ultima IV diffractometer with Cu K$_\alpha$ radiation ($\lambda = 0.15406$ nm) radiation. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer in the range of 400–4000 cm^{-1} using KBr pellets. The morphology of the samples was investigated by using scanning electron microscopy (SEM, JSM-7500F) with operating voltage at 10 kV equipped with energy dispersive spectroscopy (EDS). UV-Vis spectra were recorded using a Shimadzu UV-2450 spectrophotometer with an integrating sphere attachment within the range of 200 to 800 nm and with $BaSO_4$ as the reflectance standard. The thermogravimetric analysis (TGA) experiments were performed on a NETZSCH STA 449 F5 apparatus in the range of 30–600 °C with heating rate of 10 °C/min. The BET surface areas and pore volumes of samples were calculated using the BET method from nitrogen adsorption-desorption, using a BELSORP-max apparatus measured at liquid nitrogen temperature (77 K). The samples were degassed under vacuum at 120 °C for 6 h before measurements. Gas chromatography analysis were performed on a Thermo Scientific TRACE1300 analyzers assembled with TG-OCP 30 m × 0.25 mm × 0.25 μm (Thermo Fisher) column and a flame ionization detector. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer at room temperature and TMS as internal standard in CDCl$_3$. Elemental analysis were obtained with an Carlo-Erba 1106 elemental analyzer.

2.2 Preparation of PMO@ILCu$_2$(OH)$_3$Cl$_2$(x)

The general route for the preparation of nanomaterials PMO@ILCu$_2$(OH)$_3$Cl$_2$(x) is shown in Scheme 2. PMO support was prepared according to literature method [55, 56]. The supported catalysts PMO@ILCu$_2$(OH)$_3$Cl$_2$ were prepared following similar procedures in literatures [27, 59, 60, 64]. Typically, (3-chloropropyl) triethoxysilane (0.2 mol) and

Scheme 1 Chemical fixation of CO_2 with epoxides catalyzed by PMO@ILCu$_2$(OH)$_3$Cl$_2$
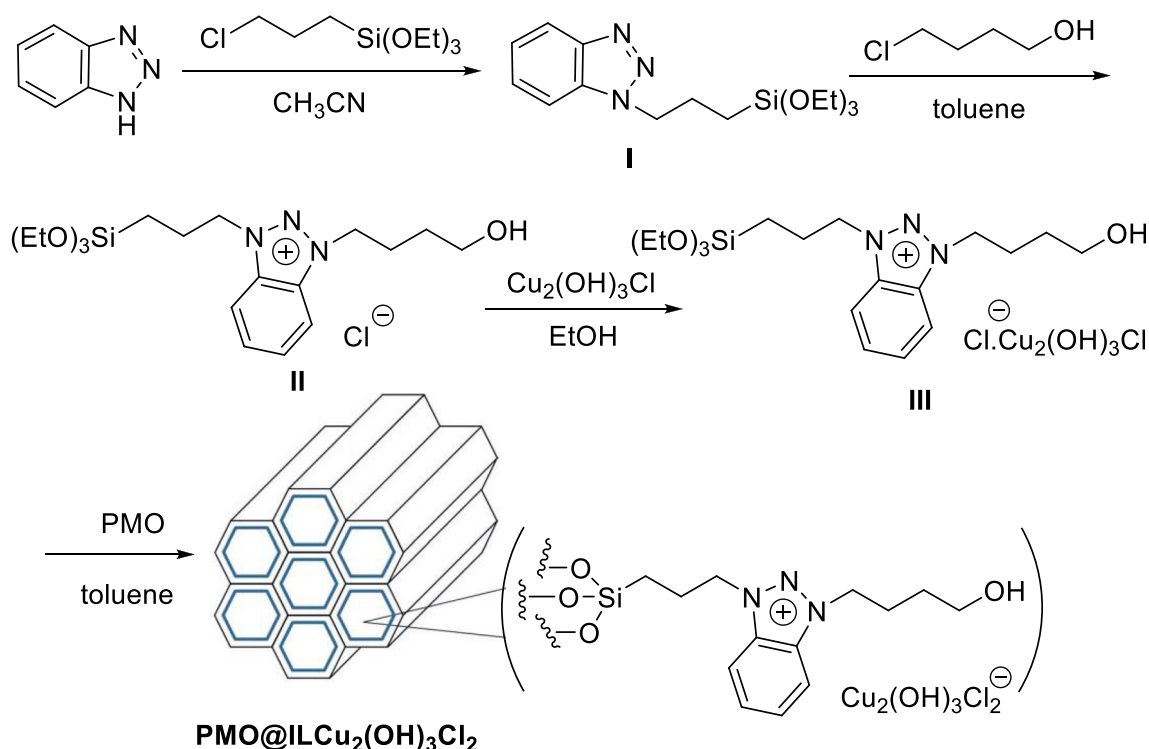
Scheme 2 Schematic illustration of synthesis process for PMO@ILCu$_2$(OH)$_3$Cl$_2$

1,2,3-benzotriazole (0.2 mol) were dispersed in acetonitrile (260 mL), and continuously stirred for 24 h at 80 °C. After the reaction, the solvent was removed by vacuum, and the crude product was washed with ethanol and dried at 60 °C for 4 h to give **I**. Then, **I** (0.1 mol) and 4-chloro-1-butanol (0.1 mol) were dissolved with 150 mL toluene in 250 mL round flask. The mixture was stirred for 24 h at 100 °C. After cooling to room temperature, the precipitate was isolated and washed with dichloromethane to give ILCl **II**. Afterwards, **II** (0.05 mol), copper oxychloride (0.05 mol), and ethanol (120 mL) were stirred at 60 °C for 48 h. The crude material was washed with ethanol-water and dried at 60 °C to give copper oxychloride anion-functionalized ionic liquid ILCu$_2$(OH)$_3$Cl$_2$ **III**. Finally, the immobilized ionic liquids with different mass ratio of ionic liquid to PMO were prepared. In a typical synthesis, PMO (1.0 g), **III** (x g) and toluene (100 mL) were refluxed for 24 h under nitrogen. After cooling to room temperature, the solid product was recovered by filtration and washed with acetone for removal the excess ionic liquid. Then the samples were dried under vacuum to give the supported nanocatalysts PMO@ILCu$_2$(OH)$_3$Cl$_2$(x).

