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Sustainable Intensification Strategies for the Production of Cyclic Carbonates from CO_2

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for being my roots ♥

ABSTRACT

Global warming, caused mostly by the increasing of greenhouse gas concentrations in the atmosphere, has became one of the most serious environmental concerns. Between the major greenhouse gases, carbon dioxide had the most significant increase. Its high availability, non-flammability, low toxicity and independency from the food supply chain, makes CO_2 utilization as a carbon feedstock an important topic from both industrial and academic perspectives. The aim of this work was to develop process intensification strategies for cyclic carbonate production from CO_2 and epoxides. Cyclic carbonates are versatile molecules which may become a future platform to introduce CO_2 as a renewable carbon feedstock into the chemical sector. Indeed, cyclic carbonates find use in a wide range of applications as electrolytes for lithium batteries, polar aprotic solvents, pharmaceutical intermediates and also as monomers in polymer production.

For the first time, zinc (II) complexes of arylhydrazones of β-diketones (AHBD) combined with ionic liquids were used as catalysts for the production of cyclic carbonates. Different cation and anion families were explored in order to understand the effect of specific functional groups on the final reaction yield and selectivity. Results confirmed the importance of the nucleophilicity of the anion, with halogens presenting the better results. Regarding the cation structure, it was possible to conclude that the bulkiness of the structure was the more important factor to have in consideration. Also the effects of pressure, temperature, type of solvent and catalyst concentration were studied and a high-pressure extraction process for an efficient product separation and recycling of the catalytic system was proposed.

Finally, in the context of developing a green continuous flow process for CO_2 conversion into cyclic carbonates, two different engineering approaches were investigated. On one hand a supported ionic liquid onto an alginate aerogel matrix was prepared, characterized and applied as catalytic system. On the other hand, a continuous flow process using a bulk ionic liquid phase as catalyst was carried out. Both processes allowed for cyclic carbonate production from a bio-based epoxide (limonene oxide) in the production of limonene carbonate, a 100% renewable cyclic carbonate.

This thesis provides new opportunities for cyclic carbonate production from CO_2 and epoxides in the context of sustainable processing.

Keywords: Carbon Dioxide, Carbonates, Green Chemistry, Epoxides, Supercritical, Ionic Liquids, Bio-based epoxides, Catalyst, Aerogel, Continuous Flow.

RESUMO

O aquecimento global provocado principalmente pelo aumento das concentrações de gases de efeito estufa na atmosfera tornou-se numa das mais sérias preocupações em termos ambientais. Entre os principais gases responsáveis pelo efeito de estufa, temos o dióxido de carbono. Pelo facto de estar bastante disponível, de ser não inflamável, ter baixa toxicidade e devido a sua independência em relação a cadeia alimentar, o uso do CO_2 como matéria-prima tem vindo a ganhar muita atenção quer do ponto de vista industrial e quer académico. O objetivo deste trabalho consiste no desenvolvimento de estratégias de intensificação do processo responsável pela produção de carbonatos cíclicos a partir da reação de epóxidos com CO_2. Por sua vez, os carbonatos cíclicos produzidos tem várias aplicações, podem ser utilizados como eletrólitos nas baterias de lítio, como intermediários farmacêuticos e também como monómeros para a produção de polímeros.

Pela primeira vez, complexos de zinco (II) de arilhidrazonas de β-dicetonas combinados com líquidos iónicos foram utilizados como catalisadores na produção de carbonatos cíclicos. Diferentes famílias de aniões e catiões foram estudadas, com o objetivo de compreender o efeito destes grupos funcionais na selectividade e no rendimento final da reação. Os resultados confirmaram a importância da nucleofilicidade do anião, com os iões de halogénios a apresentar os melhores resultados. Preservando à estrutura de catião, foi possível concluir que o tamanho da estrutura era o fator mais importante a ter em consideração. O efeito da pressão, temperatura, tipo de solvente e catalisador foram alguns dos parâmetros estudados, adicionalmente um processo de extração a alta pressão foi proposto como forma eficiente de separação do produto final e reutilização do catalisador.

Finalmente, com o objetivo de desenvolver uma tecnologia verde na conversão de CO_2 em carbonatos cíclicos duas diferentes abordagens, em termos de engenharia, foram investigadas. Primeiro, foi preparado e devidamente caracterizado um catalisador suportado, composto por uma matriz de aerogéis de alginato, para posteriormente ser testado com sistema catalítico. Segundo, foi explorada a possibilidade de realizar esta reação em modo contínuo, utilizando com líquidos iónicos em “bulk” com catalisadores. Em ambos os processos foi possível a produção de carbonatos cíclicos a partir de um epóxido proveniente de recursos naturais (óxido de limoneno) produzindo assim carbonato de limoneno, um carbonato 100% bio-renovável.

Esta tese fornece novas oportunidades para aumentar a produtividade do processo de produção de carbonatos cíclicos a partir do CO_2.

Palavras-chave: Dióxido de Carbono, Carbonatos, Química Verde, Epóxidos, Supercrítico, Líquidos Iónicos, Epóxidos bio-renováveis, Catalisador, Aerogel, Processo Continuo.

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LIST OF ABBREVIATIONS

[EMIm][B(CN)$_4$]	1-Ethyl-3-methylimidazolium tetracyanoborate
[EMIm][Br]	1-Ethyl-3-methylimidazolium bromide
[EMIm][EtSO$_4$]	1-Ethyl-3-methylimidazolium ethyl sulphate
[EMIm][NTf$_2$]	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
^{1}H NMR	Proton Nuclear Magnetic Resonance
AA	Atomic Absorption
AHBDs	Arylhydrazones of β-diketones
ALIQUAT Cl	Trioctylmethylammonium Choloride
ASILP	Aerogel Supported Ionic Liquid Phase
ATR	Attenuated Total Reflectance
B4	alginate aerogel
B4_ImpA	aerogel impregnated with Aliquat Cl
B4_ImpZ	zinc impregnated alginate aerogel
B4_ImpZA	aerogel impregnated with zinc and Aliquat Cl
BET	Brunauer, Emmett, Teller
BJH	Barrett–Joyner–Halenda
BPR	Back Pressure Regulator
CaCO$_3$	Calcium Carbonate
CC	Cyclic Carbonate
CCU	Carbon Capture and Utilization
CCS	Carbon Capture and Storage technology
CF	Carbonate formation
CHO	Cyclohexene Oxide
CO$_2$	Carbon Dioxide
DES	Deep Eutectic Solvent
EDX	Energy-Dispersive X-ray spectroscopy
EL	Ethyl lactate
EtOH	ethanol
FCT-UNL	Faculdade Ciências e Tecnologia- Universidade Nova de Lisboa
FE-SEM	Field Emission Scanning Microscopy
GDL	Glucono-δ-lactone
h	hours
H$_2$O$_2$	Hydrogen Peroxide
HCl	Hydrochlorid acid
HF	Hydrofluoric acid
IL	Ionic Liquid
ITMC	Institut für Technische und Makromolekulare Chemie
K	Kelvin

$KMnO_4$	Potassium Permanganate
LC	Limonene Carbonate
LCA	Life Cycle Assessment
LO	Limonene Oxide
MEK	Methyl ethyl ketone
MPa	Mega Pascal
NH_4OH	Ammonium Hydroxide
non-OECD	Organisation for Economic Cooperation and Development
PEG	Polyethylene Glycol
PEG	Polyethylene glycol
PO	Propylene Oxide
ppm	parts per million
PPNCl	bis(triphenyphosphine)iminium Chloride
RT	Room Temperature
RTILS	Room Temperature Ionic Liquids
RWTH	Rheinisch-Westfälische Technische Hochschule
S1	blank silica aerogel
S1_ImpZ	zinc impregnated silica aerogel
S3	silica aerogel
S3_ImpZ	zinc impregnated silica aerogel
S3_ImpZA	aerogel impregnated with zinc and Aliquat CL
$scCO_2$	Supercritical Carbon Dioxide
SCF	Supercritical Fluid
SILP	Supported Ionic Liquid Phase
SO	Styrene Oxide
STY	Space Time Yields
TBABr	Tetrabutylammonium Bromide
TBAI	Tetrabutylammonium Iodade
TMOS	Tetramethoxysilane
TOF	Turn Over Frequency
TON	Turn Over Number
WI	Wet Impregnation
Zn(II)-AHBD	Zinc(II) Complexes of Arylhydrazones of β-Diketones

The goal of this PhD thesis was the development of key steps to design an efficient catalytic system for the synthesis of cyclic carbonates via the coupling reaction between epoxides and carbon dioxide. The use of environmentally friendly conditions was of high priority, including the choice of solvent, use of renewable feedstocks, and use of non-precious metals and avoiding toxic substances, in an attempt to adhere to the 12 principles of green chemistry. Starting from basis reactions, the investigation progressed in order to obtain knowledge and understand the interaction between CO_2, epoxides and different catalysts to produce the cyclic carbonates. The thesis is divided into eight chapters along which the progress of the research is exposed in detail.

Chapter 1 provides an overview of the concepts related with the cyclic carbonate synthesis in the scientific and the industrial fields, starting with the use of CO_2 as raw material. Then some detailed information is provided about coupling reaction between CO_2 and epoxides, including some references to the traditional way based on phosgene and some of the most effective catalytic methods that have been used. The last part of this chapter approaches some modifications that can be introduced to turn the process greener and more sustainable.

In **Chapter 2** the production of cyclic styrene carbonate from CO_2 cycloaddition to styrene oxide, using tetrabutylammonium bromide (TBABr) as catalyst, was investigated. Two different reaction systems, either CO_2-rich or epoxide-rich, were studied. Reactions were performed using a visual high pressure cell, at different temperatures and pressures. High pressure phase behaviour manipulation of the reaction system was also explored and proved to be crucial for process optimization, namely to shift catalysis from homogeneous to heterogeneous, by changing operation conditions. In **Chapter 2** the versatility of using Zinc (II) complexes of arylhydrazones of β-diketones (AHBD) as catalysts combined with tetrabutylammonium bromide (TBABr) was also studied for the coupling reaction between CO_2 and epoxides. The influence of pressure and temperature on cyclic carbonate formation was investigated, as well as the catalytic activity towards different substrates (e.g. styrene oxide, propylene oxide and cyclohexene oxide). The molar ratio between metal complex and TBABr was determined for maximum catalytic activity. It was proven that the high stability and ease of preparation of these kinds of zinc complexes make them good candidates for large scale cyclic carbonate production.

In **Chapter 3** several ionic liquids were tested as solvents and co-catalysts in order to optimize the conversion of the epoxide into the cyclic carbonate product. Different cation and anion families were studied in order to understand the effect of specific functional groups on the final reaction yield. Reaction experiments were performed in a high-pressure visual apparatus using propylene oxide as model substrate. **Chapter 3** also explores the possibility of using supercritical CO_2 ($scCO_2$) technology as a second step for extracting propylene carbonate produced from the coupling reaction between propylene oxide and CO_2. The reactions were performed under biphasic gas-liquid conditions, using a zinc(II) complex of arylhydrazones of β-diketones (Zn(II)-AHBD) as metal catalyst, combined with tetrabutylammonium bromide (TBABr). Aliquat Cl was selected as the most promising solvent and $scCO_2$ extraction was effectively applied as a second step to isolate propylene carbonate from the catalyst system. Following this strategy, the catalyst system was reused three times, without significant loss of activity.

Chapter 4 establishes a framework for an efficient separation and recycling of metal catalysts. In this chapter the method of deposition of catalyst solutions on the surface of porous aerogels via wet impregnation was explored for the preparation of alginate structures supporting a Zinc complex-ionic liquid phase. This procedure originates a well-defined thin solvent film on the surface of the support materials, which provides high catalyst accessibility. Several catalytic tests were performed in a high-pressure apparatus and final products analysed by ^{1}H-NMR spectroscopy. The effect of CO_2 pressure on the reaction kinetics was also evaluated.

Chapter 5 demonstrates the possibility to perform the reaction under continuous flow mode, using naturally derived epoxides. Limonene epoxide is a bio-derived building block obtained from the epoxidation of limonene, a natural compound widely available as by-product of the citrus industry. In this Chapter, the continuous flow production of limonene carbonate from limonene epoxide and CO_2 was explored using a biphasic reaction system composed of CO_2 and an ionic liquid (IL) in a high-pressure set-up apparatus. The results under continuous-flow conditions were discussed and compared with those obtained for reactions operated at batch conditions.

Chapter 6 summarizes the thesis results as well as some concluding remarks with recommendations for future research.

Chapter 1

General introduction: reuse of carbon dioxide as a chemical feedstock for the green synthesis of organic carbonates

Green chemistry encourages the production of valuable chemicals derived from natural and renewable sources rather than using fossil fuels as starting materials. This general introduction highlights the most important aspects in the field of the utilization of CO_2 as an alternative, unlimited source of carbon for the production of chemicals. Its high tunability, low cost, relatively low toxicity and its independency from the food supply chain make CO_2 utilization as feedstock attractive from the industrial and the academic points of view.

Particularly, this chapter focus one of the most promising large-scale applications using CO_2 as C1 feedstock, the production of organic carbonates, via direct coupling between CO_2 and epoxides. These resulting cyclic organic carbonates are important low energy molecules, which find application as electrolytes for lithium batteries, pharmaceutical intermediates and monomers in polymer production.

In the last topic, an overall review was carried out taking into account the most prominent transformations according with the green chemistry principles, as a sustainable method for process intensification.

Chapter 1

1.1. Carbon capture and storage

Access to energy is a crucial factor for humanity to continue the economic, cultural and social development in the society. The world energy consumption has increased in the last years and according with predictions (Figure 1), it will continue to increase. Between 2005 and 2050, a rise of almost 60% is expected, more than half of this growth is anticipated to occur in developing nations outside the Organisation for Economic Cooperation and Development (non-OECD), including countries like China and India, where strong economic production increases are associated with a high demand for energy.

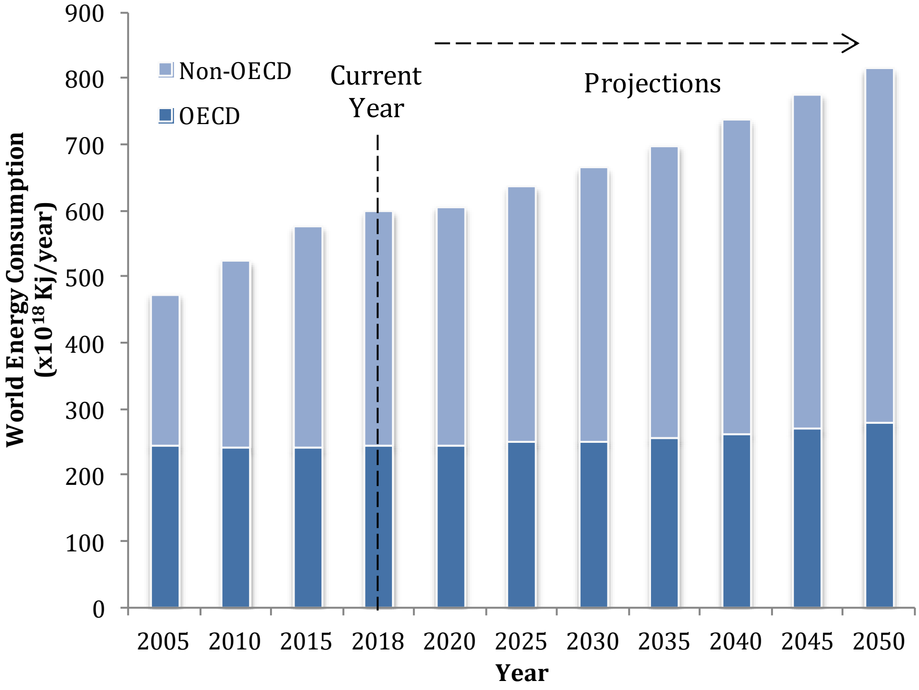


Figure 1. World energy consumption. Source: History: Energy Information Administration (EIA), International Energy Outlook 2017, web site www.eia.doe.gov/iae/. Projections: EIA, System for the Analysis of Global Energy Markets.

Despite the differences between individual nations and continents, energy production brings significant issues associated with global environmental impact [1]. The increase of energy consumption lead to environmental degradation, whether from the resource use, or from pollution point of view, as consequent irreversible adverse changes in the natural environment may occur [2, 3].

Nowadays world’s energy supplies come mainly from fossil fuels (coal, crude oil and natural gas) and beside the efforts to develop an alternative, like renewable or nuclear energy, these sources possibly will remain a predominant energy source for the next few generations [4]. Although renewable energy is the world’s faster growing source and consumption of non fossil fuels is expected to grow faster than fossil ones, fossil fuels currently represents 80% of the world’s energy sources and will very likely continue to be used for next decades (Figure 2). Associated with these carbon-based energy sources, we have inevitably production of greenhouse gases, which are responsible for the global climate change [5]. Among other greenhouse gases, such as methane and nitrous oxide, carbon dioxide (CO_2) had the most significant increase [6], indeed, the atmospheric concentration of CO_2 changed from around 300 ppm (during the preindustrial era, around 1950) to more than 400 ppm (current level) [7].

As solution to decrease the levels of CO_2 and mitigate climate change, the implementation of Carbon Capture and Storage technology (CCS) has been proposed. With this technology is possible to prevent the accumulation of large quantities of CO_2 into the atmosphere through the abatement of CO_2 [8]. CO_2 capture technologies available in the market are costly, and contribute to around 70–80% of the total cost of a full CCS system including capture, transport and storage [9]. Moreover, CCS is a complex technology and with high amount of energy required, it has been estimated to involve about 30% of the total energy produced by a power station [10].

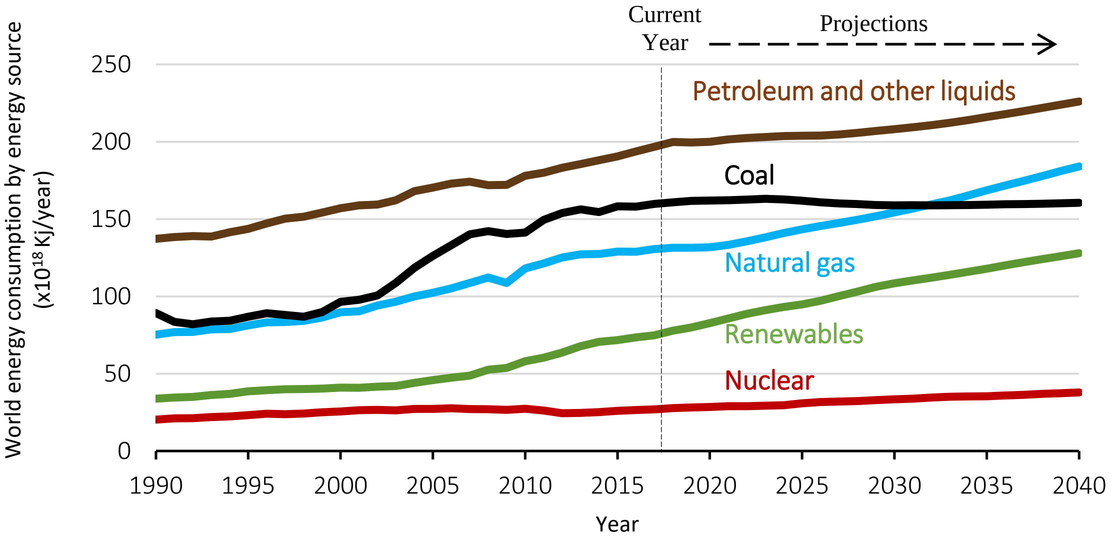


Figure 2. World energy consumption by energy source. Source: History: EIA, International Energy Outlook 2017, web site www.eia.doe.gov/iae/. Projections: EIA, System for the Analysis of Global Energy Markets.

