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Highly ordered mesoporous polymer supported imidazolium-based ionic liquid: an efficient catalyst for cycloaddition of CO_2 with epoxide to produce cyclic carbonates

Wei Zhang, Qixiang Wang, Haihong Wu*, Peng Wu, Mingyuan He*

A series of novel heterogeneous catalysts have been developed by immobilizing imidazolium-based functionalized ionic liquids on FDU-type mesoporous polymer. Various techniques such as X-ray diffraction, N2 adsorption–desorption, high resolution transmission electron microscopy have been used to characterize the physicochemical properties of the catalysts. Ionic liquid-functionalized mesoporous polymers serve as efficient catalysts in the solvent free cycloaddition reactions of CO2 with epoxides without use of any co-catalyst. The catalysts can be easily recovered and reused without significant loss of activity. In comparison with the polystyrene (PS) and mesosilica SBA-15 supports, the FDU mesopolymer possesses both mesoporous organic framework and abundant phenolic hydroxyl groups, which are key factors in improving the catalytic performance of supported ionic liquids.

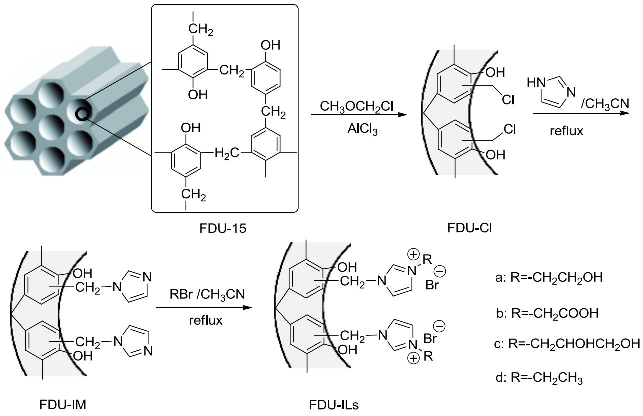
Introduction

Since carbon dioxide is expected to be a potentially abundant, cheap, non-toxic, nonflammable and renewable carbon resource in organic synthesis, many efforts have been made to develop effective processes for chemical fixation of carbon dioxide (CO_2) into valuable, economically competitive products.[1] However, the conversion and utilization of carbon dioxide are challenging for chemists due to its high thermodynamic stability.[2] One of the most promising strategies for effective fixation of CO_2 is the synthesis of valuable cyclic carbonates through the coupling reaction with epoxides.[3]

Cyclic carbonates are useful as aprotic solvents, electrolytes in secondary batteries, precursor for polymeric materials, fuel additives and green reagents etc.[4] In the past few decades, a considerable number of efficient catalytic systems have been developed for the coupling of carbon dioxide and epoxides. Numerous homogeneous catalysts associated with azaphosphatranes,[5] metal halides,[6] metal-salen complexes,[7] and ionic liquids (ILs)[8] have been employed for this transformation. Among them, ionic liquids have attracted particular attentions owing to their outstanding properties, such as negligible vapor pressure, good thermal stability and uniquely tunable structure.[9] Ionic liquids could be designed and modified by various functional groups in their cations or anions to gain the functionalities required by target reactions. The imidazolium based ILs with functional groups such as hydroxyl group (-OH) and carboxylic acid group (-COOH) have been proved to be effective to accelerate the ring opening of epoxides due to hydrogen bonding.[8a, 10] However, these homogeneous catalysts inevitably exhibit some problems such as catalyst recovery and product purification. Therefore, an increasing number of eco-friendly heterogeneous catalyst systems have been developed. ILs catalysts have been immobilized on the support materials such as silica,[11] chitosan,[12] cross-linked polymers,[13] magnetic nanoparticles,[14] carbon nanotubes,[15] and metal-organic frameworks[16] etc. It is worth noting that the presence of hydroxyl groups on solid materials could also efficiently promote the cycloaddition reaction of epoxides with $CO_{2.}$[11a, 12, 17] Although significant advances have been made in this subject, alternative immobilization strategies are still needed urgently. There is still an opportunity to develop more effective heterogeneous catalysts with a high activity, selectivity and stability for chemical fixation of $CO_{2.}$

