THE JOURNAL OF PHYSICAL CHEMISTRY C
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Anisotropic Ferricyanide Ionic Liquids and Confined SCILLs for Selective CO_2 Fixation via NHC−CO_2 Mediated Catch-and-Release Catalysis

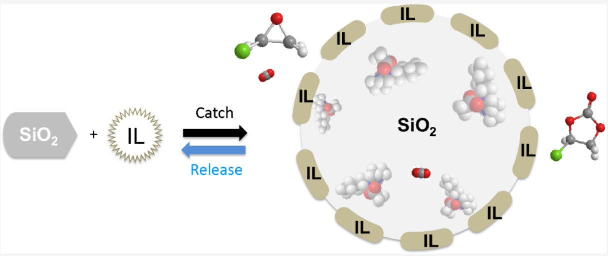
Camila P. Ebersol, Jonas X. Torres, Rafael P. das Chagas,* Luciano M. Lião, Muhammad Nisar, Pedro H. F. Matias, Heibbe Cristhian. B. de Oliveira, José S. S. Neto, Guilherme Colherinhas, and Muhammad I. Qadir*

Cite This: J. Phys. Chem. C 2025, 129, 20258−20267

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The reduction of CO_2 into value-added chemicals offers a promising approach to mitigate air pollution while simultaneously generating economic value. In this context, the chemical fixation of CO_2 into epoxides to generate cyclic carbonates is a sustainable technique due to its high atom efficiency. In this work, we report the preparation of simple iron-based ionic liquids (ILs) derived from hexacyanoferrate(III), ($Fe(CN)_6$), which exhibit remarkable activity and selectivity toward cyclic carbonate formation. Molecular dynamics (MD) simulations demonstrate that the contact ion pair organization in the IL is anisotropic, exhibiting a distinct spatial arrangement. The IL efficiently catalyzed the conversion of various epoxides using only 1.0 mol % IL under mild conditions (1−2 bar, 70−100 °C). Moreover, solid catalysts containing ionic liquid layers (SCILLs), akin to catch-and-release catalytic systems, are developed that demonstrate remarkable activity, achieving turnover numbers (TONs) of 265−729 for aliphatic epoxides and 83−668 for aromatic epoxides, with 99% selectivity toward cyclic carbonates under the same mild conditions. A monolayer of IL enhances local charge density by aligning cations and anions into distinct layers on SiO_2, therefore creating nanoconfined spaces within the SCILL (solid catalysts with IL layer). These confined domains function as a "catch-and-release" catalytic system, controlling the diffusion of epoxides, CO_2, and intermediates toward the active sites while facilitating the release of products from the microionic environment. An in situ NMR study conducted under realistic experimental conditions revealed that the reaction mechanism involves the formation of 1-*n*-butyl-3-methylimidazolium-2-carboxylate (NHC−CO_2) intermediate, thereby challenging the classical understanding of IL-assisted catalysis and providing new fundamental insights into the field.

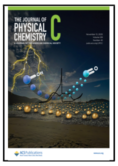


1. INTRODUCTION

The continued carbon dioxide (CO_2) emissions into the atmosphere are causing an increase in the global mean surface temperature and sea level rise. On the other hand, the presence of this abundant carbon source is also a blessing. There is an urgency to develop advanced technologies that are capable of decreasing atmospheric CO_2 through its capture and transformation into useful organic compounds. Substantial efforts are urgently required to mitigate atmospheric CO_2 through its capture and transformation into value-added organic compounds. One of the most promising approaches involves the conversion of CO_2 into fuels, lubricants, amides, esters, and cyclic carbonates via thermocatalytic and photocatalytic processes.[1−7] The development of techniques to fix CO_2 to epoxides is an ideal technique due to atom-economic and environmentally benign processes.[8,9]

Recent advancements have been made in the chemical fixing of CO_2 to generate cyclic carbonates by the use of metal complexes with sophisticated ligands, frustrated Lewis pairs (FLPs), metal halides, and carbon-based supported catalysts.[8,10−22] However, these catalytic systems have their drawbacks with the necessity of drastic conditions (high pressures and temperatures), low catalyst stability, and cost-effectiveness. Futhermore, none of these systems can perform carbon capture and utilization (CCU), either on-site or as part of a subsequent process within the same plant. In this vein, ionic liquids (ILs) have been studied as the potential media (sorbent and catalytic phase) in view of their capacity for CO_2 sorption (ad- and absorption) and catalytic fixation.[23] Among these, neat (bulk) ILs with halide anions have been exclusively studied but present a challenge in terms of separation from raw

Received: September 10, 2025
Revised: October 21, 2025
Accepted: October 22, 2025
Published: October 29, 2025



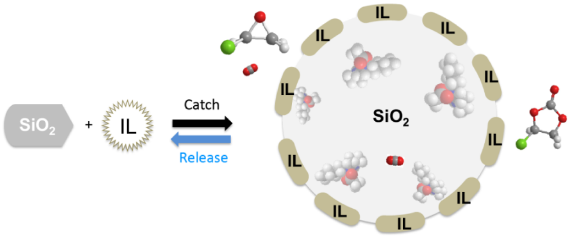
https://doi.org/10.1021/acs.jpcc.5c06371

materials and products, for recycling, limiting their extended use in cycloaddition reactions.[24−39] A limited number of studies have probed the efficacy of iron- and zinc-based, metal-containing ILs in promoting the cycloaddition of CO_2.[40−47] Only a few studies have been reported on the carbonation of epoxides to cyclic carbonates at high pressure and temperature by halide-based SILPs, but these systems exhibited low TONs.[48,49]

Recently, catch-and-release catalytic systems have been immerged as a smart technique in which a homogeneous catalyst is impregnated on a solid matrix to generate an elegant hybrid catalytic system.[50] These hybrid matrices can be designed through noncovalent immobilization of organic molecules or molecular complexes[51] enabling their release as active catalytic species into solution to promote the reaction and subsequent recapture at the end of the process.[52] To the best of our knowledge, these catalytic systems have not yet been examined for CO_2 activation. A monolayer of the ILs can be decorated onto solid supports (SiO_2 and Al_2O_3) to generate supported IL-phases (SILPs) and solid catalysts with IL-layers (SCILLs).[53] The IL in SCILL reveals a ligand effect that influences the electron properties of the support.

Herein, we prepared *n*-butyl-3-methylimidazulim ferricyanide (III), $[BMIm]_3.[Fe(CN)_6]$, IL that was examined for the efficient chemical fixation of CO_2 to various epoxides. The IL was impregnated onto commercial SiO_2, generating the "catalytic spongelike ionic assemblies" that combine the advantages of both homogeneous and heterogeneous catalysis. Our IL system is akin to a catch-release catalytic system that can dynamically control the diffusion of epoxides, intermediates, and products to the catalytic active (Scheme 1).

Scheme 1. Representation of Catch-Release of SCILL-$Fe(CN)_6$ for the CO_2 Fixation of Epoxides to Generate Cyclic Carbonates



2. EXPERIMENTAL SECTION

HPLC-grade solvents were utilized in this study. All epoxides and $K_3Fe(CN)_6$ were purchased from Sigma-Aldrich Chemicals. Silica gel (60, 0.05−0.2 mm) was obtained from Vetec (Brazil). 1-*n*-Butyl-3-methylimidazolium chloride was synthesized following a well-established method.[75] CO_2 (>99.999%) was obtained from White Martins Ltd., Brazil. The NMR spectra were acquired at 25 °C on a Bruker Avance III 500 spectrometer operating at 11.75 T, using DMSO-d_6 as a solvent.

2.1. Preparation of $[BMIm]_3·(FeCN)_6$ IL and SCILL-$Fe(CN)_6$.

A homogeneous solution of BMIm·Cl (1.05 g, 3 mmol) in an aqueous acetonitrile solution (5 mL of H_2O in 5 mL of CH_3CN) was prepared at room temperature. $K_3[Fe(CN)_6]$ (0.66 g, 2 mmol) was then added to the aqueous solution, and the mixture was stirred for 24 h. The solvents were evaporated under vacuum, resulting in the formation of a green, viscous, and homogeneous liquid. The obtained liquid was dissolved in CH_3CN (5 mL), stored in a refrigerator for 18 h, then filtered, and CH_3CN was evaporated. This process was repeated until no further white parts per trillion was observed. The resulting viscous greenish IL was stored in the refrigerator prior to further use. ^1H NMR (500 MHz, DMSO.d_6) δ 8.83 (s, 1H), 7.68 (s, 1H), 7.59 (s, 1H), 4.13 (t, J = 7.0 Hz, 2H), 3.74 (s, 3H), 1.79 − 1.69 (m, 2H), 1.27 − 1.22 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, DMSO.d_6) δ: 138.1, 124.2, 122.6, 49.3, 37.5, 31.6, 18.9, 13.4.

2.2. Preparation of SCILLs-$Fe(CN)_6$.

The SCILL-$Fe(CN)_6$ was prepared by the simple impregnation of $[BMIm]_3·(FeCN)_6$ IL onto commercially available SiO_2. Typically, 4.0 g of activated SiO_2 was added to CH_3OH (15 mL) and stirred at room temperature. Then, 1.0 g of $[BMIm]_3·(FeCN)_6$ IL was added. The reaction mixture was stirred at RT for 20 h. The resulting SCILL-$Fe(CN)_6$ was isolated by filtration, washed with dry ether (10 mL × 3), and dried at 60 °C for 16 h.

