

# Ionic liquid confined spaces controlled catalytic CO<sub>2</sub> cycloaddition of epoxides in BMIm.ZnCl<sub>3</sub> and its supported ionic liquid phases

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## ABSTRACT

Chemical fixation of CO<sub>2</sub> to epoxides is an atom-economic and environment-benign approach to generate cyclic carbonates. Herein, we report efficient activation of the different aromatic and aliphatic epoxides at ambient reaction conditions. Our n-butyl-3-methylimidazolium trichlorozincate (BMIm.ZnCl<sub>3</sub>) ionic liquid presents higher activity with 56–95% conversion for the different aromatic and aliphatic epoxides from atmospheric pressure to 5 bar pressure at 40 °C. Small sized epoxides showed higher conversion and selectivity to cyclic carbonate as compared to bulky ones suggesting that the large epoxide substrates restricted diffusion into the confined spaces of BMIm.ZnCl<sub>3</sub> IL, which limited the access of reactants to the catalytic active sites. By supporting the IL on the simple commercial SiO<sub>2</sub>, the confined SILP-ZnCl<sub>3</sub> catalyst boosted the activity with maximum conversion and yield (99%) to cyclic carbonates under 10 bar at 100 °C. This higher performance could be attributed to the formation of the IL-cages onto SiO<sub>2</sub> that enhances the local charge density and modulates the orientation of the IL near the surface to assist substantial charge transfer, leading to surface polarization and specific adsorption to ions. The reaction exemplifies a rare mechanism, supplemented by ex-situ ESI-MS analysis, in which epoxide 'O' is strongly H-bonded to the C-H of imidazolium cation, while the ZnCl<sub>3</sub> anion acts as nucleophile to facilitate the ring opening without its dissociation in chloride anion and ZnCl<sub>2</sub>, contrasting to the previous reports.

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) mitigation is one of the major challenges for the modern world due to its heavily involvement in global warming [1]. To counter the accumulation of anthropogenic CO<sub>2</sub>, various approaches have been investigated to capture and convert it into chemical feedstocks such as methanol, methane, carbon monoxide, fuels, lubricants, amides, esters and cyclic carbonates [2–7]. Among them, chemical CO<sub>2</sub> fixing to epoxides is a sustainable approach due to atom-economic and environment-benign processes [8,9]. The process gained a great interest due to the application of cyclic carbonates, such as intermediates in the synthesis of polycarbonates and polyurethanes, environmentally friendly, polar, aprotic solvents, with low odor and toxicity, and electrolytes for lithium-ion batteries [10–15].

Various strategies based on homogeneous and heterogeneous systems containing alkali metal halides, quaternary ammonium salts, polymers, molecular organic frameworks (MOFs), frustrated Lewis pairs

(FLPs), transition-metal complexes and functionalized graphene as catalysts has been widely studied for this transformation [8,16–28]. However, these catalytic systems have disadvantages such as, required the use of high pressures and/or temperatures, high catalyst loadings, low catalyst stability and cost effectiveness. Zinc-based catalysts have been employed but the reaction only occurs in the presence of tetrabutylammonium bromide (TBAB) [29,30]. Ionic liquids (ILs) have also been investigated because of their interesting properties, for example, easily fine-tuning of basicity-nucleophilicity by playing with the electronic-steric features of the both cation and anions, highly CO<sub>2</sub> absorption capacity and chemical inertness [31–45]. However they require harsh reaction conditions (>120 °C and >10 bar). Few reports based on metal-containing ILs (metal with sophisticated ligands) are examined for the cycloaddition of CO<sub>2</sub> to epoxides but required harsh reaction conditions [46–51]. Although chemical fixation of CO<sub>2</sub> to epoxide catalysed by silica supported imidazolium IL containing halides (SILP-X, X = Br, Cl, I) has been achieved, and needed high pressure (>10

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bar) and temperature, and demonstrate low TONs [52,53]. Thus, high efficiency low cost catalysts need to be preferentially explored to catalyse the CO<sub>2</sub> cycloaddition of epoxides with mild conditions. Moreover, real mechanistic insights involving the metal-halide based ILs are needed.

Herein, we now address the challenge of the use of simple *n*-butyl-3-methylimidazolium trichlorozincate (BMIm.ZnCl<sub>3</sub>) IL as a homogeneous and heterogeneous catalyst (SILP-ZnCl<sub>3</sub>). This system can drive efficiently CO<sub>2</sub> cycloaddition to different epoxides under ambient conditions (Scheme 1). Indeed, the reaction occurred in IL confined spaces that allows the control of the diffusion of reactants, intermediates and products to the catalytic active sites in the bulk IL [7,54]. Hence, IL forms ionic cages when it approaches to the solid SiO<sub>2</sub> support [55,56]. The H-bonding and hydrophobicity/hydrophilicity of the IL to SiO<sub>2</sub> enhances the local density and modulates the orientation of the IL near the surface to facilitate substantial charge transfer, leading to reconstruction of the interfacial ionic structure [57,58]. This results the surface polarization, direction, and specific adsorption to ions that can synergistically affect the structure and function of interfacial ILs [59].

## 2. Experimental

All the epoxides and ZnCl<sub>2</sub> were purchased from Sigma-Aldrich chemicals. SiO<sub>2</sub> (silicagel 60, 0.05–0.2 mm) was purchased from Vetec Brazil. BMIm.Cl (1-*n*-Butyl-3-methylimidazolium chloride) was prepared from a well-known method [60]. CO<sub>2</sub> (>99.999%) were purchased from White-Martins Ltd, Brazil. NMRs spectra were collected using a Bruker AVANCE III 500 MHz.

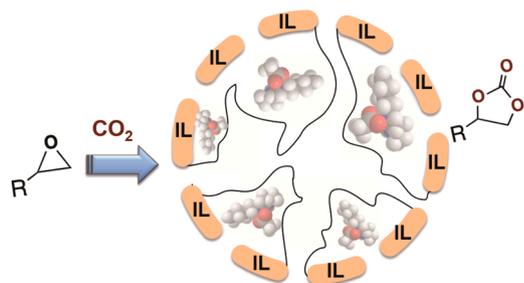
### 2.1. Catalytic CO<sub>2</sub> cycloaddition to epoxides by BMIm.ZnCl<sub>3</sub>

All the catalytic reactions were conducted in a Schelenk tube (30 mL) under atmospheric pressure of CO<sub>2</sub>. Typically, the desired epoxide (6.25 mmol) was dissolved in BMIm.ZnCl<sub>3</sub> (0.625 mmol) at room temperature. Then the tube was purged with CO<sub>2</sub> and the mixture was maintained under atmosphere of CO<sub>2</sub> using balloon. The reaction mixture was stirred and heated at the desired temperature for 24 h in silicon oil bath. The conversion and products selectivity were calculated by <sup>1</sup>H NMR.

The reactions under 5-bar pressure were tested in a homemade glass-lined stainless steel Fischer-porter reactor (24 mL). In a general procedure, the reactor was charged with BMIm.ZnCl<sub>3</sub> (6.25 mmol) and the epoxide (0.625 mmol), and flushed with CO<sub>2</sub> to remove air. Then the reactor was filled with 5-bar of CO<sub>2</sub>. The reaction was performed at 40 °C in silicon oil bath. After 24 h, the reactor was cooled down and the pressure was slowly released.

### 2.2. Catalytic CO<sub>2</sub> cycloaddition to epoxides by SILP-ZnCl<sub>3</sub>

All the catalytic reactions were performed in a Parr reactor system (model 4560 with controller model 4848) equipped with a 300 mL stainless steel vessel. Typically, the vessel was charged with SILP-ZnCl<sub>3</sub>



**Scheme 1.** Catalytic CO<sub>2</sub> cycloaddition to epoxides driven in the confined spaces of bulk IL (BMIm.ZnCl<sub>3</sub>) and its SILP.

(0.4 g) and desired epoxide (50 mmol). The system was purged with CO<sub>2</sub> to remove air. The reactor was pressurized with 10 bar and the reaction was accomplished at 100 °C for 24 h. The reactor was cooled down in ice water and the pressure was slowly released. The conversion and products selectivity were calculated by <sup>1</sup>H NMR. To avoid the volatilization of propylene oxide, the reactor was cooled down immediately in ice water for 30–40 min. Afterward, the pressure was slowly released. The sample for <sup>1</sup>H NMR was prepared and measured immediately.

