Chemical conversion of CO\textsubscript{2}: evaluation of different ionic liquids as catalysts in dimethyl carbonate synthesis

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Abstract

The CO\textsubscript{2} concentration increased considerably from 280 ppm in the pre-industrial era to a global average of 404 ppm in 2015 [1]. Energy demand, growing population and fossil fuels use are the main responsible by CO\textsubscript{2} anthropogenic emissions and are considered the major contributors to global warming, since CO\textsubscript{2} is considered the main greenhouse gas [2,3].

The current CO\textsubscript{2} emissions mitigation scenario is based on the efficient energy use, as well as in the exploitation of CO\textsubscript{2} separation, conversion and storage technologies [4,5]. Ionic liquids (ILs) are composed by organic or inorganic cations and anions, usually liquid at room temperature. They are a class of materials with excellent perspective for carbon dioxide capture and transformation in industrial valuable products, once these ionic compounds can be used as absorption solvent and catalyst [6-8].

The need for the synthesis improvement resulting in less environment aggressive process and the use of reusable raw materials are some of the Green Chemistry principles. Thus, the goal of this work was to study an alternative route for dimethyl carbonate synthesis using CO\textsubscript{2} and methanol, as raw materials and dimethoxypropane (DMP) as a drying agent to water removal. See Figure 1 [9,10].

\[
\text{2 MeOH} + \text{CO}_2 \xrightarrow{\text{IL}} \text{MeO} \text{MeO} + \text{H}_2\text{O}
\]

\[
\text{MeO} \text{MeO} + \text{H}_2\text{O} \xrightarrow{\text{IL}} \text{MeO} \text{MeO} + \text{2 MeOH}
\]

Figure 1: Two-step process for DMC synthesis.

Ionic liquid based on imidazolium and pyridine cations combined with [Cl]\textsuperscript{-}, [BF\textsubscript{4}]\textsuperscript{-}, [PF\textsubscript{6}]\textsuperscript{-}, and [Tf\textsubscript{2}N]\textsuperscript{-} anions were tested as catalysts as presented in Figure 2. The Ionic Liquid characterization was carried out using Fourier transform infrared spectroscopy (FTIR), Proton Nuclear Magnetic Resonance (1H-NMR) confirming the structure of these materials. The purity was determined using the residual chloride test. Dimethyl carbonate identification and quantification was performed using a gas chromatography equipped with a flame ionization detector (GC-FID).
Different synthesis parameters were tested. Reactions were carried out using temperatures of 413 K and 448 K, times of 12 h, 24 h and 48 h, and 4 MPa of pressure. These pressure conditions were elected for being close to the working conditions of a CO₂ capture plant in a pre-combustion process.

The results of methanol conversion and selectivity for DMC showed that these materials can be used as catalysts, but the use of a drying agent to overpass the thermodynamics barrier of the reaction is critical. The activity of the anions for this synthesis follow the order \([\text{BF}_4^-] > [\text{Cl}^-] > [\text{PF}_6^-] > [\text{Tf}_2\text{N}^-]\) for both cations in DMC synthesis. Methanol conversion is constant for both ILs cation, maintaining an average of 7.5% for the imidazolium cation compared to 7.7% for pyridine cation. Regarding the selectivity to dimethyl carbonate, the imidazolium cation is about 12% more selective, reaching 83.3% when [emim][BF₄] was used as a catalyst. Hydrophilic anions showed better selectivity for DMC than hydrophobic anions, probably due to the interaction of ILs with the water formed during the reaction hindering the hydrolysis of DMC. DMC selectivity decreases with the increase of the ILs anion volume, indicating a probable steric hindrance. With the decrease of the cation lateral carbon chain from C₄ to C₂ resulted an improvement around 27% in methanol conversion and 5% in the DMC selectivity for imidazolium cation as well as an improvement of 14% in methanol conversion and 8% in DMC selectivity to pyridine cation. This result is probably related to the hydrophilicity of the cation which decreases as the chain increases and also the reactivity and solubility of ionic liquids in methanol which also decrease with the increase of carbon chain of the cation. Five recycles were performed aiming to evaluate the catalyst regeneration capacity. The loss of the activity after 5 recycles was of 8.5%.

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Figure 2: IL used as catalyst for DMC synthesis.
References


