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Fluoro-functionalized polymeric ionic liquids: highly efficient catalysts for CO₂ cycloaddition to cyclic carbonates under mild conditions[†]

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Fluoro-functionalized polymeric ionic liquids (F-PILs) with imidazolium cations and bromide or chloride anions were designed for cycloaddition reactions of CO_2 with epoxides. It was found that the fluorine content in F-PILs significantly influenced the catalytic activity of the catalysts, and F-PIL-Br showed three times higher activity for CO_2 reacting with styrene oxide than non-fluorous PIL-Br. Moreover, F-PIL-Br could be extended to catalyse a broad range of reactants under 1 MPa CO_2 pressure, producing a series of cyclic carbonates in excellent yields (93–99%). In addition, it showed high stability and easy recyclability.

As an abundant, nontoxic, non-flammable, and renewable carbon resource, CO₂ activation and conversion for making commodity chemicals, fuels, and materials is a topic of current interest.¹ The major challenge originates from the inherent thermodynamic stability and kinetic inertness of CO_2 , which calls for a remarkable driving force to ensure efficient transformation. In this respect, employment of highenergy starting materials including epoxides/aziridines, alkenes/alkynes, activated C-H bonds and organometallics via carboxylation,^{1f} amidation,² carbonation^{2,3} and hydrogenation⁴ has been proposed for systematic exploration of CO₂ transformation. To ensure efficient conversion, coordination of CO₂ with transition metals,^{1f} amines,² N-heterocyclic carbenes (NHCs),⁵ and frustrated Lewis pairs (FLPs)⁶ is one of the most powerful ways to induce the inert CO₂ molecule to undergo chemical reactions. In addition, containing of CO2philic materials such as polyethylene glycols (PEGs) leads to increased catalytic activity through the "CO2-expansion of PEG" effect.⁷ Recently, a particular interaction of CO_2 with fluoro-containing compounds has been investigated for designing CO₂-soluble catalysts, through attachment of fluorinated chains to chelating agents, surfactants, and catalyst

ligands.^{6a,8} Hence, fluorous materials have the potential to be applied as efficient catalysts for CO_2 activation and transformation, which has rarely been reported in the literature.^{6a,9}

One of the few commercial routes using CO₂ as a raw material is the insertion of CO2 into epoxides to afford the fivemembered cyclic carbonates (Table 1), which can serve as electrolytes in secondary batteries, valuable monomers of polycarbonates and polyurethanes, aprotic polar solvents, and raw materials in a wide range of chemical reactions.^{3b,10} Although the formation of cyclic carbonate via homogeneous catalysts has been industrialized, the process requires high temperatures and pressures, and product separation is difficult. The development of a heterogeneous catalyst for synthesizing cyclic carbonate under mild conditions remains a challenge.¹¹ Generally, activation of epoxides has been considered in designing heterogeneous catalysts for cyclic carbonate production, employing metal-containing catalytic centres^{11b,c,12} or hydroxyl group-containing supports (e.g. silica),¹³ via the interaction of epoxides (O atom) with electron-deficient metal

Table 1 Cycloaddition reaction of styrene oxide with CO_2 catalyzed by F-PILs^a

		> + CO ₂ <u>Cat</u>		
Entry	Cat.	Time/h	Conv. ^b /%	Yield ^b /%
1	None	6	3	1

-				-
2	F-PIL-Cl	3	15	13
3	F-PIL-Br	3	63	58
1	F _{0.5} -PIL-Br	3	9	7
5	PIL-Br	3	4	3
5	F-PIL-Br	9	>99	96

^{*a*} Reaction conditions: styrene oxide 10 mmol, catalyst 1 mol% (mol% of imidazolium salt moieties to epoxide), 120 °C, CO₂ pressure 1 MPa. ^{*b*} Determined by ¹H NMR (CDCl₃, 400 MHz) using mesitylene as an internal standard.

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centres, or hydrogen-bond formation. Although effective, rare/ transition metals and tremendous supports are expensive, thus increasing the cost of production. Inspired by the underlying principles of CO_2 activation, He *et al.* have developed PEG-supported quaternary ammonium salt¹⁴ and fluorous polymer-bound phosphonium chloride⁹ for the cycloaddition reaction of CO_2 with epoxides, while high CO_2 pressure was still required to achieve quantitative yield of cyclic carbonates. Therefore, design and preparation of functionalized heterogeneous materials for efficient CO_2 activation and subsequent conversion under mild conditions is still urgently needed.