## 3. Results and discussion

### 3.1. Catalysts preparation and characterizations

A simple 1-*n*-butyl-3-methylimidazolium trichlorozincate (BMIm.ZnCl<sub>3</sub>) IL was prepared at 75 °C as reported earlier. [61] A white viscous liquid was obtained that was characterized by <sup>1</sup>H and <sup>13</sup>C NMRs (Fig. S1), and ESI-MS techniques, See Supporting information. Of note that ESI-MS spectra exhibited a very intense mass peaks up to *m/e* 170.83 on negative mode and *m/e* 139.12 in positive mode indicating the anion (ZnCl<sub>3</sub><sup>-</sup>) and cation (BMIm<sup>+</sup>) of the BMIm.ZnCl<sub>3</sub> IL (Fig. S2).

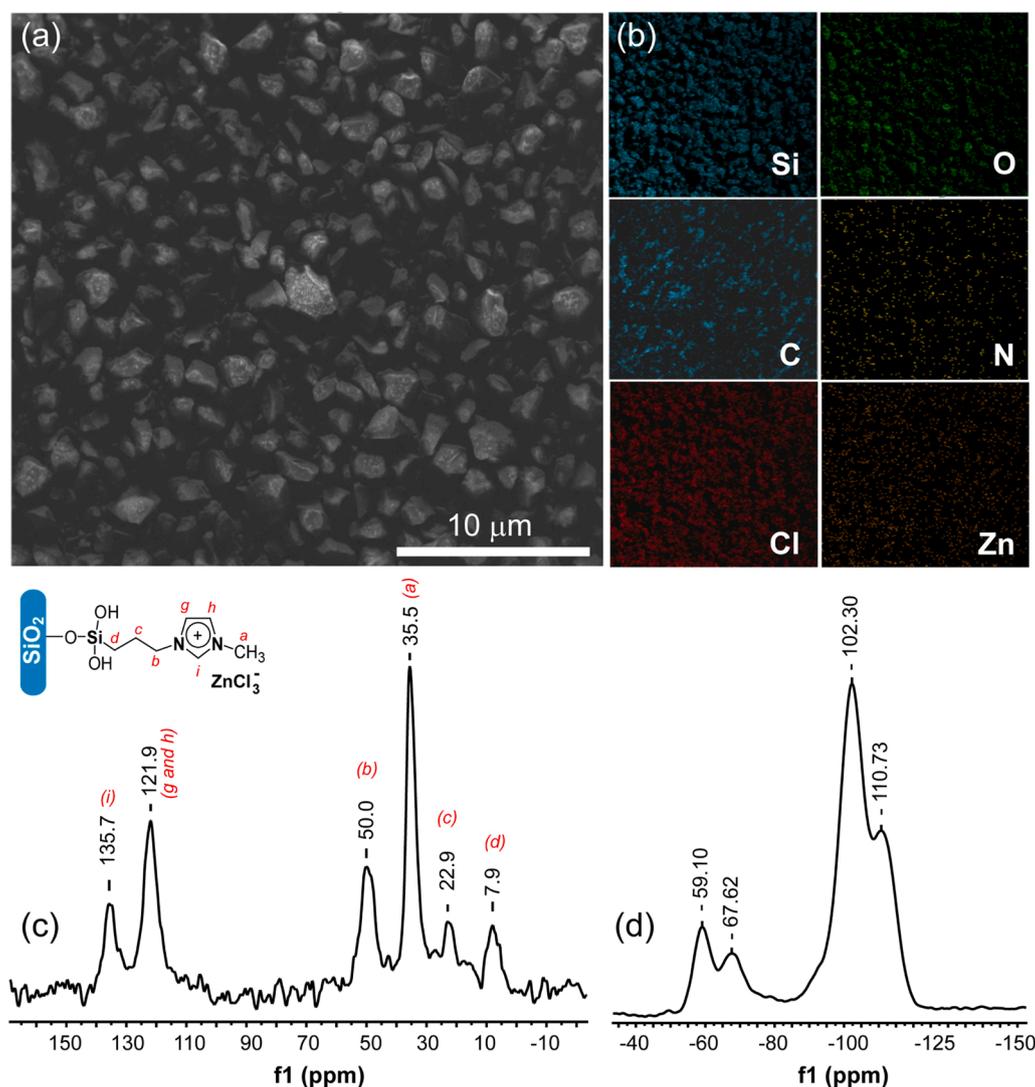
Whereas, SILP-ZnCl<sub>3</sub> was prepared by grafting the 1-methyl-3-(3-(trimethoxysilyl)propyl)-imidazolium trichlorozincate on commercially SiO<sub>2</sub> (silicagel 60, 0.05–0.2 mm) by the sol-gel method. ESI-MS spectrum of 1-methyl-3-(3-(trimethoxysilyl)propyl)-imidazolium zinc trichloride IL revealed a mass peaks about *m/e* 170.83 on negative mode, confirming the presence of ZnCl<sub>3</sub><sup>-</sup> anion (Fig. S3). The prepared SILP-ZnCl<sub>3</sub> was characterized by FTIR, scanning electron microscopy (SEM), CP-MAS solid-state NMR (<sup>13</sup>C and <sup>29</sup>Si), BET and TGA analyses. FTIR showed signals at about 3150, 3109 and 2951 cm<sup>-1</sup> characteristic to the imidazolium ring of the IL (Fig. S4).

SEM images (Fig. 1a) indicated that the SILP-ZnCl<sub>2</sub> was composed of irregular shaped particles. The EDS mapping represented for C, N, Cl, Si, O and Zn, suggesting that the IL was homogeneously anchored on the surface of SiO<sub>2</sub> (Fig. 1b).

Solid <sup>13</sup>C CP-MAS NMR spectrum of SILP-ZnCl<sub>3</sub> revealed the presence of three resonance peaks at  $\delta = 7.9, 22.9$  and  $50.0$  ppm attributed to the carbons of propylene moiety attached to the silica surface (Fig. 1c). While the signals at  $35.5, 121.9$  and  $135.7$  ppm were assigned to the carbon atoms of methylimidazolium. No signal of the methoxy groups at about 65 ppm of the silane function was observed, which confirmed that the trimethoxy-silane of 1-methyl-3-(3-(trimethoxysilyl)propyl)-imidazolium trichlorozincate IL reacted with hydroxyl groups of SiO<sub>2</sub>. <sup>29</sup>Si CP-MAS NMR spectrum of SILP-ZnCl<sub>3</sub> (Fig. 1d) displayed two peaks at  $\delta = -102.3$  and  $-110.73$  ppm that can be ascribed to the silicon atoms of silanol groups at the surface (Q<sup>n</sup>-type groups). The peaks  $-59.1$  and  $-67.62$  ppm are corresponding to the Si atoms of different environment in the 1-methyl-3-(3-(trimethoxysilyl)propyl)-imidazolium trichlorozincate, attached covalently to the silica surface (T<sup>n</sup>-type groups). The presence of signals of T<sup>n</sup>-type groups confirmed the successful functionalization of surface silanol groups through chemical bonds, not by adsorption at the surface.

The surface elemental composition and the chemical environment of surface atoms were probed by XPS. The composition of SILP-ZnCl<sub>3</sub> was obtained from the analysis of its survey scan (Fig. S6). From the areas of Zn 2p, Cl 2p, Si 2p and O 1s regions, some quantitative information on the sample's surface composition were extracted: (i) Zn and Cl represent together 5% of the atoms in sample's surface (ii) the Zn/Cl ratio in SILP-ZnCl<sub>3</sub> is 0.36, which is lower than the nominal value (0.50) for ZnCl<sub>2</sub> and also lower than value obtained from the commercial available ZnCl<sub>2</sub> XPS data (0.51). This result indicated the presence of ZnCl<sub>x</sub> (*x* = 2.8) species over SILP surface.

