



Harnessing CO₂ into Carbonates Using Heterogeneous Waste Derivative Cellulose-Based Poly(ionic liquids) as Catalysts

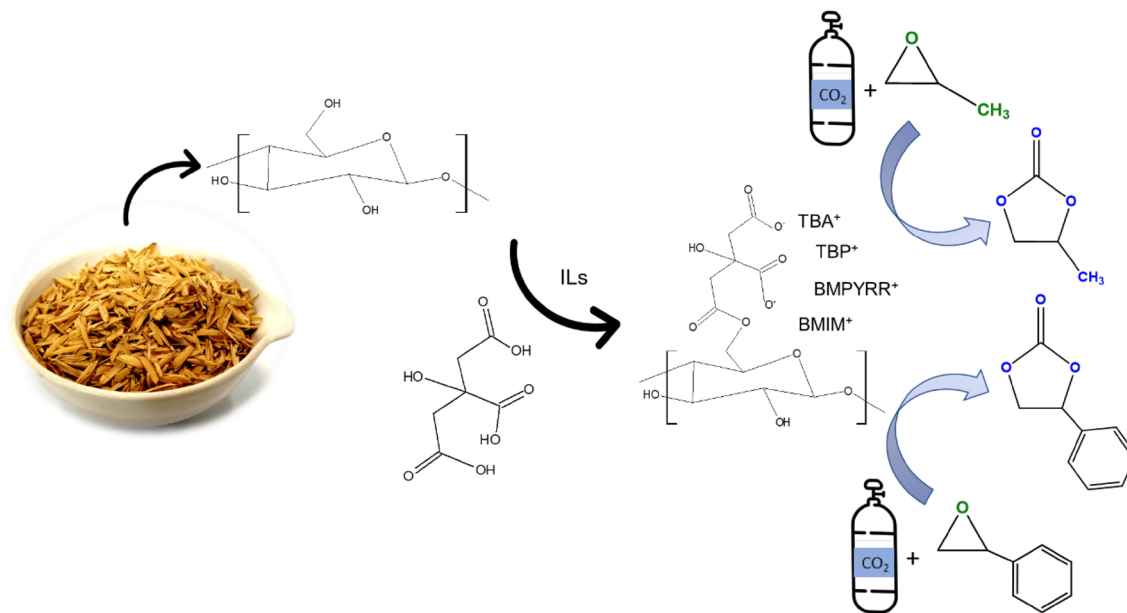
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Abstract

CO₂ chemical transformation into chemicals is an interesting option to mitigate CO₂ concentration in the atmosphere. CO₂ is an important carbon source, non-toxic, non-flammable, abundant and renewable, making it an interesting raw material. In this work, cellulose-based poly(ionic liquids) (CPILs) was synthesized from cellulose extracted from rice husk, modified with citric acid and functionalized with different cations. CPILs were used as heterogeneous catalysts for CO₂ chemical transformation into cyclic carbonates by cycloaddition of CO₂ with epoxides [propylene (PO) and styrene oxides (SO)]. The effect of the cation present in CPILs in catalytic performance, use of ZnBr₂ as a co-catalyst and catalytic reaction parameters (temperature, pressure and time) were investigated just as well. Results demonstrate that CPILs cation variation influence their catalytic activity. A higher CO₂ yield and selectivity of 81.9%/95.3% for propylene carbonate (PC) and 78.7%/100% for styrene carbonate (SC) was obtained by CPIL-TBP/ZnBr₂ at conditions of 40 bar, 110 °C and 6 h, being easily separated and recycled without significant loss of catalytic activity until the fourth cycle.

Graphical Abstract



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1 Introduction

Increasing concentrations of carbon dioxide (CO₂) in the atmosphere due to anthropological fossil fuel burning is one of climate changes determining factors. CO₂, nitrous oxide (N₂O) and methane (CH₄) are the main gases causing greenhouse effect. Although this phenomenon contributes to maintain the complex planet environmental system, human activities resulting in high gas emissions are heating the planet in a non-natural way [1]. The forecast for coming decades is that the primary source for energy generation still comes from fossil fuel burning demanding actions to CO₂ mitigation [2].

In this context, carbon capture and utilization (CCU) technologies are promising solutions for reducing CO₂ concentration in the atmosphere [3]. CO₂ chemical transformation into chemicals is an interesting option since CO₂ is an important carbon source, non-toxic, non-flammable, abundant and renewable, making it an interesting raw material [4].

CO₂ transformation into chemicals is difficult as it is the most oxidized carbon form. CO₂ is thermodynamically stable and/or kinetically inert in certain transformations making it necessary the use of high-energy starting material. The best known are unsaturated compounds, few carbon-atom-ring compounds, hydrogen and organometallic, oxidized low-energy synthetic targets such as carbonates. The use of severe reaction conditions to activate CO₂ is possible limiting the applicability of these methods [5, 6].

Although a high number of organic syntheses using CO₂ as starting material are known few have been applied in industry. CO₂ can replace toxic chemicals as phosgene, isocyanates and carbon oxide [6]. CO₂ transformation into cyclic carbonates has attracted much interest in the last decades due to the great applicability of these products in industry. The main uses are as polar aprotic solvents in chemical industry, raw material in pharmaceutical and fine chemical production, electrolytes in secondary batteries, polycarbonate precursors and other polymeric materials [4, 7].

CO₂ chemical transformation into cyclic carbonates occurs by cycloaddition of CO₂ with epoxides needing a catalyst in order to overcome the low reactivity under mild reaction conditions. Homogeneous catalysts such as transition metal complex [8], alkali metal halides [9], organic bases [10, 11], and organometallic catalysts [12, 13] are widely used and known as high-activity catalysts. However, the high cost of separating the products and the high investment required to produce these catalysts encouraged researchers to explore new catalysts [5].