2.3 Catalytic Cycloaddition of Epoxides and CO$_2$

Epoxide (0.1 mol), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) (0.2 g) were added into a stainless-steel autoclave and then was purged with CO$_2$ for three times. The reactor was pressurized with CO$_2$ to 1.5 MPa and then heated to the desired temperature,

the mixture was maintained for a desired time under vigorous stirring. After completion of the reaction, the excess CO$_2$ was vented slowly. The catalyst was easily separated from the mixture by centrifugation, and the product were injected in a gas chromatography (Agilent 7890) equipped with FID detector for a quantitative analysis. The recovered catalyst was recycled directly for the next run. All of the products were identified by comparing their physical and GC data with those of the standard compounds.

2.4 Spectroscopic Data for the Products

Propylene carbonate (Table 2, entry 1): ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm) 1.45 (dd, CH$_3$, 3H), 3.96 (t, CH, 1H), 4.54 (t, CH, 1H), 4.82–4.86 (m, CH, 1H); Elemental analysis for C$_4$H$_6$O$_3$: C 47.06, O 47.01. Found C 47.01, O 46.98.

1,2-Butylene glycol carbonate (Table 2, entry 2): ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm) 0.97 (t, CH$_3$, 3H), 1.58–1.60 (m, CH$_2$, 2H), 4.43 (d, 2H); 4.59–4.63 (m, CH, 1H); Elemental analysis for C$_5$H$_8$O$_3$: C 51.72, O 41.34. Found C 51.67, O 41.29.

1,2-Butylene glycol carbonate (Table 2, entry 3): ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm) 0.93 (t, CH$_3$, 3H), 1.56–1.62 (m, CH$_2$, 2H), 4.43 (d, 2H); 4.58–4.62 (m, CH, 1H); Elemental analysis for C$_4$H$_6$O$_4$: C 40.68, O 54.19. Found C 40.62, O 54.15.

(Chloromethyl)ethylene carbonate (Table 2, entry 4): ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm) 3.76 (dd, CH$_2$, 2H), 4.36
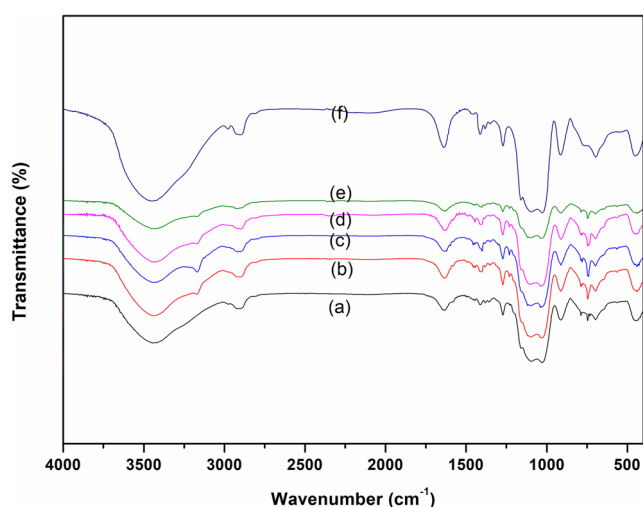
(t, CH$_2$, 1H), 4.58 (t, CH$_2$, 1H), 4.91–4.95 (m, CH, 1H); Elemental analysis for C$_4$H$_5$ClO$_3$: C 35.19, Cl 25.96, O 35.15. Found C 35.15, Cl 25.93, O 35.08.

Hexahydrobenzo[d][1,3]dioxol-2-one (Table 2, entry 5): ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm) 1.34–1.48 (m, CH$_2$CH$_2$, 4H), 1.75–1.84 (m, 2CH$_2$, 4H), 5.22 (t, 2CH, 2H); Elemental analysis for C$_7$H$_{10}$O$_3$: C 59.15, O 33.76. Found C C 59.09, O 33.73.
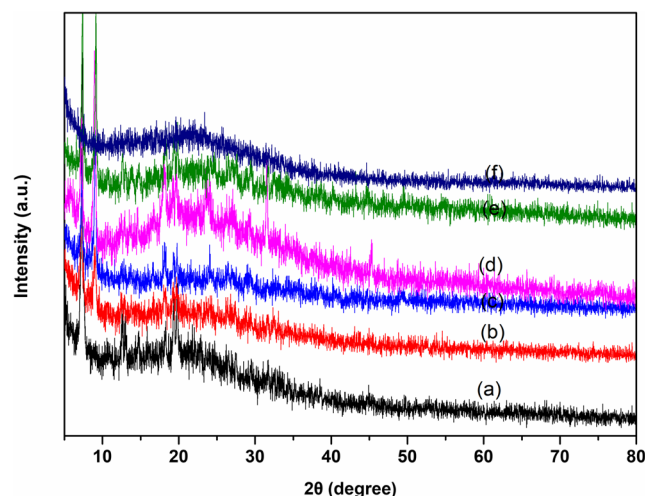
Styrene carbonate (Table 2, entry 6): ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm) 4.35 (t, CH$_2$, 1H), 4.72 (t, CH$_2$, 1H), 5.68 (t, CH$_2$, 1H), 7.28–7.40 (m, Ar-H, 5H); Elemental analysis for C$_9$H$_8$O$_3$: C 65.85, O 29.24. Found C 65.80, O 29.17.