Zn 2p<sub>3/2</sub> (Fig. 2a) and Cl 2p (Fig. 2b) high-resolution spectra were acquired for SILP-ZnCl<sub>3</sub> and for ZnCl<sub>2</sub> in order to elucidate the chemical environments and electronic state of these elements. The main results from the XPS data fitting are summarized and available Table S1 (see Supporting information). A single chemical component (at 1022.6 eV



**Fig. 1.** (a) SEM image of SILP-ZnCl<sub>3</sub>, (b) EDS elemental mapping images of SILP-ZnCl<sub>3</sub> with Si, O, C, N, Cl and Zn. The code bars for mapping images are 10 μm. For clarity of Zn mapping, see zoom Fig. S5, (c) <sup>13</sup>C CP-MAS NMR, and (d) <sup>29</sup>Si CP-MAS NMR spectrum of SILP-ZnCl<sub>3</sub>.

for ZnCl<sub>2</sub> and at 1022.3 eV for SILP-ZnCl<sub>3</sub>) was used to adjust the Zn 2p<sub>3/2</sub> peak in both spectra. The binding energies observed for this component is typical of Zn-Cl bonds, however, it is shifted to lower energy in our SILP-ZnCl<sub>3</sub> spectrum. The -0.3 eV chemical shift indicates that Zn has a higher electron density in SILP-ZnCl<sub>3</sub> than in ZnCl<sub>2</sub> due to the charge transfer between the modified support and the zinc chloride species. The analysis of Cl 2p region also indicates the presence of a single chemical environment for Cl atoms in SILP-ZnCl<sub>3</sub> and ZnCl<sub>2</sub> samples. One doublet was used to fit the data for both samples, the binding energies and spin-orbit splitting (Table S1, in supporting information) are typical for metal chlorides [62–64]. The Cl 2p doublet in SILP-ZnCl<sub>3</sub> is also shifted to lower binding energies when compared to ZnCl<sub>2</sub>, corroborating the charge transfer suggested by Zn 2p region deconvolution. These observations indicate the strength of the contact ion pair, the imidazolium cation and the halogen anion, is reduced in the confined spaces provided by the silica support [55]. This higher electron density on the Zn and Cl atoms denotes increased nucleophilicity of the anion, which is related to its presence on the surface of the SILP material.

The physicochemical properties of SILP-ZnCl<sub>3</sub> and SiO<sub>2</sub> were measured using N<sub>2</sub> adsorption (Fig. S7) that showed the decreased in surface area and pore volume of SiO<sub>2</sub> upon its functionalization with the IL. This behaviour is due to the incorporation of IL in the structure leads to a loss in micropore volume by filling and/or blocking the pores. These

findings also suggest the presence of a homogeneous and well-dispersed IL on the SiO<sub>2</sub>. The pristine SiO<sub>2</sub> contained 288.3 m<sup>2</sup>/g, 0.68 m<sup>3</sup>/g and 9.5 nm surface area, pore volume and pore area, respectively. Whereas, SILP-ZnCl<sub>3</sub> catalyst has 127.2 m<sup>2</sup>/g surface area, 0.31 m<sup>3</sup>/g pore volume and 9.9 nm pore size. Thermogravimetric measurements (Fig. S8) revealed weight loss proceeding in two steps. The first step occurred over a range of 100–220 °C due to adsorbed water from the air, whereas the second step in weight loss up to 700 °C is due to the decomposition of residual IL at the surface of the SiO<sub>2</sub>. The SILP-ZnCl<sub>3</sub> has 0.2 mmol IL, calculated from TGA [65].

### 3.2. Catalytic study

The catalytic performance of BMIm.ZnCl<sub>3</sub> IL as homogeneous catalyst (10 mol%) in the CO<sub>2</sub> cycloaddition reaction of different aliphatic and aromatic epoxides was investigated under atmospheric pressure (1 atm) of CO<sub>2</sub> at 40 °C without the use of any solvent or co-catalyst (Table 1). The catalysis evaluation was started with styrene oxide as a model substrate. No cyclic carbonate formation was observed when solely ZnCl<sub>2</sub> and BMIm.Cl IL were used. Upon the combination of ZnCl<sub>2</sub> and BMIm.Cl in the form of BMIm.ZnCl<sub>3</sub>, diminishes the activation energy for the synthesis of cyclic carbonates (57% sel.) and resulted a significant conversion (36%) of styrene oxide (Table 1, entry 1). The

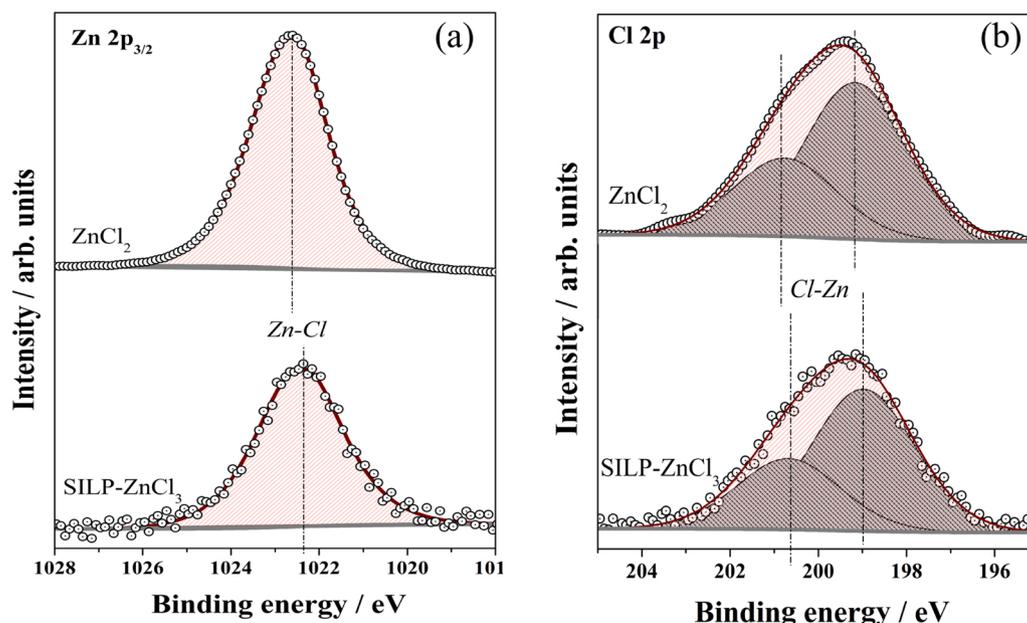
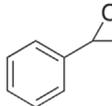
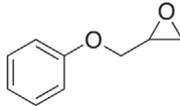
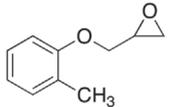
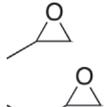
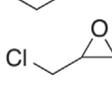
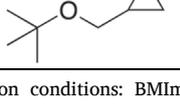


Fig. 2. XPS data and chemical components used in the analysis of Zn 2  $p_{3/2}$  (a) and Cl 2p (b) regions. A parental  $ZnCl_2$  was used to compare with our SILP- $ZnCl_3$  catalyst.

**Table 1**  
CO<sub>2</sub> cycloaddition of different epoxides by BMIm. $ZnCl_3$ <sup>a</sup>.

Entry	Substrate	P (bar)	Conv. (%) <sup>b</sup>	Sel. (%)	
				Carbonate	Diol
1		1	36	57	43
		5	95	92	8
2		1	46	89	11
		5	56	78	22
3		1	52	99	1
4		1	73	68	32
		5	83	90	10
5		1	59	80	20
		5	80	85	15
6		1	13	> 99	-
		5	15	> 99	-

<sup>a</sup> Reaction conditions: BMIm. $ZnCl_3$  (0.625 mmol), Substrate (6.25 mmol), 24 h, and 40 °C.

<sup>b</sup> Calculated from <sup>1</sup>H NMR.

formation of diol occurred due to the presence of small amount of water contents in IL absorbed from moisture during preparation. Of note, no formation of the 2-chloro-2-phenylethanol was detected. This indicates

the positive synergistic effect of BMIm. $ZnCl_3$  catalyst by the coordination of the both cationic and anionic moieties hence promoted the reaction by dual activation of the epoxide and CO<sub>2</sub>.

With the optimized conditions, a series of epoxides were examined in order to evaluate the potential of the BMIm. $ZnCl_3$  catalyst (Table 1). 46% conversion with 89% selectivity to the desired cyclic carbonate of 1,2-epoxy-3-phenylpropane was achieved (Table 1, entry 2). Whereas, its methyl substituent derivative, glycidyl 2-methylphenyl ether was converted 52% with about 99% selective to its cyclic carbonate (Table 1, entry 3). Interestingly, aliphatic epoxides showed remarkable conversion and selectivity to their carbonates. The propylene oxide (PO) gave 73% conversion with 63% selectivity to the cyclic carbonate (Table 1, entry 4). While 59% conversion of the butylene oxide was attained with 80% selectivity to carbonate (Table 1, entry 5). The epichlorohydrin and tert-butyl glycidyl ether oxide presented 57% and 13% conversion, respectively (Table 1, entries 6, 7). This may be correlated to the highly diffusion of small sized substrates into the confined spaces of BMIm. $ZnCl_3$  IL to have high access to the catalytic active sites, resulting in the high conversion and carbonate selectively [66,67].