2.3. Catalytic Fixation of CO_2 in Epoxides.

All of the catalytic tests were performed in a home-steel fisher-porter (24 mL). Typically, the desired amounts of epoxide and catalyst were introduced into the reactor, which was subsequently sealed and purged with CO_2 to remove atmospheric oxygen. The reactor was subsequently filled with the desired amount of CO_2. The mixture was subjected to magnetic stirring and heating in a silicone oil bath. After 24 h, the reactor was cooled in ice-cold water for 30 min, and the gas was carefully released. A sample for ^1H NMR was prepared in DMSO·d_6 and analyzed immediately.

3. RESULTS AND DISCUSSION

3.1. Catalyst Preparation and Characterization.

A simple ferricyanide IL was prepared by mixing 1-*n*-butyl-3-methylimidazolium chloride IL with $K_3[Fe(CN)_6]$ salt in an aqueous solution of methanol at room temperature, yielding the greenish $[BMIm]_3·[Fe(CN)_6]$, (where BMIm is 1-*n*-butyl-3-methylimidazolium) ionic liquid, hereafter denoted as BMIm·$Fe(CN)_6$. The prepared IL was air-stable and was characterized by NMR, UV−visible, and ESI-MS analyses (Supporting Information).

The molecular structure of the IL was evaluated by NMR spectroscopy, including ^1H, ^{13}C, and ^1H−^1H NOESY experiments. Figure 1c shows cross-peaks between imidazolium hydrogens and the hydrogens of the aliphatic chain, reflecting intercationic interactions. The ESI-MS spectra demonstrated intense mass peaks at m/z 139.12 in positive mode and m/z 211.95 in negative mode, corresponding to the IL cation ($BMIm^+$) and anion ($Fe(CN)_6^{3-}$) of the BMIm·$Fe(CN)_6$ IL (Figures S4 and S5).

Figure S6 displays the radial distribution functions (RDFs) between the nitrogen atoms of the anion and the carbon atoms of the $BMIm^+$ cation (C2, C4, C5, C9, and C13). All RDF curves exhibit a primary peak near 3.4 Å, indicating a characteristic interaction distance. Among the analyzed atoms, C9 exhibits the highest $g(r)$ value (∼4.7), suggesting stronger or more frequent interactions with the anion ($Fe(CN)_6^{3-}$). C2 also presents a relatively intense and sharp peak ($g(r) \approx 3.1$), indicating a notable degree of spatial association, likely due to its position adjacent to the aromatic ring and the delocalized positive charge. In contrast, the RDF for C13 is broader and less intense, implying weaker or more diffuse interactions. These findings suggest that while all sites contribute to the local ion−ion organization, C9 and C2 serve as more preferential coordination sites for the anion, driven by their supramolecular organization.[76] The observed interaction strength follows the order: C9 > C2 ≈ C4 > C5 > C13.

To further illustrate the IL structure in a more intuitive manner, spatial distribution functions (SDFs) were computed to visualize the three-dimensional probability of finding atoms around a reference molecule. In Figure 1a, the isosurface highlights the spatial distribution of $[Fe(CN)_6]^{3-}$ around the $BMIm^+$ cation. Notably, the anion preferentially accumulates near the C2 and C9 positions, in agreement with the RDF results that show enhanced $g(r)$ peaks at these sites. Figure 1b displays the complementary distribution: the C2 atom of $BMIm^+$ mapped around the $[Fe(CN)_6]^{3-}$ anion, where the density forms a ring-shaped region around the middle of the octahedral complex. This spatial arrangement supports the RDF results by showing that beyond being frequently found near the anion, C2 and C9 also tend to occupy specific regions around them, indicating a preferred orientation. Generally, the combined RDF and SDF analyses reveal that the anion $[Fe(CN)_6]^{3-}$ preferentially interacts with the C9 and C2 positions of the $BMIm^+$ cation. These results highlight the anisotropic nature of the ion pair organization, which may influence the bulk properties of the ionic liquid and its performance in redox-active environments.

It is important to note that the RDFs were calculated from an ensemble of configurations obtained under equilibrium conditions, corresponding to an average density of 1.072 g/cm^3 for the simulated ionic liquid. The results obtained are therefore coherent with the anisotropic nature of ion−ion interactions and satisfactorily reflect the structural organization characteristic of the studied ionic liquid, validating both the methodological approach and the results achieved (Table 1).

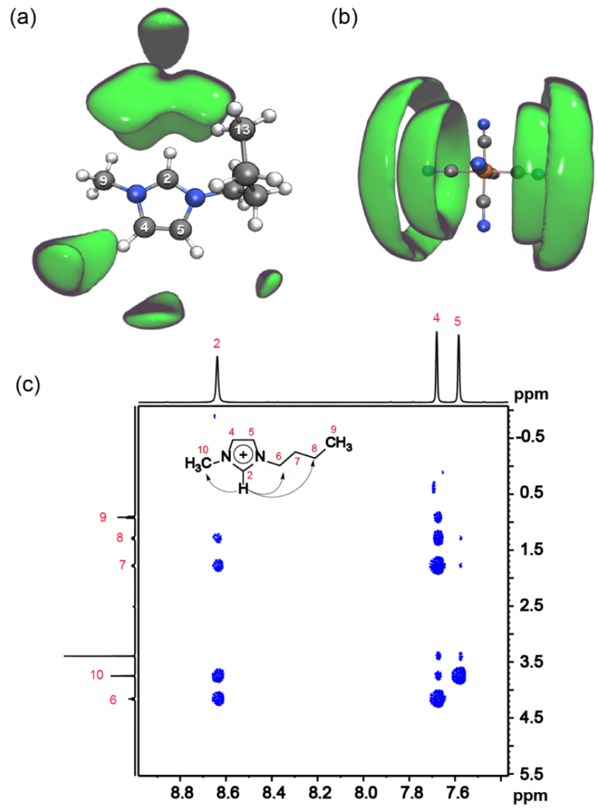


Figure 1. Radial distribution function of (a) $[Fe(CN)_6]^{3-}$ around BMIM+ and (b) C2 atom of BMIm around $[Fe(CN)_6]^{3-}$. (c) $^1H-^1H$-NOESY NMR contour map of the $BMIm \cdot Fe(CN)_6$ IL in DMSO-d_6 at 298 K. A full spectrum of $^1H-^1H$ NOESY is presented in S3.

Table 1. Literature Comparison of CO_2 Cycloaddition of Epichlorohydrin of Our Heterogeneous Catalytic System with Reported Catalysts

S. No	Cat.	Co-cat.	Temp. (C°)	P (bar)	Conv. (%)	TON	ref.
1	**SCILL-Fe(CN)$_6$**	-	**70**	**1.0**	**99**	**729.3**	**Our**
2	PQPBrCOOH	-	140	1.0	99	-	54
3	SILP-ZnCl$_3$	-	100	10	99	245	48
4	MorpholiniumIL+ ZnBr$_2$	-	25	1.0	99	-	55
5	PILs	-	60	1.0	78	200	56
6	Heteroscorpionate aluminum complexes	TBAB	25	1.0	99	-	57
7	Co^{II}-tridentate pincer type ligand (2,6-bis[[(4-methylphenyl)thio]carbonyl]pyridine)	DMAP	100	16	93	-	58
8	Zn(HBA)$_2$	TBAB	120	18	99	-	59
9	PIL microspheres grafted with pyridine (TB-Py)	-	80	10	31	-	60
10	Mn(III) meso-tetrakis(2,3-dichlorophenyl)porphyrin	TBAB	100	30	99	-	61
11	VIMEtOH][Br]-24/72	-	120	20	99	-	62
12	Imidazolium- and triazine-based ionic polymers	-	100	10	97	-	63
13	heterometallic macrocycles Ln$_8$Zn$_4$L$_6$	TBAB	120	10	99	-	64
14	NIIC-10	TBAB	40	2.0	99	-	65
15	TUD-1/Ag NPs	-	60	10	98	-	66
16	B-CN	KI	100	1.0	73	-	67
17	Al(III) phthalocyanine	PPNCl	80	10	94	-	68
18	MIL-101-N(Bnme$_2$)Br	-	100	14	96	-	69
19	CuO/paper matrices	-	100	4.0	99	-	70
20	Zn(II) Schiff base	-	110	25	98.6	-	71
21	Chalcopyrite UiO-67 MOF	-	70	10	95	-	72
22							
23	double cobaloxime salts	DMAP	100	16	98	-	73
24	NENP	TBAB	100	4.0	98.7	-	74

The SCILL-Fe$(CN)_6$ catalyst was prepared by simply grafting the BMIm·Fe$(CN)_6$ IL onto commercial silica. The resulting material was characterized by scanning electron microscopy (SEM), BET surface area analysis, and thermogravimetric analysis (TGA). SEM images revealed irregularly shaped particles, while chemical mapping (Figure 2) confirmed the homogeneous distribution of the IL within SiO_2 through the detection of Si, Fe, C, and N. TGA analysis (Figure S7) showed an initial weight loss between 30 and 100 °C, attributed to the removal of adsorbed water, followed by a second weight loss up to 700 °C, corresponding to the decomposition of the residual IL on the SiO_2 surface. SCILL-Fe$(CN)_6$ contains approximately 0.158 mmol/g of IL, as determined from the TGA results.[77] The physicochemical properties show a surface area of 236 m^2/g, a pore size of 10.3 nm, and a pore volume of 0.61 m^2/g (Table 2, entry 1, Figure S8). The decrease in surface area compared to that of pristine SiO_2 (288 m^2/g) is attributed to the incorporation of the IL into the pores of SiO_2.