3 Results and Discussion

The as-fabricated nanomaterials PMO@ILCu$_2$(OH)$_3$Cl$_2$(x) were characterized by FT-IR analysis (Fig. 1). The adsorption peaks at around 1085 cm^{-1}, 810 cm^{-1}, and 486 cm^{-1}, were assigned to the stretching vibration of Si–O. The characteristic bands at about 3518 cm^{-1}, 1635 cm^{-1} were attributed to the hydrogen-bonded stretching and bending vibrations [48–50], and the two peaks became weaker when the ionic liquid loading levels on PMO were increased. The peaks at about 1174 cm^{-1}, and 1028 cm^{-1} were attributed to N=N, and C–N stretching vibrations of triazolium ring. The characteristic bands around the range 1455 ~ 1610 cm^{-1} and 3085 cm^{-1}, were assigned to the stretching vibrations of aromatic ring [27, 65]. The characteristic bands around 2861 cm^{-1}, 1298 cm^{-1}, and 737 cm^{-1} were attributed to the stretching vibrations of CH$_2$. The characteristic bands that at around 729 cm^{-1}, 1605 cm^{-1} and 910 cm^{-1}were ascribed to the C-Cl, Cu-Cl, Cu-O vibrational modes, respectively [66]. If the
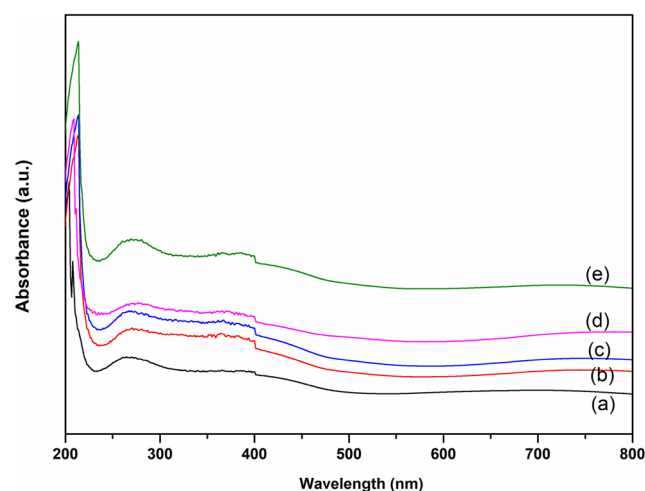
loading levels of ionic liquids were increased, it can be found that the two peaks at about 1174 cm^{-1}, 729 cm^{-1} became stronger and visible. The results indicated that the successful immobilization of functionalized benzotriazolium ionic liquid onto the PMO.

The XRD diffraction patterns for the nanomaterials PMO@ILCu$_2$(OH)$_3$Cl$_2$(x) are shown in Fig. 2. The diffraction peak about 2θ = 22.5° is the characteristic diffraction peak of PMO [54, 55, 57–60]. Other diffraction peaks at about 2θ = 5.2°, 14.8°, 20.2°, and 32.4°compared to the parent PMO were belong to the crystal planes of copper anion of ionic liquid [67, 68]. No other peaks corresponding to ionic liquid were observed, suggested that the ionic liquid sites were well-dispersed on the PMO framework. These results
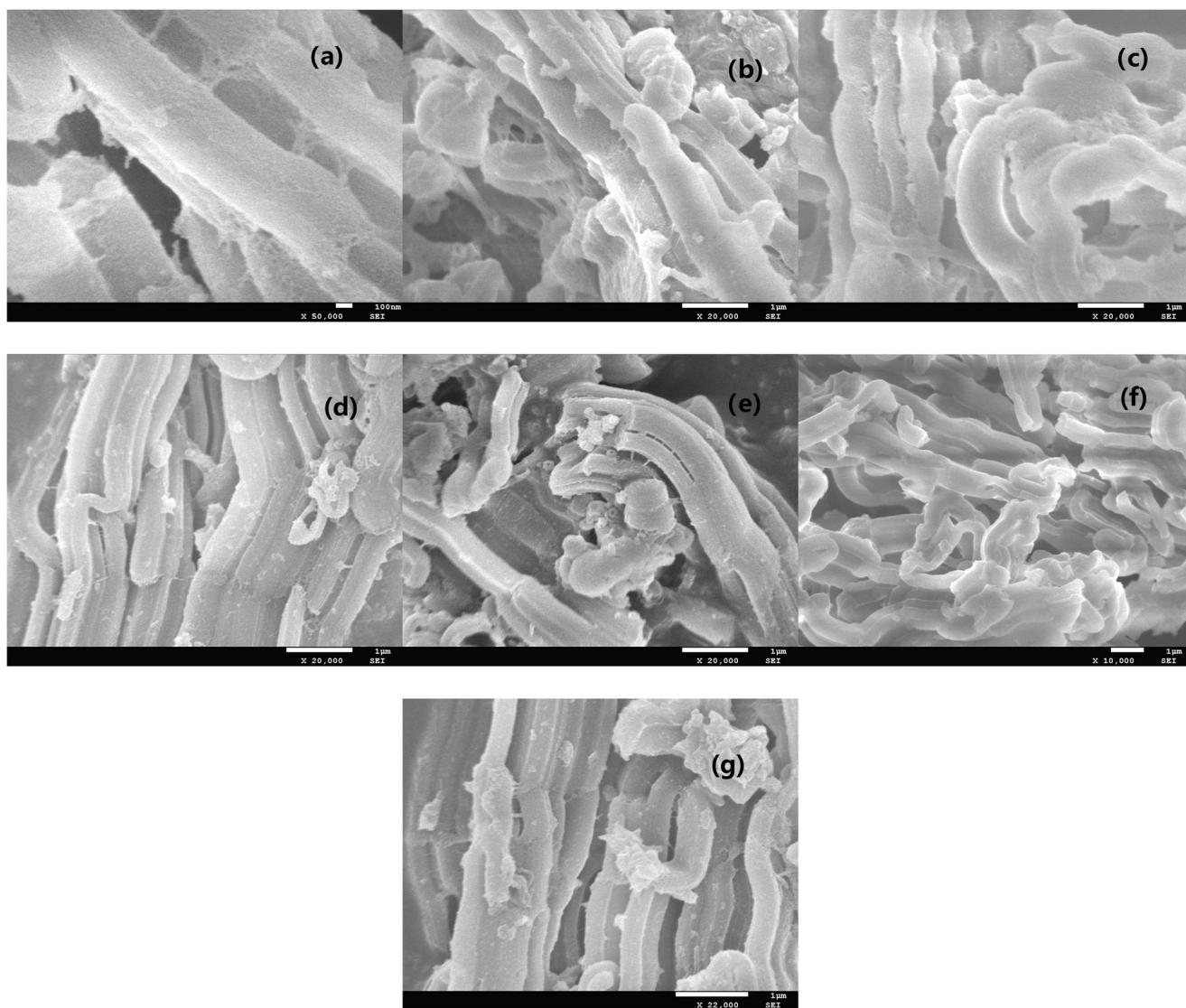