Imidazolium, ammonium, phosphonium and pyridinium-based ionic liquids have attracted great attention as

alternative homogeneous catalyst for CO₂ chemical conversion into cyclic carbonates by CO₂ cycloaddition reaction with epoxides [11, 14–18]. Ionic liquids (ILs) are special class of green solvents with melting points below 100 °C that are constituted of organic cations and inorganic and organic anions. These compounds exhibit unique properties as high thermal stability, non-flammability, negligible vapor pressure, tenability and high catalytic activity and selectivity as catalysts in CO₂ cycloaddition reactions [14, 19].

Heterogeneous catalysts such as modified zeolites [20], metal oxides [21], MOF's [9], supported catalysts [22, 23], mesoporous materials [24], silica [25], cellulose [26] and poly(ionic liquids) (PILs) [27–31] also emerged as a possibility to solve problems inherent to homogeneous catalysts. Heterogeneous catalytic system appears as an interesting option making possible catalyst reuse and ease product and catalyst separation. Yet, heterogeneous catalytic systems present higher stability when compared to homogeneous catalysis [32]. However, these catalysts present some drawbacks such as low activity, sensitivity to humidity and the need of high temperatures, limiting their application. The development of new catalysts that work at mild process conditions with good performance, being reusable, besides helping in the valorization of renewable carbon sources is of great interest [31, 33, 34]. Among heterogeneous catalysts, poly(ionic liquids) represent a new platform for developing versatile catalyst for CO₂ chemical conversion into chemicals [27–31]. PILs present in each repeating unit, ionic liquid (IL) connected through a polymeric backbone forming a macromolecular structure [35, 36]. These functional polymers combine polymer properties (mechanical stability, processing and tunable macromolecular structure) with ILs benefits [35, 36]. Leng and He, described that polymeric materials with different groups such as –NH₂, –OH and –COOH can be functionalized with ionic species such as imidazolium cation in order to obtain PILs. These PILs can be used as recyclable and efficient heterogeneous catalysts for cycloaddition reaction of epoxydes with CO₂ [37]. Recently, we reported the synthesis and characterization of new cellulose based poly(ionic liquids) (CPILs) extracted from rice husk [38]. Cellulose was functionalized with different cations (imidazolium, phosphonium, ammonium and pyrrolidinium). CPILs provides a promising approach for CO₂ capture [38]. Catalyst syntheses for CO₂ chemical fixation using cheap and nontoxic reagents are still desirable [27]. Waste-derivative PILs for use as catalyst may be an interesting option to reduce the cost and promote environmental benefits.

In this study, cellulose-based poly(ionic liquids) (CPILs) were synthesized from cellulose extracted from rice husk, modified with citric acid, and functionalized with different cations. CPILs were evaluated as heterogeneous catalysts

for CO₂ chemical transformation into cyclic carbonates by cycloaddition of CO₂ with epoxides (PO and SO). Influence of reaction temperature, time and CO₂ pressure were evaluated in catalytic activity and selectivity. The use of a metal compound as a cocatalyst was also studied as well as catalyst recyclability.

2 Experimental

2.1 Materials

Sodium hydroxide (Vetec, 97.0%), styrene oxide (Sigma Aldrich, 97.0%), propylene oxide (Sigma Aldrich, 99.0%), zinc bromide (ZnBr₂, Sigma Aldrich, 98.0%), Acetone (Vetec, 99.5%), carbon dioxide (CO₂, Air Liquid, 99.998%) ethyl ether (Vetec, 99.0%) and propylene carbonate (Alfa Aesar, 99.0%). All reagents were used as received. Cellulose-based poly(ionic liquids) (CPILs) (1-butyl 3-methylimidazolium-CPIL-BMIM, tetrabutylammonium-CPIL-TBA, tetrabutylphosphonium-CPIL-TBP and 1-butyl-1-methylpyrrolidinium-CPIL-BMPYRR), were synthesized and characterized as previously described by our group [38].

COOH group content added to modified cellulose was 2.15×10^{-4} mol/g of cellulose. ILs cations TBPB, TBAB, BMPYRR and BMIM were added to modified cellulose in contents of 1.16×10^{-4} mol/g of cellulose, 0.68×10^{-4} mol/g of cellulose, 1.57×10^{-4} mol/g of cellulose and 0.5901×10^{-4} mol/g of cellulose, respectively. Specific surface area values of CPILs TBP, TBA, BMPYRR and BMIM are non-significant (0.2398 m²/g, 0.4575 m²/g, 0.6430 m²/g, 1.7370 m²/g, 0.5901 m²/g, 0.6984 m²/g respectively) even after ILs addition [38] (Fig. 1).

2.2 Cyclic Carbonate Synthesis

All reactions were carried out in a 120 mL titanium reactor under magnetic stirring. Temperature was controlled using a thermocouple connected to a temperature controller. The reactor was kept under nitrogen and 100 mmol of epoxide, 1.0 g or 1.5 g of the CPILs and 0.625 mmol of ZnBr₂ added. CO₂ purge was used to remove N₂ then reactor was pressurized at desired CO₂ pressure. Reactions were performed under different CO₂ pressures (15 to 50 bar), temperatures (80 to 130 °C), times (3 to 9 h) and no solvent. The obtained product was filtered and washed with acetone for complete CPIL separation. All tests were performed in triplicate.