1.2. CO_2 as sustainable feedstock for production of chemicals

Instead of just store CO_2, we can use it as a sustainable feedstock for the production of chemicals, in this way, unwanted waste CO_2 can be turned into value-added chemicals [11]. At low concentrations, carbon dioxide gas has no odor, however at high concentrations irritating acidic smell can be felt. It is also colourless and denser than air. At room temperature and atmospheric pressure, it behaves like a gas, but its physical state changes according to the conditions applied (Figure 3) [12].

In fact, CO_2 is the most widely used supercritical fluid (SCF) and its critical point is around 31^{o}C and 70 bar (Critical Point, Figure 3). SCFs are highly compressed gases with intermediate properties between liquids and gases: low viscosity of a gas and the high density of a liquid. SCFs are attractive as medium for chemical reactions because of their “tunable” properties, that can be easily changed by small changes in pressure or temperature and consequent in the density [13, 14]. Scientists in the field have been exploring CO_2 physical-chemical properties and thermodynamic behaviour towards its utilization as a green solvent for more than five decades [15, 16]. For example, separation of product and catalyst can be easily controlled by changing the carbon dioxide pressure. Nowadays, supercritical carbon dioxide ($scCO_2$) is industrially used in caffeine and hops extraction, cork deodorisation, enhanced oil recovery and parts degreasing [17].

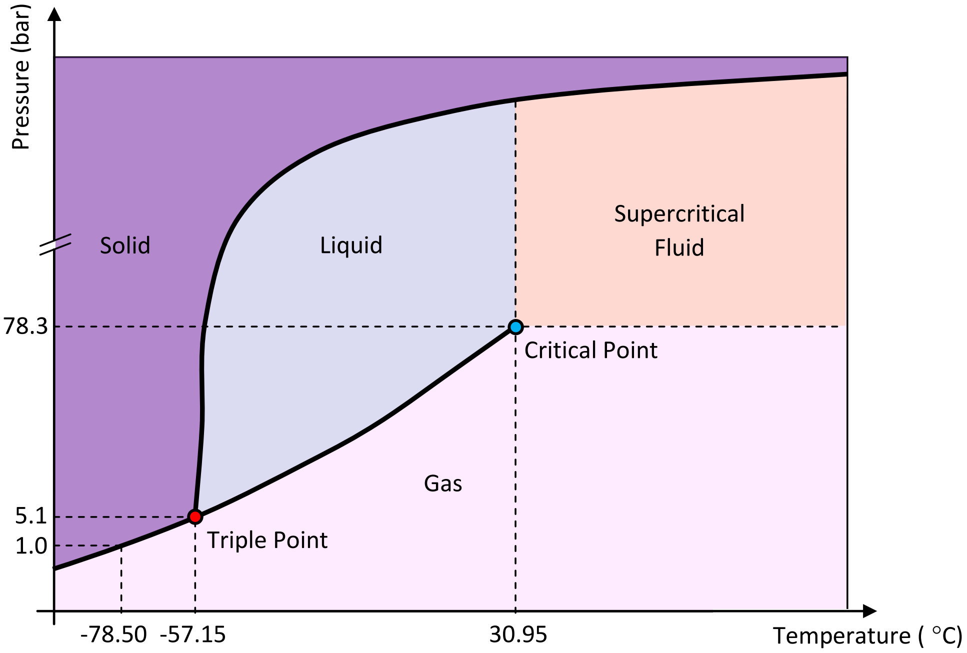


Figure 3. Carbon dioxide phase diagram.

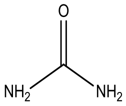
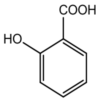
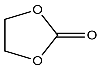
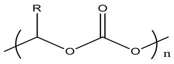
Other applications can be explored through CO_2 tunable properties in food and pharmaceutical processing to defray future liability costs, production of pharmaceutical nanoparticles for injection, polymerizations [18], emulsion polymerization of water-soluble monomers, enhanced oil recovery, and homogeneous [19] and phase-separable catalysis, including that based on ionic liquid solvents [20].

In addition to its high tunability, its high abundance, availability, low cost, less toxic alternative to traditional organic solvents [21], non-inflammability and its independency from the food supply chain, have brought CO_2 utilization as feedstock to the attention of both industry and academy [22, 23]. The CO_2 conversion into chemicals could lead to the replacement of toxic substances, such as phosgene, isocyanates or carbon monoxide in some industrial processes [24, 25]. Also, the utilization of CO_2 can lead to the formation of new materials with unique properties. Besides that, the processes could have a more efficient and economic pathway when compared with the conventional method without CO_2 [26].

Due to its highly versatile characteristics the use of CO_2 as C1 building block has been being used in different industrial applications [27]. The most successfully process for CO_2 transformation involves: employing high-energy starting material, like hydrogen, epoxides, unsaturated compounds or organometallics; the synthesis of low energy products, such as carbonates, carbamates, lactones, esters or carboxylic acids; and the process design where the equilibrium is preferable into the products by removing by-products [28].

Some important processes (Table 1), including the synthesis of urea [29] and salicylic acid [30], have been carried out on an industrial scale using CO_2. Another successfully industrialized process using CO_2 as a source of carbon in synthetic chemistry has been the catalytic production of cyclic carbonates and polycarbonates from epoxides [31].

Table 1.Industrialized processes using CO_2 as C1 feedstock [37].

Product	Molecular Formula	Annual Production	Annual CO_2 Consumption as feedstock
Urea		150 million tons	109 million tons
Salicylic Acid		170 thousand tons	50 thousand tons
Cyclic Carbonates		100 thousand tons	40 thousand tons
Polycarbonates		4.4 million tons [38]	3 million tons [39]

In all these chemical industrial applications present on Table 1, only a small fraction of the CO_2 emitted is used, around 0.5-1% [32]. However this could be a very profitable undertaking and could be used to partially offset the costs associated with CCS for the remaining carbon dioxide. Clearly, for CCU to be effective the energy requirements of the process should be very low (or the process should be linked to renewable energy), otherwise more carbon dioxide will be generated producing the required energy than is utilized in the chemical production [33].

Although the use of CO_2 as C1-bulding block may avoid the use of fossil fuels, it will not have a significant impact on climate change due to the relative scales of CO_2 emissions (10 gigatonnes in 2010) [34] and chemicals production (340 milliontonnes for the European Union, in 2010) [35] which inevitably mean that only a small amount of carbon dioxide could be recycled through Carbon Capture and Utilization (CCU) [36].

1.3. Coupling reaction of CO_2 with epoxides

As previously mentioned, one of the most successful processes using CO_2 is its reaction with epoxides, which can be controlled to form either cyclic carbonates [40] or polycarbonates [41]. The insertion of CO_2 into a carbon–oxygen bond of an epoxide is a powerful method for CO_2 fixation to produce five-member cyclic carbonates [42]. Also such use of CO_2 as building block in organic synthesis could contribute to a more sustainable use of resources.

Cyclic carbonates are valuable synthetic products, with different commercial applications, and they can be used in a wide range of chemical and technological process [43]. Cyclic carbonates can be used as monomers for the production of polycarbonates [44] and non-isocyanate polyurethanes [45] and they can also be used as electrolytes in lithium ion batteries [46], ecofriendly polar aprotic solvents and as chemical intermediates for the synthesis of a range of useful chemical products, such as dialkyl carbonates, glycols and carbamides, [47]. Their properties, such as low toxicity, high boiling and flash points, low vapour pressure, biodegradability and high solubility [48] extend their applications in the dye industry, textiles, polyacrylonitrile fibers manufacturing and cosmetics and cleaning processes [49, 37]. Additionally they can also be used as additives to fuels and hydraulic fluids [50].

This diversified range of applications and the fact that industrial processes use harsh operating conditions caused a high interest in the development of more economic processes for their manufacture, mainly from CO_2. The reaction has been reported by several authors, exploring different catalytic systems and operational conditions [51].

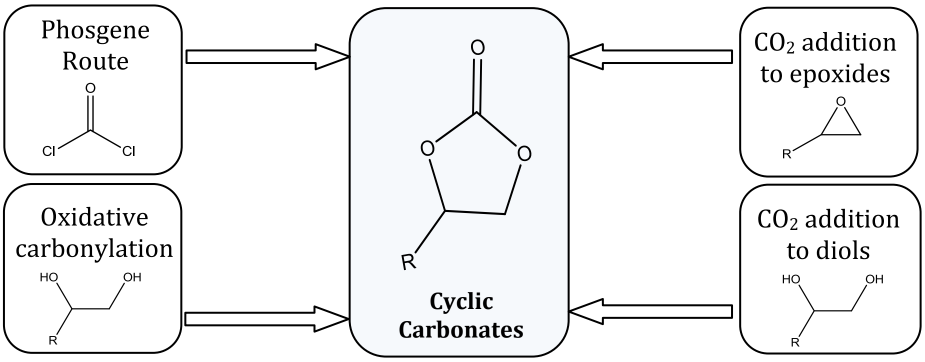


Figure 4. Cyclic carbonate synthesis by different methods.

The traditional way for the synthesis of cyclic carbonates involves the use of phosgene (Figure 4). To obtain phosgene, carbon monoxide is mixed with chlorine in an intensive energy process [52]. After phosgene is prepared, a synthesis reaction of cyclic carbonate is carried out with alkaline solution and dichloromethane, wherein the co-product of the synthesis reaction of cyclic carbonate is hydrochloric acid [26]. Due to phosgene high toxicity (considered as a chemical weapon by international treaties), high risk to human and to natural environment, difficulty to handle and the disposal of the coproduced hydrogen chloride, some alternatives have been developed [53]. A safer alternative route that excludes phosgene from the process is the insertion of CO_2 into the C-O bond of the strained heterocyclic ring of an epoxide. This coupling reaction with epoxides and CO_2 is 100% atom efficiently (Figure 4).

The production of five-membered carbonates has been industrialized since the 1950s [54]. The history of coupling CO_2 with epoxides has been known since 1969, when Inoue and co-workers discovered the possibility to use CO_2 as a C1 building block in propylene oxide copolymerization, using heterogeneous zinc catalysts in organic solvents, at 50-60 atmospheres pressure [55]. Comparable results were also obtained with other substrates such as ethylene oxide and styrene oxide [56]. Since then a lot of attention and significant efforts have been made within the past decades to investigate various relating catalysts, adjust material properties and find applications [57, 58].

The high oxidation state of the carbon in CO_2 results in elevated thermodynamic stability, which means that energy must be supplied to obtain the desired transformation. Therefore, for CO_2 utilization, high energy substrates, such as epoxides are required [59]. Furthermore a catalyst can be added to decrease the activation energy necessary for the reaction to proceed [60]. Following developments in this field were discouraged by low catalytic activities and competitive formation of polycarbonates and/or undesired by-products, such as high degrees of ether linkages in the polymer chains [61]. The cycloaddition of CO_2 to epoxides to produce cyclic carbonates strongly depends on the selection of the catalyst and several different catalysts have been studied as alkali metal salts [62], metal oxides [63], transition metal complexes [64], quaternary ammonium and phosphonium salts [65], ionic liquids [66] and supported phase catalysts [67]. Most often these are used in combination with a suitable nucleophile [68].

On the other hand, metal-free catalysts for the use of CO_2 as a C1 feedstock could represent an attractive alternative, since they are generally low cost, readily available, less toxic, stable and inert towards moisture and air [69]. In this way it is possible to avoid any toxicity issues associated with the presence of metals in the developed product, optimizing the sustainability and safety of the process [70]. Nevertheless, these catalysts preferentially work at elevated temperatures and high CO_2 pressures (>120^{o}C and >20 bar), what does not happen for catalytic systems based on transition metals, which are able to operate even at room temperature [71]. The high number of apparently redundant reports on nucleophilic organocatalysts make the question of which of these systems is the most promising for the cycloaddition of CO_2 with epoxides by low energy input beyond the laboratory scale very difficult to answer [72].

Nevertheless, emergent ionic liquid (IL) technology may solve such effort to some extent. In the last decade, widespread investigations for the production of cyclic carbonates by cycloaddition of CO_2 and epoxides using ILs as catalysts have been carried out and this significantly improved the understanding of how to activate CO_2 and the inert C–O bond of epoxides effectively. Many of these studies have been the subject of excellent recent reviews [73].

It is worth mentioning that the coupling of CO_2 with epoxides for cyclic carbonate production has been industrialized using quaternary ammonium or phosphonium salts as catalysts [74]. However, the process still suffers from major disadvantages, such as high reaction temperatures (> 120°C) and high pressures (40-80 bar of CO_2) [75]. In literature it is possible to find several reports that attempt to improve the activity of the onium salts over the combined use of other catalysts or even modifications of known catalysts with special functional groups [76].

1.4. Mechanism of the cycloaddition of CO_2 with epoxides

The cycloaddition of CO_2 with epoxides has been investigated mechanistically and theoretically [77]. Different mechanisms for the reaction of carbon dioxide with epoxides have been proposed, as they depend on the substrate, reaction conditions and also the catalyst system. The addition of CO_2 to epoxides is generally carried out in the presence of a catalytic system that can activate the CO_2 molecule, the epoxide or both molecules at the same time. As stated before, the reaction of CO_2 with epoxides can generate two types of products: cyclic carbonates and polycarbonates (a and b in Figure 5).

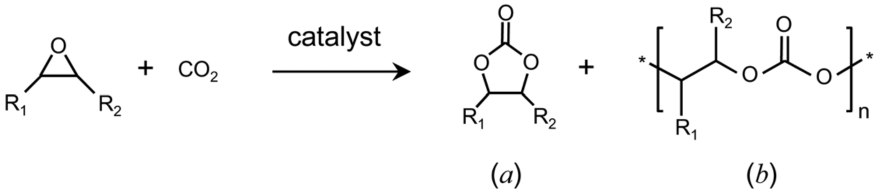


Figure 5. Reaction of CO_2 with epoxides: cyclic carbonate (a) and polycarbonate (b).

Generally the epoxide activation occurs when one of the epoxide's oxygen atoms interacts with a Lewis acid, followed by a nucleophilic attack that induces the ring opening of the epoxide [78]. The ring opening of epoxides is the key step, where the produced alkoxide species is necessary for reaction with carbon dioxide [79].

The majority of the mechanisms proposed for the reaction of CO_2 with epoxides have been derived from studies of homogeneous catalytic systems, but heterogeneous catalysts are considered to follow similar pathways [80]. The general accepted route for this reaction is shown in Figure 6, where the metal complex is used in a combination with a nucleophile, also referred as co-catalyst [81]. This route follows a three step mechanism: ring-opening, CO_2 insertion and ring closure [82].

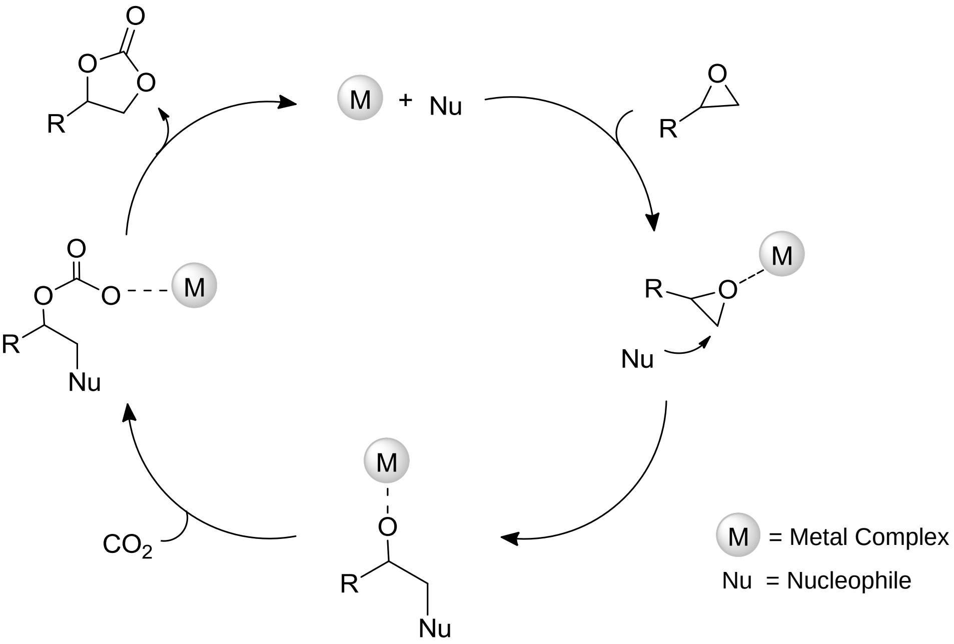


Figure 6. Mechanistic cycle for CO_2 addition to epoxides using a metal complex as catalyst [76, 77].

The first step consists on activating the epoxide by coordination to the Lewis acid metal centre, followed by the nucleophile attack in order to open the epoxide ring and formation of the metal-bound alkoxide. Then, the carbon dioxide molecule gets inserted into the metal alkoxide bond resulting in a metal carbonate intermediate which can either evolve towards a cyclic carbonate or propagate by continuous addition of epoxide and CO_2 resulting in polycarbonate.

1.5. Coupling reactions of CO_2 with epoxides – a sustainable approach

Figure 7 summarizes the 12 principles of Green Chemistry. These principles were developed by Paul Anastas and John Warner, with the purpose of reduction of toxic compounds, prevention of waste production and use of energy-efficient processes [83]. Among the most prominent transformations meeting the green chemistry principles are the coupling reactions of CO_2 with epoxides. Regarding an efficient and environmentally way for CO_2 fixation, this reaction is 100% atom efficiency, since CO_2 reacts with epoxides without formation of any by-product [84].

Beyond improving production efficiency, green chemistry and engineering also address the environmental impact of chemistry, so we could improve the process in order to make the chemical production more efficient, but also safer and greener [85]. To achieve this, the design, development and implementation of chemical products and processes, in order to reduce or completely eliminate the use and production of hazardous substances to human health and the environment is required [86].

At an industrial level, for a successful implementation of a more sustainable process, this must also be accompanied by improvements in the commercial performance [87]. However this approach towards sustainability can also make companies more competitive, not less, because adapting a properly designed environmental innovation can lower the total cost of a product or improve its value, making the company more efficient productively [88].

Figure 7. Schematic diagram with the 12 Principles of Green Chemistry.

One of the principles in Anastas's list, is the need to replace toxic and volatile organic solvents to safer and greener alternatives. The appropriate selection of solvent for a process can improve its sustainability, for that reason there has been extensive research into the application of "green solvents", such as ionic liquids and supercritical fluids, namely $scCO_2$. In this work, as mention before, we are going to explore the production of cyclic carbonates, and for that purposed CO_2 will be used, avoiding the use of the highly toxic phosgene as reagent. Another possible improvement in the direction of a greener process is the direct use of CO_2 from the industries. While pure carbon dioxide is typically used for these coupling reactions, several recent reports detail the use of impure and even post-combustion sources of CO_2 [44, 89].