Fig. 2 XRD patterns of PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.4) (a), PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.6) (b), PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.8) (c), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) (d), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.2) (e), and PMO (f)

Fig. 1 FT-IR spectras of PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.4) (a), PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.6) (b), PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.8) (c), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) (d), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.2) (e), and PMO (f)

Fig. 3 UV–Vis spectras of PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.4) (a), PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.6) (b), PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.8) (c), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) (d), and PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.2) (e)

indicated that the basic crystalline structure of PMO framework maintained even after being immobilized of ionic liquid. Figure 3 shows UV–Vis spectra of the nanomaterials PMO@ILCu$_2$(OH)$_3$Cl$_2$(x). The main absorption band at around 232 nm, corresponding to the characteristic Si-O bands absorption of PMO [54, 58–61]. It can be seen from Fig. 3a-e that, the absence of peaks of immobilized ionic liquids in these nanomaterials confirmed that the ionic liquids species were uniform and homogeneous dispersed on the support framework.

The SEM morphology of the synthesized nanomaterials is shown in Fig. 4. Figure 4f showed the characteristic morphological features of PMO [54–56]. Figures 4a-e SEM images of PMO@ILCu$_2$(OH)$_3$Cl$_2$(x) demonstrated the rope-like morphology of aggregated small spherical particles. It can be seen

that both PMO and PMO@ILCu$_2$(OH)$_3$Cl$_2$(x) exhibited similar and uniform rope-like morphology, indicating that the functional ionic liquid is attached to the inner tube wall of PMO and the immobilization of ionic liquid *do* not nearly change the surface morphology of PMO. Additionally, a more detailed investigation on the elemental composition of the nanocatalyst PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) was investigated by EDS (Fig. 5). The EDS analysis suggested that there existed the expected elemental signals of C, O, N, Cl, Cu and Si in the synthesized nanocomposites PMO@ILCu$_2$(OH)$_3$Cl$_2$(x).

The nitrogen adsorption-desorption isotherms and pore size distributions of the pure periodic mesoporous organosilica and PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) were determined (Fig. 6). Similar to the mesoporous structure of the pure PMO, the nanocatalyst exhibited the type IV isotherms with


Fig. 4 SEM images of PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.4) (a), PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.6) (b), PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.8) (c), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) (d), and PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.2) (e), PMO (f), and five times recovered PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) (g)
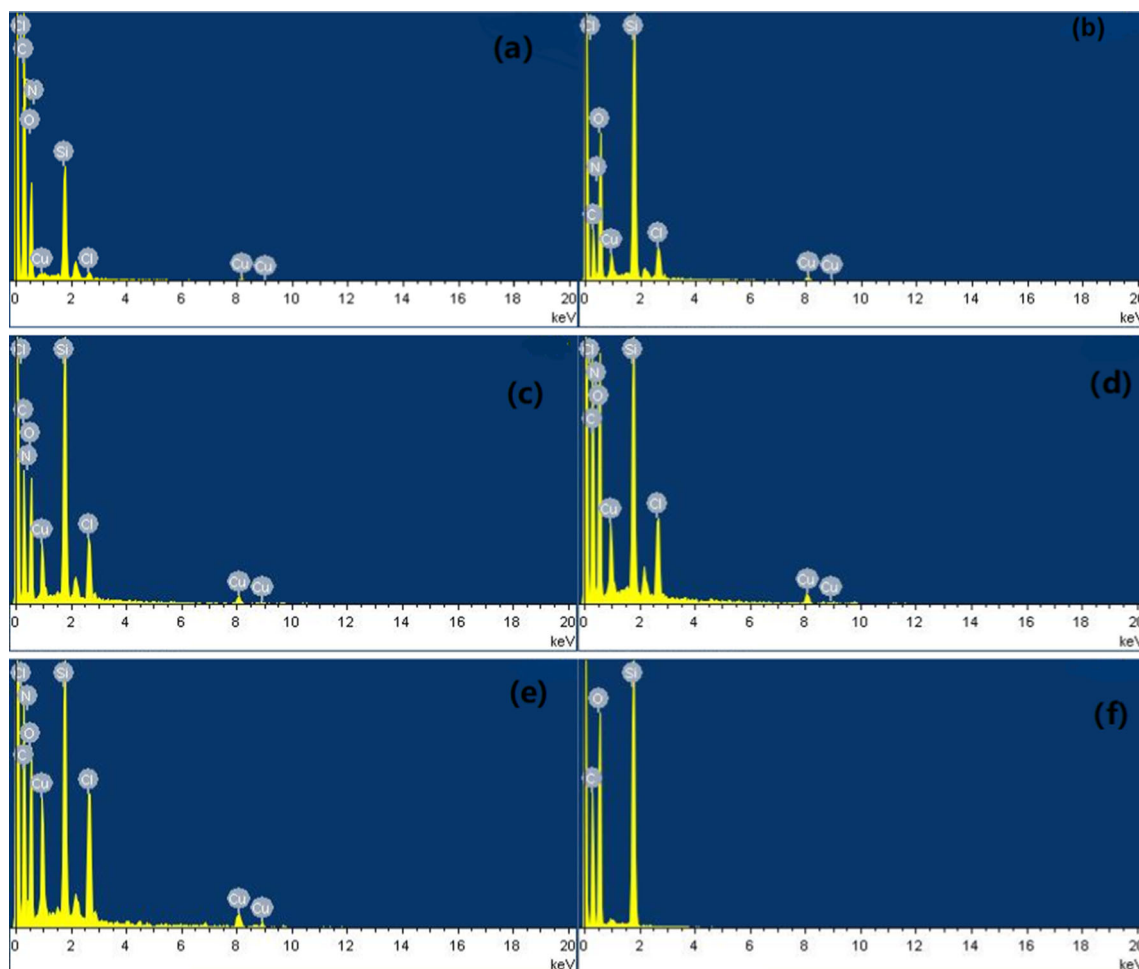
Fig. 5 EDS image of MO@ILCu$_2$(OH)$_3$Cl$_2$(0.4) (a), PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.6) (b), PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.8) (c), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) (d), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.2) (e), and PMO (f)