2.3 Product Characterization

Fourier Transform Infrared Spectroscopy (FT-IR) was used in order to confirm the propylene or styrene carbonates obtainment. Analysis was performed using Perkin-Elmer

FT-IR Spectrum 100 spectrometer in the range of 4000 cm⁻¹ to 600 cm⁻¹. Carbonates selectivity for reactions performed with propylene oxide as starting material was carried out by gas chromatographic analysis using Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector (FID) and a DB-5HT column (15 m × 0.32 mm × 0.10 μm). Quantitative analysis by direct method was used. A series of standard solutions using ethyl ether as solvent and propylene carbonate in concentrations from 10 to 50% were prepared. Chromatograms obtained from these standards were used to obtain the equation that is subsequently used to determine the propylene carbonate concentration present in the samples. Carbonate selectivity for reactions performed with styrene oxide were performed by nuclear magnetic resonance (NMR) using Varian Spectrophotometer equipment, model VNMRs 300 MHz, using chloroform-d as solvent.

3 Results and Discussion

Propylene and styrene carbonate formation was observed (see Fig. 2) by the increasing of the bands at 1780 cm⁻¹ corresponding to carbonate C=O bond and at 1162 and 1064 cm⁻¹ corresponding to the appearance of carbonate C–O bond. The disappearance of the band at 873 cm⁻¹ represents the disappearance of the epoxide ring.

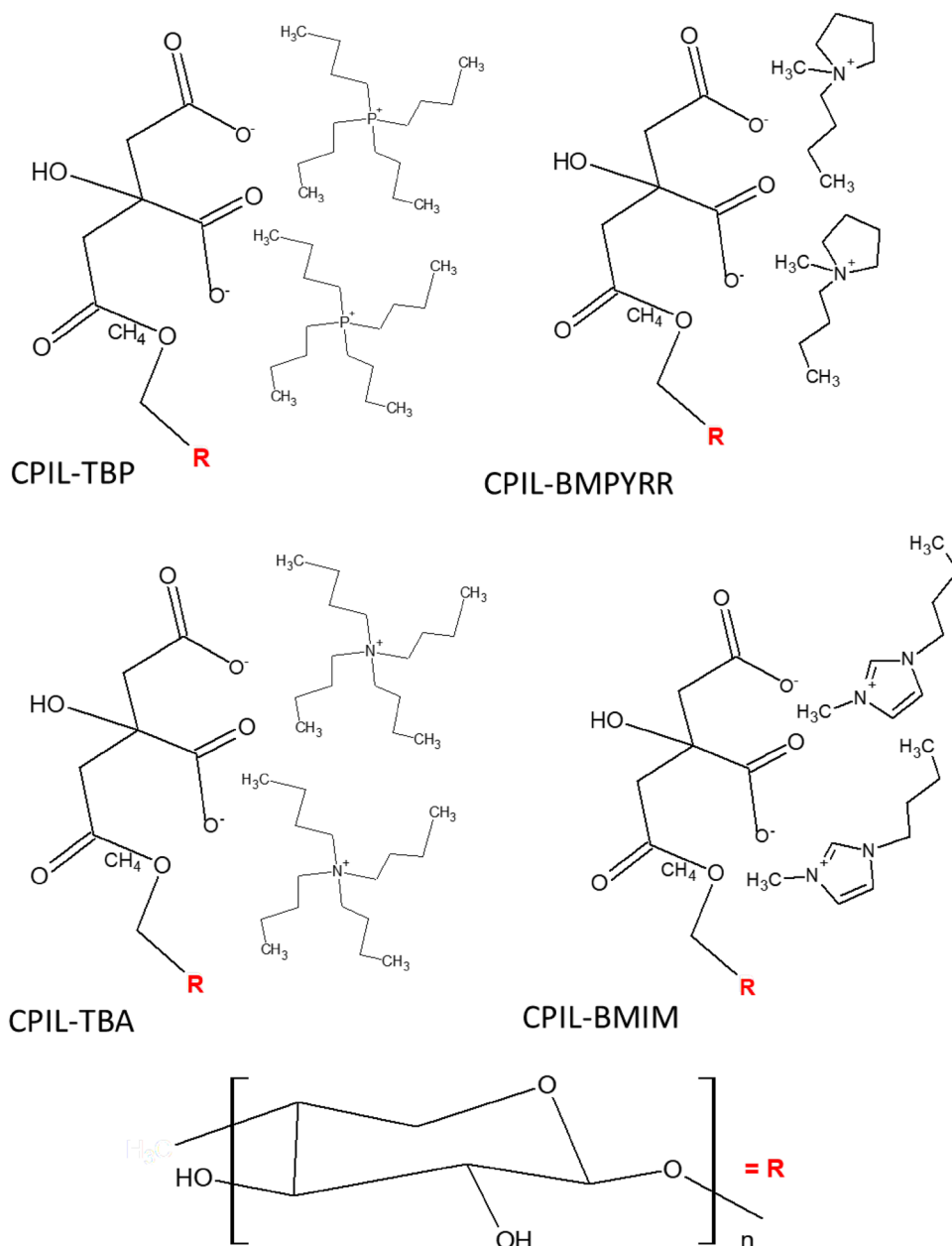
The formation of the propylene and styrene carbonates was also verified by ¹HNMR analysis. For the propylene carbonate the σ (ppm) signals are: 4.04 (t, 1H) and 4.54 (t, 1H) for CH₂ (methylene), 4.84 (dd, 1H) for CH methine and 1.43–1.50 (t, 3H) for CH₃ (methyl). Styrene carbonate signals σ (ppm) are at 4.34 (t, 1H) and 4.80 (t, 1H) for CH₂ (methylene), 5.69 (t, 1H), for CH (methine) and at 7.37–7.48 (m, 6H) for phenyl group. No other peak was detected for all reactions.