When the pressure was increased to 5 bar at 40 °C, augmentation in epoxides conversion and selectivity to cyclic carbonates were observed (Table 1). The conversion of styrene oxide reached to 92% with 95% selectivity to carbonate (Table 1, entry 1). It is important to note that our catalytic system showed higher styrene oxide conversion with selectivity to its cyclic carbonate at ambient conditions as compared to the reported sophisticated metal-based and halide containing imidazolium-based ILs (Table S2) [31,47,50,51]. The increased in the epoxide conversion and selectivity with the increased of CO<sub>2</sub> pressure may be correlated to the phase behavior of CO<sub>2</sub>-epoxide system that has two phases; one CO<sub>2</sub>-rich gas and other epoxide-rich liquid phase [68]. Hence, the CO<sub>2</sub> concentration in liquid phases increased with pressure and caused the increase of epoxides conversion. There was a slightly increased in the conversion of bulky aromatic epoxide (1,2-epoxy-3-phenylpropane) with only 56% (Table 1, entries 2) suggesting that the large epoxide substrates have restricted diffusion into the confined spaces of BMIm. $ZnCl_3$ , which limited the access of reactants to the catalytic active sites [67,69]. A similar behavior was also observed in the case of tert-butyl glycidyl ether (Table 1, entry 7). The conversion of small sized aliphatic epoxide such as propylene oxide (PO) and epichlorohydrin oxide reached to 83% and 80% conversion with the selectivity of 90% and 85%, respectively

(Table 1 entry 4, 6), higher than the previously reported [(CH<sub>2</sub>CH<sub>2</sub>OH)BIm]ZnBr<sub>3</sub> IL that required sluggish reaction conditions (120 °C and 25 bar pressure) [68].

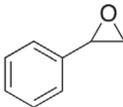
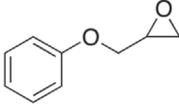
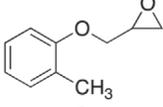
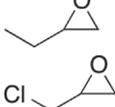
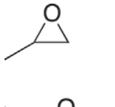
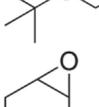
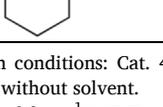
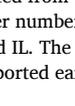
The influence of reaction temperature on styrene oxide was investigated by using BMIm.ZnCl<sub>3</sub> under 1 atm CO<sub>2</sub> for 24 h (Fig. 3). It was observed that the temperature has significant effect on the styrene oxide conversion and products selectivity. With the increase of the temperature, the styrene oxide conversion increased linearly. At room temperature 19% conversion was detected with 50% cyclic carbonate and 50% diol. The conversion was reached to 63% at 60 °C with 72% selectivity to cyclic carbonate. The Arrhenius plot (Fig. S9) was achieved based on the linear fitting of lnk vs. 1000/T from 40° to 80°C that lead to an apparent activation energy E<sub>a</sub>= 35.6 KJ mol<sup>-1</sup> which is low as compared to previously reported pyrrolidinopyridinium iodide/ZnI<sub>2</sub> binary catalyst (E<sub>a</sub>= 41.5 KJ mol<sup>-1</sup>).[70].

In order to study the heterogeneity effect, very simple silica covalent supported imidazolium-based IL containing ZnCl<sub>3</sub> anion (SILP-ZnCl<sub>3</sub>) was evaluated as a heterogeneous catalyst for a series of epoxides (Table 2). The reaction was performed in an autoclave reactor without the use of any solvent and co-catalyst at 100 °C under 10 bar pressure. The results indicated that SILP-ZnCl<sub>3</sub> could efficiently convert different aromatic and aliphatic epoxides with maximum selectivity to their corresponding cyclic carbonates. SILP-ZnCl<sub>3</sub> catalyst converted about 98% of styrene oxide to its corresponding cyclic carbonate with 99% selectivity (Table 2, entry 1) with turn over rates of 242.6. Our catalyst showed higher TONs as compared to the previously reported supported catalysts impregnated with Zn and Fe containing IL that needed high pressure and temperature [47,49] and chloride containing SILPs (Table S2). Whereas, 196.4 and 220 TONs were found for the phenylethoxy epoxide and methyl phenylethoxy epoxide with more than 97% conversion (Table 2, entries 2,3).

SILP-ZnCl<sub>3</sub> also demonstrated remarkable activity for the cycloaddition of aliphatic epoxides. A higher conversion of 98% of butyl oxide with 99% selectivity was found with SILP-ZnCl<sub>3</sub> (Table 2, entry 4). Of note that our SILP-ZnCl<sub>3</sub> catalyst showed higher conversion and selectivity for butyl oxide under milder reaction conditions as compared to previously reported SILP-Cl and SILP-Br, which needed high amount of IL (40%) [52]. The SILP-ZnCl<sub>3</sub> efficiently converted epichlorohydrin (99%), propylene oxide (81%) and tert-butyl glycidyl ether (81%) with higher selectivity (99%) to their cyclic carbonates (99%) with 245, 200.5 and 200.5 TONs (Table 2, entries 5–7), higher yield and TONs at ambient conditions as compared to the reported supported metal/IL based catalysts [47,49,50]. A low conversion of cyclohexene oxide (5%) was observed (Table 2, entry 8). The superior performance of our

**Table 2**

CO<sub>2</sub> cycloaddition of different epoxides by SILP.ZnCl<sub>3</sub><sup>a</sup>.

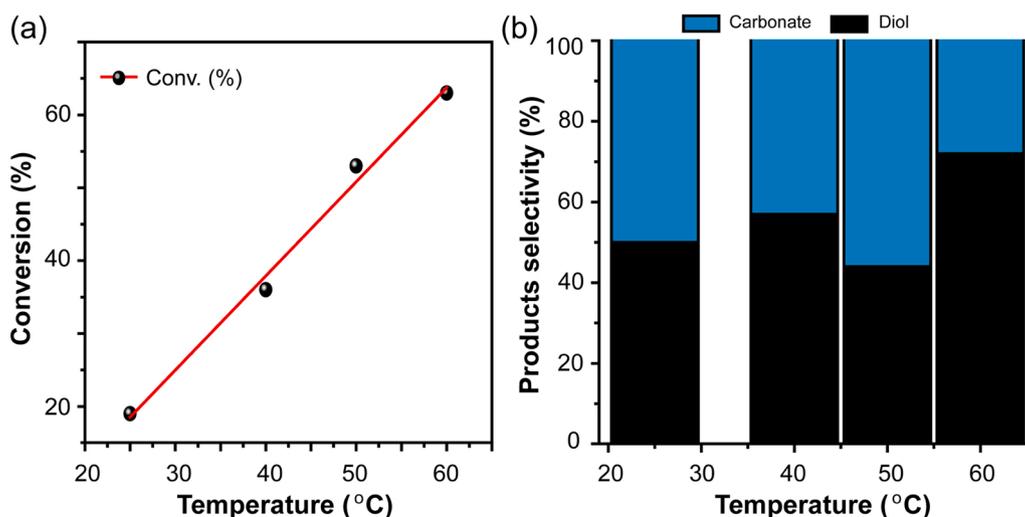
Entry	Substrate	Conv. (%) <sup>b</sup>	Carbonate (%)	TON <sup>c</sup>
1		98	> 99	242.6
2		97	81	196.4
3		99	88	220
4		98	> 99	242.6
5		99	> 99	245
6		81	> 99	200.5
7		81	> 99	200.5
8		5	> 99	12.4

<sup>a</sup> Reaction conditions: Cat. 400 mg, substrate (50 mmol), 24 h, 10 bar and 100 °C and without solvent.

<sup>b</sup> Calculated from <sup>1</sup>H NMR.