hysteresis loops of subclass H4 [55–58]. The grafting of the ionic liquid on the organosilica carrier greatly influenced its surface area and pore volume, as well as slightly smaller pore
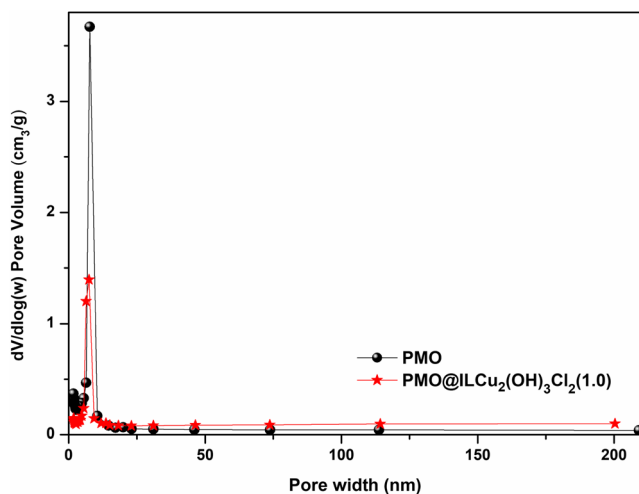

Fig. 6 N$_2$ adsorption-desorption isotherms and pore size distributions of PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0)

size. The results showed that the surface area, pore volume, pore size and were reduced from 571.59 m^2 g^{-1}, 0.76 cm^3 g^{-1} and 5.89 nm for PMO to 259.50 m^2 g^{-1}, 0.43 cm^3 g^{-1} and 5.54 nm for PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0), respectively, which was due to the immobilization of ionic liquid on the organosilica carrier. The thermal stability of PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) was determined by thermal gravimetric analysis (TGA). The nanocatalyst depict a two main step thermal decomposition (Fig. 7). The first step of weight loss (0.81%) below 200 °C related to the removal of adsorbed water (≤100 °C) and other volatile *solvent residue*s (100 ~ 200 °C), whereas the main weight loss (24.94%) from 200 to 600 °C in the second and third steps was corresponded to degradation of the organic moieties of ionic liquid. These observations demonstrated that PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) is thermally stable below 200 °C.

After the characterization of PMO@ILCu$_2$(OH)$_3$Cl$_2$(x), we intended to examine the catalytic activity for the cycload-dition of propylene oxide with CO$_2$ to produce propylene carbonate, and the results are described in Table 1. The effect of benzotriazolium-based ionic liquid loading levels on PMO

Fig. 7 Thermogravimetric analysis of PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0)
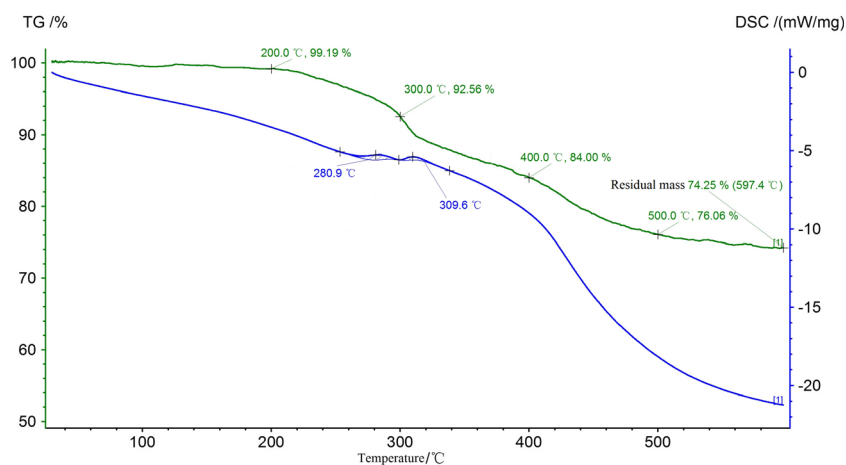
was investigated (Table 1, entries 1–5), it was found that PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) possessed the highest catalytic activities of 97% yield with excellent selectivity 99.3% (Table 1, entry 4). The comparison was then carried out using bulk ionic liquid ILCu$_2$(OH)$_3$Cl$_2$, ILCl, and PMO as catalysts (Table 1, entries 6–8) and they resulted in bad catalytic activity. As expected, no product was detected when the reaction was performed without a catalyst (Table 1, entry 9). The excellent activity observed for PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) confirms the most important copper oxychloride anion and PMO support for obtaining high catalytic activity for the synthesis of propylene carbonate under moderate reaction conditions. From the above studies, PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) could serve as the proper catalyst for the solvent-free cycloaddition. These results also revealed that the as-synthesized immobilized catalyst PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) contributes

to *the* enhancement of catalytic activity and selectivity, which was most likely due to the synergistic effect from hydroxyl active sites and strong nucleophilic anions with the appropriate cations that accelerates the CO$_2$ cycloaddition. The effect of catalyst amount on the cycloaddition reaction were studied. The conversion increased when the catalyst amount increased from 0.05 g to 0.2 g (Table 1, entries 3, 10–12), and best result was obtained with 0.2 g catalyst. However, it has been observed that further increase in the catalyst amount did not gave more product (Table 1, entry 13). Therefore, 0.2 g catalyst of PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) was employed for further investigation.