The discovery of the FDU-type periodic mesoporous polymers with rigid phenolic resin walls opens up new possibilities for the design and synthesis of new heterogeneous catalysts. The FDU mesopolymers contain three dimensionally connected benzene ring framework with plenteous phenolic hydroxyl groups, and exhibit attractive merits of tunable mesostructure, high surface area, uniform pore sizes as well as high thermal and chemical stability.[18] In comparison to conventional mesosilica-based MCM-41 and SBA-15 as well as organic-inorganic hybrid mesoporous materials, the mesoporous polymer catalysts share the advantages of both mesostructures and conventional organic polymers, which favors the development of new green chemical processes for the syntheses of various fine chemicals. [18-19] We have developed a series of FDU-type mesoporous polymer-supported catalysts by post-modification, i.e. sulfonic acid groups, amino groups and ligands functionalized mesoporous polymers, which show a good catalytic activity in various organic syntheses and the advantages of easy recycling and reuse.[20] Notably, Shen et al. have reported that phenol itself (as a Lewis acid) can catalyze the cycloaddition of epoxides with carbon dioxide in the presence of organic bases, where the phenolic hydroxyl groups play a significant role. By contrast, the combination of alcohol with organic base shows no reactivity. [21] Whiteoak et al. investigated various substituted phenolic compounds by combining $n\mathrm{Bu_4NI}$ as a co-catalyst. Those containing phenolic OH groups were more reactive than 1, 2-diaminobenzene and 1, 2-benzenedithiol, which implied a unique ability of phenolic hydroxyl groups to activate the epoxide in this reaction.[22] In view of the H-bond donating capacities among the hydroxylic groups like aliphatic hydroxyl, phenolic hydroxyl and silanol, [23] FDU mesopolymer is presumably superior to those OH group-containing support materials such as cellulose, PEG and chitosan, etc. Thus, the abundant phenolic hydroxyl groups in FDU- mesoporous polymers are expected to act synergistically with imidazolium ILs and the halide ions to accelerate the cycloaddition reaction.

Based on previous studies, we have prepared a series of FDU-type mesoporous polymers supported imidazolium-based functionalized ionic liquids. Additionally, $\mathrm{Br^-}$ was chosen as the favorable anion in the immobilized ionic liquids in accordance with its nucleophilicity and leaving ability.[13b, 24] The novel heterogeneous catalysts have been used to synthesize various cyclic carbonates through the cycloaddition reactions of CO_2 and epoxides without co-catalyst and organic solvent.



Scheme 1 Schematic illustration for preparing a series of FDU-15 mesoporous polymers supported imidazolium-based ionic liquids: (a) FDU-HEIMBr, (b) FDU-CMIMBr, (c) FDU-DHPIMBr and (d) FDU-EIMBr.

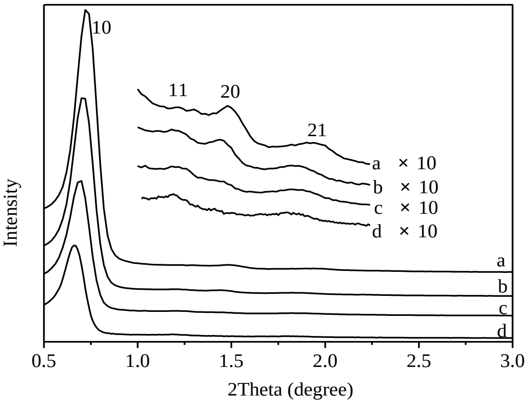


Fig.1 Small angle XRD patterns of (a) FDU-15, (b) FDU-Cl, (c) FDU-IM and (d) FDU-HEIMBr.

Results and discussion

Characterization of catalysts

According to the procedures shown in Scheme 1, the chloromethylation of FDU-15 mesoporous polymer was effectively catalyzed by anhydrous $AlCl_3$ to give FDU-Cl. We have well established this procedure for initial functionalization of mesoporous polymers.[20b-d] FDU-Cl was further functionalized with imidazole, affording FDU-IM though the reaction of $–CH_2Cl$ group with imidazolium. Further salification of FDU-IM with 2-bromoethanol gave FDU-HEIMBr. Accordingly, FDU-CMIMBr, FDU-DHPIMBr and FDU-EIMBr were synthesized by using 2-bromoacetic acid, 3-bromo-1, 2-propanediol and bromoethane instead of 2-bromoethanol respectively. The amount of grafting ionic liquid was determined by nitrogen analysis, which was 0.92 mmol g^{-1} (FDU-HEIMBr), 0.89 mmol g^{-1} (FDU-CMIMBr), 0.94 mmol g^{-1} (FDU-DHPIMBr), and 1.19 mmol g^{-1} (FDU-EIMBr), respectively.

The low-angle XRD patterns of parent FDU-15 and the mesoporous polymers after different functionalization are shown in Fig. 1 and Fig. S1. The XRD patterns of FDU-15 and its modified samples indicated a well ordered 2D hexagonal structure with *p6mm* space group as they revealed three diffraction peaks assigned to the [10], [20] and [21] planes. The well-resolved XRD patterns indicate that the highly ordered hexagonal mesostructure of FDU-15 was well preserved. The diffraction peaks shifted slightly to lower 2θ angle and decreased gradually in intensity after modifications, which indicates the pore structure was potentially affected by the introduction of the organic groups.