<sup>c</sup> Turnover number (TON): numbers of moles of cyclic carbonate per mole of immobilized IL. The quantity of IL (0.2 mmol) was obtained from TGA of SILP-ZnCl<sub>3</sub> as reported earlier.[65]

heterogeneous SILP-ZnCl<sub>3</sub> catalyst over homogeneous BMIm.ZnCl<sub>3</sub> catalyst could be attributed to its highly dispersed catalytic sites, porous framework with high surface area, and large CO<sub>2</sub> adsorption capacity as compared to its homogeneous counterpart. Moreover, the IL surface area is increased relative to its volume and the substrate can readily diffuse to the catalyst, overcoming the mass transfer limitations generated by the high viscosity of the IL [71]. Beside this, the formation of the IL-cages



**Fig. 3.** Reaction conditions: Styrene oxide (6.25 mmol), BMIm.ZnCl<sub>3</sub> (0.625 mmol), CO<sub>2</sub> (1 atm), 40 °C and 24 h.

onto SiO<sub>2</sub> enhances the local charge density and modulates the orientation of the IL near the surface to assist substantial charge transfer, leading to surface polarization and specific adsorption to ions, which also play significant role to enhance the catalytic activity.

Temperature effect for the styrene oxide was also illustrated at 10 bar CO<sub>2</sub> pressure (Fig. 4a). The rate of reaction and cyclic carbonate increased rapidly with the reaction temperature, which agrees well that raising the temperature is in favour of this reaction. The Arrhenius plot was achieved based on the linear fitting of  $\ln k$  vs.  $1000/T$  from 40° to 100°C that lead to an apparent activation energy  $E_a = 57 \text{ kJ mol}^{-1}$  (Fig. 4b). Recyclability of SILP-ZnCl<sub>3</sub> showed sustained catalytic activity and selectivity to cyclic carbonate up to six repeated cycles, displayed its catalytic stability (Fig. 4c). After fourth run, the catalytic activity was declined by a few percent with stable selectivity to carbonate. Of note, <sup>1</sup>H NMR of the reaction medium was performed that showed no IL which ruled out the leaching of IL. This decrease in activity may be due to the lose of catalyst during its washing and drying for the next run. Moreover, ESI-MS negative ion mode of the reaction mixture showed no signal around  $m/z$  170.83 which excluded the leaching of ZnCl<sub>3</sub>. FTIR of the used SILP-ZnCl<sub>3</sub> showed signals at about 3166, 3109 and 2946 cm<sup>-1</sup> characteristic to the imidazolium ring of the IL, demonstrated its stability (Fig. S10).

### 3.2.1. Mechanistic Investigation

A simple mechanistic approach is represented in Fig. 5a. It is widely

accepted that imidazolium cation acts as a Lewis acid in which H-C2 activates the epoxide and facilitates the nucleophilic attack [31]. It is been exclusively proposed (not confirmed experimentally or theoretically) that dissociation of metal-trichloride anion in molecular catalysts happened to generate Cl<sup>-</sup> anion (acts as nucleophile) and neutral ZnCl<sub>2</sub> [32,47,51]. Here we proposed that no such dissociation of the ZnCl<sub>3</sub> anion occurred. In order to confirm this hypothesis, ESI-MS analysis (negative ion mode) of the reaction mixture was performed (Fig. 5a, b). We proposed that H-C2 of the imidazolium cation ligated with the oxygen of epoxide and the nucleophilic attack of the ZnCl<sub>3</sub> anion occurred at the less hindered carbon to generate the zinc-intermediate II. Ex-site ESI-MS proved the existence of the intermediate II with  $m/z$  288.89, which excluded the dissociation of ZnCl<sub>3</sub> (Fig. 5c). It is important to note that no formation of the 2-chloro-2-phenylethanol was observed that also neglects the dissociation of ZnCl<sub>3</sub>. Then the carbonation of zinc-intermediate II with CO<sub>2</sub> followed to form an acyclic carbonate III that leads to the cyclic carbonate and regenerates the catalyst. Furthermore, ESI-MS of the crude reaction intense signal at  $m/z$  170.89 also confirmed the existence of ZnCl<sub>3</sub> (Fig. 5b).

## 4. Conclusions

In summary, we report efficient activation of the different aromatic and aliphatic epoxides at ambient reaction conditions. Our 1-*n*-butyl-3-methylimidazolium trichlorozincate (BMIm.ZnCl<sub>3</sub>) ionic liquid presented

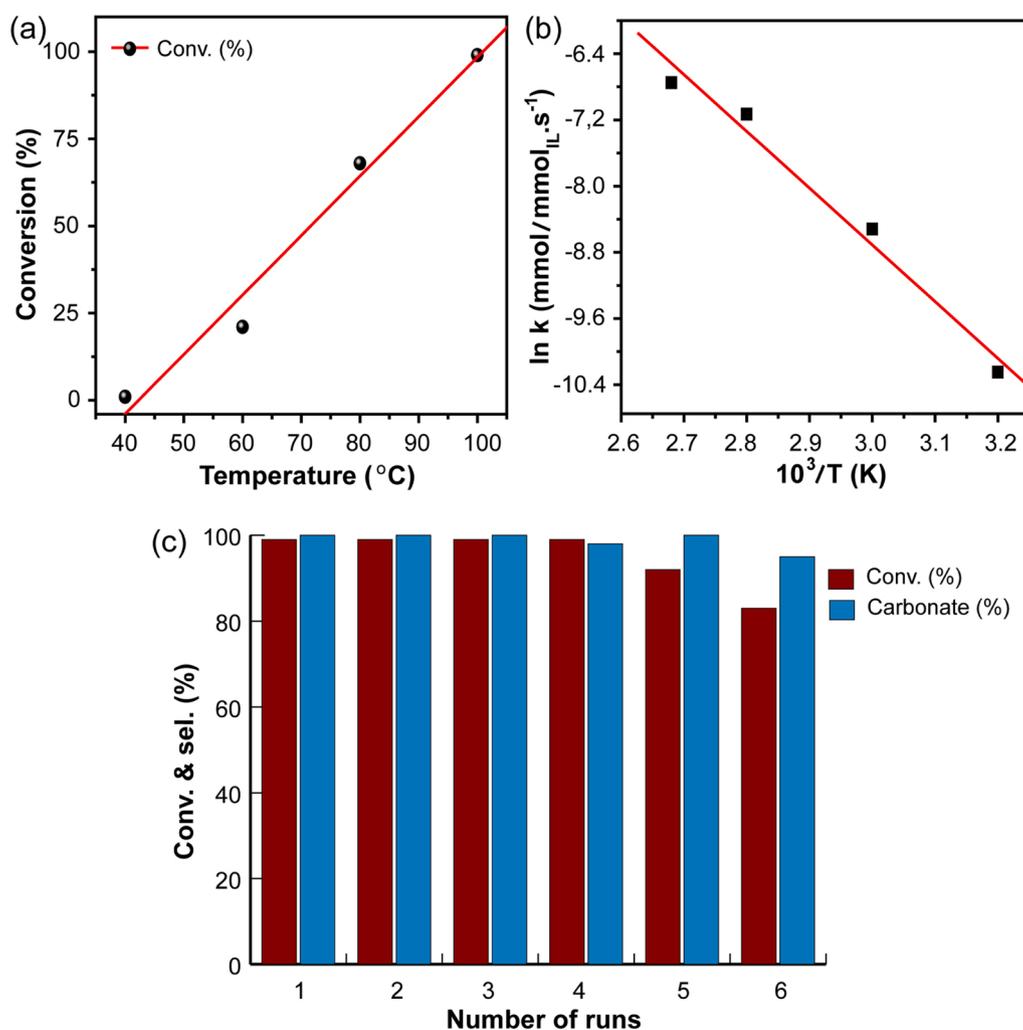
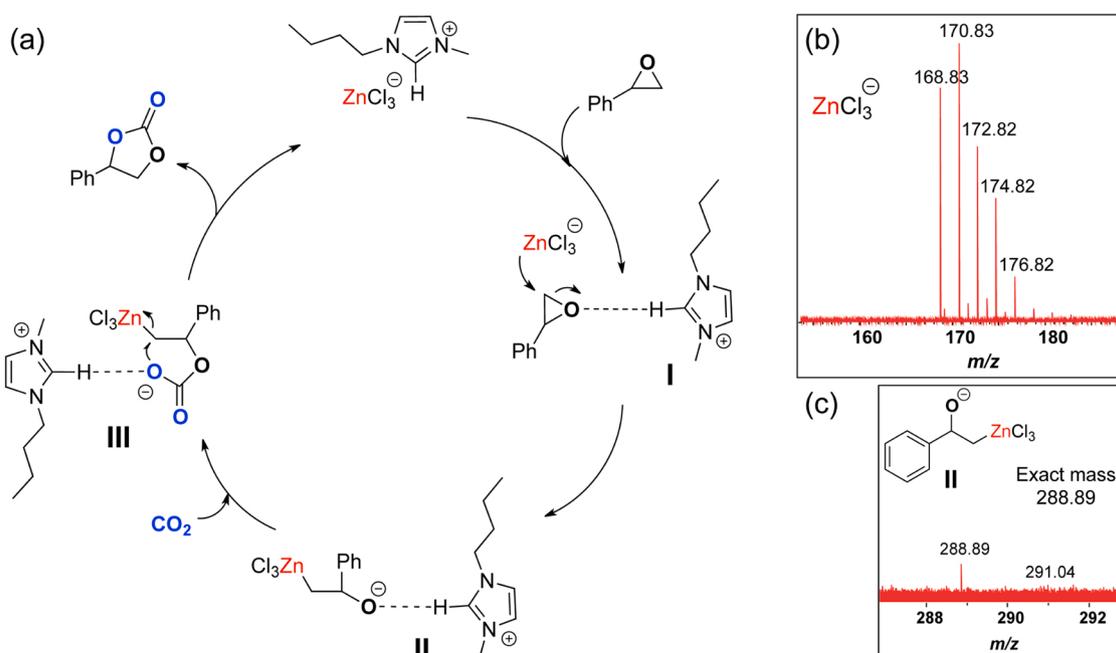