The cycloaddition of CO_2 to epoxides to produce cyclic carbonates is strongly dependent on the selection of the catalyst, and numerous catalysts have been shown to be effective for this reaction. However, many of these catalytic systems suffered from low catalytic stability or reactivity, the need for co-solvents and extreme conditions, so the design of highly effective and cheap catalysts is still desirable [90]. In search for a more efficient catalytic system, special attention should be given to catalytic systems that reveal improved activity and selectivity using mild conditions and environmentally friendly, low cost and easy to handle catalysts. Certain ionic liquids which can dissolve CO_2 favourably [91] can also be used [92].

Highlighting the potential of this reaction, the most radical and innovative step is to transfer the process from batch to continuous flow mode, with all its ‘intrinsic’ advantages, including the higher surface-to-volume ratio, enhanced mass transport, easier temperature control and automation, with consequent intensification of the process, making available systems working 24 h a day, 7 days a week [93]. Such undertakings offer very large improvements in costs and eco-efficiency, thus giving a substantial competitive advantage in light of barriers to entering new markets, highlighting maximum performance and the chemical potential of the transformations involved [94].

Still in the coupling reactions of CO_2 with epoxides one way to develop a more innovative and sustainable processes is the incorporation of epoxide monomers totally derived from renewable resources. A large number of bio-based cyclic carbonates can be produced from the cycloaddition of CO_2 and epoxides (Figure 9) [89].

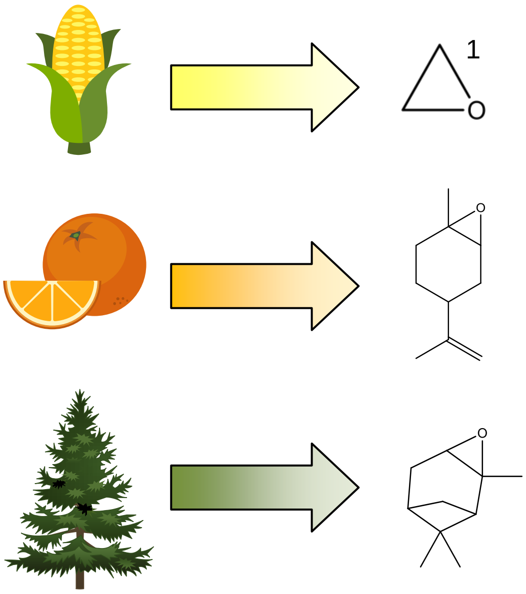


Figure 9. Epoxide starting materials that can be obtained from renewable feedstocks.

[1] Synthesis of ethylene oxide from bio ethanol

There is a need to consider the exploration of epoxides from renewable resources in order to have alternative routes for the production of 100% renewable polyesters/carbonates [95]. The epoxides may be derived from different naturally occurring sources, including from fatty acids (triglycerides) and terpenes [96]. Fatty acids, derived from vegetable oils, contain unsaturated groups which can be epoxidised. In the case of terpenes, they contain double bonds which can be epoxidised, such epoxides include limonene oxide and pinene oxide. For example, structural similarity of limonene oxide with cyclohexene oxide makes it an excellent choice as a biorenewable epoxide monomer for copolymerization with CO_2.

Limonene (by-product of the citrus industry) is the most common terpene, its abundance and low cost make it an excellent choice as a biorenewable epoxide monomer for copolymerization with CO_2. The first success of terpene derived epoxide–CO_2 came from Coates and co-workers, in 2004, who reported the successful copolymerization of limonene oxide–CO_2, using β-diiminate zinc complexes as catalyst [97].

Moreover, carbonates produced from CO_2 and epoxidized fatty acid esters and the respective triglycerides have been reported as novel precursors for the synthesis of non isocyanate polyurethanes (NIPU), as starting materials for polyesters and polycarbonates, as potential industrial lubricants, as fuel additives and polymer plasticizers [98]. In particular, their biocompatibility and biodegradability are desired properties for polymer science and sustainable materials within the biomedical field and for mitigating the end-of-life environmental impact of plastics [99, 100].

A recent Life Cycle Assessment (LCA) revealed crucial advantages regarding environmental impacts of the reported bio-based carbonates which are considered as potential plasticizers for polyvinyl chloride [101].

Other epoxides derived from terpenes should also be explored, because these alternative substrates, beside the advantage of being renewable, also offer the possibility of producing new materials with different physical-chemical properties. Indeed, some recent developments regarding epoxide carboxylation with CO_2 show potential to solve some technical issues that are limiting high scale application of this technology [102].

New and promising ways of carbonate production from CO_2 should be explored, underlining potential research opportunities, namely ionic liquids, renewable substrates and the further exploitation of supercritical conditions. In this way we could achieved an efficient use of resources and energy while reducing adverse environmental impacts.

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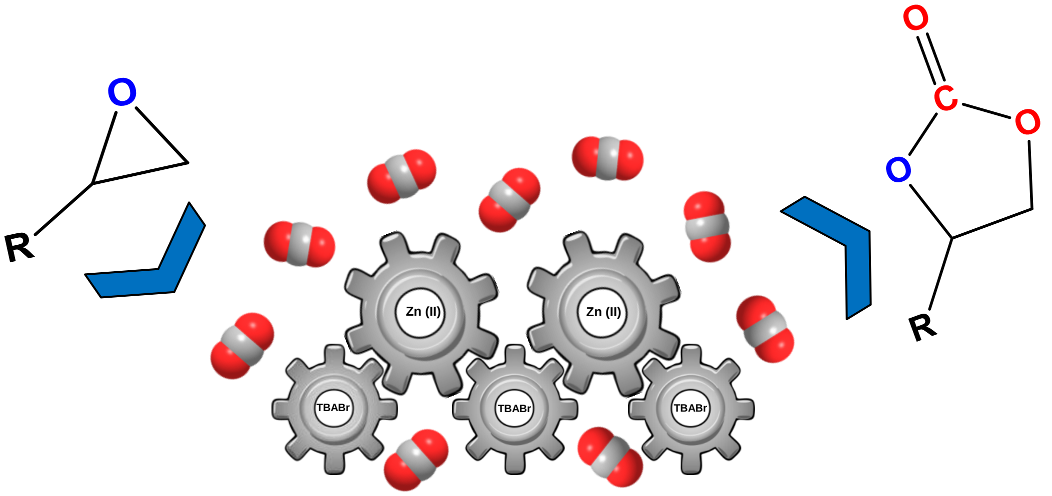
Chapter 2

Cyclic carbonate synthesis from CO_2 and epoxides using zinc(II) complexes of arylhydrazones of β-diketones combined with tetrabutylammonium bromide



First, the production of cyclic styrene carbonate from CO_2 cycloaddition to styrene oxide, using tetrabutylammonium bromide (TBABr) as catalyst, was investigated. Two different reaction systems, a CO_2-rich and an epoxide-rich were studied. High pressure phase behaviour manipulation of the reaction system was explored to shift catalysis from homogeneous to heterogeneous, by changing operation conditions.

Then, in a different approach using Zinc (II) complexes of arylhydrazones of β-diketones (AHBD) as catalysts combined with TBABr as co-catalyst, was also investigated. The influence of pressure and temperature on cyclic carbonate formation was investigated, as well as the catalytic activity towards different substrates (*e.g.* styrene oxide, propylene oxide and cyclohexene oxide). The molar ratio between metal complex and TBABr was determined for maximum catalytic activity. The carbonate formation was monitored quantitatively by using ^{1}H-NMR spectroscopy.

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Chapter 2

2.1. Introduction

2.2. Experimental Section

2.2.1. Materials

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2.3. Results and Discussion

2.3.1. TBABr as catalyst (metal free reactions)

2.3.2. TBABr as co-catalyst and Zinc(II) complex as catalysts

2.4. Conclusions

2.5. References

2.1. Introduction

The synthesis of cyclic carbonates via the coupling of CO_2 with epoxides is one of the most promising methodologies in the field of CO_2 conversion, since it can be incorporated in one step with 100% atom economy (Figure 1). Cyclic carbonates are widely used in several fields of chemical and pharmaceutical industries, such as polar aprotic solvents, production of engineering plastics, electrolytes for lithium-ion batteries, fuel additives, and as intermediates in the manufacture of fine chemicals [1-4]. In this manner the use of CO_2 (a by-product of many industrial processes) may provide access to high-value products from a nontoxic, renewable and low-cost resource, in a promising way towards reducing fossil fuels dependence [5-7]. However, the high CO_2 thermodynamic stability, mainly responsible for CO_2 successful utilization as clean solvent, poses a challenging barrier to its chemical conversion [8-12]. In this context, catalysis has a crucial role, which is motivating a lot of research under this topic [13-17].

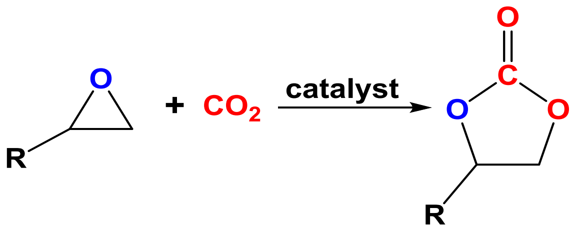


Figure 1. Synthesis of cyclic carbonates from CO_2 and epoxides.

Published works were extensively revised in 2010 by North *et al.* [2] and in 2015 by Martin *et al.* [3]. Successful catalytic systems are usually homogeneous Lewis acidic metal-based complexes, combined with a nucleophile, very often tetrabutylammonium bromide (TBABr). Usually TBABr is used as a co-catalyst, although it is also reported to efficiently catalyze the reaction alone [18, 14]. From a chemical engineering perspective, the combination, of ionic liquids with CO_2 is particularly interesting because ionic liquids are practically not soluble in CO_2, while CO_2 presents a high affinity and consequent solubility in different types of ionic liquids [19]. In addition, CO_2 is able to decrease ionic liquids melting point and so, some room temperature solid organic salts, can become liquids at determined operative conditions, completely altering the reaction system. This phenomenon of organic salts melting under CO_2 pressure, namely the influence of the cation/anion structure has been investigated by several authors [20-22]. Experimental results demonstrate that some organic salts can actually become liquid at much lower temperatures (some melting point depressions exceed 100 K), and in this case, they can also be used as ionic liquids under a supercritical CO_2 atmosphere. In this context, Scurto *et al.* [20] measured the melting point depression effect caused by high pressure CO_2 in numerous ammonium salts. For the case of TBABr a melting point depression from around 373 K to 353 K at 15 MPa was reported. Quite a few examples in literature highlight how these peculiar characteristics can be successfully explored in the implementation of process intensification strategies [8, 23], including the development of flow systems, readiness of down-stream products separation and re-utilization of catalyst [24-27]. Nevertheless, because these are non-conventional characteristics, their potentialities were still not explored for many cases and particularly not for the case of CO_2 cycloaddition to epoxides.

The generally accepted mechanism comprises an interaction between the epoxide and the Lewis acid, through M−O coordination. The epoxy ring is then subject to a nucleophilic attack by the Lewis base, which opens the epoxy ring, forming a metal-alkoxide. Attack of the metal-alkoxide intermediate on the carbon centre of the CO_2 molecule, originates a metal coordinated carbonate. Finally, the halide acts as a leaving group, closing the five-membered ring. Although the nucleophile can actually catalyse the reaction alone, the presence of a metal complex makes the ring opening procedure energetically less demanding and subsequent CO_2 insertion easier [9]. However, high catalytic activities still involve the use of harsh conditions, particularly temperatures above 373.2 K, which spoils the process overall sustainability [3].

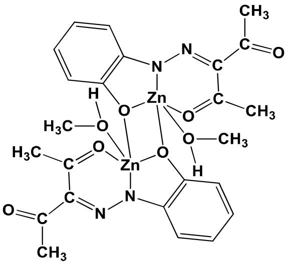
Arylhydrazones of β-diketones (AHBDs) are versatile compounds, which are easy to modify, forming a wide range of coordination compounds [28]. AHBDs can easily be prepared by diazotization with subsequent azo-coupling from cheap starting materials (aromatic amines and β-diketones) [29, 30]. AHBD complexes were reported to catalyse several reactions, namely alkane or alcohol oxidation and the nitroaldol reaction [31-34]. An important feature is that they are easy to handle, owing to their air stability and high solubility in polar solvents [31-33]. However, the capability of AHBD complexes to catalyse the CO_2 cycloaddition to epoxides has never been explored before.

In this work, two different approaches were followed, first the influence of high pressure phase behaviour on cyclic carbonates production from CO_2 and epoxides was investigated, using TBABr as the only catalyst. Styrene oxide was selected as a model substrate and reactions were performed at different temperatures, pressures and reaction mixture compositions. Then, three different Zinc (II) complexes of AHBDs (1, 2 and 3) were used for the first time as catalysts, combined with TBABr, in the coupling reaction between CO_2 and epoxides. The influence of pressure and temperature on cyclic carbonate formation was investigated, as well as the catalytic activity towards different substrates (e.g. styrene oxide, propylene oxide and cyclohexene oxide).

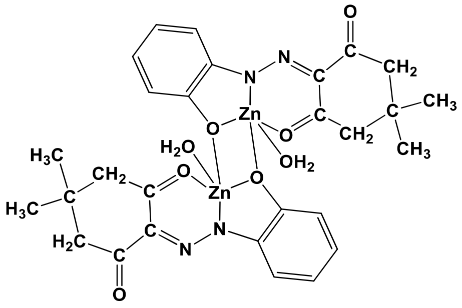
2.2. Experimental Section

2.2.1. Materials

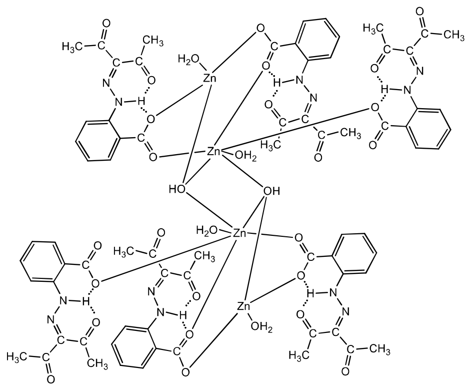
All chemicals and solvents were used as received without further purification. Carbon dioxide (99.998 mol % purity) was supplied by Air Liquid. Styrene oxide (97 mol % purity), propylene oxide (99 mol % purity), cyclohexene oxide (98 mol % purity), tetrabutylammonium bromide (TBABr) (≥ 98% purity), were purchased from Sigma-Aldrich. Zinc(II) complexes of AHBDs (Figure 2) were synthesized as previously reported [34, 35].



Complex 1: $[Zn_2(CH_3OH)_2(\mu\text{-}L^1)_2]$ (MW=631g/mol)



Complex 2: $[Zn_2(H_2O)_2(\mu\text{-}L^2)_2]$ (MW=683g/mol)



Complex 3: $[Zn_4(\mu\text{-}OH)_2(\mu\text{-}HL^3)_4(HL^3)_2(H_2O)_4]$ (MW=1851g/mol)

Figure 2. Zinc (II) complexes of arylhydrazones of β-diketones (H_2L^1 =3-(2-(2-hydroxyphenyl) hydrazineylidene)pentane-2,4-dione, H_2L^2 =2-(2-(2-hydroxyphenyl)hydrazineylidene)-5,5-dimethyl cyclohexane-1,3-dione and H_2L^3 =2-(2-(2,4-dioxopentan-3-ylidene)hydrazineyl)benzoic acid).

2.2.2. Methods

CO_2 and epoxides coupling reactions were performed in a high-pressure apparatus described elsewhere [17]. The apparatus is composed of a stainless steel cylindrical cell with an internal volume of approximately 4 cm^3 and two sapphire windows allowing a direct visual observation of the reaction mixture. The cell was first loaded with epoxide, TBABr, metal catalyst and a magnetic stirring bar. The cell was then immersed in a thermostated water bath heated by means of a controller that maintained temperature within ±0.1 ºC. Operating a CO_2-compressor, the desired pressure was brought into the cell. The pressure in the cell was measured with a pressure transducer 204 Setra calibrated between 0 MPa and 34.3 MPa (precision: 0.1%; accuracy: 0.15%, at the lowest pressure). After three hours of reaction, the high pressure cell was depressurized to atmospheric pressure into a glass trap immersed in an ice bath. Afterward, the cell was opened and the contents collected using 1 mL of chloroform, to dissolve the reaction mixture. Both contents of the cell and glass trap were mixed and prepared for further analysis as follows. Reaction mixture (0.4 mL) was transferred into a NMR tube, to which 0.1 mL of chloroform-d_1 was added. ^{1}H-NMR spectra were recorded on Bruker 500 MHz type (400 MHz). Peak frequencies were compared against solvent, chloroform-d_1 at 7.26 ppm. The epoxide carbonate formation and product yield were determined by integrating the relevant peaks in the ^{1}H-NMR spectra (see Appendix). All liquid solutions were prepared gravimetrically using analytical balance (Sartorius model R180D) with the precision of ± 0.0001 g.

2.3. Results and Discussion

2.3.1. TBABr as catalyst (metal free reactions)

Styrene oxide was selected as a model epoxide for the production of styrene carbonate by cycloaddition of CO_2. In Figure 3 is presented the experimental results obtained for styrene carbonate formation at 353.2 K and CO_2 pressures between 0.5 and 20 MPa. All reactions were performed for 3 h, using 3% mol of TBABr, in relation to the epoxide. Two different reaction mixtures were investigated, a CO_2-rich and an epoxide-rich, with styrene epoxide initial volumes of 0.2 mL and 2.0 mL, respectively, in a 4 mL high pressure visual cell. For the CO_2-rich system, reaction yield increased while increasing pressure until 4 MPa, at which nearly 60% of carbonate formation was observed. For higher pressures, the reaction yield decreased with increasing pressure until it reaches 15% at 20 MPa. At this stage, styrene oxide was completely dissolved in the CO_2 gaseous phase. On the other hand, for the epoxide-rich system, the effect of pressure was not so clear. It reached a maximum yield of 45% for 10 MPa. After 10 MPa, the reaction yield slightly decreased with increasing pressure to around 30% at 18 MPa. At these conditions, the cell was completely full of liquid styrene oxide, which expands volumetrically due to high miscibility with high pressure CO_2, forming what is often called a CO_2-expanded liquid.

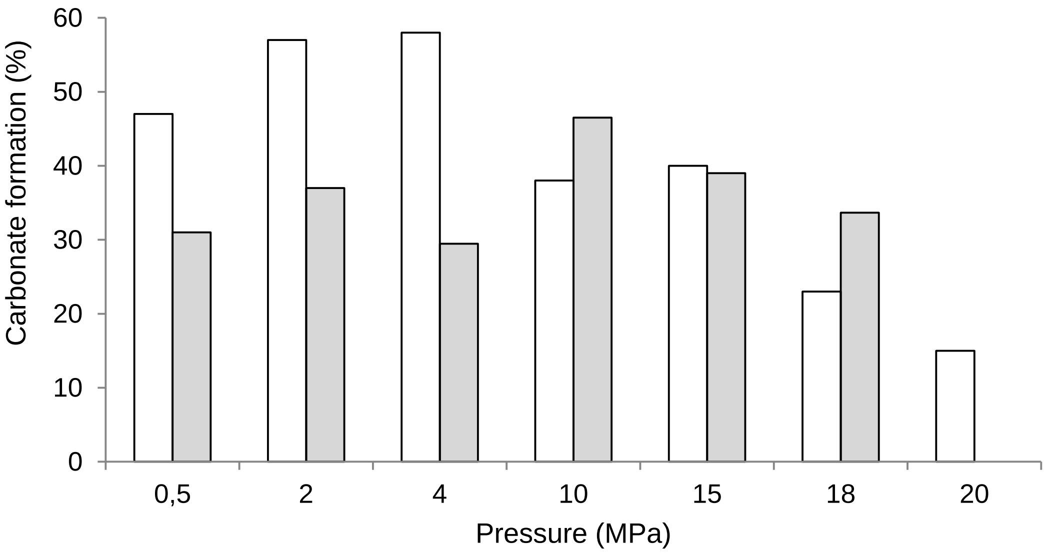


Figure 3. The effect of CO_2 pressure on styrene carbonate formation for a CO_2-rich system (blank columns) and an epoxide-rich systems (grey columns). Reactions were performed during 3h, at 353.2 K with 3% mol of TBABr in relation to styrene epoxide.

