Smart Ionic Devices of Iron-based Ionic Liquids for Carbon Dioxide Capturing and Fixation

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ABSTRACT

The reduction of carbon dioxide can be achieved by the integration of its capturing and transformations into value added chemicals and fuels. One of the effective strategies is the production of cyclic carbonates from CO_2 and epoxides, combining atomic efficiency with environmental benefits. In this study, we prepared an iron-based ionic liquid (IL) that represented a remarkable activity for the efficient chemical fixation of CO_2 in various aromatic and aliphatic epoxides. The prepared Tris-butyl-3-methylimidazolium ferricyanide $[BMIm]_3[Fe(CN)_6]$ IL showed conversions ranging from 20 to 100% with maximum selectivity to their corresponding cyclic carbonated. Our IL formed ionic containers is akin to the catalytic active membrane with confined spaces that significantly controlled the diffusion of reactants, intermediates and products. Aliphatic small sized epoxides exhibit higher conversion and selectivity to cyclic carbonate compared to bulkier ones. This suggests that larger epoxide substrates faced diffusion limitations within the confined spaces of IL, thereby restricting the reactants access to the catalytic active sites.

Keywords: CO_2 capturing; catalysis; CO_2; epoxides; ionic liquid.

INTRODUCTION

It is known that global warming is primarily caused by greenhouse gases such as water vapor, carbon dioxide, methane, and nitrous oxide, which trap heat in the Earth's atmosphere. Carbon dioxide (CO_2), which remains in the atmosphere longer than other gases, is a major contributor to global warming and climate change. CO_2 is naturally produced and consumed in the carbon cycle. However, the current burning of large amounts of stored carbon in the form of fossil fuels and coal results in excessive CO_2 emissions into the atmosphere. Additionally, oceans, which act as natural CO_2 absorbers, are unable to absorb all the CO_2 emitted [1]. One of the major current challenges is implementing strategies to reduce CO_2 emissions, given its significant contribution to global warming. To reduce CO_2 accumulation in the atmosphere, 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].

The chemical fixation of CO_2 into epoxides has emerged as a sustainable solution due to its atom-economic efficiency and environmental benefits. This process is of great interest due to the application of the formed cyclic carbonates, which serve as intermediates in the synthesis of products such as polyurethanes and polycarbonates, and can also act as green, polar, aprotic solvents [3].

Various methodologies for this transformation have been described, involving homogeneous and heterogeneous systems such as alkali metal halides, quaternary ammonium salts, polymers, molecular organic frameworks, frustrated Lewis pairs, transition-metal complexes, and functionalized graphene. However, these systems have drawbacks, such as the need for high pressures and temperatures, large amounts of catalyst, low stability, and high cost. In this context, ionic liquids (ILs) have gained attention for their advantageous properties, such as the ability to adjust basicity and nucleophilicity by manipulating the electronic and steric features of cations and anions, high CO_2 absorption capacity, and chemical inertness [4]. Herein, Fe-based IL, $[BMIm]_3[Fe(CN)_6]$, is prepared that revealed efficient CO_2 capturing and fixation in different kind of epoxides at low pressure and temperature.

MATERIALS AND METHODS

All the epoxides and $K_3Fe(CN)_6$ were purchased from Sigma-Aldrich chemicals. BMIm.Cl (1-n-Butyl-3-methylimidazolium chloride) was prepared from a well-known method [5]. CO_2 (>99.999%) were purchased from White-Martins Ltd, Brazil. NMRs spectra were collected using a Bruker AVANCE III 400MHz. The $[BMIm]_3[Fe(CN)_6]$ IL was prepared by reacting a mixture of 1-n-butyl-3-methylimidazolium chloride in acetonitrile with a solution of $K_3Fe(CN)_6$ at room temperature, which was characterized by ^1H and ^{13}C NMR analyses.

All catalytic reactions were carried out in a homemade glass reactor (24 mL) under CO_2 pressure. The epoxide of interest (12 mmol) was dissolved in $[BMIm]_3[Fe(CN)_6]$ (0.13 mmol, 1 mol%) at room temperature. The reactor was then purged with CO_2 to remove air and subsequently filled with CO_2 to 2-bar. The reaction mixture was stirred and heated to the desired temperature for 24 hours in a silicon oil bath. After 24 hours, the reactor was cooled and the pressure was slowly released. Conversion and product selectivity were determined by ^1H NMR.