Fig. 4. Reaction condition: SILP-ZnCl<sub>3</sub> (400 mg), styrene oxide (50 mmol) and pressure (10 bar). (a) Conv. Vs Temperature, (b) Arrhenius plot, and (c) recyclability of SILP-ZnCl<sub>3</sub> for styrene oxide.



**Fig. 5.** (a) A proposed mechanism for the CO<sub>2</sub> cycloaddition of styrene oxide by BMIm.ZnCl<sub>3</sub> IL, (b) ESI-MS mass spectrum in the negative ion mode of crude reaction mixture during CO<sub>2</sub> cycloaddition of styrene oxide at 40 °C of anion ZnCl<sub>3</sub> (II) *m/z* 170.83178, and (c) reactive intermediate II *m/z* 288.89999. Reaction conditions for ESI-MS; BMIm.ZnCl<sub>3</sub> (0.625 mmol), styrene oxide (6.25 mmol), 24 h, 1 atm, and 40 °C.

higher activity with 56–95% conversion for the different aromatic and aliphatic epoxides under 1–5 bar pressure at 40 °C. Small sized epoxides showed higher conversion and selectivity to cyclic carbonate as compared to bulky ones suggesting that the large epoxide substrates restricted diffusion into the confined spaces of BMIm.ZnCl<sub>3</sub> IL, which limited the access of reactants to the catalytic active sites. By supporting the IL on the SiO<sub>2</sub>, the confined SILP-ZnCl<sub>3</sub> catalyst boosted the activity with maximum conversion and yield (99%) to cyclic carbonates under 10 bar at 100 °C. This higher performance could be attributed to the formation of the IL-cages onto SiO<sub>2</sub> that enhances the local charge density and modulates the orientation of the IL near the surface to assist substantial charge transfer, leading to surface polarization and specific adsorption to ions. The SILP-ZnCl<sub>3</sub> catalyst can be recovered and reused at least six times, showing good chemical stability and reusability. Furthermore, mechanistic investigations followed by ex-situ ESI-MS analysis confirmed that the imidazolium cation of BMIm.ZnCl<sub>3</sub> IL acted as Lewis acid and its anion, ZnCl<sub>3</sub> anion, acts as nucleophile to facilitate the ring opening without its dissociation into chloride anion and ZnCl<sub>2</sub>, contrasting to the previous reports.

#### CRediT authorship contribution statement

Vinicius K. Tomazett performed the experiments, synthesized the catalysts, performed the catalytic experiments, interpreted data and wrote the manuscript; Gustavo Chacon discussed and performed the experiments. Graciane Marin discussed and performed the experiments. Marcus V. Castegnaro performed the XPS analysis and interpreted data; Rafael P. das Chagas discussed and interpreted data; Luciano M. Lião interpreted NMRs data; Jairton Dupont coordinated the experiments, discussed results and co-wrote the manuscript; M. I. Qadir planned the experiments, synthesized the catalysts, performed the catalytic experiments, interpreted data and wrote the manuscript.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Data will be made available on request.

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#### CRediT authorship contribution statement

The manuscript was written through contributions of all authors.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2023.102400](https://doi.org/10.1016/j.jcou.2023.102400).

#### References

- [1] Y. Ou, C. Roney, J. Alsalam, K. Calvin, J. Creason, J. Edmonds, A.A. Fawcett, P. Kyle, K. Narayan, P. O'Rourke, P. Patel, S. Ragnauth, S.J. Smith, H. McJeon, Deep mitigation of CO<sub>2</sub> and non-CO<sub>2</sub> greenhouse gases toward 1.5 °C and 2 °C futures, *Nat. Commun.* 12 (2021) 6245.
- [2] J. Dupont, Across the board: jairton dupont, *ChemSusChem* 8 (2015) 586–587.
- [3] M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T.E. Müller, Chemical technologies for exploiting and recycling carbon dioxide into the value chain, *ChemSusChem* 4 (2011) 1216–1240.
- [4] M. North, R. Pasquale, C. Young, Synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>, *Green. Chem.* 12 (2010) 1514–1539.
- [5] S. De, A. Dokania, A. Ramirez, J. Gascon, Advances in the design of heterogeneous catalysts and thermocatalytic processes for CO<sub>2</sub> utilization, *ACS Catal.* 10 (2020) 14147–14185.
- [6] E.C. Ra, K.Y. Kim, E.H. Kim, H. Lee, K. An, J.S. Lee, Recycling carbon dioxide through catalytic hydrogenation: recent key developments and perspectives, *ACS Catal.* 10 (2020) 11318–11345.
- [7] M.I. Qadir, F. Bernardi, J.D. Scholten, D.L. Baptista, J. Dupont, Synergistic CO<sub>2</sub> hydrogenation over bimetallic Ru/Ni nanoparticles in ionic liquids, *Appl. Catal. B: Environ.* 252 (2019) 10–17.
- [8] L. Guo, K.J. Lamb, M. North, Recent developments in organocatalyzed transformations of epoxides and carbon dioxide into cyclic carbonates, *Green. Chem.* 23 (2021) 77–118.

