



## Capturing and Fixation of Carbon Dioxide in Confined Spaces Supported Ionic Liquid Phases

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### ABSTRACT

Chemical fixation of CO<sub>2</sub> for the formation of cyclic carbonates is an excellent strategy to reduce this gas in the atmosphere and invest in the production of value-added chemical products. The utilization of ionic liquids (ILs) immobilized on metal oxide supports represents a significant strategy for atmospheric CO<sub>2</sub> mitigation, particularly through the fixation of CO<sub>2</sub> into epoxides. In this regard, 1-methyl-3-(3-(trimethoxysilyl)propyl)imidazolium trichlorozincate IL incorporated onto Al<sub>2</sub>O<sub>3</sub> was prepared, showing remarkable catalytic activity for the chemical fixation of CO<sub>2</sub> with various epoxides, achieving 80-90% conversion. The catalytic activity is influenced by the electron-withdrawing groups or low steric hindrance of epoxides.

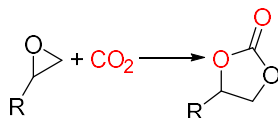
**Keywords:** CO<sub>2</sub>, Chemical fixation, cyclic carbonates, SILPs.

### INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) capturing and activation with more efficient catalysts, is an excellent strategy to reduce this gas in the atmosphere and, at the same time, invest in the production of value-added chemical products. This approach is particularly notable in the formation of cyclic carbonates, formaldehyde and methanol. Fixation of CO<sub>2</sub> to generate cyclic carbonates (Figure 1) is widely recognized as one of the most efficient synthetic routes due to its atom economy and broad applicability. Synthesizing cyclic carbonates from CO<sub>2</sub> and epoxides is attractive for converting greenhouse gases into useful products [1].

Ionic Liquids (ILs) are of great interest due to their CO<sub>2</sub> absorption capacity, chemical stability, and tunable properties, making them potential catalysts or co-

catalysts in CO<sub>2</sub> conversion [1]. This work proposes investigating Supported Ionic Liquid Phase (SILP) catalysts for converting epoxides into cyclic carbonates under mild reaction conditions.



**Figure 1.** General reaction for the synthesis of cyclic carbonates through the fixation of CO<sub>2</sub> in epoxides.

## MATERIALS AND METHODS

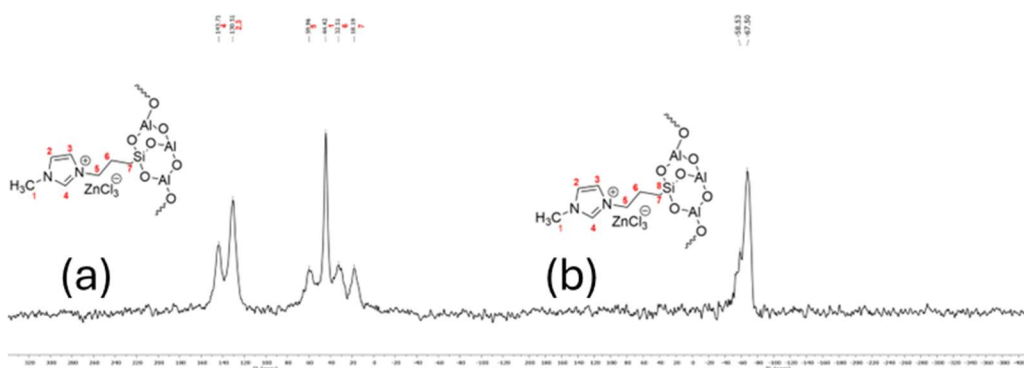
All chemicals were purchased from Sigma-Aldrich chemicals. Al<sub>2</sub>O<sub>3</sub> Neutral (Synth, 70-210 mesh). CO<sub>2</sub> (>99.999%) were purchased from White-Martins Ltd, Brazil. NMRs spectra were collected using a Bruker AVANCE III 400 MHz. SILP.ZnCl<sub>3</sub> catalyst was prepared in two steps. In first step 1-n-butyl-3-(3-trimethoxysilylpropyl)-imidazolium zintrochloride was prepared by mixing an equimolar quantity of 1-n-butyl-3-(3-trimethoxysilylpropyl)-imidazolium chloride and ZnCl<sub>2</sub> at 75 °C [2]. The resulting product (3.0 g) was dissolved in CH<sub>3</sub>CN and added to 9.0 g aluminum oxide, refluxed and vigorously stirred at 120 °C for 72 h to produce the support material. The alumina immobilized with the IL was then washed, centrifuged, and dried to produce the support. The prepared SILP-ZnCl<sub>3</sub> was characterized by Fourier Transform Infrared (IR), Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy (EDS), CP-MAS solid state NMR (<sup>13</sup>C and <sup>29</sup>Si) and Thermogravimetric (TGA) analyses. The catalytic reactions were conducted in a Fisher-Porter stainless steel reactor.