The effects of reaction temperature on the cycloaddition were studied and results were displayed in Fig. 8a. With the increase in reaction temperature, the conversion of propylene oxide and the yield of propylene carbonate was significantly

**Table 1** Screening of catalysts for the synthesis of propylene carbonate

Entry	Catalyst	Catalyst (g)	Time (h)	Yield (%)[a]	Selectivity (%)[b]
1	PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.4)	0.2	5	79.5	98.6
2	PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.6)	0.2	3	88.4	98.4
3	PMO@ILCu$_2$(OH)$_3$Cl$_2$(0.8)	0.2	2.5	93	99.1
4	PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0)	0.2	2.5	97	99.3
5	PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.2)	0.2	2.5	96.7	99
6	ILCu$_2$(OH)$_3$Cl$_2$	0.2[c]	7	85	93.7
7	ILCl	0.2[c]	12	43	89.4
8	PMO	0.2[c]	12	18	86.5
9	–	–	24	0	0
10	PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0)	0.05	4	57	99
11	PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0)	0.1	4	81.7	99.3
12	PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0)	0.15	2.5	93	99.2
13	PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0)	0.25	2.5	96.5	99.2

Reaction conditions: propylene oxide (0.1 mmol), CO$_2$ pressure (1.5 MPa), catalyst, 60 °C.

[a] Isolated yields of pure products

[b] Determined by GC analysis

[c] Reaction temperature at 100 °C
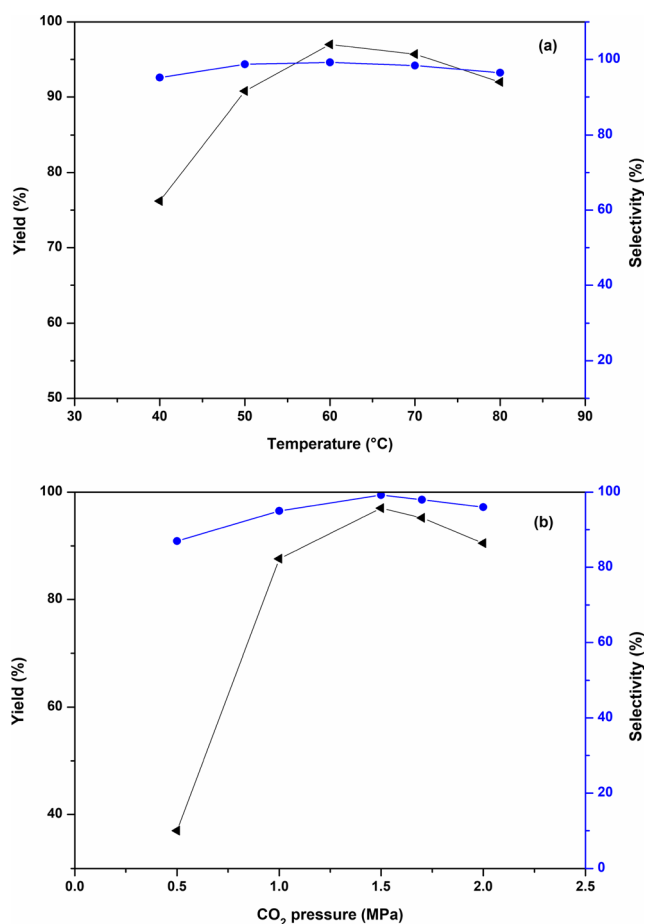
Fig. 8 (a) Effects of reaction temperature: propylene oxide (0.1 mmol), CO_2 pressure (1.5 MPa), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) 0.2 g, 2.5 h; (b) Effects of initial pressure: propylene oxide (0.1 mmol), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) 0.2 g, 60 °C, 2.5 h

increased, followed by a slight increase in the of propylene carbonate. However, the yield and selectivity of propylene carbonate exhibited a slight decrease after the temperature goes 60 °C. This may be due to the side reactions of isomerization and ring opening of propylene oxide occurred at overly high temperatures (determined by GC analysis). Thus, 60 °C was adopted as the appropriate reaction temperature. In addition, the effects of initial pressure on the catalytic was also investigated (Fig. 8b). It can be observed that the yield and selectivity of propylene carbonate were obviously facilitated when the increase CO_2 pressure from 0.5 MPa to 1.5 MPa, then displayed a visible decrease when CO_2 pressure was above1.5 MPa. It was because higher CO_2 pressures caused the increased concentration of the substrates in the low-pressure region, thus resulting in high yields and selectivities. Too high CO_2 pressure may retard the interaction of the substrates and the catalyst, and reduced the propylene oxide concentration to give low yields and selectivities [13–16]. Hence, 1.5 MPa of carbon dioxide was the optimum pressure.