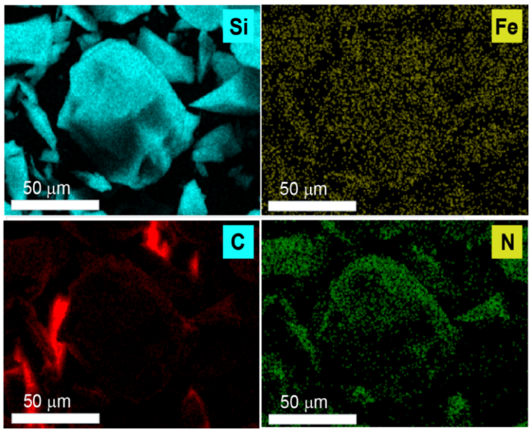


Figure 2. SEM with chemical mapping of the SCILLs-Fe$(CN)_6$.

Table 2. Physiochemical Properties of Catalysts

Entry	Cat.	Surface area (m^2/g)[bb]	Pore size (nm)[aa]	Pore volume (m^2/g)[aa]
1	SCILL-Fe$(CN)_6$	236	10.3	0.61
2	SiO_2	288	9.5	0.68

[a]Calculated from the N_2 adsorption and sorption isotherm using the BJH method. [b]Calculated from N_2 sorption using the BET method.

3.2. Catalytic Chemical Fixation of CO_2.

The prepared BMIm·Fe$(CN)_6$ IL was evaluated for the chemical fixation of CO_2 with different epoxides at 70 °C under 1−2 bar of CO_2 using 0.13 mmol of IL. Our IL represented efficient activity and selectivity to their respective cyclic carbonates. Using epichlorohydrin as the model substrate under 1 bar of CO_2, a conversion of 99% was obtained with 97% selectivity for the corresponding cyclic carbonates. A small amount of diols was also detected, which is associated with the confined water within ILs that is challenging to eliminate from them. The reaction progress was monitored as a function of time (Figure 3). Interestingly, the reaction reached 22% conversion after 1 h of reaction with >99% selectivity toward its cyclic carbonate. The conversion was augmented with the increases of time. After 2 h, about 32% conversion was achieved that reached 61% at 4 h, while maintaining >99% selectivity for cyclic carbonate.

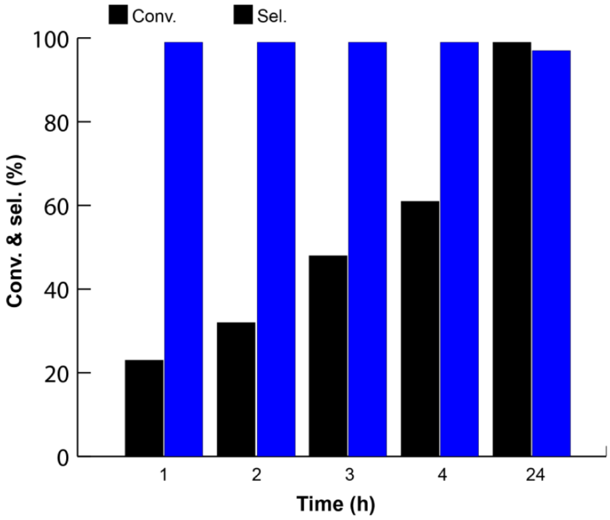


Figure 3. Epichlorohydrin conversion vs time. Reaction conditions; IL (0.13 mmol) and epichlorohydrin (12.0 mmol), temperature (70 °C) and 1-bar of CO_2.

The catalytic activity of our IL toward different kinds of aliphatic epoxides was also investigated (Figure 4). It was observed that the conversion of the aliphatic epoxides decreased as the number of carbon atoms increased. At 70 °C, propylene oxide (**2c**, Figure 4) achieved 46% conversion with >99% selectivity to the cyclic carbonate, while 39, 20, and 0% conversion were obtained with butyl epoxide (**2b**), butyl glycidyl ether (**2g**), and tert-butyl glycidyl ether (**2h**), respectively. The decrease in catalytic activity is related to low diffusion of large-sized substrates into the confined spaces of the IL, which restricts access to the active sites and reduces conversion and carbonate selectivity. In bulk and/or dilute phases, the presence of hydrogen bonding, along with polar and nonpolar domains, generates the distinct spatial confinement and dominant surface forces at short length scale that offer unique phases transition and depressed transport properties.[53,78] As a result, nanoconfined spaces akin to the catalytic active membrane/sponge structure are formed that control the diffusion of reactants, products, and intermediates to the catalytic active sites. These transport properties are attributed to the dynamical interplay of the contact ion pairs of the IL in bulk phases.[79]

Our IL also demonstrated efficient activity for the aromatic epoxides. At 70 °C, a lower activity (37%) was observed with styrene oxide (**2d**). On increasing the temperature to 100 °C, the conversion was reached >99% with maximum selectivity, while 1,2-epoxy-3-phenylpropane (**2e**) and glycidyl 2-methylphenyl ether (**2f**) afforded 97 and 70% conversion, respectively. The higher activity may be related to the presence of electron-donating oxygen, which activates the epoxide ring through its electron-donating capability.

To elucidate the heterogeneous effect, impregnation of the BMIm·Fe$(CN)_6$ IL on simple SiO_2 was prepared and obtained the SCILL-Fe$(CN)_6$ catalyst. Our SCILL-Fe$(CN)_6$ showed efficient activity for different aliphatic and aromatic epoxides at 100 °C and 2-bar CO_2 (Table 3). Notably, our catalyst showed remarkable activity with the turnover numbers of 729.3 with 99% conversion and 97% selectivity to its cyclic carbonate under 1 bar of CO_2 at 70 °C. Our catalytic system exhibited

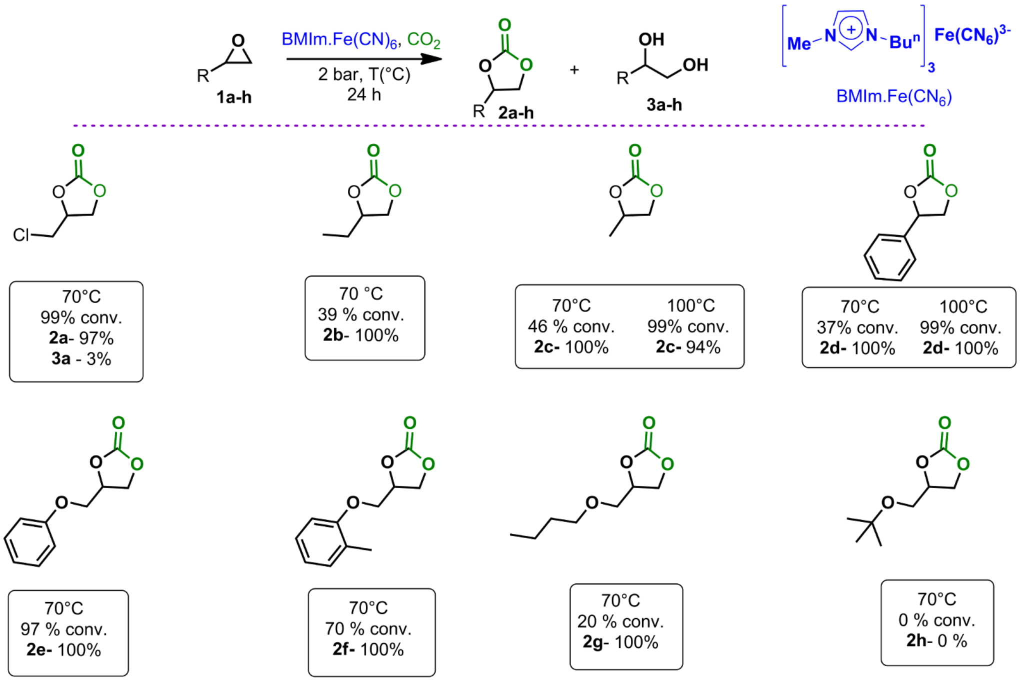
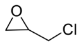
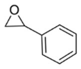
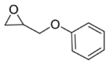
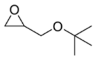
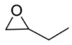
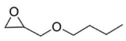


Figure 4. CO_2 chemical fixation in different epoxides by BMIm·Fe(CN)$_6$ IL. Reaction conditions; IL (0.13 mmol) and epoxide (12.0 mmol). The reaction was performed at 2 bar of CO_2, except epichlorohydrin. Conversion and selectivity were calculated by ^{1}H NMR. CO_2 (1.0 bar) for epichlorohydrin.