3.1 Catalytic Activity Evaluation of CPILs in Propylene Carbonate Synthesis

In order to evaluate CPILs catalytic activity we used similar reaction conditions (0.1 mol do propylene epoxide; reaction temperature 110 °C; reaction time 6 h and CO₂ pressure = 40 bar) described in literature for cycloaddition reactions employing poly(ionic liquids) (PILs) and ILs as [14, 31, 39–41].

Table 1 presents yield and selectivity values for cycloaddition reactions employing pure and citric acid modified cellulose, TBAB and TBPB ILs to compare with CPILs, and CPILs with or without ZnBr₂ as cocatalyst. When pure and citric acid modified celluloses were used as catalyst, no catalytic activity was observed for cycloaddition reactions (see entries 1 and 2, Table 1). For reactions where CPIL-BMIM and CPIL-BMPYRR were used as catalysts,

Fig. 1 Chemical structure of CPILs used as catalysts



low yield values were obtained (< 5% as seen in entries 3 and 4, Table 1). We previously described a computational study of CO₂, COO⁻ anionic group, BMIM, BMPYRR, TBA and TBP cation interaction [42]. The most important interaction occurs between the COO⁻ and CO₂ (binding energy COO⁻ and CO₂—19 kJmol⁻¹) in relation to the other involved species. BMIM cation, besides presenting a considerable coordination with CO₂ (binding energy BMIM and CO₂—14 kJmol⁻¹), strongly coordinates to COO⁻ site by the imidazolium ring diffculting COO⁻/CO₂ interaction. This may explain the lower catalytic activity presented by the CPIL-BMIM. Cation/CO₂ interaction decreases in the following order BMIM > BMPYRR > TBP > TBA (binding

energies cation/CO₂—14 kJ mol⁻¹ > 9.3 kJ mol⁻¹ > 6.7 kJ mol⁻¹ > 3.7 kJ mol⁻¹ respectively) [42]. The BMPYRR/CO₂ high interaction can be pointed out as one of the reasons for lower catalytic activity presented by CPIL-BMPYRR. TBA and TBP cations, in addition to exhibiting the lowest interactions with CO₂ when compared to BMIM and BMPYRR, are non-coordinating cations as well. The poor coordination of these cations to COO⁻ allows this active site to be free for interacting with CO₂. This behavior is probably responsible for higher catalytic activity observed for CPILs with TBA and TBP. When the ionic liquids TBAB and TBPB were used as catalysts in the same proportions of ILs inserted in the modified cellulose, higher catalytic

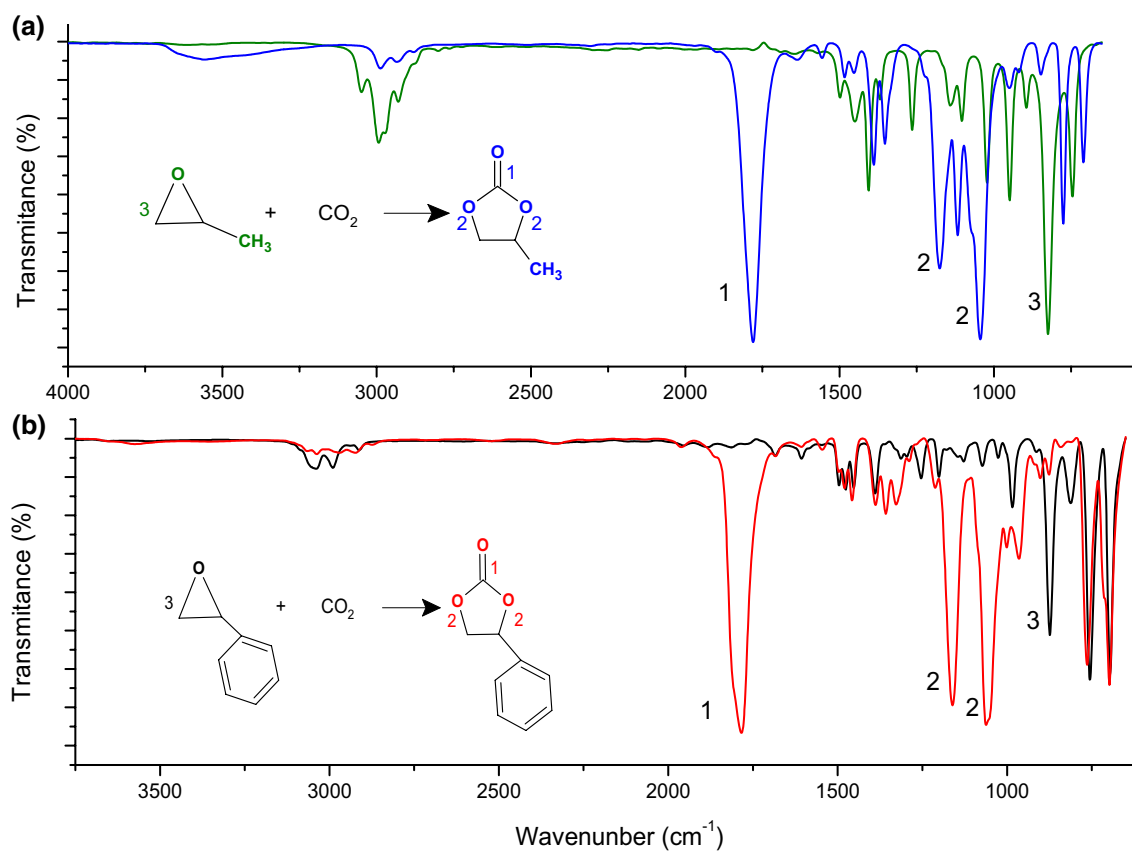


Fig. 2 Typical spectrogram of products of reactions **a** propylene carbonate and **b** styrene carbonate