- [9] R.R. Shaikh, S. Pornpraprom, V. D'Elia, Catalytic strategies for the cycloaddition of pure, diluted, and waste CO<sub>2</sub> to epoxides under ambient conditions, *ACS Catal.* 8 (2018) 419–450.
- [10] B. Schäffner, F. Schäffner, S.P. Verevkin, A. Börner, Organic carbonates as solvents in synthesis and catalysis, *Chem. Rev.* 110 (2010) 4554–4581.
- [11] M. North, P. Villuendas, A. Chiral, Solvent effect in asymmetric organocatalysis, *Org. Lett.* 12 (2010) 2378–2381.
- [12] S.B. Lawrenson, R. Arav, M. North, The greening of peptide synthesis, *Green. Chem.* 19 (2017) 1685–1691.
- [13] M. Sathish, K.J. Sreeram, J. Raghava Rao, B. Unni Nair, Cyclic carbonate: a recyclable medium for zero discharge tanning, *ACS Sustain. Chem. Eng.* 4 (2016) 1032–1040.
- [14] M.E. Boot-Handford, J.C. Abanades, E.J. Anthony, M.J. Blunt, S. Brandani, N. Mac Dowell, J.R. Fernández, M.-C. Ferrari, R. Gross, J.P. Hallett, R.S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R.T.J. Porter, M. Pourkashanian, G.T. Rochelle, N. Shah, J.G. Yao, P.S. Fennell, Carbon capture and storage update, *Energy Environ. Sci.* 7 (2014) 130–189.
- [15] X. Wei, W. Xu, M. Vijayakumar, L. Cosimbescu, T. Liu, V. Sprenkle, W. Wang, TEMPO-based catholyte for high-energy density nonaqueous redox flow batteries, *Adv. Mater.* 26 (2014) 7649–7653.
- [16] Y. Chen, R. Qiu, X. Xu, C.-T. Au, S.-F. Yin, Organoantimony and organobismuth complexes for CO<sub>2</sub> fixation, *RSC Adv.* 4 (2014) 11907–11918.
- [17] X.-B. Lu, D.J. Darensbourg, Cobalt catalysts for the coupling of CO<sub>2</sub> and epoxides to produce polycarbonates and cyclic carbonates, *Chem. Soc. Rev.* 41 (2012) 1462–1484.
- [18] C.M. Miralda, E.E. Macias, M. Zhu, P. Ratnasamy, M.A. Carreon, Zeolitic imidazole framework-8 catalysts in the conversion of CO<sub>2</sub> to chloropropene carbonate, *ACS Catal.* 2 (2012) 180–183.
- [19] M. Zhu, D. Srinivas, S. Bhogesarwarao, P. Ratnasamy, M.A. Carreon, Catalytic activity of ZIF-8 in the synthesis of styrene carbonate from CO<sub>2</sub> and styrene oxide, *Catal. Commun.* 32 (2013) 36–40.
- [20] D.-H. Lan, L. Chen, C.-T. Au, S.-F. Yin, One-pot synthesized multi-functional graphene oxide as a water-tolerant and efficient metal-free heterogeneous catalyst for cycloaddition reaction, *Carbon* 93 (2015) 22–31.
- [21] D.-H. Lan, H.-T. Wang, L. Chen, C.-T. Au, S.-F. Yin, Phosphorous-modified bulk graphitic carbon nitride: Facile preparation and application as an acid-base bifunctional and efficient catalyst for CO<sub>2</sub> cycloaddition with epoxides, *Carbon* 100 (2016) 81–89.
- [22] D.-H. Lan, Y.-X. Gong, N.-Y. Tan, S.-S. Wu, J. Shen, K.-C. Yao, B. Yi, C.-T. Au, S.-F. Yin, Multi-functionalization of GO with multi-cationic ILS as high efficient metal-free catalyst for CO<sub>2</sub> cycloaddition under mild conditions, *Carbon* 127 (2018) 245–254.
- [23] W.-H. Zhang, P.-P. He, S. Wu, J. Xu, Y. Li, G. Zhang, X.-Y. Wei, Graphene oxide grafted hydroxyl-functionalized ionic liquid: a highly efficient catalyst for cycloaddition of CO<sub>2</sub> with epoxides, *Appl. Catal. A: Gen.* 509 (2016) 111–117.
- [24] G. Fiorani, W. Guo, A.W. Kleij, Sustainable conversion of carbon dioxide: the advent of organocatalysis, *Green. Chem.* 17 (2015) 1375–1389.
- [25] N. Kihara, N. Hara, T. Endo, Catalytic activity of various salts in the reaction of 2,3-epoxypropyl phenyl ether and carbon dioxide under atmospheric pressure, *J. Org. Chem.* 58 (1993) 6198–6202.
- [26] L.-N. He, H. Yasuda, T. Sakakura, New procedure for recycling homogeneous catalyst: propylene carbonate synthesis under supercritical CO<sub>2</sub> conditions, *Green. Chem.* 5 (2003) 92–94.
- [27] S.L.S. Ribeiro, C.G. Silva, G.E.T.O. Prado, Á.F.A. da Mata, J.L.S. Milani, P. R. Martins, R.P. das Chagas, Nickel–cobalt hydroxide catalysts for the cycloaddition of carbon dioxide to epoxides, *Res. Chem. Intermed.* 48 (2022) 1907–1921.
- [28] A. Decortes, A.M. Castilla, A.W. Kleij, Salen-complex-mediated formation of cyclic carbonates by cycloaddition of CO<sub>2</sub> to epoxides, *Angew. Chem. Int. Ed.* 49 (2010) 9822–9837.
- [29] K. Yin, L. Hua, L. Qu, Q. Yao, Y. Wang, D. Yuan, H. You, Y. Yao, Heterobimetallic rare earth metal–zinc catalysts for reactions of epoxides and CO<sub>2</sub> under ambient conditions, *Dalton Trans.* 50 (2021) 1453–1464.
- [30] J.L.S. Milani, Wd.A. Bezerra, A.K.S.M. Valdo, F.T. Martins, L.T.Fd.M. Camargo, V. H. Carvalho-Silva, S.S. dos Santos, D. Cangussu, R.P. das Chagas, Zinc complexes with 1,2-disubstituted benzimidazole ligands: experimental and theoretical studies in the catalytic cycloaddition of CO<sub>2</sub> with epoxides, *Polyhedron* 173 (2019), 114134.
- [31] A.-L. Girard, N. Simon, M. Zanatta, S. Marmitt, P. Gonçalves, J. Dupont, Insights on recyclable catalytic system composed of task-specific ionic liquids for the chemical fixation of carbon dioxide, *Green. Chem.* 16 (2014) 2815–2825.
- [32] Y.J. Kim, R.S. Varma, Tetrahaloindate(III)-based ionic liquids in the coupling reaction of carbon dioxide and epoxides to generate cyclic carbonates: H-bonding and mechanistic studies, *J. Org. Chem.* 70 (2005) 7882–7891.
- [33] Z.-Z. Yang, Y.-N. Zhao, L.-N. He, J. Gao, Z.-S. Yin, Highly efficient conversion of carbon dioxide catalyzed by polyethylene glycol-functionalized basic ionic liquids, *Green. Chem.* 14 (2012) 519–527.
- [34] R. Yao, H. Wang, J. Han, Polyethylene glycol-supported ionic liquid as a highly efficient catalyst for the synthesis of propylene carbonate under mild conditions, *Front Chem. Sci. Eng.* 6 (2012) 239–245.
- [35] W.-L. Wong, L.Y.S. Lee, K.-P. Ho, Z.-Y. Zhou, T. Fan, Z. Lin, K.-Y. Wong, A green catalysis of CO<sub>2</sub> fixation to aliphatic cyclic carbonates by a new ionic liquid system, *Appl. Catal. A: Gen.* 472 (2014) 160–166.
- [36] X. Zhang, D. Su, L. Xiao, W. Wu, Immobilized protic ionic liquids: efficient catalysts for CO<sub>2</sub> fixation with epoxides, *J. CO<sub>2</sub> Util.* 17 (2017) 37–42.
- [37] B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang, S.-J. Zhang, Fixation of CO<sub>2</sub> into cyclic carbonates catalyzed by ionic liquids: a multi-scale approach, *Green. Chem.* 17 (2015) 108–122.
- [38] Á.F. Arruda da Mata, N. Glanzmann, P.H. Fazza Stroppo, F. Terra Martins, R.P. das Chagas, A.D. da Silva, J.L.S. Milani, Single-component, metal-free, solvent-free HO-functionalized 1,2,3-triazole-based ionic liquid catalysts for efficient CO<sub>2</sub> conversion, *N. J. Chem.* 46 (2022) 12237–12243.
- [39] G. Li, S. Dong, P. Fu, Q. Yue, Y. Zhou, J. Wang, Synthesis of porous poly(ionic liquid)s for chemical CO<sub>2</sub> fixation with epoxides, *Green. Chem.* 24 (2022) 3433–3460.
- [40] Y. Lei, H.Q.N. Gunaratne, L. Jin, Design and synthesis of pyridinamide functionalized ionic liquids for efficient conversion of carbon dioxide into cyclic carbonates, *J. CO<sub>2</sub> Util.* 58 (2022), 101930.
- [41] P. Goodrich, H.Q.N. Gunaratne, J. Jacquemin, L. Jin, Y. Lei, K.R. Seddon, Sustainable cyclic carbonate production, utilizing carbon dioxide and azolate ionic liquids, *ACS Sustain. Chem. Eng.* 5 (2017) 5635–5641.
- [42] J. Hu, J. Ma, H. Liu, Q. Qian, C. Xie, B. Han, Dual-ionic liquid system: an efficient catalyst for chemical fixation of CO<sub>2</sub> to cyclic carbonates under mild conditions, *Green. Chem.* 20 (2018) 2990–2994.
- [43] X. Meng, Z. Ju, S. Zhang, X. Liang, N. von Solms, X. Zhang, X. Zhang, Efficient transformation of CO<sub>2</sub> to cyclic carbonates using bifunctional protic ionic liquids under mild conditions, *Green. Chem.* 21 (2019) 3456–3463.
- [44] Z. Zhang, F. Fan, H. Xing, Q. Yang, Z. Bao, Q. Ren, Efficient synthesis of cyclic carbonates from atmospheric CO<sub>2</sub> using a positive charge delocalized ionic liquid catalyst, *ACS Sustain. Chem. Eng.* 5 (2017) 2841–2846.
- [45] N. Fajul-Mosteirín, C. Jehanno, F. Ruipérez, H. Sardon, A.P. Dove, Rational study of DBU salts for the CO<sub>2</sub> insertion into epoxides for the synthesis of cyclic carbonates, *ACS Sustain. Chem. Eng.* 7 (2019) 10633–10640.
- [46] J. Cheng, C. Lu, B. Zhao, Cycloaddition of carbon dioxide and epoxides catalyzed by rare earth metal complexes bearing a Trost ligand, *N. J. Chem.* 45 (2021) 13096–13103.
- [47] J. Gao, Q.-W. Song, L.-N. He, C. Liu, Z.-Z. Yang, X. Han, X.-D. Li, Q.-C. Song, Preparation of polystyrene-supported Lewis acidic Fe(III) ionic liquid and its application in catalytic conversion of carbon dioxide, *Tetrahedron* 68 (2012) 3835–3842.
- [48] L. Han, M.-S. Park, S.-J. Choi, Y.-J. Kim, S.-M. Lee, D.-W. Park, Incorporation of metal ions into silica-grafted imidazolium-based ionic liquids to efficiently catalyze cycloaddition reactions of CO<sub>2</sub> and epoxides, *Catal. Lett.* 142 (2012) 259–266.
- [49] M.-I. Kim, S.-J. Choi, D.-W. Kim, D.-W. Park, Catalytic performance of zinc containing ionic liquids immobilized on silica for the synthesis of cyclic carbonates, *J. Ind. Eng. Chem.* 20 (2014) 3102–3107.
- [50] D. Kim, Y. Moon, D. Ji, H. Kim, D. Cho, Metal-containing ionic liquids as synergistic catalysts for the cycloaddition of CO<sub>2</sub>: a density functional theory and response surface methodology corroborated study, *ACS Sustain. Chem. Eng.* 4 (2016) 4591–4600.
- [51] M.K. Leu, I. Vicente, J.A. Fernandes, I. de Pedro, J. Dupont, V. Sans, P. Licence, A. Gual, I. Cano, On the real catalytically active species for CO<sub>2</sub> fixation into cyclic carbonates under near ambient conditions: dissociation equilibrium of [BmIm][Fe(NO)<sub>2</sub>Cl<sub>2</sub>] dependant on reaction temperature, *Appl. Catal. B: Environ.* 245 (2019) 240–250.
- [52] Q. Su, Y. Qi, X. Yao, W. Cheng, L. Dong, S. Chen, S. Zhang, Ionic liquids tailored and confined by one-step assembly with mesoporous silica for boosting the catalytic conversion of CO<sub>2</sub> into cyclic carbonates, *Green. Chem.* 20 (2018) 3232–3241.
- [53] O. Martínez-Ferraté, G. Chacón, F. Bernardi, T. Grehl, P. Brüner, J. Dupont, Cycloaddition of carbon dioxide to epoxides catalysed by supported ionic liquids, *Catal. Sci. Technol.* 8 (2018) 3081–3089.
- [54] M.I. Qadir, N.M. Simon, J. Dupont, Catalytic Properties of Metal Nanoparticles Confined in Ionic Liquids, in: *Nanoparticles in Catalysis*, 2021, pp. 123–138.
- [55] L. Luza, C.P. Rambor, A. Gual, F. Bernardi, J.B. Domingos, T. Grehl, P. Brüner, J. Dupont, Catalytically active membranelike devices: ionic liquid hybrid organosilicas decorated with palladium nanoparticles, *ACS Catal.* 6 (2016) 6478–6486.
- [56] L. Luza, C.P. Rambor, A. Gual, J. Alves Fernandes, D. Eberhardt, J. Dupont, Revealing hydrogenation reaction pathways on naked gold nanoparticles, *ACS Catal.* 7 (2017) 2791–2799.
- [57] R.M. Lynden-Bell, M.G. Del Pópolo, T.G.A. Youngs, J. Kohanoff, C.G. Hanke, J. B. Harper, C.C. Pinilla, Simulations of ionic liquids, solutions, and surfaces, *Acc. Chem. Res.* 40 (2007) 1138–1145.
- [58] Y. Wang, H. He, C. Wang, Y. Lu, K. Dong, F. Huo, S. Zhang, Insights into ionic liquids: from Z-bonds to quasi-liquids, *JACS Au* 2 (2022) 543–561.
- [59] C. Wang, Y. Wang, Z. Gan, Y. Lu, C. Qian, F. Huo, H. He, S. Zhang, Topological engineering of two-dimensional ionic liquid islands for high structural stability and CO<sub>2</sub> adsorption selectivity, *Chem. Sci.* 12 (2021) 15503–15510.
- [60] V. Farmer, T. Welton, The oxidation of alcohols in substituted imidazolium ionic liquids using ruthenium catalysts, *Green. Chem.* 4 (2002) 97–102.
- [61] M.B. Alves, A.P. Umpierre, V.O. Santos Jr, V.C.D. Soares, J. Dupont, J.C. Rubim, P. A.Z. Suarez, The use of Differential Scanning Calorimetry (DSC) to characterize phase diagrams of ionic mixtures of 1-n-butyl-3-methylimidazolium chloride and niobium chloride or zinc chloride, *Thermochim. Acta* 502 (2010) 20–23.
- [62] A. Abidli, One-pot direct synthesis route to self-assembled highly ordered Zn-decorated mesoporous aluminium oxide toward efficient and sustainable metathesis heterogeneous catalyst design, *RSC Adv.* 5 (2015) 92743–92756.
- [63] S.A. Schmidt, N. Kumar, A. Shchukarev, K. Eränen, J.-P. Mikkola, D.Y. Murzin, T. Salmi, Preparation and characterization of neat and ZnCl<sub>2</sub> modified zeolites and alumina for methyl chloride synthesis, *Appl. Catal. A: Gen.* 468 (2013) 120–134.