Figure 4 illustrates a sequence of images, showing phase changes, with adding and increasing CO_2 pressure, for both systems. It is possible to observe from photographs presented in Figure 4, that pressure increase had complete different effects on the phase behaviour of the reaction mixture, depending if the system is a CO_2-rich, or an epoxide-rich.

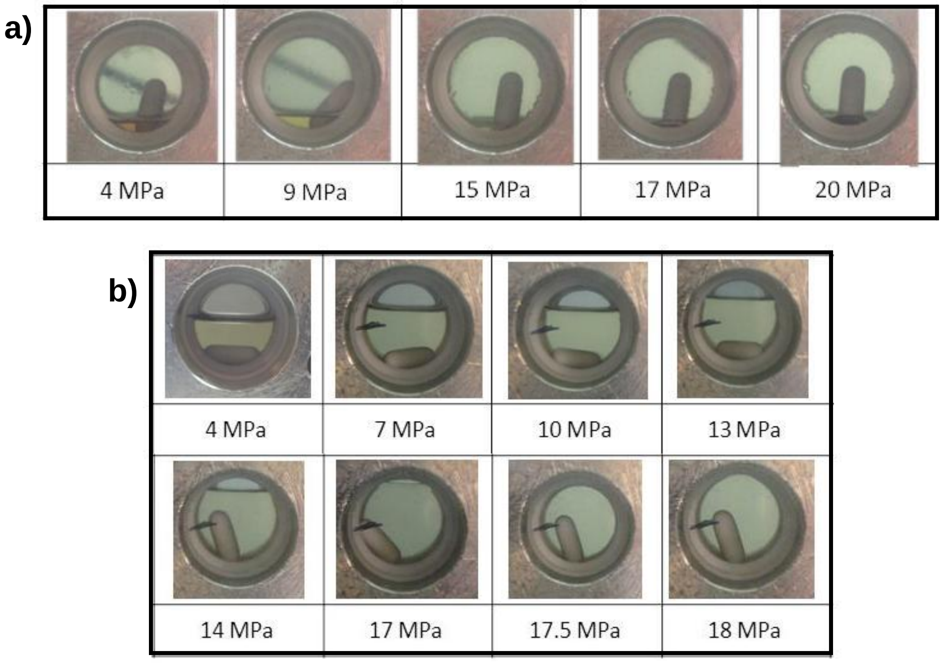


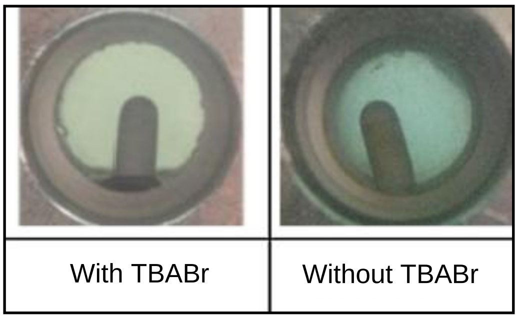
Figure 4. The effect of pressure on reaction phase conditions at 353.2 K, for a CO_2-rich (a) and an epoxide-rich (b) system. The CO_2-rich systems is composed of 0.2 mL of SO and TBABr 3% mol. The epoxide-rich system is composed of 2 mL of SO and TBABr 3% mol.

These observations along with the experimental results presented in Figure 3, demonstrate the importance of studying the influence of phase behaviour on the reaction yield. Tassaing and co-workers [36] have reported the phase behaviour of carbon dioxide/epoxide mixtures for different pressures, temperatures and epoxides (cyclohexene oxide, propylene oxide and styrene oxide). From pressure-composition phase diagrams, it is possible to conclude that complete miscibility between CO_2 and epoxides is easily attained between 8 and 20 MPa, depending on the epoxide and working temperature, with lower temperatures requiring lower pressures (as expected). However, for reaction mixtures, the presence of catalyst has to be considered. Indeed, solid metallic complexes and/or ionic salts, present in very low quantities, have very likely no significant effect on binary CO_2/epoxide equilibrium at mild pressures. But an increase in CO_2 pressure will eventually lead to catalyst precipitation, due to high mutual miscibility between CO_2 and epoxides. This should happen mainly for CO_2-rich systems, which actually stands for most of the reported systems in literature [37]. This behaviour was visually observed in this work and is illustrated in Figure 4a. The precipitation of a catalyst-rich phase was observed at around 15 MPa, originating a physical barrier to mass transfer. Nevertheless, percentages of styrene carbonate formation of around 40%, 20% and 15%, for 15, 18 and 20 MPa respectively, were still observed. At these pressures, TBABr is acting as a heterogeneous catalyst phase (although non-supported).

It noteworthy that from the sapphire window of the high pressure cell, a relatively dense and clear liquid phase, instead of a white solid (physical aspect of TBABr), was visualized. This is in accordance with experimental data reported by Scurto *et al.* [20] on the melting behaviour of TBABr under high pressure CO_2. According to the authors, at 353.2 K and 15 MPa of CO_2, TBABr melts, behaving as an ionic liquid, which according to results presented in this work, was able to catalyze the reaction of CO_2 insertion into styrene oxide. These high pressure heterogeneous conditions, although presenting lower carbonate formations, can bring some process advantages, namely concerning product separation from the reaction mixture and/or avoid the utilization of an organic solvent, for cases in which the catalyst and the substrate (epoxide) are not soluble.

For the epoxide-rich system, the influence of pressure was not so clear. Indeed when 2 mL of epoxide, in a 4 mL high pressure cell, were put in contact with CO_2 at 353.2 K, the reaction system was biphasic with approximately equal volumes of liquid and gas phase (Figure 4b). As CO_2 was added to the cell, it solubilised into styrene oxide liquid phase, considerably expanding its volume, until monophasic conditions were attained at approximately 18 MPa [36].

Results presented in Figure 3 shows that styrene carbonate formation tends to increase with the increase of pressure until 10 MPa, after which, it started to slightly decrease due to a dilution effect caused by the expansion of the reacting liquid phase. This behaviour was well documented for several reactions and was also observed in this work [8, 37]. Two reactions without adding TBABr (blank reactions) were performed at 4 MPa (for epoxide-rich system) and at 18 MPa (for CO_2-rich system), both presenting negligible reaction yields. Figure 5 presents a picture of the blank reaction performed at 18 MPa (for the CO_2-rich system) showing a complete homogeneous system, in which styrene oxide is completely dissolved in the CO_2 gaseous phase.



With TBABr

Without TBABr

Figure 5. CO_2-rich system at 353.2 K and 18 MPa, with 3% mol TBABr (heterogeneous system) and without TBABr (homogeneous system).

Figure 6 shows how the CO_2-rich system is affected by temperature, at lower pressure (4 MPa) and at higher pressure (18 MPa). In both cases, styrene carbonate formation is significantly favoured by temperature increase, which is a common effect already described by other authors [14].

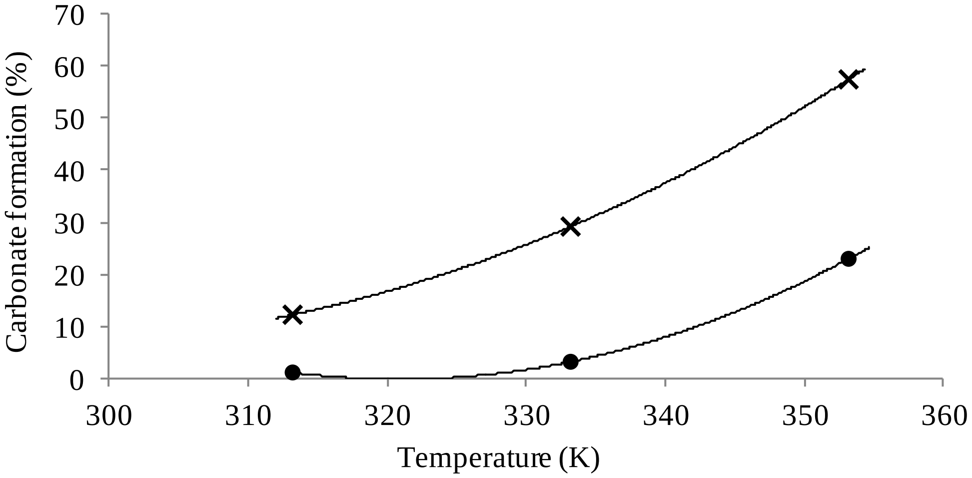


Figure 6. The effect of temperature on styrene carbonate formation for CO_2-rich system (0.2 mL of SO, TBABr 3% mol, 3h) at 4 MPa (x) and 18 MPa (●).

The reaction kinetic was also studied. As presented in Figure 7, at the beginning of both reactions (4 MPa and 18 MPa), styrene carbonate formation percentages were very similar. However, a significant increase of styrene carbonate formation after 3 h was observed for reaction at 4 MPa in respect to reaction at 18 MPa. Indeed, at 18 MPa, the reaction rate was limited not by kinetic but by the rate at which reactants found its way into the catalyst liquid phase, which is a consequence of catalyst liquid phase precipitation. This rate strongly depends on the solubility of CO_2 in the catalyst phase. Finally, several authors have tested the effect of small quantities of additives in the chemical yield of CO_2 cycloaddition to epoxides. For example Zhang *et al.* [38] has reported a significant increase in chemical yield by adding water to the reaction system. In this work, the effect of polyethylene glycols with molecular weight 400 and 1000 g mol^{-1}(PEG400 and PEG1000) and water were tested as additives in an attempt to increase product formation.

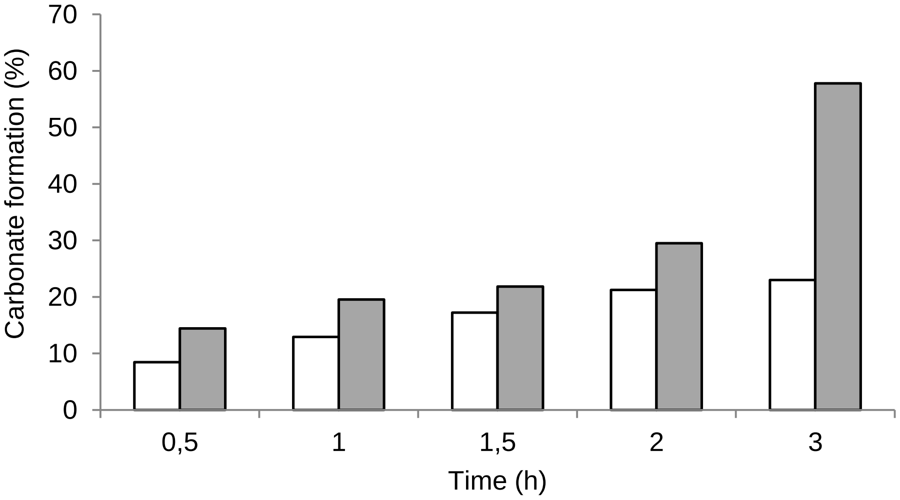


Figure 7. Styrene carbonate formation as a function of time for CO_2-rich system (0.2 mL of SO, TBABr 3% mol, 3h) at 4 MPa (grey columns) and 18 MPa (blank columns) at 353.2 K.

As presented in Figure 8, both PEG 400 and PEG 1000 slightly increased product formation from 23% (without additives) to 31% and 30%, respectively. Water exhibited slightly higher rise of product formation to 33%, which can be attributed to the activation of the epoxide by hydrogen bonding.

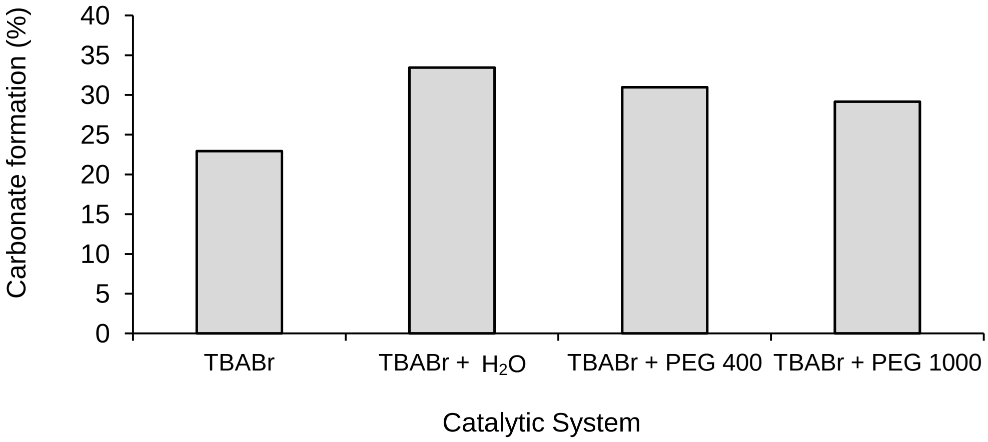


Figure 8. The effect of different additives (2 mL) on styrene carbonate formation for a CO_2-rich system at 18 MPa and 353.2 K.

2.3.2. *TBABr as co-catalyst and Zinc(II) complex as catalysts*

Following the previous results on the use of TBABr as catalyst for the CO_2 cycloaddition to styrene oxide, three different temperatures (313, 333 and 353 K) were investigated at 4 MPa. All reactions were performed for 3 hours, using 3% mol of TBABr and 0.5% mol of Zinc (II) complex, in relation to the epoxide. Results obtained are shown in Figure 9.

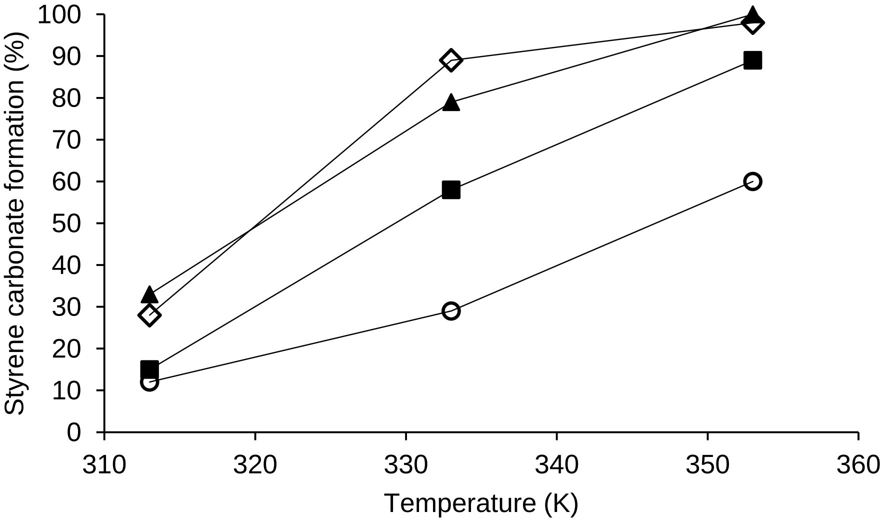


Figure 9. Styrene carbonate formation after 3 hours at 4 MPa, using: 3 % mol of TBABr (○); and 3 % mol of TBABr / 0.5 % mol of complex **1** (▲); 3 % mol of TBABr / 0.5 % mol of complex **2** (■); 3% mol of TBABr / 0.5 % mol of complex **3** (◇).

It is thus clear that Zn(II)-AHBD complexes 1−3 significantly improved the reaction yield, when compared with the catalytic activity of TBABr alone. Among them, Zn(II)-AHBD complex 1 and 3 presented the highest activities, showing a slightly greater percentage of carbonate formation. Another critical factor was the temperature. For all systems, and as already observed by other authors, cyclic carbonate formation is significantly favoured by the increase of that parameter.

As part of our interest in using CO_2 both as reactant and reaction solvent [17, 39, 40], this study was extended to the influence of pressure on the catalytic activity of Zn(II)-AHBD complex 3. Experiments were performed at 353 K for 3 hours, using 3% mol of TBABr and different quantities of Zn(II)-AHBD complex (0.5% mol and 1% mol), in relation to the epoxide. Results are shown in Figure 10. As also noticed in a paper by Taherimehr *et al.* [41], for epoxides such as styrene oxide that readily dissolves the catalyst, there is no advantage in working under high CO_2 pressure. Experimental results presented in Figure 9 show that carrying on increasing the pressure, had an overall negative effect on styrene carbonate formation. Nevertheless, this influence was not observed at all for 1% mol of the Zn(II)-AHBD catalyst. This general pressure negative effect is a result of the reaction mixture separation due to CO_2 addition to the reaction system; as CO_2 pressure increases, the epoxide totally solubilises into the gas phase, precipitating the catalyst.

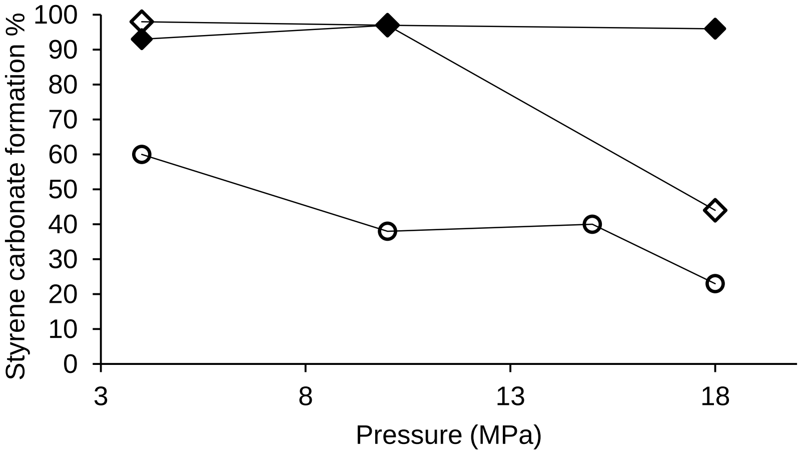


Figure 10. Styrene carbonate formation after 3 hours at 353 K and different pressures, using: 3% mol of TBABr (○); and 3% mol of TBABr+0.5% mol of Zn(II)-AHBD complex 3 (◇); 3% mol of TBABr+1% mol of Zn(II)-AHBD complex 3 (◆).

However, reaction still occurs with relatively good yields, with TBABr/Zn(II)-AHBD complex acting as a heterogeneous (although non-supported) catalyst phase. Experimentally, at 18 MPa it is possible to visualise the catalyst phase through the reactor sapphire window. It consists of a melted TBABr phase in which the Zn(II)-AHBD complex is apparently dissolved. At 353 K and 18 MPa, TBABr precipitates as a melted phase due to well-known melting point reduction effect (under high CO_2 pressure) [42]. These phenomena can be explored for cases in which the catalytic system is not soluble in the substrate, avoiding the use of a harmful organic solvent.

The catalytic activity of Zn(II)-AHBD complex 3 was further tested for two other epoxides, namely, propylene oxide and cyclohexene oxide (Figure 11).