Fig.2 and Fig.S2 shows the N_2 adsorption-desorption isotherms and their corresponding pore size distributions of the FDU-15 mesoporous materials supported functionalized-ionic liquids. All the samples displayed a typical IV type isotherm with an apparent H1-type hysteresis loop and the pore size distributions all possessed relatively narrow peaks centered at ~6.8 nm, implying the presence of uniform mesoporous structures even

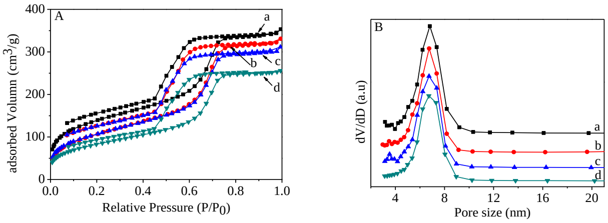


Fig.2 The Nitrogen adsorption–desorption isotherms (A) and BJH pore size distribution curves (B) of (a) FDU-15, (b) FDU-Cl, (c) FDU-IM and (d) FDU-HEIMBr.

Table 1 Textural properties of parent FDU-15 and grafted samples.

Sample	S_{BET}^{a} (m^2 g^{-1})	V_P^{a} (cm^3 g^{-1})	D_P^{b} (nm)
FDU-15	500	0.55	6.80
FDU-Cl	414	0.51	6.74
FDU-IM	386	0.47	6.74
FDU-HEIMBr	218	0.40	6.72

[a] Given by N_2 sorption at 77 K. [b] By BJH analysis.

after functionalizations [18a]. As expected, the BET surface areas, pore volume and pore diameter gradually decreased after post-modification (Table 1), probably due to that the organic groups (imidazole group) grafted to the inner channel of FDU-15 reduced the surface area and blocked the pores partially.

Fig.3 shows the representative transmission electron microscopy (TEM) images of FDU-HEIMBr. The results confirmed that same as the parent FDU-15, the array of the mesopores in FDU-HEIMBr was still of a typical 2D hexagonal mesostructure. Similar to FDU-HEIMBr, the well-ordered mesostructure were maintained precisely in FDU-EIMBr, FDU-CMIMBr and FDU-DHPIMBr (Fig.S3) after chemical grafting.

Fig. 4 shows the FT-IR spectra of FDU-15 mesoporous polymer and after stepwise modification. The chloromethylation of parent material developed a new band at 696 cm^{-1} (Fig. 4a and 4b), which is attributed to the stretching vibration of the C–Cl bond.[20b, 20c] This indicates that CH_2Cl groups were successfully grafted on the walls FDU-15 as a result of the chloromethylation with aromatic rings. Notably, in comparison with FDU-Cl, the observed bands of CH_2Cl group disappeared in the spectrum of FDU-IM (Fig. 4c). In turn, new bands appeared at 1653, 1562, 1106 and 1076 cm^{-1}, which are assigned to the imidazolium ring skeleton stretching vibrations[13b]. Besides, the band appeared at 3143 cm^{-1} assigned to newly appeared aromatic C–H stretching vibration of imidazole.[11c] After FDU-IM was further quaternized, the observed bands are similar (Fig. 4d), however, the intensity of imidazolium ring-related vibration slightly decreased, which is probably due to the effect by organic groups (-CH_2CH_2-OH). The solid state ^{13}C MAS NMR spectra of FDU-15, FDU-IM and FDU-HEIMBr are shown in Fig. 5. All samples show distinct signals at 29, 127 and 151 ppm, which are corresponding to the methylene bridges, phenolic hydroxyl substituted and other carbon in phenol ring, respectively [18a]. In comparison with FDU-15, the FDU-IM (Fig. 5b) and FDU-HEIMBr samples (Fig. 5c) display a new shoulder band at 134 ppm, which is attributed to the C_2 of imidazole ring carbon atoms.[25] The cis-carbons of imidazolium ring (C4 and C5 atoms) are unobvious and hidden by the enhanced peak of aromatic carbon at around 129 ppm. The distinct peaks at 33 ppm are presumably attributed to the methylene of 2-bromoethanol.[24b, 25-26]

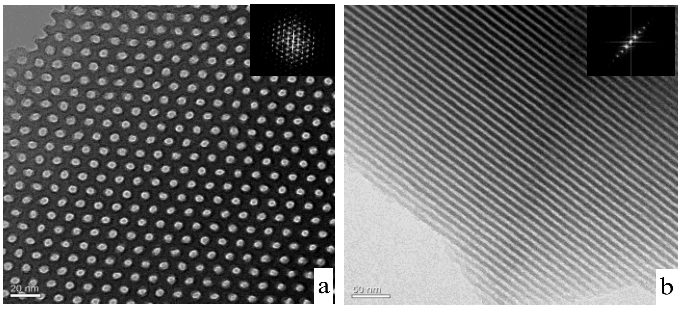


Fig.3 TEM images of FDU-HEIMBr taken along (a) [11] direction and (b) along [10] direction.