The reactor was charged with 0,1 g of catalyst and 6,25 mmol of the epoxides and pressurized with 4 bar of CO<sub>2</sub>. The reaction was performed at 120° C for 24 h in a silicone oil bath. <sup>1</sup>H NMR analysis was used to determine the conversion and selectivity of the products in CDCl<sub>3</sub>.

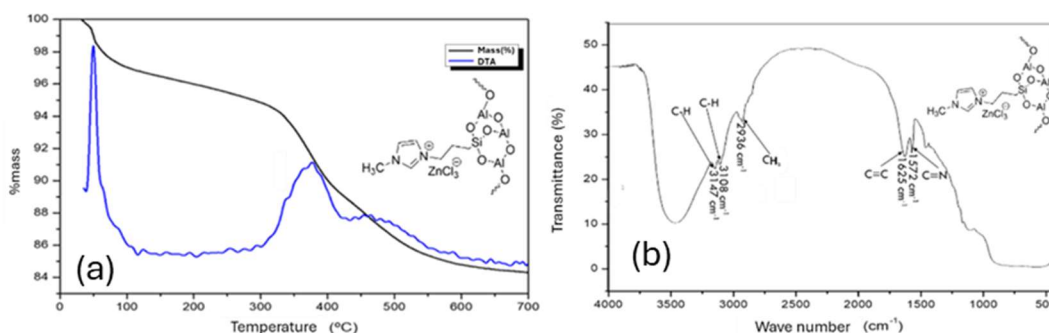
## RESULTS AND DISCUSSION

The solid <sup>13</sup>C CP-MAS NMR spectrum revealed the presence of the resonance peaks at δ = 44,42, 130,51, and 143,71 ppm, which were attributed to the carbon atoms of the methylimidazolium moiety. The chemical shift

corresponding to the carbon bonded to the nitrogen in the imidazolium ring was identified by the signal at  $\delta = 59,96$  ppm. The signal at  $\delta = 18,19$  ppm was attributed to the carbon bonded to the silicon atom (Figure 2a). However, no signals were detected for the methoxy groups of the silane functionality. The Solid  $^{29}\text{Si}$  CP-MAS NMR spectrum of SILP- $\text{ZnCl}_3$  exhibited two peaks at  $\delta = -58,53$  and  $-67,50$  ppm (Figure 1b), corresponding to silicon atoms in different environments, indicating the formation of a covalent bond to the surface of aluminum oxide through the presence of T<sup>n</sup>-type groups.



**Figure 2.** (a) The solid  $^{13}\text{C}$  CP-MAS NMR spectrum and (b)  $^{29}\text{Si}$  NMR spectrum of SILP- $\text{ZnCl}_3$ .

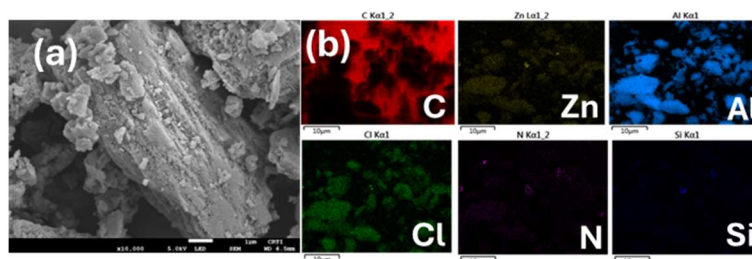


**Figure 3.** (a) TGA profile (b) IR of SILP- $\text{ZnCl}_3$ .

The TGA profile showed mass loss occurring specifically in two regions (Figure 3a). The first region exhibited a mass loss in the range of 51-84 °C, which could be attributed to the loss of adsorbed moisture. The second stage involved the decomposition of organic functions along with the degradation of the ILs bonded to the surface of the support. The TGA of the catalyst determined the amount of IL immobilized on the aluminum oxide support, as demonstrated in the literature [3]. The amount of IL supported on the catalyst was found to be 0.03 mmol. IR peaks

were identified at 3147, 3108, 2936, 1625, and 1572  $\text{cm}^{-1}$ , corresponding to the imidazolium ring of the IL (Figure 3b).