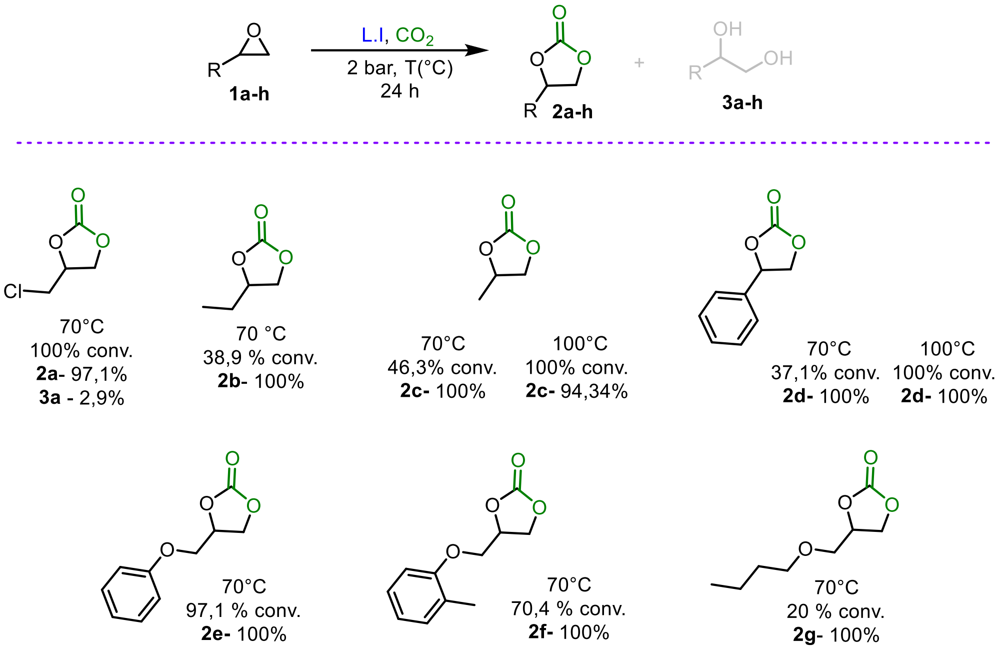
RESULTS AND DISCUSSION

The catalytic activity of IL $[BMIm]_3[Fe(CN)_6]$ was evaluated as in the CO_2 cycloaddition reaction with various aliphatic and aromatic epoxides, under a CO_2 pressure of 2 bar at 70 °C, as shown in Figure 1. The reaction was initially performed with epichlorohydrin as the model substrate (Figure 1, entry 1). About 99% conversion and 97% selectivity for the carbonate formation were observed, with 3% of the corresponding diol. The formation of the diol was attributed to the presence of a small amount of water absorbed by the IL during its preparation.

We examined the structure-activity relationship (SAR) of our catalyst against other aliphatic epoxides. For example, a low conversion of 46% was observed for 2-methyloxirane with 100% selectivity for the carbonate (Figure 1, 2c). Increasing the temperature to 100 °C resulted in a conversion of 94%. The 2-ethyloxirane at 70 °C also showed a low conversion of 39%, with 100% selectivity for cylic carbonate (Figure 1, 2b). For 2-(butoxymethyl)oxirane, the conversion was only 20%, with 100% selectivity for the carbonate (Figure 1, 2g). The ILs works as catalytic active membrane that have confined spaces and can modulate the diffusion of reactants, intermediates and products to catalytic active sites. Small sized epoxides displayed higher conversion and selectivity to cyclic carbonate compared to bulkier ones. This advocates that larger sized epoxide substrates faced diffusion limitations within the confined spaces of our $[BMIm]_3[Fe(CN)_6]$ IL, thereby restricting the reactants access to the catalytic active sites.

The potential of our catalyst was also tested for different kind of aromatic epoxides under our standard reaction conditions. When using styrene oxide, a conversion of only 37% was observed with higher selectivity (> 99%) for its cyclic carbonate (Figure 1, 2d). Increasing the temperature to 100 °C resulted in a significant increase in conversion to 100%, with no diol formation observed. For the cyclic epoxide 2-(phenoxymethyl)oxirane, the conversion was 97%, with 100% selectivity for the corresponding carbonate (Figure 1, 2e). The cyclic carbonate derived from 2-((o-tolyl)oxy)methyl)oxirane was obtained with a 71% conversion and 100% selectivity (Figure 1, 2f).

Figure 1: Catalytic CO_2 fixing in different epoxides by $[BMIm]_3[Fe(CN)_6]$



[a] Reaction conditions: $[BMIm]_3[Fe(CN)_6]$ (0.13 mmol, 1.0 mol%), substrate (12 mmol), 24 h.[b] Calculated by ^1H NMR.

CONCLUSIONS

The results obtained highlight the efficiency in activating the different aromatic and aliphatic epoxides. The ionic liquid $[BMIm]_3[Fe(CN)_6]$ demonstrated significant activity, with conversions ranging from 20 to 100% for the various epoxides, under a pressure of 2 bar and at temperatures of 70 °C and 100 °C. A structure-activity relationship studies showed that our catalyst generated ionic cages with confined spaces that significantly controlled the diffusion of reactant epoxides, intermediates and products to catalytic active sites.

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