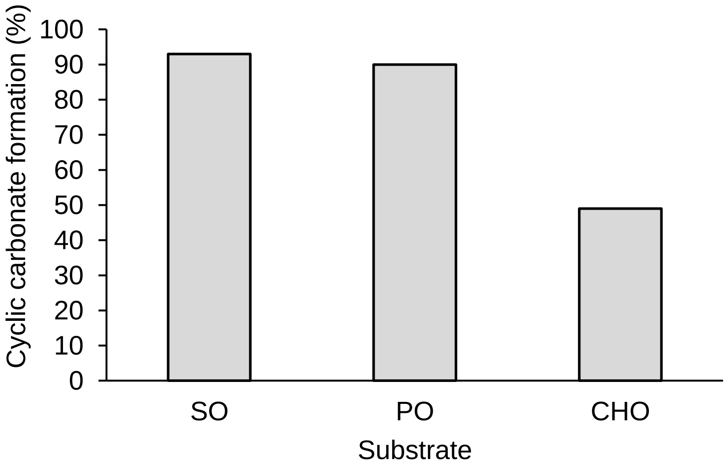


Figure 11. Cyclic carbonate formation after 3 hours at 353 K and 4 MPa, using 3 % mol of TBABr, 1 % mol of Zn(II)-AHBD complex 3. SO: styrene oxide; PO: propylene oxide; CHO: cyclohexene oxide.

For propylene oxide (terminal epoxide), the Zn(II)-AHBD complex 3 presented a similar catalytic activity when compared with styrene oxide, for the same reaction conditions. The catalytic activity of Zn(II)-AHBD complex 3 was however less effective for the case of cyclohexene oxide (internal epoxide). This behaviour is explained by the difficulty posed by the restricted geometry of the cyclohexene ring to the formation of the carbonate ring. It should be noted that internal epoxides are considered much more challenging substrates, due to widely natural occurrence. However, these natural epoxides have proven to be mostly unreactive often requiring high pressures [3].

It is known that the outcome of the coupling reactions between CO_2 and epoxides, besides being considerably affected by temperature, is also very sensitive to the proportion between the components of the catalytic mixture. In particular, the reaction is affected by the nature of the co-catalyst and its ratio with respect to the metal catalyst. Therefore, a systematic study was performed at 353 K and 4 MPa during 3 hours, in order to find out an optimum molar ratio between Zn(II)-AHBD complex 3 and TBABr for styrene carbonate formation (Table 1).

Table 1. Optimization of molar ratio between Zn(II)-AHBD complex 3 and TBABr for styrene carbonate formation. TOFs were calculated based on the amount of Zn(II)-AHBD complex used. Reactions were performed using 0.2 mL of styrene oxide for 3 hours at 353 K and 4 MPa.

TBABr Catalysts (mol %)	Zn(II)-AHBD complex 3 Catalyst (mol %)	Molar ratio Zn/IL (mol %)	Carbonate Formation (%)	TOF (h^{-1})
0.5	0	0.00	9	0
	0.1	0.20	56	186
	0.25	0.50	29	39
	0.5	1.00	7	5
1	0	0.00	52	0
	0.17	0.17	78	153
	0.34	0.34	54	53
	0.5	0.50	44	30
	1	1.00	14	5
2	0	0,00	55	0
	0.34	0.17	55	54
	0.5	0.25	43	29
	1	0.50	32	11
	2	1.00	15	3
3	0	0,00	58	0
	0,5	0,17	98	65
	1	0,33	94	32
	3	1,00	54	6

From Table 1, it is possible to observe that, for all molar percentages of TBABr (0.5%, 1%, 2%, 3%), there was always a specific complex amount yielding the best results. Furthermore, Zn(II)-AHBD complex 3/TBABr molar ratios of around 0.17−0.20 were the ones leading to optimal yields. Additionally, the best balance between reaction yield (% mol) and TOF (h^{-1}) was achieved for 1% (mol) of TBABr. In an attempt to further tune this value, similar reactions were performed reducing the catalyst amount, but maintaining the optimal ratio of 0.17 between Zn(II)-AHBD complex 3 and TBABr.

As can be seen from the results in Table 2 and Figure 12, the best compromise between reaction yield and reaction TOF was achieved for TBABr molar percentages of 0.75 % and Zn(II)-AHBD complex 3 molar percentages of 0.125 %. Under these conditions, the catalyst system is operating at its maximum efficiency, with a reaction yield and reaction TOF of 75 % and 200 h^{-1}, respectively, and presents the highest activity when compared with Zn(II)-AHBD complexes 1 and 2 (Figure 13).

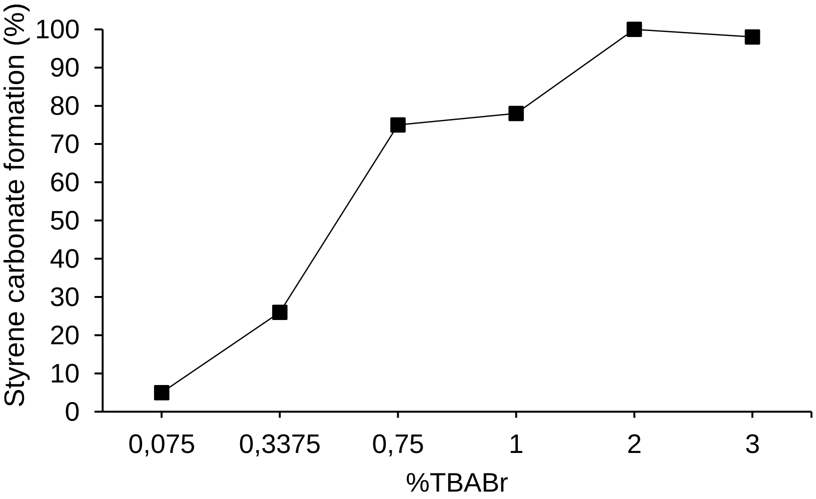


Figure 12. Styrene carbonation formation using different quantities of Zn(II)-AHBD complex 3 and TBABr (SO 0,2 mL). The mol ration was Zn(II)-AHBD complex 3/TBABr=0.17. Reactions were performed for 3 hours at 353 K and 4 MPa. TOFs were calculated using the amount of Zn(II)-AHBD complex used. Note that the dashed line is just showing the tendency of the obtained data.

Table 2. Obtained TOF for the experiments shown in Figure 12. TOFs were calculated based on the amount of Zn(II)-AHBD complex used. Reactions were performed using 0.2 mL of styrene oxide for 3 hours at 353 K and 4 MPa.

TBABr Catalysts (mol %)	Zn(II)-AHBD complex 3 Catalysts (mol %)	Carbonate Formation (%)	TOF (h^{-1})
0.075	0.0125	5	143
0.3375	0.0563	26	154
0.75	0.125	75	213
1	0.17	78	153
2	0.34	100	98
3	0.5	98	65

These results seem to reflect approximately the double number of active metal sites for Zn(II)-AHBD complex 3, showing that the zinc centers retain the catalytic activity in the tetrametallic structure, however a structure-activity relationship study is needed to establish the influence of ligands electronic and steric properties on the reaction TOF.

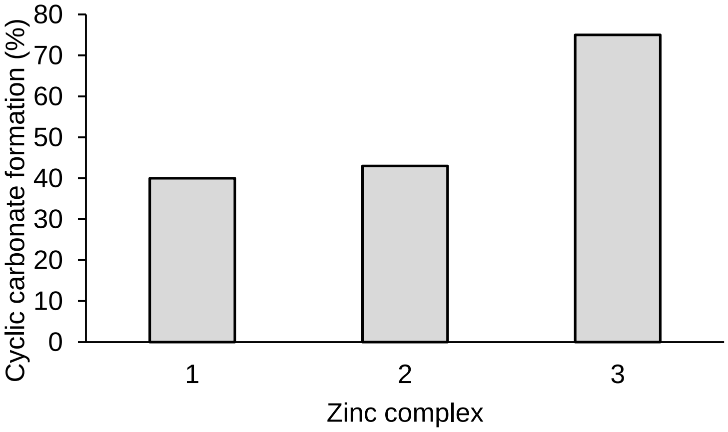


Figure 13. Catalytic activities of different Zn(II)-AHBD complexes, at best reaction conditions. Reactions were performed for 3 hours at 353 K and 4 MPa, using 0,75 % of TBABr and 0.125 % of Zn(II)-AHBD complex (molar percentages in relation to 0.2 mL of SO).

It should be noted that for all conditions studied reaction selectivity toward cyclic carbonate was always >97%. Furthermore there was no detectable catalytic activity in the absence of TBABr, for conditions explored in this work. The observed results for different Zn(II)-AHBD complex and TBABr ratios, allow us to propose a similar mechanism of related reported catalytic systems (Figure 14) [43–45].

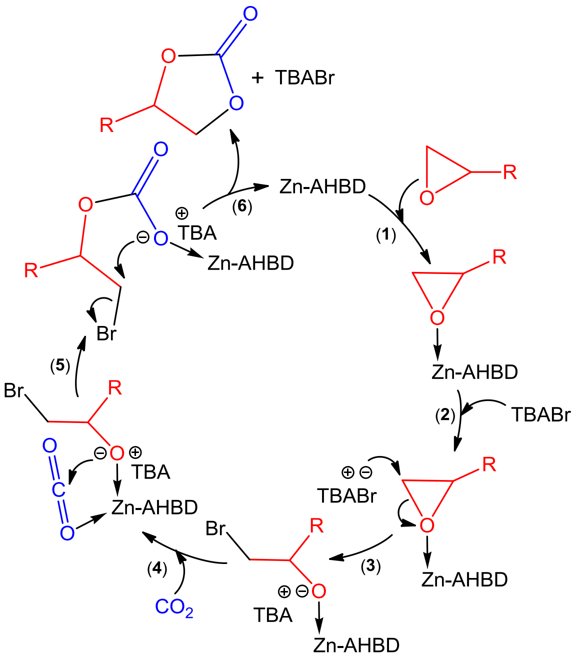


Figure 14. Proposed mechanistic cycle for the coupling reaction of epoxide with CO_2 catalyzed by Zn(II)-AHBD and TBABr.

The mechanism involves the activation of the epoxide by Zn(II)-AHBD complex (step 1) and subsequent ring-opening with bromide of TBABr (steps 2 and 3). CO_2 could then be inserted into the Zn–O bond with ring-closure giving the cyclic carbonate (steps 4, 5 and 6). Nevertheless, further studies are necessary to corroborate this assumption.

The interest in exploring AHBD ligands besides their high air stability and synthetic accessibility, arises from their different molecular conformations upon metal complexation and possibility to easy modulate the environment around the metal center. Indeed, from the point of view of large scale manufacturing, the search for a sustainable and versatile catalyst system continues to challenge scientists in the field [46].

The yields and TOFs for styrene carbonate formation observed in this work were compared with those reported for other zinc homogeneous complexes. A direct comparison between different catalysts is not possible due to differences in experimental conditions, however the Zinc(II) complexes of AHBD ligands used in this work showed encouraging activities in comparison with other catalysts as resumed in Table 3. Besides, temperature, pressure, catalyst loading, kind of co-catalyst and time, the mixture composition is also a relevant parameter [17], which further depends on the volume of the reactor used. It is feasible however, to contextualize yield and TOF values obtained for styrene carbonate formation in this work, taking into account experimental differences from those reported in literature.

Table 3. Comparison of catalytic activity for styrene carbonate formation using homogeneous Zn(II)-AHBD complexes bellow 373.2 K. For comparison, TOF obtained in this work was recalculated per mol of zinc.

Catalyst	Conditions T(K), p(MPa), time (h)	Yield %	TOF (h^{-1})
Zn(II)-AHBD + TBABr (this work)	353.2 K, 4 MPa, 3 h	75	50
Zn- Salphen + TBABI [41]	318.2 K, 4 MPa	86	12
Zn-btsc + TBABI [47]	318.2 K, 1 MPa, 18 h	29	2
Zn-bpb + TBABr [48]	353.2 K, 5 MPa, 20h	27	7

For example, Taherimehr *et al.* [41] reported the use of ZN(II)-AHBD complexes of N,N’-phenylene-1,2-bis-salicylidene (Salphen ligands) as catalyst and TBAI as co-catalyst for the production of cyclic carbonates. Using a monometallic complex structure, the authors attained a styrene carbonate yield of 86%, at 318K and 4 MPa which corresponds to a TOF of 11.5h^{-1}, as well as, a styrene carbonate yield of 90%, at 318K and 1 MPa which corresponds to a TOF 12h^{-1}.

In another work from the same group, Anselmo *et al.* [47] reported the use of Zinc complexes of bis-thiosemicarbazonato (btsc ligands). The authors attained a styrene carbonate conversion of 29% using a monometallic structure and TBAI as co-catalyst, at 318K and 1 MPa which corresponds to a TOF of 1.6h^{-1}. Furthermore, in 2015 Adolph *et al.* [48] reported the use of Zinc complexes based on the N,N-bis-(2-pyridinecarboxamide)-1,2-benzene (bpb ligands) as catalysts for CO_2 cycloaddition to epoxides. The authors attained a styrene carbonate conversion of 27% using monometallic catalyst structure and TBABr as co-catalyst, at 353 K and 5 MPa which corresponds to a TOF of 6.8h^{-1}. In this context, Zinc (II) complexes of AHBD ligands used in this work as catalysts in the CO_2 cycloaddition to epoxides (for the first time) showed encouraging activities, although in some of the cited studies, Zn(II)-based catalysts were used at milder conditions.

2.4. Conclusions

The reaction between CO_2 and styrene oxide for the production of styrene carbonate was investigated at different high pressure phase conditions. The obtained results indicate that the role of phase behaviour is of crucial importance and should be considered for process optimization purposes. For CO_2-rich systems, which are the majority of reported systems in literature, high CO_2 pressures lead to catalyst precipitation. When TBABr is used as the only catalyst, this phenomenon can be explored to shift catalysis, from homogeneous to heterogeneous, simply by tuning operation conditions.

Zinc (II) complexes of arylhydrazones of β-diketones have been used for the first time as catalysts towards the coupling reaction between CO_2 and epoxides. Good catalytic activities and selectivities were achieved at a moderate temperature range of 333-353 K. The reaction requires the use of tetrabutylammonium bromide, but this organic salt can also be used as a liquid heterogeneous support phase for the Zinc metal complex (at high pressures). Furthermore, the four potentially Zinc active sites of complex 3 provided almost the double catalytic activity in comparison with the bimetallic complexes 1 and 2. Although it has been proved that the Zinc metal sites in tetrametallic structure have maintained it catalytic activity, there was no advantage in using a tetrametallic instead of bimetallic (for the conditions studied in this work). Nevertheless, the high stability and ease of preparation of these kinds of Zinc complexes make them good candidates for large scale cyclic carbonate production.

2.5. References

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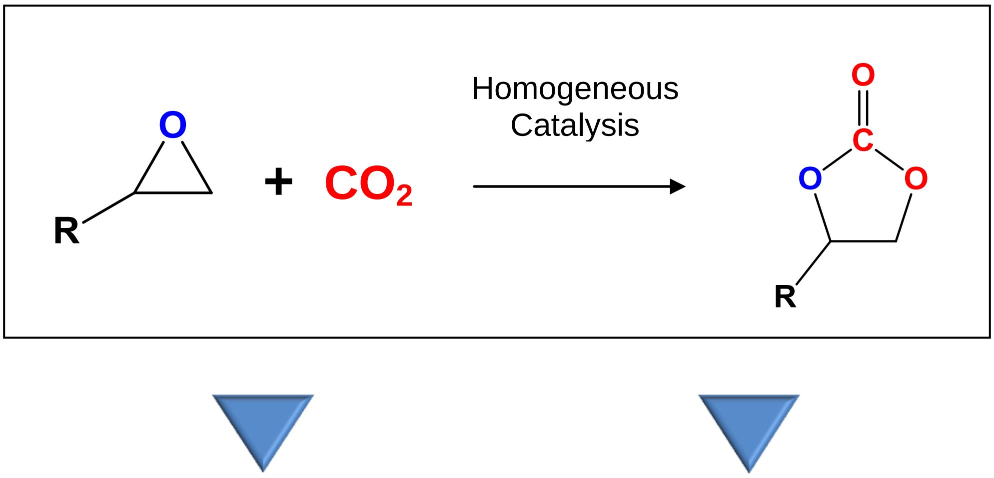
Chapter 3

CO_2 + ionic liquid biphasic system for reaction/product separation in the synthesis of cyclic carbonates from CO_2 and epoxides using Zn(II) complexes of arylhydrazones of β-diketones



IL as co-catalysts

IL as solvents

Successful systems reported, often include the presence of a homogeneous metal complex in combination with an ionic salt, usually tetrabutylammonium bromide. The role of ionic liquids (ILs) on the cycloaddition reaction between CO_2 and epoxides was studied. Different ILs combined with a Zinc (II) complex of arylhydrazone of ß-diketones (Zn(II)-AHBD), were explored as co-catalysts and/or as solvents, for the production of propylene carbonate from CO_2 and propylene oxide. As co-catalysts, different combinations between task-specific anions and cations were evaluated. Furthermore, several commercial room temperature ionic liquids (RTILS) were applied as reaction solvents and results correlated with their hydrophilicity, except for [Aliquat Cl] that acted both as solvent and reaction catalyst.

The possibility of using supercritical CO_2 ($scCO_2$) technology as a second step for extracting propylene carbonate produced from the coupling reaction between propylene oxide and CO_2, was also investigated. ALIQUAT Cl was selected as the most promising solvent and $scCO_2$ extraction was effectively applied as a second step to isolate propylene carbonate from the catalyst system. Following this strategy, the catalyst system was reused three times, without loss of activity.

The results present in this Chapter were published in The Journal of Supercritical Fluids 132 (2018) 71–75. Ana B. Paninho was involved in part of the experimental work and discussion of the results together with Alexandre L.R. Ventura.

Chapter 3

3.1. Introduction

Carbon dioxide ($CO_{2)}$ has been widely explored as feedstock for the production of cyclic carbonates [1]. In recent years, the importance of this topic has grown significantly due to the belief that being a versatile molecule, cyclic carbonates, may become a platform to introduce CO_2 as a renewable feedstock into different areas of the chemical industry. Indeed cyclic carbonates are already in use as polar aprotic solvents, fuel additives, electrolytes for lithium batteries, fine chemicals intermediates as well as monomers in the production of polymers [2].

One of the most attractive routes for the production of cyclic carbonates is the atom economic coupling reaction between CO_2 and highly energetic epoxides [3, 4]. General accepted mechanism involves the epoxide ring-opening by a nucleophile and the CO_2 insertion followed by an intramolecular backbiting to cyclic carbonate formation and catalyst regeneration. Ionic liquids (ILs) have been widely described as playing an important role as catalysts in this reaction, with the anion being responsible for the nucleophilic attack to the epoxide ring and the cation for the stabilization of the ring-opened alkoxide intermediate [5].

Different families of ILs have been investigated and several reviews have extensively discussed the effect of different cations and anions in the reaction yield and selectivity [6-12]. It is current knowledge that halides are the most active anions, due to their strong nucleophilic character. The activity depends on both the nucleophilicity and leaving group ability in the order $I^- > Br^- > Cl^- > F^-$. Furthermore it is well known that the cation has determinant influence on the anion reactivity. Bulky cations keep the anion away from the centre of the structure, exhibiting weaker electrostatic interactions, which leaves the anion more available for the nucleophilic attack [13-15]. Nevertheless, in some cases, completely opposite behaviours were observed, as additional factors have to be considered. For example Zhang and co-workers [16] showed that the presence of water improved the activity of various onium salts but also changed anion reactivity. The activity of anions varied in the order $I^->Br^->Cl^->PF_6^->BF_4^-$ in the presence of water, while it was $Br^->Cl^->I^->PF_6^->BF_4^-$ without water. Also Endo and co-workers [17] observed that the nature of the solvent had a significant effect on the catalyst performance. Protic solvents such as 1-methoxy-2-propanol proved to be more suitable, which was attributed to the activation of the epoxide by hydrogen bonding. Finally, the substrate itself may be the cause of different behaviours observed. Indeed, for more sterically crowded epoxides some authors reported an increase activity of Cl^- in comparison with Br^- due to smaller stearic hindrance of Cl^- than Br^- [18].