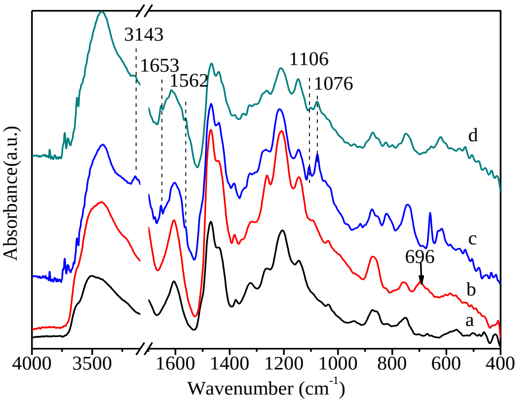


Fig. 4 FT-IR spectra of (a) FDU-15, (b) FDU-Cl, (c) FDU-IM and (d) FDU-HEIMBr

Additionally, the samples before and after functionalization were further characterized by EDX spectroscopy after surface-sputtered with Pt (Fig. 6). The characteristic peak of elemental

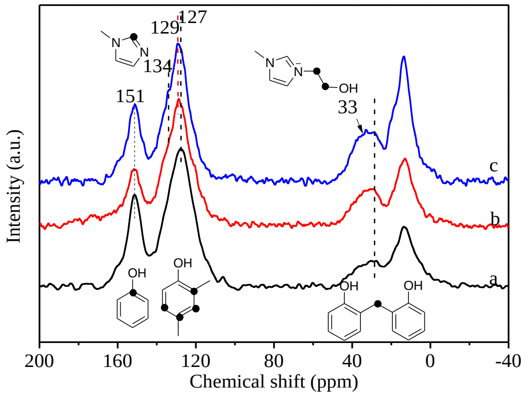


Fig.5 ^{13}C MAS NMR spectra of (a) FDU-15, (b) FDU-IM and (c) FDU-HEIMBr.

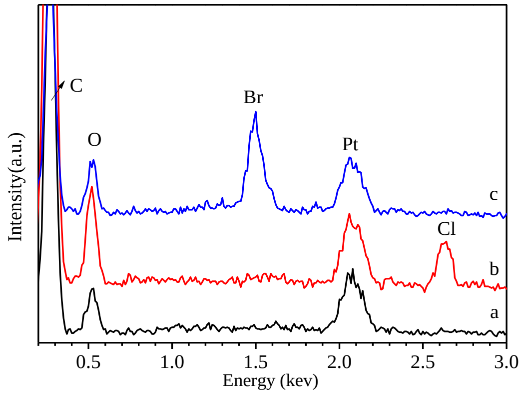


Fig.6 EDX spectra of (a) FDU-15, (b) FDU-Cl and (c) FDU-HEIMBr.

Cl was observed after the chloromethylation of FDU-15 (Fig.6b). After the reaction of 2-bromoethanol with FDU-IM, a new characteristic peak corresponding to elemental Br was developed, while the Cl peak disappeared in the spectrum of FDU-HEIMBr. These spectra confirmed the complete functionalization of FDU-Cl with imidazole and a successful immobilization of 1-(2-hydroxylethyl)-imidazolium bromide on the FDU-15 support, which was in agreement with the FT-IR analysis.

Catalytic cycloaddition of peroxides with CO_2

The cycloaddition reaction of propylene oxide (PO) and CO_2 to propylene carbonate (PC) was used as a model reaction to evaluate the catalytic performance of FDU-15 supported functionalized-ionic liquids. The influence of the reaction parameters was investigated using FDU-HEIMBr as a catalyst and the results are summarized in Table 2.