To test the reusability of the catalyst, the catalyst was easily recovered from the reaction mixture by filtration
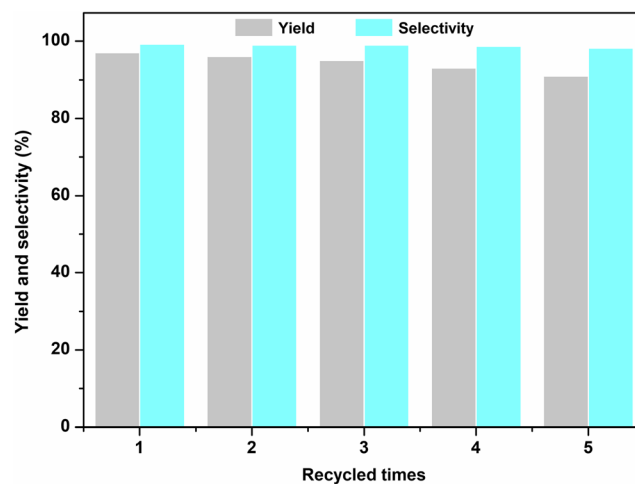
Fig. 9 Recyclability chart of PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0)

and then reused directly for a subsequent similar reaction. We have examined the reusability of this heterogeneous catalyst for the cycloaddition of propylene oxide with CO_2 to produce propylene carbonate under the optimized reaction conditions (Fig. 9). It was observed that the catalyst could be recycled and reused for at least five consecutive runs without significant losses in its catalytic activity. The recovered catalyst after five runs was characterized by FT-IR, which showed similar spectra with fresh catalyst, indicating the stability of the catalyst (Fig. 10). In addition, SEM image of the recovered catalyst after five runs showed similar morphology to that of the original one (Fig. 4g). The above results provide further evidence for the high stability of the catalyst PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0).

The catalytic performance of PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) has also been studied using other epoxides for the synthesis of corresponding cyclic carbonates. As can be seen in Table 2, the cycloaddition proceeded smoothly to give the
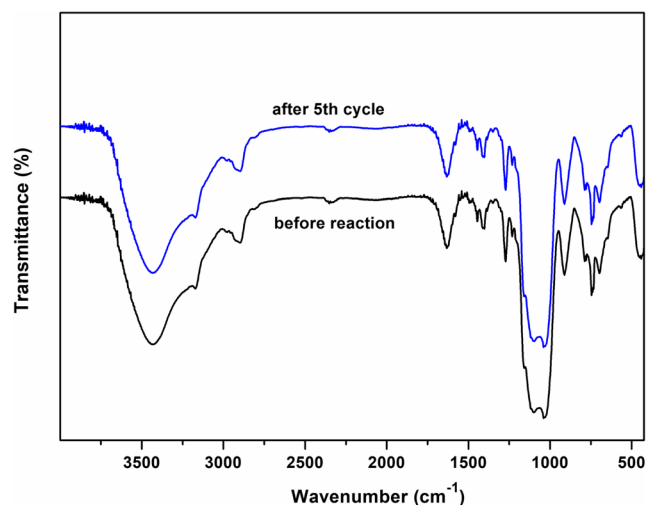
Fig. 10 FT-IR spectra of PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) before reaction and after 5th cycle of the reaction

Table 2 Cycloaddition of CO_2 to different epoxides over PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0).

Entry	Epoxide	Product	Time (h)	Yield (%)[a]	Selectivity (%)[b]
1			2.5	97	99.3
2			2.5	95	99.5
3			2	98	99.4
4			2	93	99.2
5			5	88	99
6			4	90	99.1

Reaction conditions: epoxide (0.1 mol), PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) 0.2 g, CO_2 (1.5 MPa), 60 °C.

[a] Isolated yields.

[b] Determined by GC analysis.

corresponding cyclic carbonates from the terminal epoxides within 5 h, which exhibited high yields (89% ~ 98%) and extremely excellent selectivities (99% ~ 99.5%). Pleasingly, epoxides containing electron withdrawing and electron donating groups were converted to the desired products and showed the good functional group tolerance. While the reaction of styrene oxide and cyclohexene oxide showed lower activity, and *longer times needed to* obtain good yields (Table 2, entries 5 and 6), probably due to the low reactivity of the β-carbon atom and the high steric hindrance of cyclohexyl group.

Based on the above and other reported data in the literature [14–21], a possible mechanism is predicated as shown in Scheme 3. In the proposed catalytic cycle, epoxide could be activated through the coordination of hydroxyl group sites of PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) and the O atom of epoxide, resulting in the polarization of C–O bond, so as to form the intermediate **A**, together with the adsorption and activation of CO_2 by the alkaline anion of copper oxychloride to form carbonate species. Then, intermediate **B** is formed via an
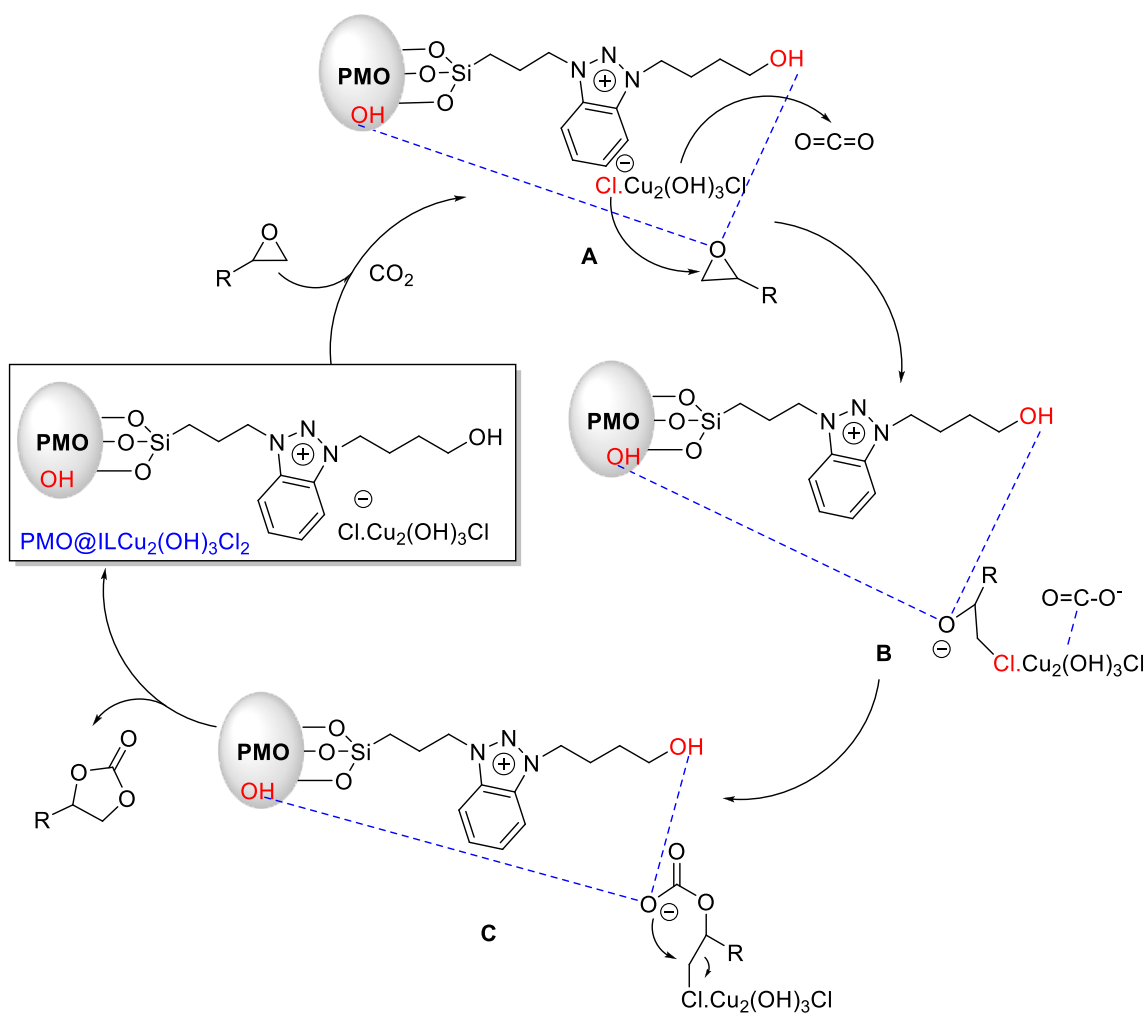
Scheme 3 Proposed reaction mechanism for the synthesis of cyclic carbonates