Furthermore, when ionic liquids are used together with homogeneous metal complexes, substantial higher catalytic activities are observed [3,4]. It was reported that due a synergetic effect, various cyclic carbonates are produced from corresponding epoxides even at room temperature with good yields [9]. The epoxide coordinates to the Lewis acidic metal centre, significantly facilitating the halide ring opening step. Theoretical density functional theory (DFT) calculations have determined considerably lower energy barriers which may be crucial if one wants to explore less reactive epoxides [19]. Most efficient reported ligands on the metal centres are usually salen [20], salphen [21], amino phenolate [22] and porphyrins [23]. When metal complexes are used possible interactions between metal centre and ionic liquids might have to be considered, moreover the IL ratio with respect to the metal catalyst dramatically influence the outcome of the reaction [24].

One popular strategy, regarding homogeneous catalyst reutilization relies on catalyst retention by using a CO_2/ionic liquid (IL) biphasic system [25]. It consists in retaining the catalyst in the IL stationary phase inside the reactor, while products are transported out of the reactor by a mobile CO_2 supercritical phase. The aim is to effectively separate the products from the reaction mixture and extend the use of the catalyst increasing the catalyst's turnover number (TON) [26]. Actually, the combination of CO_2 with ILs have drawn a lot of attention, since ILs are not soluble in CO_2, while CO_2 presents a high affinity and dissolves very well in several ILs. Furthermore, the presence of CO_2 often decreases IL's viscosity considerably improving mass transfer, which favours reaction kinetics [27]. Several examples in literature report successful CO_2/ILs biphasic systems used for product separation, catalyst retention and reutilization.

As part of our on-going interest in using Zinc(II) complexes of Arylhydrazones of β-diketones (Zn(II)-AHBD) as homogeneous catalysts for the coupling reaction between CO_2 and epoxides [28], the effect of different ionic liquids as co-catalysts were investigated and also the possibility of using scCO_2 for product extraction followed by catalyst reutilization using an ionic liquid as solvent.

3.2. Experimental Section

3.2.1. Materials

All chemicals and solvents were used as received without further purification. Carbon dioxide (99.998 mol % purity) was supplied by Air Liquid. Zn(II)-AHBD complex 3 was synthesized as previously reported [29] (Figure 1). The other ILs were synthesized by Solchemar Lda. Compounds ([N1,1,2,2OH]Br) and ([N1,6,2,2OH]Br) were synthesized in FCT-UNL, Lab 4.10 by Andreia Forte [30].

Propylene oxide (99.5% purity), Tetrabutylammonium bromide (TBABr) (≥ 98% purity), Methyl ethyl ketone (MEK) (≥ 99.50% purity), Polyethylene glycol (PEG), Ethyl lactate (≥98% purity), 1-Ethyl-3-methylimidazolium ethyl sulfate ([EMIm][EtSO$_4$]) (≥ 95% purity), 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm][NTf$_2$]) (≥ 97% purity), 1-Ethyl-3-

methylimidazolium bromide ([EMIm][Br]) (≥ 97% purity), 1-Ethyl-3-methylimidazolium tetracyanoborate ([EMIm][B(CN)$_4$]) (≥ 97% purity), Trioctylmethyl ammonium chloride ([ALIQUAT][Cl]) (≥95% purity), Bis(triphenylphosphine)iminium chloride (PPNCl) (≥ 97% purity), Tetrabutylammonium bromide ([TBA][Br]) (≥ 98% purity), Tetrabutylammonium chloride ([TBA][Cl]) (≥ 97% purity) were purchased from Sigma Aldrich.

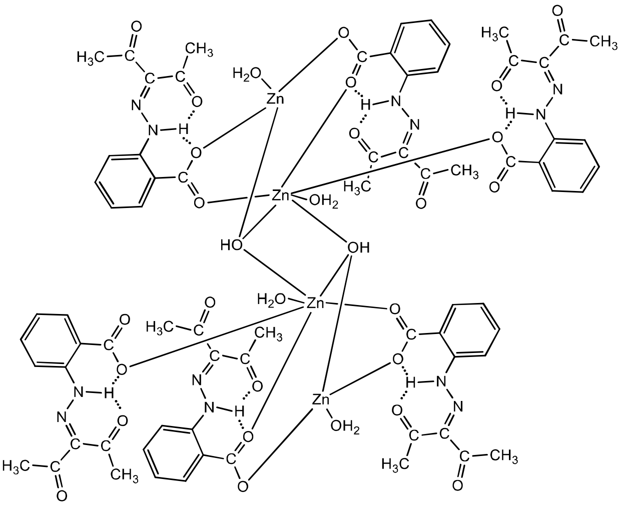


Figure 1. Zinc(II) complex of arylhydrazones of β-diketones (complex 3).

3.2.2. Methods

3.2.2.1. CO$_2$ coupling reactions with epoxides

Coupling reactions between CO$_2$ and epoxides were carried out in a high-pressure apparatus as earlier described [31, 32]. The apparatus is composed by a stainless steel small cylindrical reactor with a volume of approximately 11 cm^3. Two sapphire windows at the top and bottom of the reactor allow the visualization of the entire reactor volume. Reaction procedure was initiated by the loading of the reactor with solvent (1 mL when used), epoxide (1 mL), metal catalyst, TBABr, and a magnetic stirring bar. The reactor was then immersed in a thermostated water bath heated by means of a controller that maintained temperature within ± 0.1 ºC. The required CO$_2$ pressure was introduced into the reactor by operating a CO$_2$-compressor. Pressure was measured with a pressure transducer 204 Setra calibrated between 0 MPa and 34.3 MPa (precision: 0.1%; accuracy: 0.15%, at the lowest pressure). At the end of the reaction, the high pressure reactor was very slowly depressurized to atmospheric pressure into a glass trap immersed in an ice bath. Afterward, the reactor was opened and the contents collected using 1 mL of chloroform, to dissolve the reaction mixture. Both contents of the reactor and glass trap were mixed and prepared for further analysis.

3.2.2.2. *Supercritical CO_2 extraction of final product*

Extraction experiments were performed using the same high pressure apparatus described in section 4.2.2.1, with some modifications.

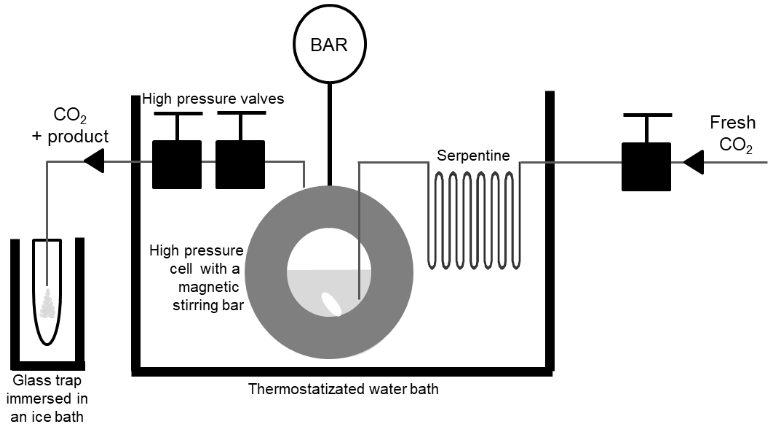


Figure 2. Scheme illustrating the experimental apparatus used for the supercritical CO_2 extraction of the final product (cyclic carbonate) from the reaction mixture (ionic liquid + binary catalytic system).

The CO_2 inlet tube was extended through a serpentine that was immersed in the water bath to allow the CO_2 to be heated before entering the reactor. The tube was connected to the reactor in such a way that the end of the tube was immersed in the reaction mixture as can be observed in Figure 2. At the outlet of the reactor, two high-pressure valves were connected at the top of the reactor, and further connected to a glass trap immersed in an ice bath. The two high-pressure valves were slowly released and manipulated to control the CO_2 flow and maintain constant the pressure inside the system. Extraction experiments were carried out at 353.2 K and 11.5 MPa, during approximately 3 h.

3.2.2.3. *Analytical method*

For analytic purposes, a sample of the reaction mixture or of the extracted product, was transferred into a NMR tube, to which chloroform-d_1 was added. ^{1}H-NMR spectra were recorded on Bruker 500 MHz type (400 MHz). Peak frequencies were compared against solvent, chloroform-d_1 at 7.26 ppm. The carbonate formation was determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture. The calculations were made using the signals from the epoxy groups and from the cyclic carbonate groups. Errors in the carbonate formation measurements were estimated by comparing the results of at least 3 integrations of each spectrum. The error introduced into the final results was lower than 10%. Please note that the selectivity for cyclic carbonate products in all cases was determined to be >99%.

Reaction Turnover number (TON) were calculated by dividing the molar percentage of cyclic carbonate produced (CC) by the molar percentage of metal catalyst used (Zn(II)-AHBD).

3.3. Results and Discussion

3.3.1. High Pressure Reactions

Following our interest in the use of Zn(II)-AHBD complexes as catalyst for the CO_2 cycloaddition to epoxides, in this work propylene oxide was used as a model substrate to investigate the effect of different ionic liquids in the reaction kinetics. Primary reactions were performed in neat propylene oxide using different quantities of Zn(II)-AHBD complex 3 and TBABr (the most used ionic liquid). All reactions were performed at 4MPa for 3 hours. The effect of pressure was first investigated at different temperatures (323.2 K and 353.2 K). Results are presented in Figure 3.

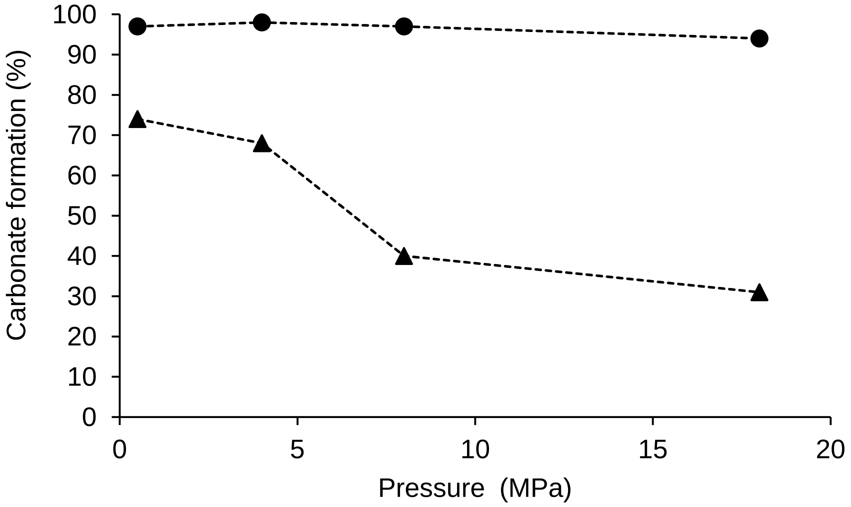


Figure 3. Propylene carbonate formation as a function of pressure under solvent-free conditions, after 3 hours of reaction for different temperatures: 353.2 K (●); and 323.2 K (▲). 0.25% Zn(II)-AHBD complex 3 and 1% TBABr were used (molar percentages in relation to substrate).

As observed earlier by us [28, 31] and also by other authors [3], pressure has an overall negative effect on the reaction kinetic. This effect is mostly related with the high solubility of CO_2 in the organic substrate, which increases with pressure, causing liquid expansion followed by catalyst precipitation with a negative effect on the kinetics. Furthermore, the solubility of CO_2 in the liquid phase decreases with temperature, which is consistent with the non-visualization of this phenomenon at 353.2 K.

The same behaviour has been observed for reactions carried out at milder conditions, as observed in Figure 4. At room temperature (RT), the pressure negative effect was very marked. Nevertheless, the catalytic system under investigation has confirmed to be active under very mild conditions as room temperature and around 0.5 MPa.

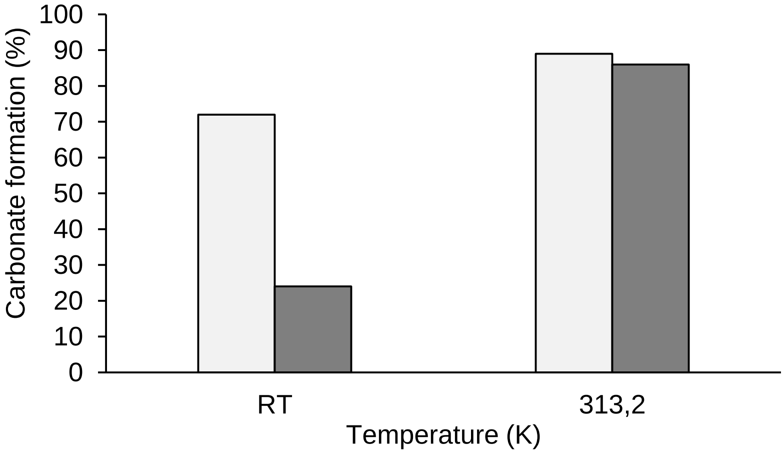


Figure 4. Propylene carbonates formation after 24 hours at room temperature (293.2 K) and 313.2 K, at different pressures: 4 MPa (light grey columns) and 0.5 MPa (dark grey columns). 0.25% Zn(II)-AHBD complex 3 + 1% TBABr were used (molar percentages in relation to substrate).

The same behaviour have been observed for reactions carried out at milder conditions, as observed in Figure 4. At room temperature (RT), the pressure negative effect was very marked. Nevertheless, the catalytic system under investigation has confirmed to be active under very mild conditions as room temperature and around 0.5 MPa.

Figure 5 shows the effect of Zn(II)-AHBD complex 3 on the reaction kinetics. In fact for 353.2 k it is possible to observe that the reaction proceeds even in the absence of a metal complex. However, the addition of only 0.05% mol, drastically increase propylene carbonate formation from 25% to 95%.

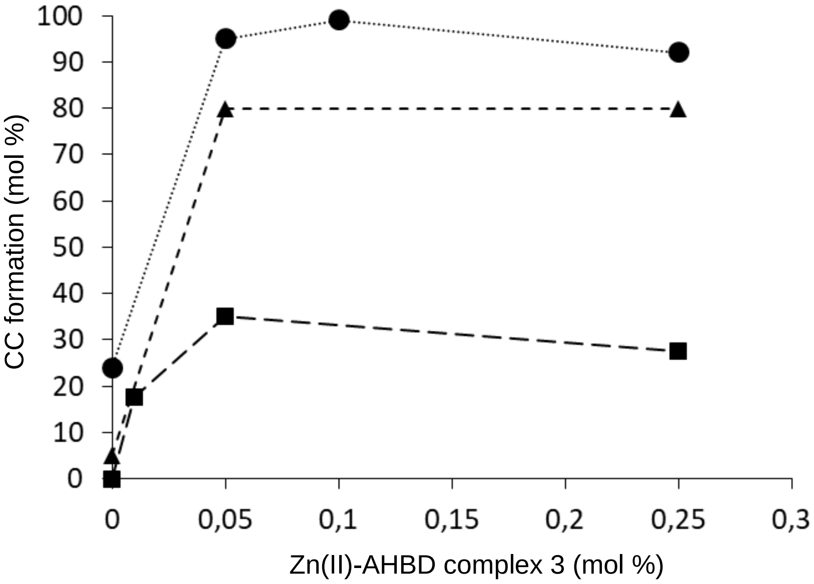


Figure 5. Cyclic Propylene carbonate formation as a function of molar percentages of Zn(II)-AHBD complex 3 for 1%(mol) of TBABr, 4 MPa, 3 hours and different temperatures: 353.2 K (●); 333.2 K (▲) and 313.2 K (■). Molar percentages were calculated in relation to substrate.

On the other hand for lower temperatures the need for a metal catalyst is crucial, as for example at 313 K the reaction does not proceed without the presence of Zn(II)-AHBD. Moreover, an increase in the amount of metal catalyst in relation to [TBA]Br, increases cyclic carbonate formation, although a maximum seems to be reached, after which there is no advantage in increasing the quantity of metal complex. This behaviour was earlier observed by us and is related with the importance of metal/nucleophile ratio also reported by other authors [28].

Figure 6 shows the effect of increasing [TBA]Br molar percentage, for a fixed quantity of Zn(II)-AHBD. It is possible to conclude that the reaction simply does not proceed without the presence of the ionic liquid for all selected temperatures. Also, the increase of the [TBA]Br molar percentage showed a positive effect on the reaction kinetics.

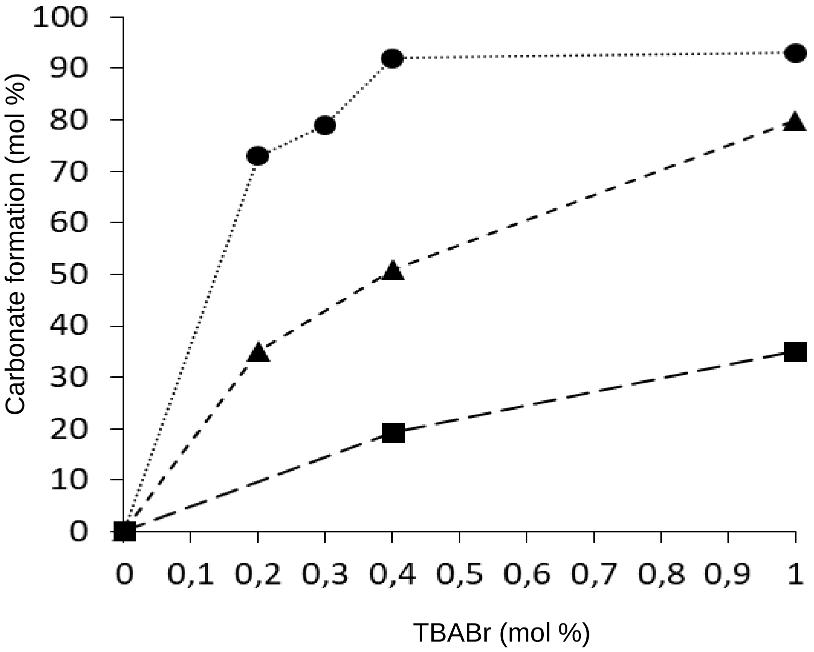


Figure 6. Propylene carbonate formation as a function of molar percentages of TBABr for 0.05%(mol) of Zn(II)-AHBD complex 3, 4 MPa, 3 hours and different temperatures: 353.2 K (●); 333.2 K (▲) and 313.2 K (■). Molar percentages were calculated in relation to substrate.

These results highlight the involvement of [TBA]Br in the rate-determining reaction step that is the opening of the epoxide ring. In parallel, the metal complex considerably facilitates this reaction step, by lowering the activation energy, although it does not catalyse this reaction alone. This observation can justify why for a fixed amount of [TBA]Br, there is a limit after which there is no advantage in increasing of the metal complex concentration. These results are in accordance with the most general accepted reaction mechanism in which the metal complex activates the epoxide, facilitating the ring opening step by the nucleophile.