Table 3. Cycloaddition Reaction of Different Epoxides Catalyzed by BMIm·Fe(CN)$_6$ IL[a,b]

Entry	Substrate	Temp. (°C)	Conv. (%)[b]	Carb. Sel. (%)	TON
1		70	94	97	729.3
2		100	11	>99	83.5
3		100	88	>99	668.3
4		100	35	>99	265.8
5		100	94	>99	713.9
6		100	18	>99	136.7

[a] Reaction conditions: Cat. 100 mg, substrate (12.0 mmol), 24 h. Turnover number (TON): numbers of moles of cyclic carbonate per mole of immobilized IL. The quantity of IL (0.158 mmol/g) was obtained from TGA of SCILL·Fe(CN)$_6$ as reported earlier.[77]
[b] Calculated by ^{1}H NMR.

higher activity compared to previously reported heterogeneous catalysts under mild reaction conditions (Table 1).

We investigated the effect of the temperature on the activity of our catalysts (Figure 5a−c). At 25 °C, no product was observed. The reaction started at 40 °C with a conversion of 9%, while at 50 °C, a conversion of 22% with 165 TONs was obtained. As the temperature increased, the catalytic activity also increased, demonstrating the positive effect of temperature. When the temperature reached 70 °C, a conversion of 94% with 729.4 TONs was achieved (Table 3, entry 1). The high selectivity of >97% for cyclic carbonate was maintained across different temperatures (Figure 5b).

Our SCILL·Fe(CN)$_6$ catalyst also exhibited remarkable activity toward various aliphatic epoxides (Table 3). Butyl epoxide, tert-butyl glycidyl ether, and butyl glycidyl ether achieved conversions of 94, 35, and 18, respectively (Table 3, entries 5, 4, and 6). The observed decline in catalytic activity correlates with the increasing molecular size of the epoxides. Bulkier epoxides experience restricted diffusion within the confined spaces of SCILL·Fe(CN)$_6$, thereby limiting their access to the catalytic active sites.[80,81] On the other hand, about 11 and 88% conversion with TONs of 83.5 and 668.3 were achieved for styrene and phenyl glycidyl ether, respectively (Table 3, entries 2−3).

The anisotropic ion pair organization in IL is an important structural feature that influences the bulk properties of the liquid and its performance in “redox-active environments”. When an imidazolium IL interacts with the solid surface (SiO_2), its strong H-bonding exhibits a high affinity for the host solid surface. A monolayer of IL readily enhances the local charge density and modulates the orientation of cations and anions at the surface, wherein the first layer consists of imidazolium cations absorbed onto the solid, followed by a layer of IL anions.[82] These distinct orientations of the IL contact pair generate unique microenvironments/confined spaces, thereby facilitating faster diffusion (Figure 5d).[83] Additionally, the high surface-to-volume ratio of the immobilized IL facilitates enhanced substrate diffusion, effectively mitigating the mass transfer constraints imposed by the high viscosity of IL.[48] These features are responsible for the higher activity of the heterogeneous catalyst (SCILL·Fe(CN)$_6$) compared to that of the bulk IL.

To evaluate the stability of the SCILL·Fe(CN)$_6$ catalyst, recycling tests were carried out. Unfortunately, the catalytic

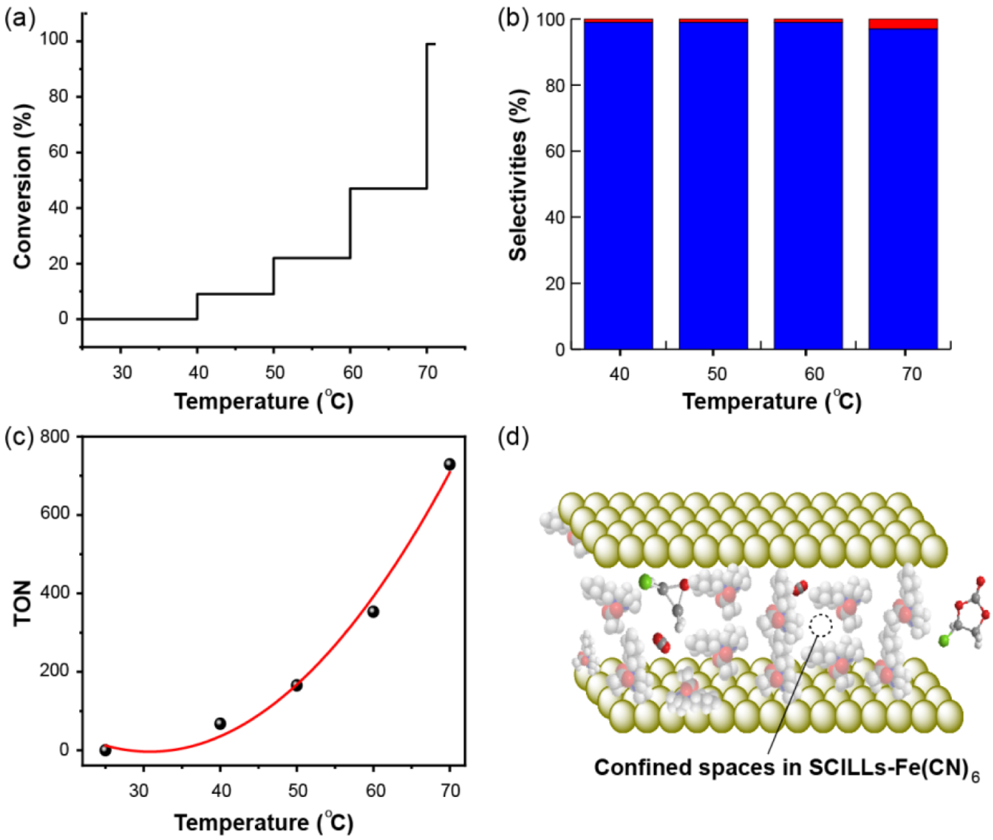


Figure 5. (a–c) Conversion vs temperature; cat. (100 mg), epichlorohydrin (12.0 mmol), CO_2 (1.0 bar) and 24 h; and (d) schematic representation of confined spaces in SCILL-Fe$(CN)_6$.

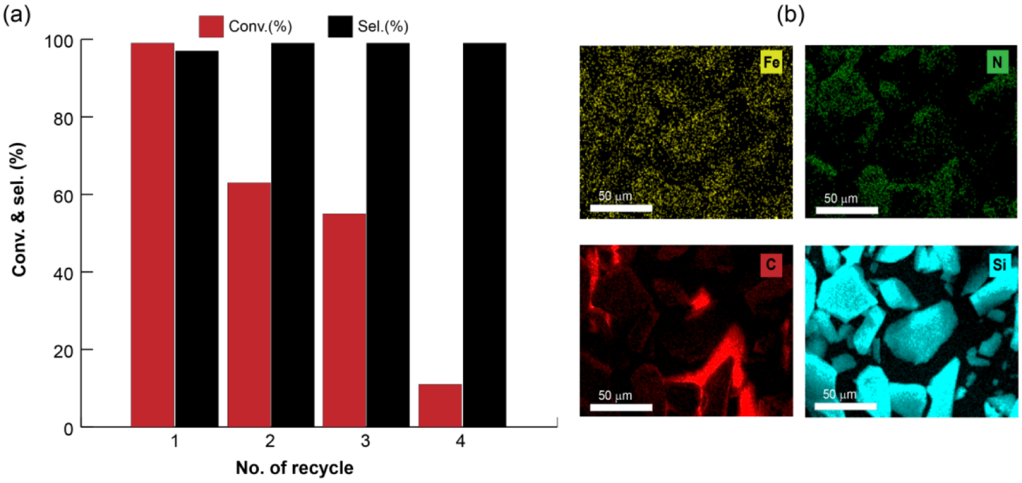


Figure 6. (a) Recycling tests of SCILL-Fe$(CN)_6$ (100 mg), epichlorohydrin (12.0 mmol), CO_2 (1.0 bar), and 24 h and (b) SEM with chemical mapping of SCILL-Fe$(CN)_6$ after 4th cycle.

activity decreased sharply after the first cycle, dropping from 99% conversion to about 60% (Figure 6a). This decline in activity continued in subsequent cycles, which is most likely attributable to leaching of the immobilized ionic liquid from the SiO_2 surface. The ^1H NMR spectrum of the crude reaction mixture confirmed the partial leaching of the IL (Figure S16). However, it is difficult to quantify the concentration of the leached IL because the fresh SCILL·Fe$(CN)_6$ catalyst contains only a very small amount of IL (0.0158 mmol). Since the IL concentration was extremely low, no notable conversion of epichlorohydrin was observed when the reaction was performed in the filtrate having leached IL. Moreover, SEM-EDS chemical mapping (Figure 6b) revealed the presence of Si, Fe, C, and N from the IL on SiO_2, confirming that the IL was not completely leached from SiO_2.