As shown in Table 2, the PC yield remarkably increased from 79% to 99% when the reaction temperature was raised from 90 ^{o}C to 110 ^{o}C (entries 1-2), whereas higher temperatures caused a significant decreased in the product selectivity (entries 3-4).The reaction at high temperatures may accelerate the side reactions like polymerization of PC and isomerization of PO to acetone. The influence of reaction pressure on the yield and selectivity of PC was studied at 110 ^{o}C for 3 h, when the CO_2 pressure gradually increased from 0.5 MPa to 1 MPa, the PC yield dramatically increased from 71% to 99% (entries 2 and 5). With an increasing system pressure, the PC yield decreased slightly (entries 6-8). A similar pressure effect was reported by Xie et al [13a] and Yang et al [24a] respectively. The reaction maintained a high PC yield within a wide range of CO_2 pressure (1-4 MPa) under mild conditions. Moreover, a reaction time of 3 h and a catalyst amount of 0.5 mol% were optimal for the synthesis of cyclic carbonate in this study (entries 9-12). Thus, the optimal conditions were that 30 mmol PO, 0.5 mol% catalyst, 1 MPa, 3 h and 110 ^{o}C. The good PC yield were obtained under the mild conditions which were probably ascribed to that FDU-HEIMBr catalyst possessed abundant hydrogen bonding interacted with the propylene oxide and its high surface and mesopores can in principle accelerate the interfacial mass and energy transfer.

Table 2 The influence of reaction parameters on the cycloaddition reaction of CO_2 with propylene oxide. [a]

Entry	T /^{o}C	P /MPa	T/h	Yield (%) [b]	Selectivity (%) [b]
1	90	1	3	79	99
2	110	1	3	99	>99
3	130	1	3	95	97
4	150	1	3	87	90
5	110	0.5	3	71	96
6	110	2	3	95	>99
7	110	3	3	93	99
8	110	4	3	92	99
9	110	1	1	85	98
10	110	1	2	96	>99
11[c]	110	1	3	83	99
12[d]	110	1	3	98	99

[a] Reaction conditions: PO (30 mmol, 1.74 g), FDU-HEIMBr (0.5 mol%, 160 mg). [b] Determined by GC using biphenyl as an internal standard. [c] FDU-HEIMBr (0.25 mol%, 80 mg). [d] FDU-HEIMBr (0.75 mol%, 240 mg).

A comparison of activities among various catalysts

Under the optimized reaction conditions, the catalytic activities of various catalysts for the cycloaddition of carbon dioxide and propylene oxide were investigated, and the corresponding results were listed in table 3. Either the parent material FDU-15 or FDU-Cl could scarcely catalyze the cycloaddition reaction (entries1-2). And FDU-IM gave a low yield of 32% with the selectivity of 95% in the cycloaddition reaction, suggested that without Br^- anion the presence of only imidazole groups (basic active sites) and phenolic hydroxyl groups could not provide highly active centers for this cycloaddition (entry 3). After the quaterisation, all the FDU-15 supported imidazolium-based

Table 3 Cycloaddition of CO_2 to propylene oxide over various catalysts.[a]

Entry	Catalyst	Yield (%)[b]	Selectivity (%)[b]	TON [c]
1	FDU-15	trace	-	-
2	FDU-Cl	2	5	-
3	FDU-IM	32	95	64
4	FDU-HEIMBr	99	>99	198
5	FDU-CMIMBr	98	99	196
6	FDU-DHPIMBr	98	>99	196
7	FDU-EIMBr	91	99	182
8	EMIMBr	67	>99	134
9	HEMIMBr	87	99	174
10	PS-HEIMBr	67	>99	134
11	SBA-15-HEIMBr	65	98	130

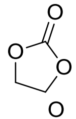
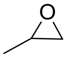
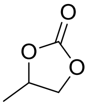
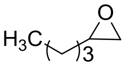
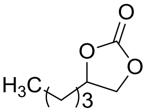
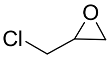
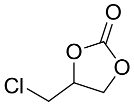
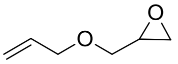
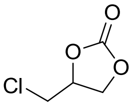
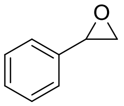
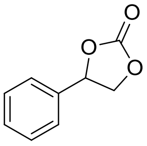
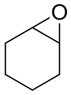
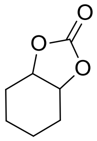
[a] Reaction conditions: PO (30 mmol, 1.74 g), 0.5 mol% catalyst, CO_2 pressure: 1 MPa, 110 ^{o}C, 3 h. [b] Determined by GC using biphenyl as an internal standard. [c] Turnover number (TON): moles of synthesized propylene carbonate per mole of immobilized imidazolium salts.