SEM images (Figure 4a) indicated that the SILP- $\text{ZnCl}_3$  was composed of irregular shaped particles. EDS analysis (Figure 4b) of these images unequivocally revealed the presence of a homogeneous distribution of the chemical elements originating from the IL supported on the surface of the aluminum oxide.



**Figure 4.** (a) SEM image of SILP- $\text{ZnCl}_3$ , (b) EDS elemental mapping images of SILP- $\text{ZnCl}_3$  with Al, Si, C, N, Cl and Zn.

**Table 1.**  $\text{CO}_2$  cycloaddition of different epoxides by SILP. $\text{ZnCl}_3$  catalyst (0.1 g)

Entry	Substrate	T (°C)	Conv. (%)	Sel. Carb. (%)	Sel. Diol(%)
1		120	25.9	88.5	11.5
2		120	87.3	84.8	15.2
3		120	78.1	83.2	16.8
4		120	66.4	88.4	11.6
5		120	54.3	74.8	25.2
6		120	99.4	87.8	12.2
7		120	33.7	84.3	15.7

\* Carb. (cyclic carbonate). Reaction time (24 h).

The catalytic results are shown in Table 1. The formation of diol occurred due to the presence of small amount of water contents in IL absorbed from moisture during preparation. The catalyst showed the efficient conversion of aromatic epoxides having electron donating groups under 4 bar  $\text{CO}_2$  and 120 °C. The styrene



oxide showed about 26% conversion with 88% selectivity to its cyclic carbonate (Table 1, entry 1). The conversion of the aromatic increased with the inclusion of electron donating group (oxygen). 1,2-epoxy-3-phenylpropane and glycidyl 2-methylphenyl ether achieved 87.3% and 78.1% conversion, respectively. Moreover, aliphatic epoxide also showed efficient conversion and selectivity to carbonates. The conversion decreased with the increase of carbon chain length of the epoxides, except in the case of epichlorohydrin, which is related to the confined space of the catalyst. The smaller aliphatic epoxide can diffuse and reached effectively to the catalytic active sites and showed higher conversion. The propylene oxide gave 66.4% conversion with 88.4% selectivity to the cyclic carbonate (Table 1, entry 4).

## CONCLUSION

The SILP catalyst demonstrated significant potential as a heterogeneous catalyst for CO<sub>2</sub> fixation reactions with epoxides. Subsequently, a catalytic study was conducted with SILP-ZnCl<sub>2</sub> to evaluate the effects of pressure, temperature, and catalyst quantity. The results obtained under milder pressure and temperature conditions were highly promising, showing high conversion rates and selectivity for both aliphatic and aromatic epoxides. The catalytic activity is related to the electron donating and confine space properties of the catalyst. These findings highlight the catalyst's excellent capability in the production of cyclic carbonates.

## ACKNOWLEDGMENT

Authors are thankful to CNPq for financial support.

## REFERENCES

- [1] Thanh, H. T., Le, O. K., & Chihaia, V. (2024). Carbon dioxide conversion to methanol on a PdCo bimetallic catalyst. *Physical Chemistry Chemical Physics*, 26(5), 3963-3973. <https://doi.org/10.1039/D3CP05146C>.
- [2] Foppa, L, *et al.* (2015). Sputtering-deposition of Ru nanoparticles onto Al<sub>2</sub>O<sub>3</sub> modified with imidazolium ionic liquids: synthesis, characterisation and catalysis. *Dalton Transactions*, 44(6), 2827-2834. <https://doi.org/10.1039/C4DT03039G>.
- [3] Mohamedali, M., Ibrahim, H., & Henni, A. (2018). Incorporation of acetate-based ionic liquids into a zeolitic imidazolate framework (ZIF-8) as efficient sorbents for carbon dioxide capture. *Chemical Engineering Journal*, 334, 817-828. <https://doi.org/10.1016/j.cej.2017.10.104>.