To confirm the proposed catch-and-release mechanism, we performed CO_2 sorption–desorption experiments. The sorption behavior of SCILL·Fe$(CN)_6$ was evaluated at 4 bar of CO_2 and 45 °C (Figure 7). The SCILL·Fe$(CN)_6$ exhibited an efficient CO_2 uptake of about 0.89 mmol of CO_2 per gram of catalyst. The recyclability of the sorption process was confirmed through multiple sorption–desorption cycles, with

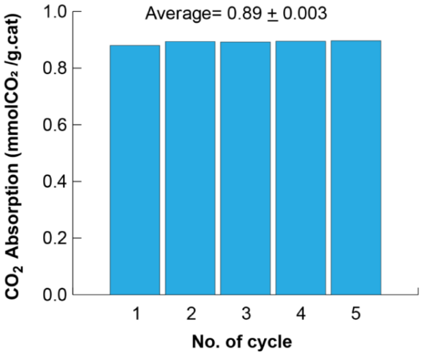


Figure 7. CO_2 sorption values of the SCILL·Fe(CN)$_6$ catalyst at 4 bar and 45 °C.

desorption carried out at 55 °C under vacuum. The SCILL·Fe(CN)$_6$ catalyst maintained a nearly constant chemisorption performance, and the CO_2 uptake/desorption process could be repeated at least five times without a significant loss of efficiency, thereby demonstrating the robustness of the system. These findings provide direct evidence supporting the proposed catch-and-release behavior of the catalyst.

3.2.1. Mechanistic Study. We propose a mechanism involving the formation of the 1-butyl-3-methylimidazolium-2-carboxylate adduct (NHC−CO_2) (Figure 8a). The formation of NHC−CO_2 species from imidazolium cations has been reported for CO_2 fixation in epoxides.[18,84] The first step involves the generation of a carbene by deprotonation, followed by the insertion of CO_2 to yield the NHC−CO_2 adduct (I).[85,86] The nucleophilic attack of the NHC−CO_2 adduct on epichlorohydrin affords an alkoxide (II), which subsequently undergoes intramolecular cyclic elimination to produce the cyclic carbonate.[87,88] The formed carbene reacts with a molecule of CO_2 to regenerate the NHC−CO_2 species. To confirm our hypothesis, in situ ^{13}C NMR was performed at 60 °C (Figure 8b). The formation of the NHC−CO_2 adduct was observed at 155 ppm after 2 h of reaction, and its quantity increased over time (Figure 8b).

4. CONCLUSIONS

A simple and inert ferricyanide (III)-based IL was developed, exhibiting anisotropic contact-ion-pair organization, as revealed by MD simulations. The prepared IL demonstrated higher activity and selectivity for the chemical fixation of CO_2 into various aliphatic and aromatic epoxides under low pressures (1−2 bar) and moderate temperatures (70−100 °C). Remarkably, its heterogeneous form (SCILL·Fe(CN)$_6$) demonstrated an even higher catalytic activity. The prepared SCILL-Fe(CN)$_6$ exhibited turnover numbers (TONs) ranging from 265 to 729 for aliphatic epoxides and from 83 to 668 for aromatic epoxides, maintaining 99% selectivity toward their cyclic carbonates under mild conditions. The nanoconfined spaces in SCILL-Fe(CN)$_6$, formed due to the distinct orientation of cations and anions, function as catch-release ionic catalytic systems. These confined spaces regulate the diffusion of reactants, products, and intermediates to and from the catalytically active sites. The reaction mechanism involves the generation of an NHC−CO_2 adduct, which was confirmed by in situ NMR studies under realistic reaction conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.5c06371.

NMRs analyses, SEM, BET, recyclability tests, and ESI-MS analysis (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Muhammad I. Qadir − *Instituto de Química, Universidade Federal de Goiás-UFG, Goiânia, Goiás 74690-900, Brazil;* orcid.org/0000-0001-7172-8427; Email: irfan@ufg.br

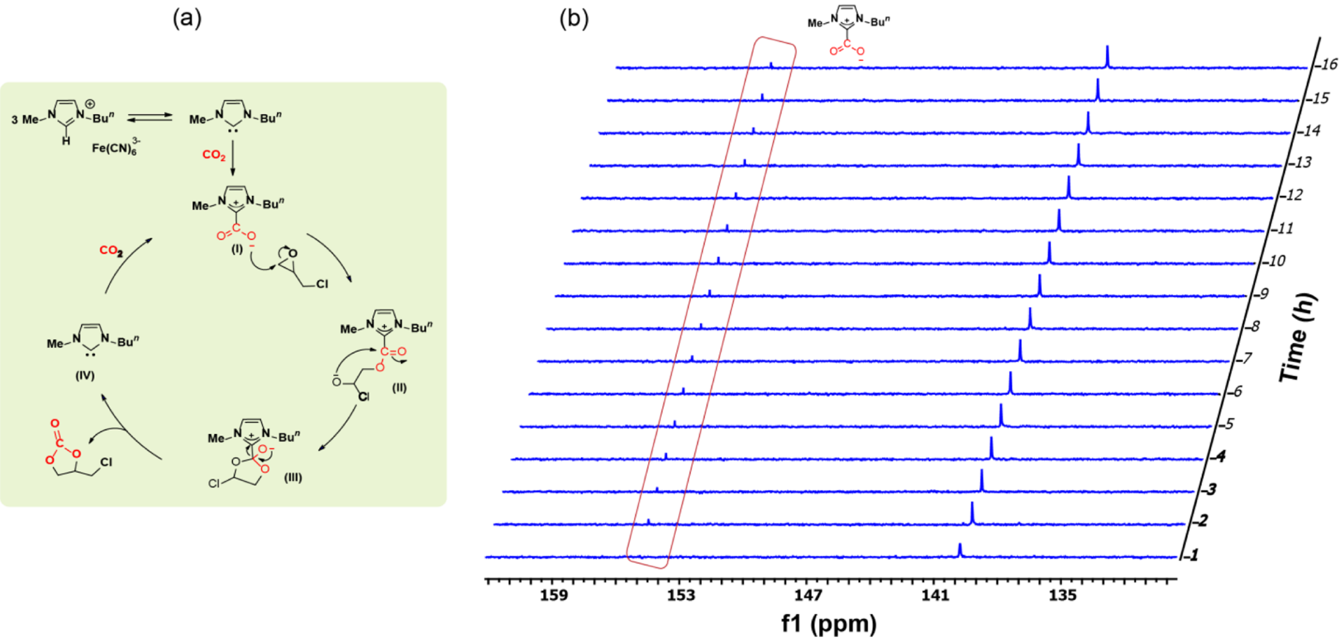


Figure 8. (a) A plausible mechanistic approach and (b) in situ ^{13}C-NMR analysis, reaction conditions; epichlorohydrin (200 mg), BMIm·Fe(CN)$_6$ (200 mg), DMSO-d6 (5.0 mL) and 60 °C. The reaction mixture was bubbled with CO_2.

Rafael P. das Chagas − *Instituto de Química, Universidade Federal de Goiás-UFG, Goiânia, Goiás 74690-900, Brazil;* orcid.org/0000-0002-4671-8697; Email: rpchagas@ufg.br

Authors

Camila P. Ebersol − *Instituto de Química, Universidade Federal de Goiás-UFG, Goiânia, Goiás 74690-900, Brazil*

Jonas X. Torres − *Instituto de Química, Universidade Federal de Goiás-UFG, Goiânia, Goiás 74690-900, Brazil*

Luciano M. Lião − *Instituto de Química, Universidade Federal de Goiás-UFG, Goiânia, Goiás 74690-900, Brazil;* orcid.org/0000-0001-9985-2980

Muhammad Nisar − *Departamento de Ingeniería Eléctrica, Facultad de ingeniería, Universidad Católica de la Santísima Concepción, Concepción 2850, Chile;* orcid.org/0000-0002-1305-5188

Pedro H. F. Matias − *Instituto de Química, Universidade Federal de Goiás-UFG, Goiânia, Goiás 74690-900, Brazil;* orcid.org/0009-0000-0612-3018

Heibbe Cristhian. B. de Oliveira − *Instituto de Química, Universidade Federal de Goiás-UFG, Goiânia, Goiás 74690-900, Brazil;* orcid.org/0000-0002-6937-9982

José S. S. Neto − *Instituto de Química, Universidade Federal de Goiás-UFG, Goiânia, Goiás 74690-900, Brazil;* orcid.org/0000-0003-4157-3481

Guilherme Colherinhas − *Instituto de Física, Universidade Federal de Goiás-UFG, Goiânia, Goiás 74690-900, Brazil*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpcc.5c06371

Author Contributions

C. P. Ebersol planned the experiments, prepared the catalysts, performed the catalytic experiments, interpreted data, and wrote the manuscript. J. Xavier performed experiments, interpreted data, and wrote the manuscript. R. P. das Chagas designed experiments, interpreted data, and wrote the manuscript. L. M. Lião and José S. S. Neto analyzed NMR data. M. Nisar prepared catalysts and interpreted data. P. H. F. Matias, H. C. B. de Oliveira, and Guilherme Colherinhas performed computational study. M. I. Qadir planned, supervised, discussed results, and wrote the manuscript. All authors have given approval to the final version of the manuscript.