Table 1 CPILs catalytic performances

Entry	Catalyst	Weight (g)	Cocatalyst	Yield(%)	Selectivity (%)
1	Cellulose	1.0	–	ND	–
2	Citric acid modified cellulose ^a	1.0	–	ND	–
3	CPIL-BMIM ^b	1.0	–	2.7 ± 1.4	–
4	CPIL-BMPyRR ^c	1.0	–	4.3 ± 1.6	–
5	TBPB	0.3	–	73.6 ± 2.1	94.8
6	TBAB	0.3	–	63.0 ± 1.8	100
7	ZnBr ₂	0.1	–	ND	–
8	CPIL-TBP ^d	1.0	–	53.2 ± 1.7	92.5
9	CPIL-TBP	1.0	ZnBr ₂	71.7 ± 1.7	94.5
10	CPIL-TBP	1.5	–	59.5 ± 2.0	95.1
11	CPIL-TBP	1.5	ZnBr ₂	81.9 ± 2.9	95.3
12	CPIL-TBA ^e	1.0	–	39.7 ± 1.4	87.8
13	CPIL-TBA	1.0	ZnBr ₂	70.0 ± 2.4	90.8
14	CPIL-TBA	1.5	–	43.9 ± 1.8	93.3
15	CPIL-TBA	1.5	ZnBr ₂	71.1 ± 1.6	91.0

Reaction conditions: 0.1 mol of propylene epoxide; reaction temperature 110 °C; reaction time 6 h

^a0.003 mol of COOH

^b0.00157 mol of ILs/ g cellulose

^c0.00095 mol of ILs/g cellulose

^d0.00198 mol of ILs/ g cellulose

^e0.00122 mol of ILs/ g cellulose, CO₂ pressure = 40 bar

activity and selectivity (see entries 5 and 6, Table 1) were observed when compared to their respective CPILs without cocatalyst addition under the same reaction conditions (see entries 9 and 11, Table 1). This behavior was expected as ILs behaves as homogeneous catalyst, soluble in the epoxide, dispersing better in reaction mixture when compared to CPILs [31, 42].

The use of ZnBr_2 as cocatalyst in reactions with CPIL-TBP and CPIL-TBA as catalyst promoted a higher catalytic activity (CPIL-TBP from 53.2 to 71.7% and CPIL-TBA from 39.7 to 70.0%) and similar to net ILs TBPB and TBAB (TBPB 73.6% and TBAB 63.0%). This behavior occurs due to the combination of the Zn high reactivity with bromide nucleophilicity facilitating the epoxide ring opening [14, 43, 44]. However, unlike ILs, CPILs are easily separated from reactional media requiring only a simple filtration being easily reused in a new reaction. Heterogeneous catalysts favor product separation lowering separation step costs. CPILs IL content is extremely low (0.00095 mol of ILs/g cellulose) being a very important

issue since ILs are high cost chemicals. When ZnBr_2 was singly used no catalytic activity was observed. This behavior is in agreement with previous studies [14, 44]. An increase in catalyst weight of 50% was tested (see entries 10, 11, 14 and 15, Table 1). For CPILs tested, both yield and selectivity showed a slight increase, with the amount 1 g of catalyst being considered optimal. CPIL-TBP presented the best yield and selectivity results in the reaction conditions presented in Table 1 to be used in the following optimization study. CPILs present higher catalytic activity when compared to PILs using TBA as cation, described in literature [30] as efficient catalysts for cyclic carbonates production from CO_2 reaction with epoxides, such as modified chitosan (PC yield = 47.0%), modified cellulose (PC yield = 40.0%) and modified PEG6000 (PC yield = 37.0%). When CPILs are compared to an urethane based poly(ionic liquid) (PUDA-BMIM) (PC yield = 78.4%) [31] at same reaction conditions we observe similar catalytic activity. CPILs bring the advantage of being produced from rice husk an abundant, no toxic and biodegradable waste.