ionic liquids showed good catalytic activities (entries 4-7). Interestingly, the activity of FDU-EIMBr without hydroxyl group in ILs (entry 7) was close to those with hydroxyl group (entries 4-6). On the contrary, the homogeneous catalyst 1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide (HEMIMBr) with hydroxyl group showed much higher activity than 1-ethyl-3-methylimidazolium bromide (EMIMBr) without hydroxyl group (entries 8-9). After the graft of ionic liquids onto FDU support, the difference between HEMIMBr and EMIMBr was almost leveled-up, and the activity for cycloaddition was also enhanced. Quite differently, HEMIMBr grafted on other two supports of polystyrene (PS) and SBA-15 (entries 10-11) obviously showed poorer activity than HEMIMBr under this mild condition (entry 9). In order to further display the advantage of our FDU support, the catalytic performance were compared and the turn over numbers (TON) calculated in the present study were superior to that of the most of the previously reported analogous catalysts.[27] For instance, a TON of 198 could be achieved by FDU-HEIMBr (Table 3, entry 4), which was much higher than that of previously reported catalysts (Table S1, entries 1-5). Notably, Roshan et al. used a very efficient microwave synthesized methyl iodide-quaternized cellulose (mQC-1.I) (Table S1, entry 6) and obtained a TON as high as 242 with a yield of PC 97%.[28] However, the reported pressure of 1.2 MPa and the temperature of 120 ^{o}C for the reaction were both higher than those (1MPa, 110 ^{o}C) in our study. All these results suggest that FDU support contribute greatly to this cycloaddition, where the abundant phenolic hydroxyl group of FDU-15 may facilitate the ring opening of epoxide and thus distinctly enhance the activity for cycloaddition. It was reported that strong chelating ability through hydrogen bonding with the oxygen atom of epoxide enabled the ring opening more easily. A similar catalysis effect was reported by Shen et al, [21] which proposed that Lewis acid phenol through hydrogen bonding can catalyze the cycloaddition reaction of epoxides with CO_2 in the presence of organic bases. In short, both mesoporous organic framework (high surface area) and abundant phenolic hydroxyl groups of FDU-15 could highly improve the catalytic performance of supported ionic liquids by the synergistic effect.

Cycloaddition of CO_2 with other epoxides

The catalytic properties of FDU-HEIMBr for the reactions of various epoxides with CO_2 were examined under the optimized reaction conditions, the results are summarized in Table 4. The reactions of terminal epoxides with both electron-withdrawing and electron-donating substituents proceeded well and all gave high yields and selectivity (entries1–6). However, the cyclohexene oxide exhibited relatively low yield with higher CO_2 pressure and prolonging the reaction time to 24 h, which presumably due to a steric hindrance obstruct the nucleophilic attack of Br^-.

Table 4 Cycloaddition of CO_2 with various epoxides catalyzed by FDU-HEIMBr.[a]

Entry	Epoxide	Product	Yield [b](%)	Selectivity [b] (%)
1			99	99
2			99	99
3			97	99
4			96	98
5			99	99
6[c]			95	99
7[d]			70	97

[a] Reaction conditions: epoxides 30 mmol, 0.5 mol% FDU-HEIMBr, CO_2 pressure 1 MPa, 110^{o}C, 3 h; [b] Determined by GC; [c] Reaction time 5h; [d] CO_2 pressure 2 MPa, 24 h.

Recycling of catalysts

Experiments were carried out to test the reusability of the FDU-HEIMBr catalyst under the optimal reaction conditions. In each run, the catalyst was separated by simple filtration, washed with

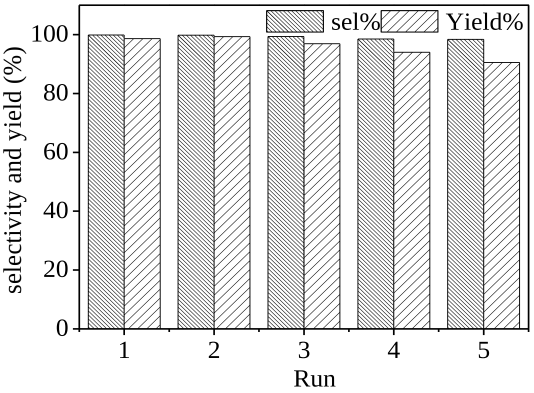


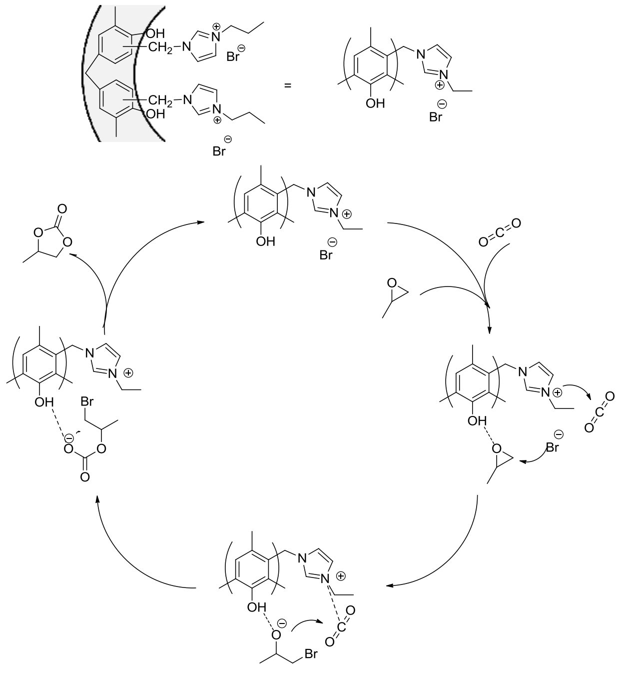
Fig. 7 Recycling of FDU-HEIMBr in the cycloaddition of CO_2 to propylene oxide. Reaction conditions: PO (30 mmol, 1.74 g), 0.5 mol% catalyst, CO_2 pressure: 1 MPa, 110 ^{o}C, 3 h.