Funding

The authors thank CNPq (406422/2022-2) and FAPEG (202310267000259, 202310267001383) for financial support. M. Nisar thanks the Chilean Agency for Research and Development (ANID) under the FONDECYT (11251269). The Article Processing Charge for the publication of this research was funded by the Coordenacao de Aperfeicoamento de Pessoal de Nivel Superior (CAPES), Brazil (ROR identifier: 00x0ma614).

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Dupont, J. Across the Board: Jairton Dupont. *ChemSuschem* **2015**, *8* (4), 586−587.

(2) Peters, M.; Köhler, B.; Kuckshinrichs, W.; Leitner, W.; Markewitz, P.; Müller, T. E. Chemical Technologies for Exploiting and Recycling Carbon Dioxide into the Value Chain. *ChemSuschem* **2011**, *4* (9), 1216−1240.

(3) North, M.; Pasquale, R.; Young, C. Synthesis of cyclic carbonates from epoxides and CO2. *Green Chem.* **2010**, *12* (9), 1514−1539.

(4) De, S.; Dokania, A.; Ramirez, A.; Gascon, J. Advances in the Design of Heterogeneous Catalysts and Thermocatalytic Processes for CO2 Utilization. *ACS Catal.* **2020**, *10* (23), 14147−14185.

(5) Ra, E. C.; Kim, K. Y.; Kim, E. H.; Lee, H.; An, K.; Lee, J. S. Recycling Carbon Dioxide through Catalytic Hydrogenation: Recent Key Developments and Perspectives. *ACS Catal.* **2020**, *10* (19), 11318−11345.

(6) Qadir, M. I.; Bernardi, F.; Scholten, J. D.; Baptista, D. L.; Dupont, J. Synergistic CO2 hydrogenation over bimetallic Ru/Ni nanoparticles in ionic liquids. *Appl. Catal., B* **2019**, *252*, 10−17.

(7) Luo, P.; Shi, P.; Yan, Z.; Han, J.; Wang, J.; Li, Y.; Ban, H.; Cai, W.; Li, C. Ternary synergistic interaction of Cu-ZnO-ZrO2 promoting CO2 hydrogenation to methanol. *Appl. Catal., A* **2025**, *689*, 120006.

(8) Guo, L.; Lamb, K. J.; North, M. Recent developments in organocatalysed transformations of epoxides and carbon dioxide into cyclic carbonates. *Green Chem.* **2021**, *23* (1), 77−118.

(9) Shaikh, R. R.; Pornpraprom, S.; D'Elia, V. Catalytic Strategies for the Cycloaddition of Pure, Diluted, and Waste CO2 to Epoxides under Ambient Conditions. *ACS Catal.* **2018**, *8* (1), 419−450.

(10) Chen, Y.; Qiu, R.; Xu, X.; Au, C.-T.; Yin, S.-F. Organoantimony and organobismuth complexes for CO2 fixation. *RSC Adv.* **2014**, *4* (23), 11907−11918.

(11) Lu, X.-B.; Darensbourg, D. J. Cobalt catalysts for the coupling of CO2 and epoxides to provide polycarbonates and cyclic carbonates. *Chem. Soc. Rev.* **2012**, *41* (4), 1462−1484.

(12) Miralda, C. M.; Macias, E. E.; Zhu, M.; Ratnasamy, P.; Carreon, M. A. Zeolitic Imidazole Framework-8 Catalysts in the Conversion of CO2 to Chloropropene Carbonate. *ACS Catal.* **2012**, *2* (1), 180−183.

(13) Zhu, M.; Srinivas, D.; Bhogeswararao, S.; Ratnasamy, P.; Carreon, M. A. Catalytic activity of ZIF-8 in the synthesis of styrene carbonate from CO2 and styrene oxide. *Catal. Commun.* **2013**, *32*, 36−40.

(14) Lan, D.-H.; Chen, L.; Au, C.-T.; Yin, S.-F. One-pot synthesized multi-functional graphene oxide as a water-tolerant and efficient metal-free heterogeneous catalyst for cycloaddition reaction. *Carbon* **2015**, *93*, 22−31.

(15) Lan, D.-H.; Wang, H.-T.; Chen, L.; Au, C.-T.; Yin, S.-F. Phosphorous-modified bulk graphitic carbon nitride: Facile preparation and application as an acid-base bifunctional and efficient catalyst for CO2 cycloaddition with epoxides. *Carbon* **2016**, *100*, 81−89.

(16) Lan, D.-H.; Gong, Y.-X.; Tan, N.-Y.; Wu, S.-S.; Shen, J.; Yao, K.-C.; Yi, B.; Au, C.-T.; Yin, S.-F. Multi-functionalization of GO with multi-cationic ILs as high efficient metal-free catalyst for CO2 cycloaddition under mild conditions. *Carbon* **2018**, *127*, 245−254.

(17) Zhang, W.-H.; He, P.-P.; Wu, S.; Xu, J.; Li, Y.; Zhang, G.; Wei, X.-Y. Graphene oxide grafted hydroxyl-functionalized ionic liquid: A highly efficient catalyst for cycloaddition of CO2 with epoxides. *Appl. Catal., A* **2016**, *509*, 111−117.

(18) Fiorani, G.; Guo, W.; Kleij, A. W. Sustainable conversion of carbon dioxide: The advent of organocatalysis. *Green Chem.* **2015**, *17* (3), 1375−1389.

(19) Kihara, N.; Hara, N.; Endo, T. Catalytic activity of various salts in the reaction of 2,3-epoxypropyl phenyl ether and carbon dioxide under atmospheric pressure. *J. Org. Chem.* **1993**, *58* (23), 6198−6202.

(20) He, L.-N.; Yasuda, H.; Sakakura, T. New procedure for recycling homogeneous catalyst: Propylene carbonate synthesis under supercritical CO2 conditions. *Green Chem.* **2003**, *5* (1), 92−94.

(21) Ribeiro, S. L. S.; Silva, C. G.; Prado, G. E. T. O.; da Mata, Á. F. A.; Milani, J. L. S.; Martins, P. R.; Das Chagas, R. P. Nickel−cobalt hydroxide catalysts for the cycloaddition of carbon dioxide to epoxides. *Res. Chem. Intermed.* **2022**, *48* (5), 1907−1921.

(22) Decortes, A.; Castilla, A. M.; Kleij, A. W. Salen-Complex-Mediated Formation of Cyclic Carbonates by Cycloaddition of CO2 to Epoxides. *Angew. Chem. Int. Ed.* **2010**, *49* (51), 9822−9837.

(23) Qadir, M. I.; Dupont, J. Thermo- and Photocatalytic Activation of CO2 in Ionic Liquids Nanodomains. *Angew. Chem., Int. Ed.* **2023**, *62* (31), No. e202301497.

(24) Girard, A.-L.; Simon, N.; Zanatta, M.; Marmitt, S.; Gonçalves, P.; Dupont, J. Insights on recyclable catalytic system composed of task-specific ionic liquids for the chemical fixation of carbon dioxide. *Green Chem.* **2014**, *16* (5), 2815−2825.

(25) Yao, R.; Wang, H.; Han, J. Polyethylene glycol-supported ionic liquid as a highly efficient catalyst for the synthesis of propylene carbonate under mild conditions. *Front. Chem. Sci. Eng.* **2012**, *6* (3), 239−245.

(26) Wong, W.-L.; Lee, L. Y. S.; Ho, K.-P.; Zhou, Z.-Y.; Fan, T.; Lin, Z.; Wong, K.-Y. A green catalysis of CO2 fixation to aliphatic cyclic carbonates by a new ionic liquid system. *Appl. Catal., A* **2014**, *472*, 160−166.

(27) Arruda da Mata, Á. F.; Glanzmann, N.; Fazza Stroppa, P. H.; Terra Martins, F.; Das Chagas, R. P.; da Silva, A. D.; Milani, J. L. S. Single-component, metal-free, solvent-free HO-functionalized 1,2,3-triazole-based ionic liquid catalysts for efficient CO2 conversion. *New J. Chem.* **2022**, *46* (25), 12237−12243.

(28) Li, G.; Dong, S.; Fu, P.; Yue, Q.; Zhou, Y.; Wang, J. Synthesis of porous poly(ionic liquid)s for chemical CO2 fixation with epoxides. *Green Chem.* **2022**, *24* (9), 3433−3460.

(29) Lei, Y.; Gunaratne, H. Q. N.; Jin, L. Design and synthesis of pyridinamide functionalized ionic liquids for efficient conversion of carbon dioxide into cyclic carbonates. *J. CO2 Util.* **2022**, *58*, 101930.

(30) Fanjul-Mosteirín, N.; Jehanno, C.; Ruipérez, F.; Sardon, H.; Dove, A. P. Rational Study of DBU Salts for the CO2 Insertion into Epoxides for the Synthesis of Cyclic Carbonates. *ACS Sustainable Chem. Eng.* **2019**, *7* (12), 10633−10640.

(31) Masoom Nataj, S. M.; Kaliaguine, S.; Fontaine, F.-G. CO2 fixation reaction over pyrimidinium-based dicationic ionic liquid in MIL-101(Cr). *Appl. Catal., A* **2025**, *697*, 120186.