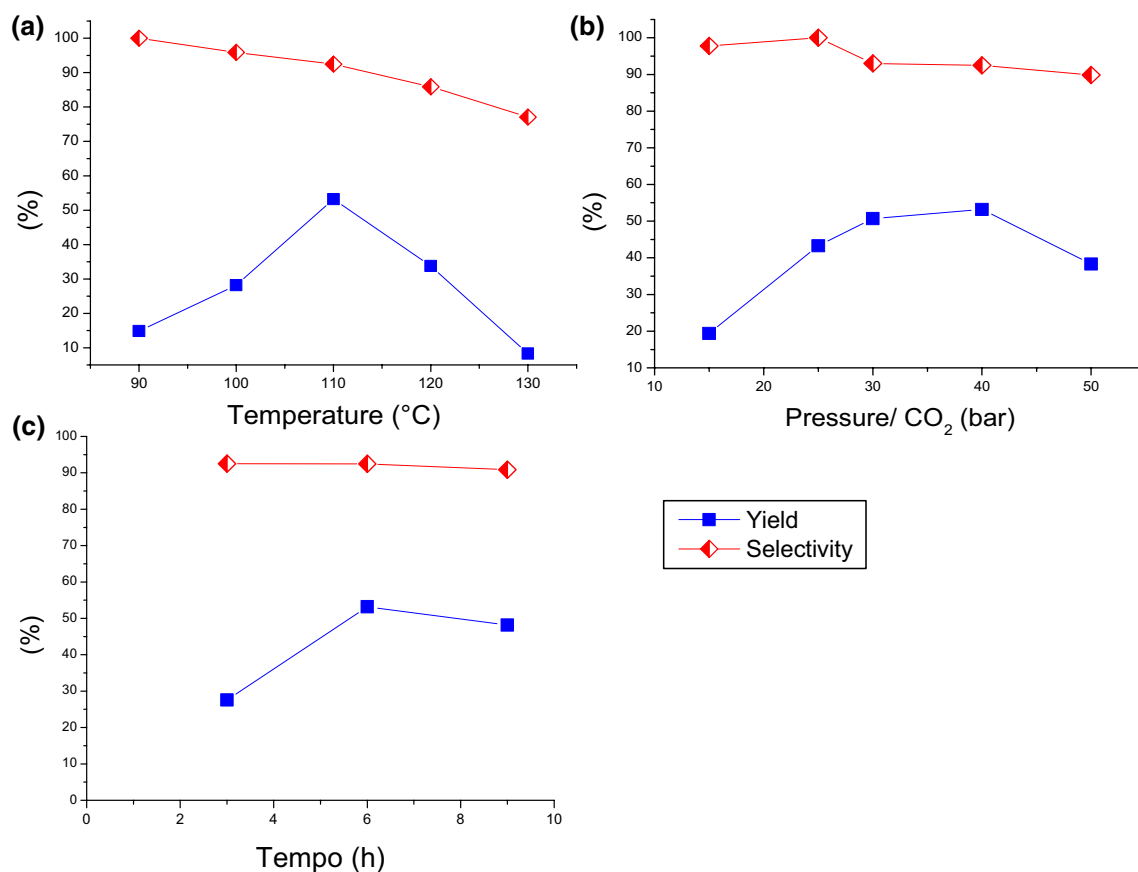


Fig. 3 Influence of temperature (a), CO_2 pressure (b) and reaction time (c) in yield and selectivity for cycloaddition reactions of CO_2 with propylene oxide using CPIL-PBP as catalyst

3.2 Influence of Reaction Conditions in Catalyst Activity

Temperature effect in cycloaddition reactions of CO₂ with propylene oxide was investigated by maintaining CO₂ pressure at 40 bar for 6 h, varying the temperature from 90 to 130 °C. Figure 3a evidenced that reaction yield strongly depends on reaction temperature. Increasing temperature from 90 to 110 °C increases from 14.8 to 53.2% in yield of PC. Increasing reaction temperature above 110 °C significantly decreases yield of 53.2% to 8.3% at 130 °C. This behavior could be attributed to secondary reaction in higher temperatures resulting in PO isomerization and PC polymerization [14, 31, 43, 45].

As temperature, pressure variation significantly influences PC yield as presented in Fig. 3b. Reactions were performed at 110 °C for 6 h. Carbonate yield increases with CO₂ pressure until reaching a maximum point at 40 bar. Increasing CO₂ pressure above this point decreases carbonate yield as previously described in literature [14, 22, 45]. This behavior is probably related with CO₂/PO molar ratio. There is an optimum CO₂/PO molar ratio and consequently submitting the system to lower or higher CO₂ pressures causes a yield decrease [14, 46, 47]. According to [43], cycloaddition reactions occur in a multiphase system and the behavior of each phase is important being responsible for yield increase or decrease. When low CO₂ pressure is applied, phase volume remains almost constant whilst CO₂ concentration in organic phase increases. CO₂ concentration increase in organic phase is probably responsible for carbonate yield increase. However, increasing CO₂ concentration above the optimum point results in organic phase reactants dilution difficulting epoxide and catalyst interaction, consequently decreasing carbonate yield [14, 45]. Reaction time influence was investigated by varying reaction time from 3 to 9 h, maintaining temperature at 110 °C and CO₂ pressure at 40 bar. Figure 3c shows reaction yield increases when time was increased from 3 to 6 h, slightly decreasing from 6 to 9 h of reaction time. Unlike, selectivity was constant with reaction time increase. Results indicate that in 6 h the CO₂ cycloaddition reaction with OP was complete [47, 48].

Cycloaddition reaction catalytic activity was evaluated under different CO₂ pressures (25 to 40 bar) using CPIL-TBA/ZnBr₂ and CPIL-TBP/ZnBr₂ catalytic systems. Previously defined as best reactional conditions (110 °C for 6 h) (see Table 2) were used for all reactions. Increasing CO₂ pressure increases carbonate yield and decreases reaction selectivity. Using ZnBr₂ as cocatalyst results in similar yield (see Table 2) for reactions performed at 40 and 25 bar pressures. So, we can point out the use of 25 bar of CO₂ pressure as the ideal pressure in cycloaddition reactions in which the CPIL-TBA/ZnBr₂ and CPIL-TBP/ZnBr₂

Table 2 Catalytic performance of CPIL-TBA and CPIL-TBP using ZnBr₂ as cocatalyst and varying CO₂ pressure

Entry	Catalyst	Pressure (bar)	Yield (%)	Selectivity (%)
1	CPIL-TBP	40	71.3 ± 1.7	94.5
2	CPIL-TBP	30	69.4 ± 1.6	95.6
3	CPIL-TBP	25	68.2 ± 2.6	97.5
4	CPIL-TBA	40	70.0 ± 2.4	90.8
5	CPIL-TBA	30	69.0 ± 1.5	91.23
6	CPIL-TBA	25	67.3 ± 0.3	93.58

Reaction conditions: 0.1 mol of propylene epoxide; reaction temperature 110 °C; reaction time 6 h; catalyst weight: 1.0 g; ZnBr₂: 0.625 mmol

are used as catalytic system. Thus, when comparing reaction conditions of this work with those of other studies reporting the use of immobilized catalysts [49] one can conclude that CPIL-TBA/ZnBr₂ and CPIL-TBP/ZnBr₂ are active solvent-free catalytic systems under mild reaction conditions.