Fluorine-containing compounds or materials have been reported to have CO₂-philic properties,¹⁵ which presumably could facilitate CO2 conversion with increasing activity. Herein, we designed fluoro-functionalized polymeric ionic liquids (F-PILs) with imidazolium cations and bromide or chloride anions for catalyzing the cycloaddition reactions of CO₂ with epoxides, which were synthesized under catalyst-free conditions as illustrated in Scheme 1. All the as-synthesized PILs were effective to catalyse the reaction of CO₂ with styrene oxide under 1 MPa CO₂ pressure and solvent-free conditions. Interestingly, the fluorine content in the PILs significantly influenced the catalytic activity of the catalysts, following the order: PIL-Br < F0.5-PIL-Br < F-PIL-Br. Notably, F-PIL-Br showed three times higher activity for this reaction than nonfluorous PIL-Br, together with a broad range of reactants, excellent product yields (93-99%), high stability and easy recyclability.

In this study, a two-step alkylation has been designed to produce polyimidazolium salts under catalyst-free conditions



Scheme 1 Synthetic route and structures of the polymeric ionic liquids (PILs).

(Scheme 1). Fluorine linkages were directly involved in the backbone of the PILs. For comparison, PILs with different fluorine content and the corresponding non-fluorous PIL were synthesized. The formation of F-PILs was revealed by Fourier transform infrared (FTIR) spectroscopy, elemental analysis and cross-polarization magic-angle spinning (CP/MAS) ¹³C NMR. In FTIR spectra of **F-PIL-Br** (Fig. 1A and Fig. S1, ESI†), the imidazolium structures were confirmed by the characteristic bands of 1160 (C–N⁺), 1560 (C=C) and 1635 (C=N) cm⁻¹. The FTIR bands located at 1035 cm⁻¹ correspond to C–F stretching



Fig. 1 (A) FTIR spectra of F-PIL-Br (fresh and recycled). (B) CP/MAS 13 C NMR spectra of the PILs. F-PIL-Br: 31.9, 36.0, 42.8, 115.6, 122.5, 137.1, 144.4; F-PIL-Cl: 32.1, 35.5, 42.2, 115.6, 122.3, 136.1, 144.0; F0.5-PIL-Br: 42.0, 50.6, 116.7, 119.3, 125.2, 128.4, 129.9, 134.8, 139.5, 143.4; PIL-Br: 51.3, 53.4, 123.8, 125.1, 128.8, 130.2, 135.3, 137.6. (C) TGA analysis of the PILs under air up to 600 °C at a rate of 20 °C min⁻¹.



Fig. 2 Catalytic activity of PILs for the reaction between styrene oxide and CO₂. Reaction conditions: styrene oxide 10 mmol, catalyst 1 mol% (mol% of imidazolium salt moieties to epoxide), 120 °C, CO₂ pressure 1 MPa. Yield and conversion were determined by ¹H NMR (CDCl₃, 400 MHz) using mesitylene as an internal standard.

mode and the respective bands for the methylene group appeared around 2960 cm⁻¹.¹⁶ The presence of chemical shifts in the range of 115.6–144.4 ppm in CP/MAS ¹³C NMR spectra of PILs (Fig. 1B) belonged to the aromatic carbons in the backbone, and those at 31.9–42.8 ppm to methylene carbon. Thermogravimetric analysis (TGA) indicated that the resulting PILs were stable up to 300 °C in an air environment (Fig. 1C).