The effect of different anions and cations on propylene carbonate formation was also studied. Figure 7 illustrate the direct comparison between the most common used anions (Br^- versus Cl^-) and cations (quaternary ammonium versus imidazolium).

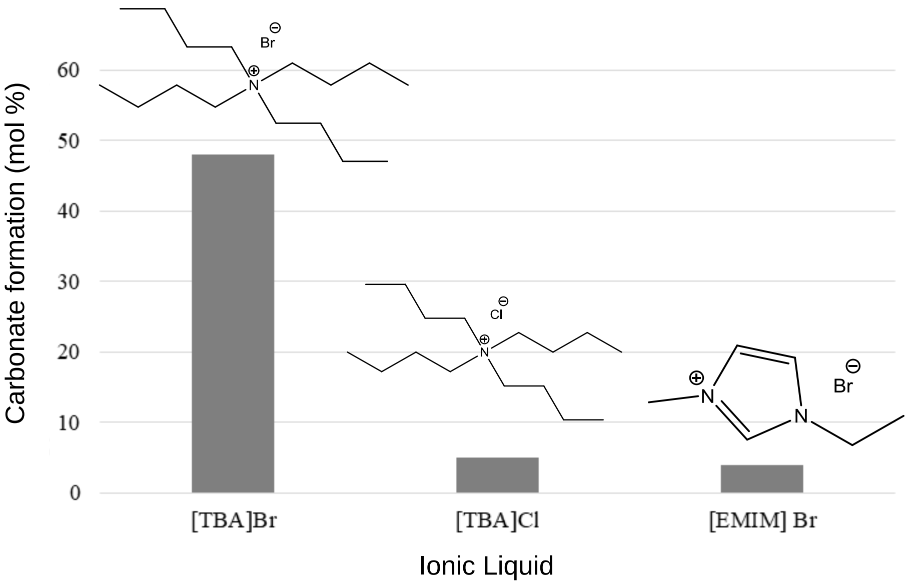
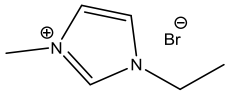
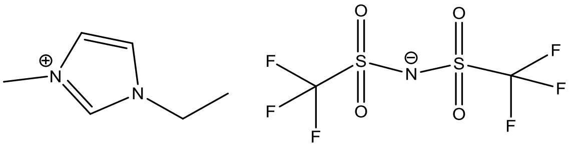
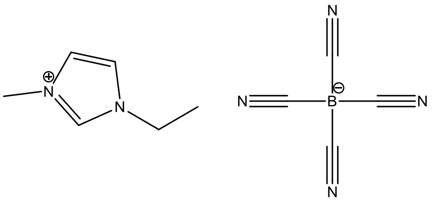
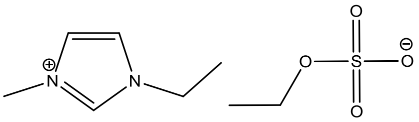


Figure 7. Propylene carbonate formation with different ionic liquids as co-catalysts, using 0.05% (mol) Zn(II)-AHBD complex 3 and 0.4% (mol) Ionic liquid, during 3 hours of reaction for a temperature of 333.2 K and pressure of 4 MPa. Molar percentages were calculated in relation to substrate.

It is observed a very significant difference comparing the catalytic performance of [TBA]Br and other salts. It is clear that bromide is a better nucleophile as well as leaving group than chloride, which favours the formation of cyclic carbonate. Between the cations used, [TBA] is considerable bulkier pushing the bromide away from the centre of the structure, leaving it more available for a nucleophilic attack on the epoxide. On the other hand, [EMIM] structure allows the stabilization of the charge due to the ionic bonding between species. The strength of ionic bond between the planar five-member ring [EMIM] and bromide is stronger than the interaction between [TBA] and bromide. These results are in accordance with behaviours reported for coupling reactions between CO_2 and epoxides using other metal complexes. Furthermore, for the same imidazolium cation [EMIM], other non-halogenated anions were tested as [NTf_2], [$B(CN)_4$] and [$EtSO_4$] without success.

Table 1 illustrates the effect of the cation using chloride as the anion for different ionic liquids in the coupling reaction. As can be observed in table, although all ionic liquids showed very low conversions, both bis(triphenyphosphine)iminium chloride [PPN][Cl] and tetrabytlyammonium chloride [TBA][Cl] were distinguish by presenting a detectable formation of cyclic carbonate. Indeed, very low similar conversions were obtained for [TBA][Cl] and [PPN][Cl] very likely due to their bulkiness when compared to the other investigated cations.

Table 1. Anion interference as co-catalyst in the coupling reaction with 0.05% of Zn(II)-AHBD complex 3 and 0.4% of co-catalyst, at 333 K, 4 MPa, 3 h.

[EMIm][X]	CC Formation (%) [a]	Ionic liquid structure
[EMIm][Br]	6%	
[EMIm][NTf_2]	0%	
[EMIm][$B(CN)_4$]	0%	
[EMIm][$EtSO_4$]	0%	

[a] Cyclic carbonate formation determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture.

Based on the fact reported in the literature that hydroxyl-functionalized ionic liquids show increased catalytic activity due to epoxide activation through hydrogen bonding, the effect of two functionalized tetra-ammonium salts was explored as indicated in Figure 8.

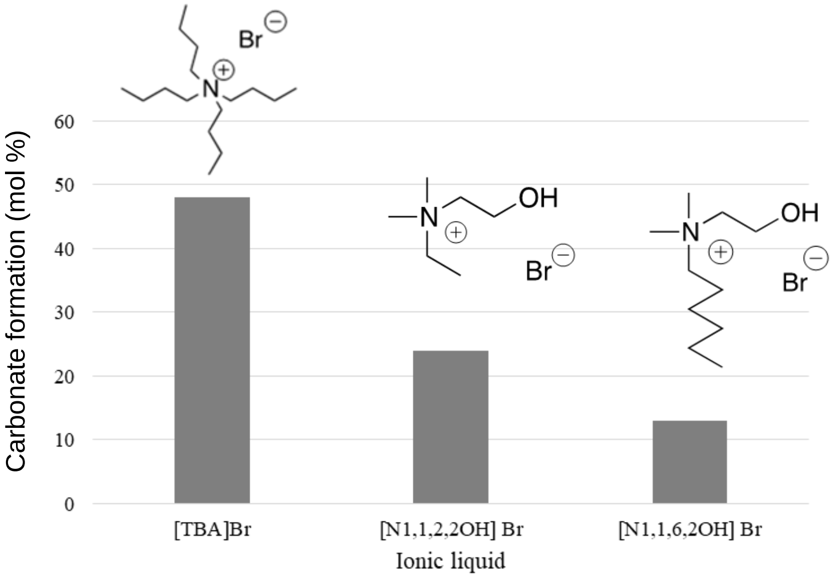


Figure 8. Propylene carbonate formation using different ionic liquids as co-catalysts (0.4% mol of Ionic Liquid), combined with 0.05% (mol) Zn(II)-AHBD complex 3, after 3 hours of reaction for different a temperature of 333.2 K and 4 MPa. Molar percentages were calculated in relation to substrate.

For the two functionalized ionic liquids studied ([N1,1,2,2OH]Br and [N1,1,6,2OH]Br), lower conversions were obtained. The difference between both ionic liquids is the presence of hexyl unit for [N1,1,6,2OH]Br, which contrasts with the presence of ethyl group for [N1,1,2,2OH]Br. Better results for the cation with ethyl group can be explained by the steric hindrance that exists in the six carbon chain structure, which difficult the activation of the epoxide via hydrogen bonding with the oxygen of the epoxide ring. On the other hand when compared with the non-functionalized ionic liquid, it turns out very clearly that it is again the bulkiness of the cation (in this case that results from the four butyl groups from [TBA]) that by affecting the nucleophile reactivity, stands as the most important factor to consider, supplanting the potential epoxide activation.

3.2.2. High pressure reactions using a solvent

In order to explore the possibility of using ILs as reactions solvents, several room temperature ionic liquids (RTILs) were investigated as reaction media for the reaction. Table 2 summarizes the results obtained with different selected ionic liquids.

Table 2. Effect of different ionic liquids (1 mL) as solvents in the coupling reaction between CO_2 and PO using 1 mL of substrate, with 0.25% mol of Zn(II)-AHBD complex 3 and 1% mol of TBABr, at 333 K, 4 MPa, 3 h.

Ionic Liquid	CC Formation (%) [a]
[EMIm] [$B(CN)_4$]	10
[EMIm] [$EtSO_4$]	20
[EMIm] [Otf]	10
[BMIm] [Otf]	15
[BMIm] [Ntf_2]	10
[Aliquat] Cl *	30
[Aliquat] Cl **	15

[a] Conversion determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture.

* Results published by us in an earlier work [26] and presented here for comparison.

** Reaction performed without adding catalysts.

The catalytic performance indicated in Table 2 is in agreement with the hydrophilicity of the tested ionic liquids. Among three [EMIM] based ionic liquids ([EMIM] [X]; X=$B(CN)_4$,$EtSO_4$,TfO); [EMIM] [$EtSO_4$] as the most hydrophilic, showed the best result of 20% of cyclic carbonate formation. Similar behaviour was observed comparing the performance between Otf and NTf_2, [BMIM][NTf_2] again the most hydrophilic IL gave the best results. Finally, [Aliquat]Cl possessing a more hydrophobic cation give one of the best results. In addition, this later is composed of the chloride anion which may favour the reaction kinetics by interfering in the reaction. This possibility was confirmed by performing a reaction without the addition of catalysts that showed that [Aliquat]Cl acts both as solvent and reaction catalyst.

3.3.3. High Pressure Reactions followed by product extraction and catalyst reutilization

A set of three experiments (reactions, followed by product extraction) were performed using [Aliquat][Cl] as the reaction solvent and $scCO_2$ as the extraction solvent for product recovery. Reactions were performed at 353.2 K, 4 MPa, for 3 hours. Subsequent extractions were also performed at 353.2 K and 11.5 MPa for more 3 hours. For these sequential experiments, the overall process yield was calculated by weighting the product recovered in each cycle and comparing with the substrate initially introduced into the reactor. Zn(II)-AHBD complex 3 + TBABr catalyst system was reused 3 times. Results are presented in Table 3.

Table 3. Yields and cumulative reaction TONs obtained in catalyst recycling experiments for propylene oxide coupling reaction with CO_2 at 353.2K, 4MPa and 3 hours. 1 mL Aliquat Cl, 0.25% Zn(II)-AHBD complex 3 + 1% TBABr were used (molar percentages in relation to substrate). Reactions were followed by product extraction at 353.2K and 11.5MPa during 3 hours.

Cycles	Overall yield (%)	TON
1	48	192
2	60	434
3	53	644

The ionic solvent selected ([Aliquat][Cl]) was effective in solubilising and retaining the catalyst system inside the reactor. On the other hand, both propylene carbonate produced and unreacted propylene oxide, were extracted using supercritical CO_2. However, due to high volatility difference, product and substrate were separated during continuous CO_2 flow depressurization and temperature decrease. Propylene carbonate precipitated and was recovered in the glass trap immersed in an ice bath, whereas the highly volatile propylene oxide was dragged with CO_2 out of the system. ^{1}H-NMR analysis demonstrated that the product was recovered completely free of solvent, catalyst and substrate. This procedure allowed catalyst reutilisation for 3 times, without loss of activity and with good reproducibility.

3.4. Conclusions

In this work the synergistic catalytic effect between Zn(II)-AHBD and different ionic liquids was investigated. The combination between anions and cations from ILs can influence the reaction performance. It is clear that bromide is the best anion and [TBA] the most active cation from all of our examples. Detailed studies showed a significant effect of Zn(II)-AHBD in lowering the activation energy by coordination with epoxide. The design of new task-specific ILs inspired in the adequate combination between bromide as anions and tetra-alkylammonium can be very promising. Several ionic liquids were also explored as reaction media where [Aliquat]Cl showed the best results but clearly acting both as solvent and catalyst due to the presence of the chloride anion.

Beside that a high-pressure CO_2/[ALIQUAT][Cl] biphasic mixture was successfully used to carry out the CO_2 cycloaddition reaction with propylene oxide. [ALIQUAT][Cl] presented superior results in comparison with [EMIm][$EtSO_4$], very likely due interference of the chloride anion as nucleophile in the reaction catalysis. In order to reuse the catalyst system, propylene carbonate extraction was performed using supercritical CO_2 extraction step at 353.2 K and 11.5 MPa for 3 hours. [Aliquat][Cl] was effective in solubilising and retaining the catalyst system inside the reactor. Propylene carbonate was recovered completely free of solvent, catalyst and substrate. The catalyst system was reused three times, without loss of activity and with good reproducibility.

3.5. References

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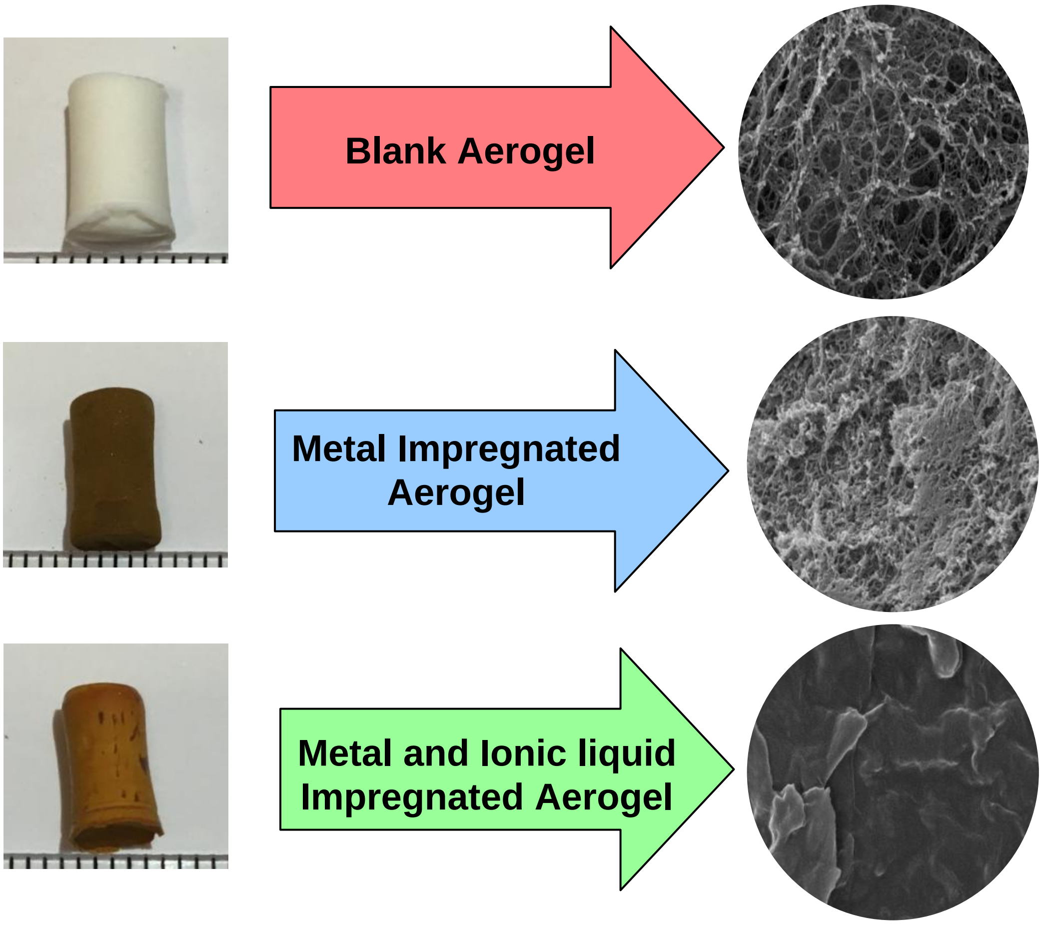
Chapter 4

Addressing the Advantage of Using a Supported Ionic Liquid Phase (SILP) on the Coupling Reaction between CO_2 and Epoxides



In this chapter the method of deposition of catalyst solutions on the surface of porous aerogels via wet impregnation was explored for the preparation of alginate structures supporting a Zinc complex-ionic liquid phase. This procedure originates a well-defined thin solvent film on the surface of support materials, which provide high catalyst accessibility. Final materials were characterised by Fourier Transform Infrared Spectra, N_2 Adsorption-Desorption Analysis, X-ray diffraction, Atomic Absorption and Field Emission Scanning Microscopy. Several catalytic tests were performed in a high-pressure apparatus and final products analysed by ^{1}H-NMR spectroscopy. The effect of CO_2 pressure on the reaction kinetic is discussed.

Chapter 4

4.1. Introduction

Ionic liquids (IL) have been widely used as organic catalysts for the cycloaddition reaction between CO_2 and epoxides showing appreciable performances, as presented in the previous Chapters. In fact the possibility of developing a metal-free catalytic process has attracted a high interest from the green chemistry point view [1]. However, other issues are also important to evaluate and have to be taken into account, as catalyst reutilization and the possibility of further converting the process into continuous flow mode. Regarding continuous flow processes using ionic liquids as solvents and/or catalysts, several works have been focusing on their utilization covalently attached or physically adsorbed onto solid materials suitable for fixed bed operations. This approach is also known as Supported Ionic Liquid Phase (SILP) catalysis and although the resulting material is indeed a solid, the active species (e.g metal complexes) are usually dissolved in the ionic liquid phase acting as homogeneous catalysts [2].

SILP brings together advantages of both homogeneous (high rates and good selectivity) and heterogeneous (easy separation, recyclability and continuous operation) catalysis [3, 4]. With this technology is possible to reduce the quantity of IL used, retaining their properties [5]. The SILP concept results in a more efficient and economic use of the IL, because of relatively short diffusion distances for the reactants compared to the conventional biphasic reaction systems, where generally a large amount of IL is required [6]. Furthermore, ILs negligible vapour pressure, large liquid range and high stability ensure that the IL remains on the support in its fluid state even at elevated temperatures; this makes SILP particularly suitable for continuous processes [5, 7]. Over the last decade, SILPs have been used in different applications, namely as supports of catalysts, surface modifying agents, stationary phases in separation technologies, and electrodes in electrochemistry [8, 9].

The immobilization of IL on porous support material can be achieved by two different methods: chemical bonding to the support of one of the ions that compose the IL or physisorption via van der Waals and dipole forces [9]. Although physisorption is an easier method of preparation, the IL film can be more susceptible to be removed from the support, especially if polar solvents are used like in a liquid-liquid biphasic system [10]. SILP materials can be prepared from a broad range of ILs at loads varying from 5 to 60% (w/w) [11]. A variety of support materials can be chosen, with alumina [12], silica [13], titania [14] or active carbon [15] among the most commonly used.

The combination of supercritical carbon dioxide ($scCO_2$) as the mobile phase with SILP is particularly attractive as it allows developing a practicably “solvent-free” process. These systems are based on the fact that CO_2 have high solubility in most ILs, while ILs are insoluble in CO_2.