3.3 Catalytic Mechanism

When CPIL-TBP and CPIL-TBA were used as catalyst, yield of 53.2% and 39.7% were obtained respectively (see Table 1, entries 8 and 12). With cocatalyst addition, an increase in yield carbonate was observed (71.7% for CPIL-TBP, entry 9 and 70.0% for CPIL-TBA, entry 13). Based on the findings this is possible that two catalytic pathways for cyclic carbonates synthesis reactions using CPILs and CPIL/cocatalyst as catalysts may occur. Figure 4a describes the probable mechanism involving CPIL/cocatalyst system and Fig. 4b when only CPIL is acting as catalyst. The first mechanism (see Fig. 4a) proposed for CO₂ cycloaddition with epoxide predicts that the metal halide interacts with the epoxide oxygen allowing CPILs anionic specimen [COO⁻] to attack the more available ring carbon resulting in ring opening. In the next step an oxoanionic specimen is formed. CO₂ carbon atom interacts with this anionic specimen producing an anionic alkylcarbonate, which is finally converted to cyclic carbonate by cyclic intermolecular elimination [14].

In the second proposed mechanism (Fig. 2b), COO⁻ (hard base) presents a higher interaction with CO₂ (hard acid) than with epoxide resulting in an anionic specimen [O-CO₂]⁻ formation. Cations (TBP or TBA) could be favoring species formation interacting with the oxygen of CO₂ molecule, turning the CO₂ carbon more electro-deficient and vulnerable to nucleophilic attack. In a second moment the anionic specimen [O-CO₂]⁻ reacts with the epoxide more available carbon atom forming an oxy-anionic specimen, which later

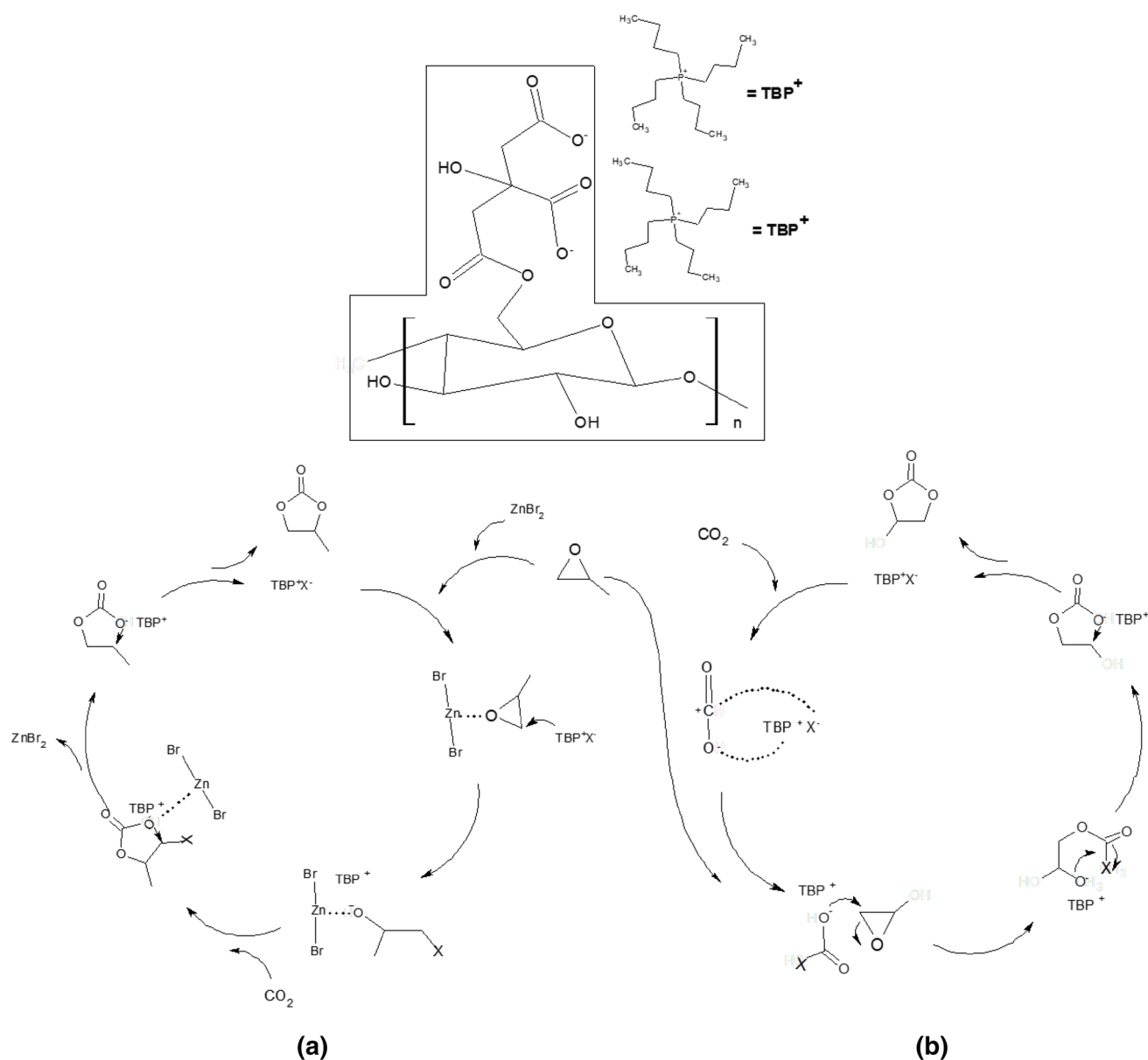


Fig. 4 Proposed catalytic mechanisms for CO₂ cycloaddition with epoxides. **a** with CPIL as catalyst and ZnBr₂ as cocatalyst **b** with CPIL as catalyst

is converted to cyclic carbonate by cyclic intermolecular elimination [31, 50].