acetone and then dried in vacuum and then used directly for the next cycle. As shown in Fig.7, there was no remarkable decrease in PC yield after five runs, which indicated a high stability and reusability of the prepared catalyst.

In addition, the reused FDU-HEIMBr catalyst was characterized by the XRD and TEM analysis, as shown in Fig. S4 and Fig. S5, there was no significant difference between the XRD patterns and TEM image of the fresh and the fifth-used catalyst, which provided further evidences for the good structural stability of FDU-HEIMBr. Compare to fresh FDU-HEIMBr, the FT-IR spectra of the used catalyst were retained except for the presence of a new band at 1785 cm^{-1} (Fig. S6), which is attributed to the asymmetric vibration of the C=O groups in cyclic carbonate. A similar result was observed in the reported literature.[25, 29] Cyclic carbonate may occupy the active sites of the catalyst, and then decreased the activity of the catalyst. Moreover, the TG analysis curves confirmed that FDU-HEIMBr catalyst was stable up to 240^{o}C (Fig. S7). Xiong et al. have reported that the weight loss of the used catalyst appeared slightly earlier in TGA curves [30], which was due to desorption of the residual cyclic carbonate. The same phenomenon was observed in our test.

Plausible reaction mechanism of cycloaddition reaction

The plausible reaction mechanism were deduced on the basis of the previous literatures,[11a, 11c, 12, 21-22] as well as the results in our study. As shown in Scheme 2, the polarization of C−O bonds of the epoxide first occurs by hydrogen bonding between the epoxide and the phenolic hydroxyl group of FDU-EIMBr. Meanwhile, the ring opening of the epoxide via nucleophilic attack of the halide anion Br^{-} occurs on the less sterically hindered-carbon atom of the epoxide. Then, the activated CO_2 by the tertiary ammonium from the IL-catalyst further interacts with the ring-open intermediate. Finally, the cyclic carbonate is formed by succeeding intramolecular ring-closure with simultaneous releasing of Br^{-} and regeneration of the catalyst.



Scheme 2 The proposed mechanism for cycloaddition of epoxide and CO_2 catalyzed by FDU-EIMBr.

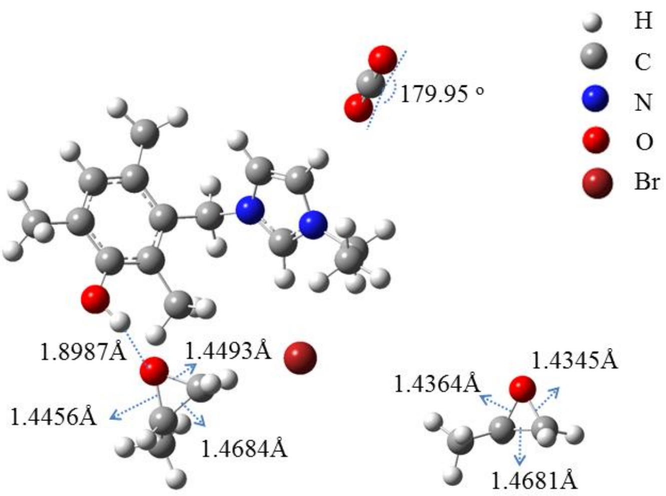


Fig. 8. Interaction of reactant complex with PO, CO_2 and FDU-EIMBr from the DFT.

Additionally, the interaction mentioned between reactant complex was further investigated using the density functional theory (DFT) method implemented in the Gaussian 09 package.[30] The geometry optimizations and frequency calculations were carried out with the B3LYP using the 6-311++G (d, p) basis set. A strong hydrogen-bonding interaction formed between phenolic hydroxyl group and PO, while the length of C−O bonds in polarized PO were elongated to 1.4456 Å and 1.4493 Å, respectively (Fig. 8). As expected, the distance (1.8987 Å) between phenolic H atom and the O atom of PO was significantly shorter than that of chitosan (1.969 Å, 2.038 Å) [12], which further demonstrated the superiority of the FDU support. Moreover, it was observed that the bond angle of linear CO_2 bended from 180 ° to 179.95 °, which indicated that the imidazolium ring moiety could activate CO_2. All the results of DFT study, to a certain extent, verified the proposed reaction mechanism.