Styrene carbonate synthesis from CO₂ and styrene oxide was carried out catalyzed by the resulting PILs, and the results are shown in Table 1 and Fig. 2. It was found that almost no reaction occurred in the absence of any catalyst under the experimental conditions (Table 1, entry 1), while the as-prepared PILs were effective. F-PIL-Br showed much higher activity than F-PIL-Cl though both of them had the same cation (entry 2 vs. 3), probably owing to the superior leaving ability and nucleophilicity of Br⁻ over Cl⁻.¹⁷ Notably, the catalytic efficiency of PILs with different cations decreased in the order: \mathbf{F} -PIL⁺ > F0.5-PIL⁺ > PIL⁺ (Fig. 2), which increased with the fluorine content in the cations. Little catalytic activity of PIL-Br and F0.5-PIL-Br was observed within 3 h, while increasing the fluorine content, i.e. F-PIL-Br, gave much higher yield of styrene carbonate under the same conditions (Fig. 2). In addition, the F-PIL⁺ cation with CO₂-philic fluorine linkages showed the highest activity (89%), whereas the cation without fluorine linkages gave much lower activity (25%) within 6 h. Hence, incorporation of fluoro atoms into the PIL skeleton played important roles in CO2 activation and deserved much higher catalytic activity for subsequent CO₂ transformation. 96% yield of styrene carbonate was obtained when the reaction time was 9 h catalyzed by F-PIL-Br under 1 MPa CO_2 pressure (Table 1, entry 6), which was superior (1 MPa, 120 °C) to most of the metal-free heterogeneous catalysts reported before. For example, harsh reaction conditions were needed to obtain a quantitative yield of cyclic carbonates for fluorous polymer immobilized phosphonium chlorides (8 MPa, 150 °C),9 tubular microporous organic networks (3 MPa, 160 °C),¹⁸ cross-linked polymeric nanoparticles (3 MPa, 160 °C),¹⁹ supported glycidyl-group-containing ILs (6 MPa, 130 °C)^{13a} and polyaniline salts (5 MPa, 115 °C).²⁰ In addition, fluorine-functionalized PIL (**F-PIL-Br**) was much more effective than the homogeneous imidazolium IL (4 MPa, 110 °C)²¹ and the carboxylic acid-group containing IL (8 MPa, 140 °C).²² From the above results, it can be deduced that the fluorine in the as-prepared catalysts promoted the activities of the catalysts. The exact promotion mechanism by fluorine was unclear, which presumably derived from the interaction between the fluorine atom (strongly electronegative) and the carbonyl carbon atom (electropositive) of CO₂, thus leading to activation of CO₂ and to the increased concentration of CO₂ around the catalytic centre as well, and facilitating CO₂ conversion with increasing activity.¹⁵

The generality of **F-PIL-Br** catalysing CO_2 reacting with more epoxides was also examined and the results are summarized in Table 2. It was demonstrated that terminal epoxides with both

 Table 2
 Cyclic carbonate synthesis catalyzed by F-PIL-Br^a

 O
 O



^{*a*} Reaction conditions: epoxide 10 mmol, **F-PIL-Br** 1 mol% (mol% of imidazolium salt moieties to epoxide), CO₂ 1 MPa, 120 °C, 9 h. ^{*b*} Determined by ¹H NMR (CDCl₃, 400 MHz) using mesitylene as an internal standard.



Fig. 3 Recycle test of **F-PIL-Br**. Conversion of styrene oxide and the yield of styrene carbonate were determined by ¹H NMR using mesitylene as the internal standard.

electron-donating (Table 2, entries 1–5) and electron-withdrawing groups (Table 2, entry 6) could be transformed to the corresponding cyclic carbonates with almost quantitative yields (93–99%) within 9 h under 1 MPa CO_2 pressure at 120 °C.

To test the catalyst reusability, the reaction of styrene oxide with CO_2 catalyzed by a catalytic amount of **F-PIL-Br** was performed. The catalyst was recovered through centrifugation after the reaction mixture was washed with dichloromethane, dried and then used directly for the next run without any further purification. The results shown in Fig. 3 indicate that the yield of styrene carbonate was almost constant after five successive recycles. Peaks in the FTIR spectra of the catalyst showed no difference between the fresh and the recycled catalyst (Fig. 1A), suggesting that **F-PIL-Br** had excellent stability under the experimental conditions.

Conclusions

F-PILs were designed for the cycloaddition reaction of CO_2 with epoxides. The catalytic activity of the resulting F-PILs increased with the fluorine content in the cations, and F-PIL-Br showed the highest efficiency, producing a series of cyclic carbonates with excellent yields (93–99%) under 1 MPa CO_2 pressure. In addition, it showed high stability and easy recyclability. Design and application of other fluorous materials for CO_2 activation and transformation is under investigation in our lab.

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