Table 3 Comparison of as-prepared catalyst with various previously reported catalyst for cycloaddition of CO_2 to epoxides

Entry	Catalyst	Conditions	Time (h)	Yield/ Selectivity (%)	References
1	[La{N(SiHMe$_2$)$_2$}$_2${κ^3-bpzcp}]/TBAB	propylene oxide, CO_2 (1 MPa), 70 °C	16	95/95	[10]
2	DBU/NIS	cyclohexene oxide, CO_2 (0.1 MPa), 60 °C	12	37/–	[13]
3	lignin/KI	styrene oxide, CO_2 (2 MPa), 140 °C	12	87/–	[15]
4	B_2O_3/n-Bu$_4$NBr	propylene oxide, CO_2 (2 MPa), 100 °C	2	90/99	[16]
5	amino-MIL-101(Al)@Fe$_3$O$_4$@SiO$_2$ /DMF	styrene oxide, CO_2 (0.1 MPa), 100 °C	16	80/100	[19]
6	NH$_3$I-Zn/SBA-15 (0.12)	styrene oxide, CO_2 (0.1 MPa), 130 °C	12	71/99	[20]
7	WP-KI	propylene oxide, CO_2 (1.5 MPa), 120 °C	3	94/–	[21]
8	Ti(HPO$_4$)$_2$·H$_2$O /n-Bu$_4$NBr	propylene oxide, CO_2 (1 MPa), R.T.	6	90/–	[25]
9	[P$_{4\,4\,4\,4}$][bzim]	cyclohexene oxide, CO_2 (1 MPa), 100 °C	3	71.2/99	[33]
10	PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0)	propylene oxide, CO_2 (1.5 MPa), 60 °C	2.5	97/99.3	This work

nucleophilic attack on the less sterically hindered carbon atom of epoxide. After that, followed by the nucleophilic interaction of **B** and CO_2, resulted in the formation of intermediate **C**. Subsequently, the intramolecular substitution of anion gave the final desired product and releases the catalyst for the next catalytic cycle. The presence of the alkaline anion of copper oxychloride probably have a synergetic effect on effective activation of CO_2 and presence of hydroxyl groups can significantly activate the epoxides, which provide sufficient catalytic sites and promote the catalytic cycloaddition.

To understand the advantage of the catalytic system, we compared the as-prepared catalyst with previously reported catalysts. As shown in Table 3, PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) catalyst presented superior features of excellent catalytic activities. These results demonstrated that the catalytic performance of PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) for the cycloaddition of CO_2 with epoxides to produce cyclic carbonates can be considered as quite promising, indicating that PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) is an *appropriate catalyst* for the cycloaddition of CO_2 to epoxides.

4 Conclusion

In conclusion, a novel type of copper oxychloride anionic benzotriazolium ionic liquid-modified periodic mesoporous organosilicas nanoparticles were synthesized, characterized and used as practical heterogeneous nanocatalysts for the synthesis of cyclic carbonates by the cycloaddition of CO_2 with epoxides. The synergistic effects between the hydroxyl groups sites on PMO framework and the active sites (hydroxyl groups/ copper oxychloride anion) of IL contributes to improving *the* catalytic sites of the catalyst. Among the different *loading* levels benzotriazolium-based ILs, PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) exhibited the most highly improved catalytic *activity* for the reaction with high yields and

selectivities *under solvent-* and cocatalyst-free conditions. Also, the catalyst PMO@ILCu$_2$(OH)$_3$Cl$_2$(1.0) displayed high thermal stability and could be easily recovered and recycled for five runs. Notably, considering the homogeneous catalytic cycloaddition/heterogeneous separation of this nanocatalyst, an efficient and environmentally benign strategy has been developed for the chemical fixation of CO_2 with epoxides.

Compliance with Ethical Standards

Conflict of interest There is no conflict of interest for each contributing author.

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