(32) Numpilai, T.; Pham, L. K. H.; Witoon, T. Advances in Ionic Liquid Technologies for CO2 Capture and Conversion: A Comprehensive Review. *Ind. Eng. Chem. Res.* **2024**, *63* (46), 19865−19915.

(33) Neto, B. A. D.; Souza, R. Y. D.; Dupont, J. Can any Basic/Nucleophile Quaternary Salt Promote the Carbonatation of Epoxides? A Review. *ACS Omega* **2025**, *10* (33), 36824−36865.

(34) Rodríguez, H.; Gurau, G.; Holbrey, J. D.; Rogers, R. D. Reaction of elemental chalcogens with imidazolium acetates to yield imidazole-2-chalcogenones: Direct evidence for ionic liquids as proto-carbenes. *Chem. Commun.* **2011**, *47* (11), 3222−3224.

(35) Chen, J.; Wu, X.; Ding, H.; Liu, N.; Liu, B.; He, L. Tolerant Bimetallic Macrocyclic [OSSO]-Type Zinc Complexes for Efficient CO2 Fixation into Cyclic Carbonates. *ACS Sustainable Chem. Eng.* **2021**, *9* (48), 16210−16219.

(36) Li, F.; Hou, X.; Zhou, Y.-H. Dicationic ionic liquid-grafted UiO-66 as efficient catalyst for CO2 conversion into cyclocarbonate under cocatalyst-free and solventless conditions. *Appl. Organomet. Chem.* **2024**, *38* (11), No. e7640.

(37) Liu, Y.; Ding, W.; Li, Y.; Li, M.; Liu, Y.; Li, Y.; Su, Q.; Yang, Z. Cost-effective fixation of CO2 into cyclic carbonates catalyzed by Zn bromide-based deep eutectic ionic liquid. *Tetrahedron* **2023**, *140*, 133453.

(38) Zhang, Z.; Fan, F.; Xing, H.; Yang, Q.; Bao, Z.; Ren, Q. Efficient Synthesis of Cyclic Carbonates from Atmospheric CO2 Using a Positive Charge Delocalized Ionic Liquid Catalyst. *ACS Sustainable Chem. Eng.* **2017**, *5* (4), 2841−2846.

(39) Honores, J.; Quezada, D.; Camarada, M. B.; Ramirez, G.; Isaacs, M. Integrated experimental and theoretical insights into CO2 fixation: Tetraazamacrocyclic catalysts in ionic liquids for cyclic carbonate formation. *RSC Sustainability* **2025**, *3* (7), 2927−2937.

(40) Cheng, J.; Lu, C.; Zhao, B. Cycloaddition of carbon dioxide and epoxides catalyzed by rare earth metal complexes bearing a Trost ligand. *New J. Chem.* **2021**, *45* (29), 13096−13103.

(41) Gao, J.; Song, Q.-W.; He, L.-N.; Liu, C.; Yang, Z.-Z.; Han, X.; Li, X.-D.; Song, Q.-C. Preparation of polystyrene-supported Lewis acidic Fe(III) ionic liquid and its application in catalytic conversion of carbon dioxide. *Tetrahedron* **2012**, *68* (20), 3835−3842.

(42) Han, L.; Park, M.-S.; Choi, S.-J.; Kim, Y.-J.; Lee, S.-M.; Park, D.-W. Incorporation of Metal Ions into Silica-Grafted Imidazolium-Based Ionic Liquids to Efficiently Catalyze Cycloaddition Reactions of CO2 and Epoxides. *Catal. Lett.* **2012**, *142* (2), 259−266.

(43) Kim, M.-I.; Choi, S.-J.; Kim, D.-W.; Park, D.-W. Catalytic performance of zinc containing ionic liquids immobilized on silica for the synthesis of cyclic carbonates. *J. Ind. Eng. Chem.* **2014**, *20* (5), 3102−3107.

(44) Kim, D.; Moon, Y.; Ji, D.; Kim, H.; Cho, D. Metal-Containing Ionic Liquids as Synergistic Catalysts for the Cycloaddition of CO2: A Density Functional Theory and Response Surface Methodology Corroborated Study. *ACS Sustainable Chem. Eng.* **2016**, *4* (9), 4591−4600.

(45) Leu, M. K.; Vicente, I.; Fernandes, J. A.; de Pedro, I.; Dupont, J.; Sans, V.; Licence, P.; Gual, A.; Cano, I. On the real catalytically active species for CO2 fixation into cyclic carbonates under near ambient conditions: Dissociation equilibrium of [BMIm][Fe(NO)-2Cl2] dependant on reaction temperature. *Appl. Catal., B* **2019**, *245*, 240−250.

(46) Barrulas, R. V.; Tinajero, C.; Ferreira, D. P. N.; Illanes-Bordomás, C.; Sans, V.; Carrott, M. R.; García-González, C. A.; Zanatta, M.; Corvo, M. C. Poly(ionic liquid)-based aerogels for continuous-flow CO2 upcycling. *J. CO2 Util.* **2024**, *83*, 102771.

(47) Niu, J.; Wang, G.; Qiao, H.; Yan, L.; Wu, J.; Gao, Y.; Han, L.; Zhu, N. Acetate-based ionic liquid immobilized Fe-MIL-101-NH2: A highly efficient heterogeneous catalyst for the conversion of CO2 into oxazolidinones with N-aryl epoxy amines. *J. Environ. Chem. Eng.* **2024**, *12* (5), 113503.

(48) Tomazett, V. K.; Chacon, G.; Marin, G.; Castegnaro, M. V.; Das Chagas, R. P.; Lião, L. M.; Dupont, J.; Qadir, M. I. Ionic liquid confined spaces controlled catalytic CO2 cycloaddition of epoxides in BMIm.ZnCl3 and its supported ionic liquid phases. *J. CO2 Util.* **2023**, *69*, 102400.

(49) Martínez-Ferraté, O.; Chacón, G.; Bernardi, F.; Grehl, T.; Brüner, P.; Dupont, J. Cycloaddition of carbon dioxide to epoxides catalysed by supported ionic liquids. *Catal. Sci. Technol.* **2018**, *8* (12), 3081−3089.

(50) Gruttadauria, M.; Giacalone, F.; Noto, R. "Release and catch" catalytic systems. *Green Chem.* **2013**, *15* (10), 2608−2618.

(51) Qi, M.; Chew, B. K. J.; Yee, K. G.; Zhang, Z.-X.; Young, D. J.; Hor, T. S. A. A catch−release catalysis system based on supramolecular host−guest interactions. *RSC Adv.* **2016**, *6* (28), 23686−23692.

(52) Paul, I.; Mittal, N.; De, S.; Bolte, M.; Schmittel, M. Catch−Release System for Dosing and Recycling Silver(I) Catalyst with Status of Catalytic Activity Reported by Fluorescence. *J. Am. Chem. Soc.* **2019**, *141* (13), 5139−5143.

(53) Dupont, J.; Leal, B. C.; Lozano, P.; Monteiro, A. L.; Migowski, P.; Scholten, J. D. Ionic Liquids in Metal, Photo-, Electro-, and (Bio) Catalysis. *Chem. Rev.* **2024**, *124* (9), 5227−5420.

(54) Yin, K.; Hua, L.; Qu, L.; Yao, Q.; Wang, Y.; Yuan, D.; You, H.; Yao, Y. Heterobimetallic rare earth metal−zinc catalysts for reactions of epoxides and CO2 under ambient conditions. *Dalton Trans.* **2021**, *50* (4), 1453−1464.

(55) Shang, Y.; Gong, Q.; Zheng, M.; Zhang, H.; Zhou, X. An efficient morpholinium ionic liquid based catalyst system for cycloaddition of CO2 and epoxides under mild conditions. *J. Mol. Liq.* **2019**, *283*, 235−241.

(56) Li, C.; Liu, F.; Zhao, T.; Gu, J.; Chen, P.; Chen, T. Highly efficient CO2 fixation into cyclic carbonate by hydroxyl-functionalized protic ionic liquids at atmospheric pressure. *Mol. Catal.* **2021**, *511*, 111756.

(57) de la Cruz-Martínez, F.; Castro-Osma, J. A.; Lara-Sánchez, A. Carbon dioxide fixation into cyclic carbonates at room temperature catalyzed by heteroscorpionate aluminum complexes. *Green Chem. Eng.* **2022**, *3* (3), 280−287.

(58) Gamze Sogukomerogullari, H.; Delidogan, A.; Aytar, E.; Köse, A.; Sönmez, M. Pd(II), Ni(II), Cu(II) and Co(II) complexes bearing "SNS" pincer type Ligand: Application as catalysts for chemical CO2 conversion to obtain cyclic carbonates. *Inorg. Chim. Acta* **2022**, *539*, 121040.

(59) Ge, Y.; Liu, W.; Zou, Y.; Cheng, G.; Ke, H. A solid Zn complex catalyst for efficient transformation of CO2 to cyclic carbonates at mild conditions. *Tetrahedron* **2022**, *119*, 132857.