Conclusions

A series of FDU-15 mesopolymer supported imidazolium-based ionic liquids were successfully prepared. They proved to be efficient heterogeneous catalysts for the cycloaddition of CO_2 with epoxides in the absence of any co-catalyst and organic solvent. The phenolic hydroxyl groups played a key role in promoting the reaction in cooperation with quaternary ammonium halides. Compared with traditional solid supports of polystyrene and SBA-15 mesosilica, the mesoporous organic framework and abundant phenolic hydroxyl groups of FDU-15 possessed the advantages of significantly improving the catalytic performance of supported ionic liquids. Additionally, the catalyst can be separated by simple filtration and reused for five times without significant loss of activity. The obtained exciting results appeal for the further development of new mesoporous phenolic supports.

Experimental

General

All reagents were commercially available (Aldrich) and were directly used without further purification. The X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE instrument using Cu-Kα radiation (λ= 1.5418 Å) at 35 kV and 30 mA. Nitrogen adsorption–desorption isotherms were measured on a Quancachrome Autosorb-3B instrument after evacuating the samples at 423 K for 6 h. The specific surface areas were evaluated using Brunauer–Emmett–Teller (BET) method and the pore distribution was calculated by BJH method from adsorption branches of isotherms. The TEM images were recorded using a JEOL-JEM-2010 microscope after the specimens were dispersed in ethanol and placed on holey copper grids. The IR spectra were recorded on a Nicolet NEXUS 670 infrared spectrometer. N elemental analyses were performed on an Elementar VarioEL III CHN elemental analyser. ^{1}H spectra were acquired on a Bruker DRX500 spectrometer at 400 MHz in $CDCl_3$ with TMS was as an internal standard. The resulting reaction mixture was analyzed by GC-mass spectrometry (GC-MS) for product identification, which was performed on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. The conversion and selectivity of products were quantified on Agilent's 7890A GC equipped with a flame ionization detector and a DB-WAX column (30 m × 0.32 mm × 0.25μm) using biphenyl as an internal standard.

Preparation of FDU-IM

FDU-15 mesopolymer was prepared according to previously reported procedures [18a]. FDU-15 was chloromethylated with chloromethyl methyl ether to obtain FDU-CH_2Cl using $AlCl_3$ as a catalyst[20b-d]. FDU-CH_2Cl (18.0 g) was further functionalized with imidazole (3.3 g) in acetonitrile (100 mL) under reflux for 24 h. The obtained material was separated by filtration and dispersed in 50 mL acetone under mild ultrasonication for 1 h to remove physisorbed imidazole. The resulting suspension was filtered and dried at 60 ^{o}C under vacuum for 24 h to give FDU-IM.

Preparation of FDU mesopolymers supported functionalized-ionic liquids

For a typical synthesis procedure of FDU-15 supported 1-(2-hydroxylethyl)-imidazolium bromide (FDU-HEIMBr), FDU-IM (10.0 g) was added into 80 mL acetonitrile, then 2-bromoethanol (2.5 g) was added slowly with vigorous stirring and the mixture was refluxed for 24 h. The solid phase was filtered and washed repeatedly with acetone and then dried overnight at 80 ^{o}C. The resulting solid was denoted as FDU-HEIMBr. According to the above similar procedure, the other FDU-15 supported imidazolium-based ionic liquids, FDU-CMIMBr, FDU-DHPIMBr and FDU-EIMBr, were synthesized respectively by using 2-bromoacetic acid, 3-bromo-1, 2-propanediol and bromoethane instead of 2-bromoethanol.

Typical procedure for the synthesis of cyclic carbonate from epoxide and CO_2

In a typical catalytic cycloaddition, propylene oxide (30 mmol), catalyst (0.5 mol%, according to the amount of ionic liquid) and biphenyl (0.2 g, internal standard for GC analysis) were placed in a 25 mL stainless-steel autoclave equipped with a magnetic stirrer. CO_2 was then charged in the autoclave. The reaction was carried out at specified temperature and a constant pressure for a desired period of time. After the reaction, the reactor was cooled in an ice-water bath and slowly depressurized. The catalyst was washed with acetone, dried, and reused without any further activation. The products were also identified by ^{1}H NMR spectra. (See supporting information).

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Notes and references

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Graphical abstract

A series of imidazolium-based ionic liquids were supported on FDU-15 mesoporous polymer with abundant phenolic hydroxyl groups, which proved to be efficient for the cycloaddition of CO_2 with epoxides in the absence of any co-catalyst and organic solvent.