3.4 Catalytic Recycling Tests

In order to investigate CPILs recycling capacity, CPIL-TBP was reused for four consecutive cycles. After each reaction CPIL-TBP was simply filtered, acetone washed, oven-dried and then reused in the next reaction. The tests were carried out under the best reaction conditions determined in

previous experiments (40 bar, 6 h and 110 °C). The first recycling test was performed using CPIL-TBP as catalyst with no further addition during cycles. In the second test CPIL-TBP was used as catalyst and ZnBr₂ as cocatalyst with no catalyst and cocatalyst addition during the cycles. In the third experiment, CPIL-TBP was used as catalyst (no further addition) and ZnBr₂ as cocatalyst being re-added after each cycle (0.625 mmol).

Figure 5 presents PC yield for recycle tests. For all cases selectivities were higher than 90%. When CPIL-TBP was

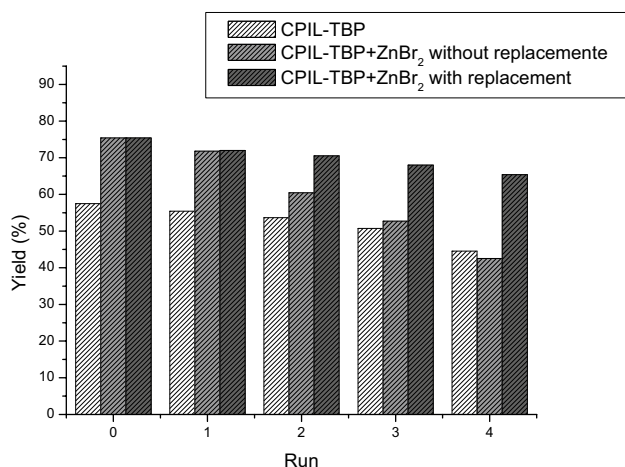


Fig. 5 Recycle reaction tests using CPILs as catalyst and ZnBr₂ as cocatalyst

used as catalyst a yield decreasing of less than 7.1% was observed from the first to third recycling test. In the fourth cycle a yield loss of almost 11.6% was observed. These results evidenced that CPIL-TBP remained stable up to three recycles. When the CPIL-TBP/ZnBr₂ system was tested without catalyst and cocatalyst addition after each cycle, catalytic activity was constant by only one recycle. After that, there was a considerable decrease of 14.9%, 22.6% and 32.8% in the second, third and fourth recycle, respectively.

PC yield values for these three recycles are close to those of the CPIL-TBP tests without cocatalyst (see Fig. 5), indicating as a possible cause for catalytic activity decrease cocatalyst loss during wash. Reactions were also carried out using CPIL-TBP/ZnBr₂ system, adding cocatalyst (0.625 mmol) for each recycle. A slight yield decrease was observed until the fourth cycle. However, for the fifth recycle a decrease of 10.0% in PC yield was observed.

3.5 Catalytic Activity Evaluation of CPILs in Styrene Carbonate Synthesis

CPIL-TBP was used as catalyst for CO₂ cycloaddition reaction with styrene oxide (SO) using reactional conditions defined as optimal for PC formation (40 bar, 6 h and 110 °C). For reactions using pure cellulose and citric acid modified cellulose as catalyst no catalytic activity was observed as shown in Table 3. As for PC synthesis using IL as catalyst a higher yield in SC synthesis was obtained. Yet, pressure increasing and cocatalyst addition also increase SC yield.

4 Conclusion

Cellulose-based poly(ionic liquids) synthesized from rice husk and modified with ionic liquids are promising catalysts for CO₂ transformation into cyclic carbonates. Carbonate yield is strongly influenced by the cation type present in the CPIL chain. Higher interaction between cation and the COO⁻ group of polymeric chain decreases cyclic carbonates yield. CPIL-TBP is the most active catalyst and TBP the less coordinate cation. The use of ZnBr₂ as cocatalyst increases carbonate yield. Reaction conditions also influence catalytic activity. The best yield result was obtained at 110 °C of temperature, 6 h of reaction time and 40 bar of CO₂ pressure. CPILs are easily recovered by simple filtration and can be recycled up to 4 times without significant catalytic activity loss. In addition, reactions are solvent-free. Results suggest new green catalysts for cyclic carbonates synthesis from CO₂ reaction with epoxides, showing a significant catalytic activity, selectivity and recyclability.

Table 3 Catalytic performance of CPIL-TBP in styrene carbonate synthesis

Entry	Catalyst	Weight (g)	Cocatalyst	P _{CO₂} (bar)	Yield (%)	Selectivity (%)
16	Cellulose	1	–	40	ND	–
17	Citric acid modified cellulose	1	–	40	ND	–
18	TBPB	0.3	–	40	80.9 ± 2.3	100
19	CPIL-TBP	1	–	40	67.2 ± 3.2	100
20	CPIL-TBP	1	–	30	63.2 ± 1.9	100
21	CPIL-TBP	1	–	25	41.9 ± 1.7	100
22	ZnBr ₂	0.14	–	40	ND	–
23	CPIL-TBP	1	ZnBr ₂	40	78.7 ± 2.7	100

Reaction conditions: 0.1 mol of styrene epoxide, reaction temperature 110 °C, reaction time 6 h and 0.00198 mol of ILs/g cellulose

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