- [64] W. Hoisang, T. Uematsu, T. Torimoto, S. Kuwabata, Surface ligand chemistry on quaternary Ag(In<sub>x</sub>Ga<sub>1-x</sub>)S<sub>2</sub> semiconductor quantum dots for improving photoluminescence properties, *Nanoscale Adv.* 4 (2022) 849–857.
- [65] L. Han, S.-W. Park, D.-W. Park, Silica grafted imidazolium-based ionic liquids: efficient heterogeneous catalysts for chemical fixation of CO<sub>2</sub> to a cyclic carbonate, *Energy Environ. Sci.* 2 (2009) 1286–1292.
- [66] J.E. Warren, C.G. Perkins, K.E. Jelfs, P. Boldrin, P.A. Chater, G.J. Miller, T. D. Manning, M.E. Briggs, K.C. Stylianou, J.B. Claridge, M.J. Rosseinsky, Shape selectivity by guest-driven restructuring of a porous material, *Angew. Chem. Int. Ed.* 53 (2014) 4592–4596.
- [67] S. Horike, M. Dincă, K. Tamaki, J.R. Long, Size-selective lewis acid catalysis in a microporous metal-organic framework with exposed Mn<sup>2+</sup> coordination sites, *J. Am. Chem. Soc.* 130 (2008) 5854–5855.
- [68] M. Liu, F. Wang, L. Shi, L. Liang, J. Sun, Zn-based ionic liquids as highly efficient catalysts for chemical fixation of carbon dioxide to epoxides, *RSC Adv.* 5 (2015) 14277–14284.
- [69] J.E. Warren, C.G. Perkins, K.E. Jelfs, P. Boldrin, P.A. Chater, G.J. Miller, T. D. Manning, M.E. Briggs, K.C. Stylianou, J.B. Claridge, M.J. Rosseinsky, Shape selectivity by guest-driven restructuring of a porous material, *Angew. Chem. Int. Ed.* 53 (2014) 4592–4596.
- [70] A. Rehman, V.C. Eze, M.F.M.G. Resul, A. Harvey, Kinetics and mechanistic investigation of epoxide/CO<sub>2</sub> cycloaddition by a synergistic catalytic effect of pyrrolidinopyridinium iodide and zinc halides, *J. Energy Chem.* 37 (2019) 35–42.
- [71] L. Foppa, L. Luza, A. Gual, D.E. Weibel, D. Eberhardt, S.R. Teixeira, J. Dupont, Sputtering-deposition of Ru nanoparticles onto Al<sub>2</sub>O<sub>3</sub> modified with imidazolium ionic liquids: synthesis, characterisation and catalysis, *Dalton Trans.* 44 (2015) 2827–2834.