(60) Lu, J.; Liu, S.; Xu, A.; Jin, L.; Chi, H.; Li, Y.; Li, B.; Dong, L.; Fan, M. Surface functionalized ionic liquid polymer microspheres as efficient solid catalysts for chemical fixation of CO2 into cyclic carbonates. *Mater. Chem. Phys.* **2021**, *272*, 124899.

(61) Milani, J. L. S.; Meireles, A. M.; Cabral, B. N.; de Almeida Bezerra, W.; Martins, F. T.; da Silva Martins, D. C.; Das Chagas, R. P. Highly active Mn(III) meso-tetrakis(2,3-dichlorophenyl)porphyrin catalysts for the cycloaddition of CO2 with epoxides. *J. CO2 Util.* **2019**, *30*, 100−106.

(62) Mujmule, R. B.; Kim, H. Efficient imidazolium ionic liquid as a tri-functional robust catalyst for chemical fixation of CO2 into cyclic carbonates. *J. Environ. Manage.* **2022**, *314*, 115045.

(63) Cai, K.; Liu, P.; Chen, P.; Yang, C.; Liu, F.; Xie, T.; Zhao, T. Imidazolium- and triazine-based ionic polymers as recyclable catalysts for efficient fixation of CO2 into cyclic carbonates. *J. CO2 Util.* **2021**, *51*, 101658.

(64) Yang, H.; Xie, Y.; Chen, W.; Tang, X.; Hu, M.; Shu, Y.; Wang, L.; Liu, W. Gridlike 3d-4f heterometallic macrocycles for highly efficient conversion of CO2 into cyclic carbonates. *J. CO2 Util.* **2021**, *54*, 101780.

(65) Bondarenko, G. N.; Ganina, O. G.; Lysova, A. A.; Fedin, V. P.; Beletskaya, I. P. Cyclic carbonates synthesis from epoxides and CO2 over NIIC-10 metal-organic frameworks. *J. CO2 Util.* **2021**, *53*, 101718.

(66) Keshri, K. S.; Bhattacharjee, S.; Singha, A.; Bhaumik, A.; Chowdhury, B. Synthesis of cyclic carbonates of different epoxides using CO2 as a C1 building block over Ag/TUD-1 mesoporous silica catalyst: A solvent free approach. *Mol. Catal.* **2022**, *522*, 112234.

(67) Chand, H.; Choudhary, P.; Kumar, A.; Kumar, A.; Krishnan, V. Atmospheric pressure conversion of carbon dioxide to cyclic carbonates using a metal-free Lewis acid-base bifunctional heterogeneous catalyst. *J. CO2 Util.* **2021**, *51*, 101646.

(68) Gonzalez, A. C. S.; Felgueiras, A. P.; Aroso, R. T.; Carrilho, R. M. B.; Pereira, M. M. Al(III) phthalocyanine catalysts for CO2 addition to epoxides: Fine-tunable selectivity for cyclic carbonates versus polycarbonates. *J. Organomet. Chem.* **2021**, *950*, 121979.

(69) Xu, A.; Chen, Z.; Jin, L.; Chu, B.; Lu, J.; He, X.; Yao, Y.; Li, B.; Dong, L.; Fan, M. Quaternary ammonium salt functionalized MIL-101-NH2(Cr) as a bifunctional catalyst for the cycloaddition of CO2 with epoxides to produce cyclic carbonates. *Appl. Catal., A* **2021**, *624*, 118307.

(70) Aggrawal, S.; Sharma, R.; Mohanty, P. CuO immobilized paper matrices: A green catalyst for conversion of CO2 to cyclic carbonates. *J. CO2 Util.* **2021**, *46*, 101466.

(71) Wu, Y.; Shi, S.; Su, X.; Zhang, Z.; Liu, P.; Oderinde, O.; Yi, G.; Xiao, G.; Zhang, Y. Experimental and computational studies of Zn (II) complexes structured with Schiff base ligands as the efficient catalysts for chemical fixation of CO2 into cyclic carbonates. *Mol. Catal.* **2021**, *515*, 111894.

(72) Helal, A.; Alahmari, F.; Usman, M.; Yamani, Z. H. Chalcopyrite UiO-67 metal-organic framework composite for CO2 fixation as cyclic carbonates. *J. Environ. Chem. Eng.* **2022**, *10* (3), 108061.

(73) Alhafez, A.; Aytar, E.; Kilic, A. Enhancing catalytic strategy for cyclic carbonates synthesized from CO2 and epoxides by using cobaloxime-based double complex salts as catalysts. *J. CO2 Util.* **2022**, *63*, 102129.

(74) Sharma, R.; Chaudhary, M.; Pandey, A.; Biswas, P.; Mohanty, P. Catalytic conversion of CO2: Electrochemically to ethanol and thermochemically to cyclic carbonates using nanoporous polytriazine. *J. CO2 Util.* **2021**, *52*, 101676.

(75) Farmer, V.; Welton, T. The oxidation of alcohols in substituted imidazolium ionic liquids using ruthenium catalysts. *Green Chem.* **2002**, *4* (2), 97−102.

(76) Corvo, M. C.; Sardinha, J.; Menezes, S. C.; Einloft, S.; Seferin, M.; Dupont, J.; Casimiro, T.; Cabrita, E. J. Solvation of Carbon Dioxide in [C4mim][BF4] and [C4mim][PF6] Ionic Liquids Revealed by High-Pressure NMR Spectroscopy. *Angew. Chem., Int. Ed.* **2013**, *52* (49), 13024−13027.

(77) Han, L.; Park, S.-W.; Park, D.-W. Silica grafted imidazolium-based ionic liquids: Efficient heterogeneous catalysts for chemical fixation of CO2 to a cyclic carbonate. *Energy Environ. Sci.* **2009**, *2* (12), 1286−1292.

(78) Lu, Y.; Chen, W.; Wang, Y.; Huo, F.; Zhang, L.; He, H.; Zhang, S. A space-confined strategy toward large-area two-dimensional crystals of ionic liquid. *Phys. Chem. Chem. Phys.* **2020**, *22* (4), 1820−1825.

(79) Zhang, Q.; Xu, Y.; Wang, Q.; Huang, W.; Zhou, J.; Jiang, Y.; Xu, H.; Guo, L.; Zhang, P.; Zhao, J.; et al. Outstanding catalytic performance in the semi-hydrogenation of acetylene in a front-end process by establishing a "hydrogen deficient" phase. *Chem. Commun* **2019**, *55* (99), 14910−14913.

(80) Horike, S.; Dinca, M.; Tamaki, K.; Long, J. R. Size-Selective Lewis Acid Catalysis in a Microporous Metal-Organic Framework with Exposed Mn2+ Coordination Sites. *J. Am. Chem. Soc.* **2008**, *130* (18), 5854−5855.

(81) Warren, J. E.; Perkins, C. G.; Jelfs, K. E.; Boldrin, P.; Chater, P. A.; Miller, G. J.; Manning, T. D.; Briggs, M. E.; Stylianou, K. C.; Claridge, J. B.; et al. Shape Selectivity by Guest-Driven Restructuring of a Porous Material. *Angew. Chem. Int. Ed* **2014**, *53* (18), 4592−4596.

(82) Zhang, S.; Zhang, J.; Zhang, Y.; Deng, Y. Nanoconfined Ionic Liquids. *Chem. Rev.* **2017**, *117* (10), 6755−6833.

(83) Wang, Y.; He, H.; Wang, C.; Lu, Y.; Dong, K.; Huo, F.; Zhang, S. Insights into Ionic Liquids: From Z-Bonds to Quasi-Liquids. *JACS Au* **2022**, *2* (3), 543−561.

(84) Souleymanou, M. Y.; El-Ouahabi, F.; Masdeu-Bultó, A. M.; Godard, C. Cooperative NHC-based Catalytic System Immobilised onto Carbon Materials for the Cycloaddition of CO2 to Epoxides. *ChemCatchem* **2021**, *13* (7), 1706−1710.

(85) Alkorta, I.; Montero-Campillo, M. M.; Elguero, J. Trapping CO2 by Adduct Formation with Nitrogen Heterocyclic Carbenes (NHCs). *Theor. Study* **2017**, *23* (44), 10604−10609.

(86) Zhang, L.; Lei, M.; Cao, Z. The Crucial Role of Lewis Basicity of N-Heterocyclic Carbenes in the CO2 Hydroboration Reduction: Comprehensive Insights from Density Functional Theory Calculations and Microkinetic Simulations. *ACS Catal.* **2025**, *15* (4), 2772−2784.

(87) Zhou, H.; Zhang, W.-Z.; Liu, C.-H.; Qu, J.-P.; Lu, X.-B. CO2 Adducts of N-Heterocyclic Carbenes: Thermal Stability and Catalytic Activity toward the Coupling of CO2 with Epoxides. *J. Org. Chem.* **2008**, *73* (20), 8039−8044.

(88) Goodrich, P.; Gunaratne, H. Q. N.; Jacquemin, J.; Jin, L.; Lei, Y.; Seddon, K. R. Sustainable Cyclic Carbonate Production, Utilizing Carbon Dioxide and Azolate Ionic Liquids. *ACS Sustainable Chem. Eng.* **2017**, *5* (7), 5635−5641.