Cole Hamilton and co-workers have applied the first SILP continuous flow system with supercritical CO_2 transport in the hydroformylation of 1-octene into aldehydes [16]. SILPs with different IL loadings of 14 wt%, 29 wt% and 44 wt% supported on silica gel provided high reaction rates for all cases with near no dependence on the IL loading. The authors concluded that the supercritical transport provided excellent diffusion of the substrate into the catalyst in such a way that transport diffusion was no longer the rate limiting step (as happens in other SILP processes). This was an important advantage brought by the use of supercritical CO_2 to homogeneous catalysis and after the work of Cole-Hamilton, several papers were published reporting successful applications of SILP processes with supercritical transport. For example Leitner and co-workers have applied this approach to the enantioselective hydrogenation of dimethyl itaconate by using a chiral transition-metal catalyst supported ionic liquid phase [17]. SILP materials with IL loadings of 45 wt% were prepared using dehydroxylated silica as support. The utilization of $scCO_2$ flow mobile phase allowed developing a fully integrated process with product separation, which allowed obtaining the pure product without the need for any organic solvent.

In fact most published works developing successful SILP processes using $scCO_2$ as the mobile phase were specifically applied for reactions in which one of the reactants is a gas. On the context of our interest in the utilization of CO_2 as a reactant in cyclic carbonates formation we have foreseen that this methodology should be particularly advantageous for processes in which CO_2 is used both as reactant and solvent. Curiously and to the best of our knowledge, there is only one report in the literature exploring $scCO_2$ together with SILP supported on SiO_2, as catalyst for the cycloaddition reaction between CO_2 and epoxides [18]. The SILP material was prepared with an ionic liquid ($[C_4mim][BF_4]$) loading of 20%wt and was used in a batch reactor at supercritical conditions (T= 160^oC, P=8 MPa). Good reaction yields (> 85%) and selectivities (> 97%) were attained. Based on the observation that the reaction product, propylene carbonate, precipitates out of the supercritical phase as it forms, the authors stated that this procedure could be applied to the development of fixed-bed continuous flow reactors, avoiding the use of organic solvent to isolate the products. However, this is actually not the optimal phase behaviour for the development of fixed-bed reactors, since the liquid phase formed during the reaction can accumulate inside the reactor and cause the leaching of the SILP material. Instead, operating conditions for which both reactant and product are soluble in the supercritical phase should be selected. Only in this way the $scCO_2$ phase is able to take the reactants and the products into and out of the reactor in continuous mode.

Nevertheless the work of Wang *et al.* was the only one approaching the utilization of CO_2 also as the mobile phase and though taking advantage of supercritical conditions. All other published studies on the cyclic carbonate formation from CO_2 and epoxides focus on developing SILP materials for performing reactions in the liquid phase [19]. This is probably the reason why the majority of the authors also use the chemical bond between the IL and the support instead of simple physical absorption.

Furthermore several different supports were reported [20]. Silica is by far the most explored material for SILP preparation, and in this case a catalytic synergetic effect was reported. Sakakura and co-workers reported that silica-supported onium salts turned out hundred times higher catalytic activities compared to onium salts alone [21]. In these systems, the cooperative action of the silanol groups and the nucleophile promotes oxygen atom coordination and the nucleophilic ring opening of the epoxide [22]. Similar results were reported by Takashi Sakai *et al.* [23]. In this last work, it was also found that the pore size of silica affected the catalysis, mesoporous silica with the mean pore size of 19 nm exhibited much better performance than silica with that of 6 nm.

Other type of materials as carbon nanotubes were investigated, Han *et al*. [24] reported on the reaction between CO_2 and allyl glycidyl ether using carbon nanotubes as support for immidazolium-based ionic liquids. The material could be reused and showed satisfactory activities, five consecutive runs were the product selectivity remain constant (98%). Also polymers as polystyrene and polyethylene glycol have been used [25]. The utilization of biopolymers as supports for ionic liquids is recent but very attractive since biopolymer sources are established, relatively cheap and accessible at industrial scale [26]. In a recent study, a dicationic ionic liquid was supported in the biopolymer chitosan for the cycloaddition reaction of CO_2 [27]. Different epoxides were studied, under solvent-free conditions in high yield and selectivity, without the addition any metal as co-catalyst. It was possible to reuse the catalyst five times without losing activity.

Finally, another important key feature of a good support material is to have a high surface area where the IL can be deposited with a very high dispersion. Regarding these characteristics, aerogels materials which have an open structure, large specific surface area, high porosity, mesoporous pore size distribution and low bulk density compose an interesting support family for SILP preparation, also known as ASILP (Aerogel Supported Ionic Liquid Phase) [28]. Recently graphene oxide aerogels were applied as heterogeneous catalyst for the synthesis of cyclic carbonates through CO_2 cycloaddition toward epoxides [29]. The aerogels were impregnated with thiamine derivates and no solvent or co-catalyst was added. The aerogels could be reused five times, with a small loss of activity showing an efficient and stable catalytic system.

On the context of our interest in developing a green technology for CO_2 conversion into organic carbonates, in this chapter we have supported an ionic liquid into an alginate aerogel matrix and applied it as a catalyst for the cycloaddition reaction between CO_2 and a bio-based epoxide. This is the first time that an aerogel made from a biopolymer is used as support for an ionic liquid. Alginate is a natural polysaccharide biopolymer mainly derived from brown algae and consists of α-L-guluronic acid and β-D-mannuronic acid (M) residues, linearly linked by 1,4-glycosidic linkage [30]. Due to its biodegradability, low cost, non-toxicity and stability it is an attractive candidates for aerogel production.

Beside that if we want to have a more sustainable process it is interesting to explore the production of carbonates using epoxides derived from natural sources. Studies with naturally occurring epoxides are still limited and usually the authors focus on petroleum-based compounds such as propylene oxide and cyclohexene oxide [31, 32]. In this work natural terpenes were explored as potential renewable raw materials and as an alternative to the fossil fuel derivates epoxides. Terpenes can be found in many essential oils and limonene is the most common terpene and is mostly obtained from waste orange peel [33]. In particular limonene (a by-product of the citrus industry) was studied.

4.2. Experimental

4.2.1. Materials

All chemicals and solvents were used as received without further purification. Carbon dioxide (>99.95 mol % purity) was supplied by Air Liquide and Carburos Metálicos. Limonene oxide (97 mol % purity), Aliquat Cl (Trioctylmethylammonium chloride), chloroform, chloroform deuterated, alginic acid sodium salt from brown algae (low viscosity, 4–15 cP), calcium carbonate ($CaCO_3$) and glucono-δ-lactone (GDL), tetramethoxysilane (TMOS), methanol, ammonium hydroxide (NH_4OH) were purchased from Sigma-Aldrich. Zinc (II) complexes of Arylhydrazones of β-diketones (Zn(II)-AHBD) complex 2 was prepared as reported method [34, 35] (Figure 6).

4.2.2. Preparation of alcogels

4.2.2.1. Silica alcogels synthesis

Hydrophilic silica alcogels were produced based on a sol-gel technique with two different approaches. In the first approach TMOS was mixed with methanol and the solution of ammonium hydroxide-water was added drop by drop under stirring conditions. A molar ratio of 1 mol TMOS : 3 mol MeOH : 4 mol H_2O : 5×10^{-3} mol NH_4OH was used [36]. In the second approach we use the molar ratio 1 mol TMOS : 2.4 mol MeOH : 1.3 mol H_2O : 1×10^{-5} mol HCl: 7.7×10^{-4} mol NH_4OH [37]. TMOS was mixed with water, methanol, and hydrochloric acid. The reaction mixture was stirred at room temperature for 30 minutes. In the second step a solution of ammonium hydroxide-water was added drop by drop under stirring conditions. For both approaches a specific volume of the mixture was then pipetted into molds and covered with parafilm for jellification to take place. After fifteen minutes, the gels formed were immersed into methanol for aging process, which was maintained at least 7 days. The solvent was changed at least twice during aging to completely remove excess water and traces of excess of reactants from the sol-gel reactions from the alcogels.

4.2.2.2. Alginate alcogels synthesis

Alginate hydrogel was prepared by a method of internal gelation based on lowering of pH as described elsewhere [38, 39]. Sodium alginate was dissolved in distilled water under stirring conditions of 400 rpm overnight to allow complete dispersion to obtain a 2% (w/v). In this work, calcium carbonate was used as Ca^{2+} divalent cations source to create cross-linking of alginate-Ca^{2+} and form alginate gels. The $CaCO_3$ was added into the solution and stirred for 1 h. This was followed by the addition of GDL to liberate the Ca^{2+}, reduce the pH of the solution and to allow the solution to become a gel. The resulting mixture was poured into molds, covered with parafilm and stored in refrigerator ($4^{o}C$) for 18 h, period during which it solidified. The monoliths of alginate hydrogels were then immersed in ethanol-water solution (stepwise from 30, 50, 70, 90% v/v and twice with pure ethanol, every 24 h) to substitute the water content from the hydrogel with alcohol prior to the supercritical drying.

4.2.3. Aerogels Impregnation

Wet impregnation (WI) was used to impregnate Zn(II)-AHBD complex 2 into the aerogels matrix [40]. In the WI method, the absorption of substance into the alcogels was carried out at the end of the solvent exchange period. First, the Zn(II)-AHBD complex 2 was dissolved in an organic solvent to produce a saturated compounds solution, ethanol in the case of alginate aerogels and methanol for silica aerogels. We use 0.45g of Zn(II)-AHBD complex 2 in 30 mL of solvent (ethanol or methanol). This quantity of Zn(II)-AHBD complex 2 is equivalent of 15000 ppm. The solution was then put into contact with the alcogels that had been aged for at least a week, and kept in contact to allow compounds diffusion into the pores of alcogels until equilibration was reached. Subsequently, the solvent was extracted by supercritical CO_2 drying, leading to the precipitation of the compounds on the surface and pores of aerogels due to their insolubility in CO_2. It is important to note that the appropriate diffusion of the compounds into the pores of alcogels depends on the time of diffusion, concentration of the compounds solution and the porosimetry properties of the alcogels. About 12 alcogel monoliths (aged for 7 days) were added and maintained into the solution for 48 hours.

In the case of the impregnation with Zn(II)-AHBD complex 2 and Aliquat Cl the procedure was exactly the same, the only difference was that we use 0,45g of Zn(II)-AHBD complex 2 in 20 mL of solvent, plus 10 mL of Aliquat Cl. Also 12 alcogel monoliths (aged for 7 days) were added and maintained into the solution for 48 hours.

Only alginate aerogels were tested with Aliquat Cl alone. The procedure was also the same, the only difference was that we did not use any Zn(II)-AHBD complex 2 and we tested two different solutions for the impregnation: A1 with 20 mL of Aliquat Cl and 10 mL of ethanol, and A2 with 15 mL of Aliquat Cl and 15 mL of ethanol. The 12 alcogel monoliths (aged for 7 days) were added and maintained into the solution for 24, 48 and 72 hours.

4.2.4. Supercritical drying of alcogels

The alcogels (silica and alginate) were subjected to supercritical drying by CO_2 at 14 ± 0.5 MPa and 45 °C, employing the procedure and equipment described in a previous work (Figure 1) [41]. About 12 alcogels monoliths were placed in the drying chamber, which was then filled with solvent (ethanol in the case of alginate and methanol in the case of silica) to prevent damage of alcogel structure during the pressurization of the system. The system was slowly pressurized to the desired pressure at a rate of 0.4 MPa/min. After the operating conditions of drying were reached, the solvent in the chamber was slowly removed by opening the lower valve. By doing this, a continuous circulation of CO_2 began to extract the solvent from the alcogels. The drying process was conducted in three cycles of 60 min minimum in each cycle. After the three cycles of CO_2 circulation were completed, the system was slowly depressurized at a rate of 0.2 MPa/min in order to avoid shrinkage or damage of aerogels.

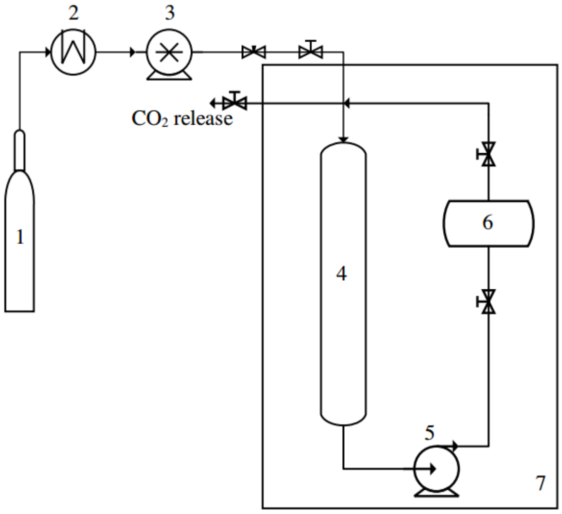


Figure 1. Supercritical CO_2 drying setup; (1) CO_2 tank, (2) cooler, (3) pump, (4) CO_2 buffer, (5) pump, (6) view cell chamber and (7) oven.

4.2.5. CO_2 and epoxides coupling reactions

CO_2 and epoxides coupling reactions were performed in a high-pressure apparatus, as shown in Figure 2, described in detail elsewhere [42]. Briefly, this apparatus is built around a stainless steel cylindrical cell with two sapphire windows and an internal volume of approximately 11 cm^3. Inside the cell was introduced a metal net to avoid any contact between the aerogel and the liquid phase, see details in Figure 2. A magnetic stirring bar was introduced inside the cell in order to homogenise the solution.

The cell was first loaded with limonene oxide, catalyst (SILP or bulk), then immersed in a thermostated ethylene glycol bath heated by means of a controller that maintained temperature within ± 0.1 ºC. Operating a CO_2-compressor, the desired pressure was brought into the cell. The pressure in the cell was measured with a pressure transducer 204 Setra (± 0,073% full scale accuracy). At the end of the reaction, the high pressure cell was cooled and then slowly depressurized to atmospheric pressure into a glass trap immersed in an ice bath. Afterward, the cell was opened and the contents collected. Both contents of the cell and glass trap were mixed and prepared for further analysis as follows.

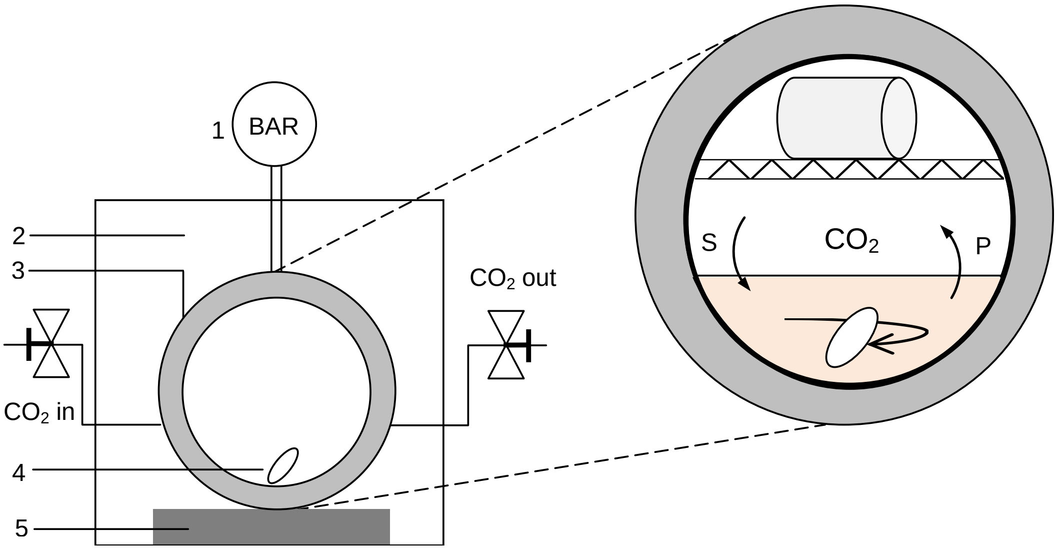


Figure 2. High pressure apparatus: 1 - Pressure transducer, 2 - Thermostated water bath, 3 - Stainless steel cylindrical cell, 4 - Magnetic stirring bar, 5 - Stir Plate.

The reaction mixture was then analyzed by NMR using deuterated chloroform as a solvent. NMR spectres were recorded on Bruker 500 MHz type (400 MHz). Peak frequencies were compared against solvent, chloroform-d at 7.26 ppm. All liquid solutions were prepared gravimetrically using analytical balance (Sartorius model R180D) with the precision of ± 0.0001 g. The carbonate formation was determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture. The calculations were made using the signals from the epoxy groups of limonene oxide (δ= 2.9-3.1 ppm) and from the cyclic carbonate groups (δ= 4.3-4.5 ppm) [43]. Errors in the carbonate formation measurements were estimated by comparing the results of at least 3 integrations of each spectrum. The error introduced into the final results was lower than 10%.

4.2.6. Aerogels Characterization

The aerogel structure was studied by Fourier transform infrared spectra. The spectra were acquired between 4000 and 400 cm^{-1} with a 4 cm^{-1} step using an attenuated total reflectance (ATR) sampling accessory (Smart iTR) equipped with a single-bounce diamond crystal on a Thermo Nicolet 6700 Spectrometer.

Textural characteristics of aerogels, mainly specific surface area, mean pore diameter and pore size distribution, were determined by N2 adsorption-desorption analysis at low temperature (NOVA 3000e). The specific pore volume is determined by the single point adsorption method. The shown average pore diameter is based on the desorption isotherm of the Barrett–Joyner–Halenda (BJH) method. Prior to the determination, the alginate and silica aerogels were degassed at 70 and 200 ◦C, respectively, under vacuum (<1 mPa) for 20h. The specific area was calculated by the method of Brunauer, Emmett, Teller (BET) and the pore size distribution was calculated from the desorption isotherm.

The crystallinity of the impregnated Zn(II)-AHBD complex 2 particles was analyzed by X-ray diffraction (Discover D8-Bruker). A JEOL field emission microscope, model JEM-FS2200 HRP, operating at 200 kV was used for EDX (Energy-Dispersive X-ray spectroscopy).

Particle morphology was analyzed by Field Emission Scanning Microscopy (FE-SEM JEOL 7001F). Before analysis particles were covered with approximately 300A˚ of gold by a sputter-coater in argon atmosphere (Polaron).

Metal loading was determined by atomic absorption (AA) using a VARIAN SPECTRA 220FS analyzer. Digestion of the samples was performed with HCl, H_2O_2 and HF using microwave at 250 °C.

4.3. Results and Discussion

4.3.1. Infrared spectra studies

Prepared aerogels with and without impregnation of Zn(II)-AHBD complex 2 and ionic liquid (Aliquat Cl) were analysed by FTIR. Figures 3, 4 and 5 shows the results of FTIR assays of the impregnated aerogels with Alginate, Silica 1 and Silica 3, respectively, compared with the blank aerogels, the pure Zn(II)-AHBD complex 2 catalyst and the pure Aliquat Cl. The y axe scale is the same for all curves.

The corresponding absorption bands of the Zn(II)-AHBD complex 2 catalyst were not possible to observe clearly in the impregnated samples, this can be due the lower amount that is impregnated into the aerogels.

For the blank alginate aerogel (Figure 3, B4) it is possible to observe several characteristic absorption bands at 3450 cm^{-1} (O-H stretching) and the alginic acid bands between 700 and 1800 cm^{-1} [40]. The corresponding absorption bands of pure Aliquat Cl (Figure 3, Aliquat) can be seen at 1480 cm^{-1} (CH_2 blending) and between 2800 and 3000 cm^{-1} (C-H stretching) [44]. The obtained spectrum of pure Aliquat Cl was compared with the Aliquat Cl impregnated alginate aerogels (Figure 3, B4_ImpZA and B4_ImpA) and it was observed that Aliquat Cl characteristic peaks also appeared in the spectrum, which indicates that Aliquat Cl was successfully impregnated into the alginate aerogels.

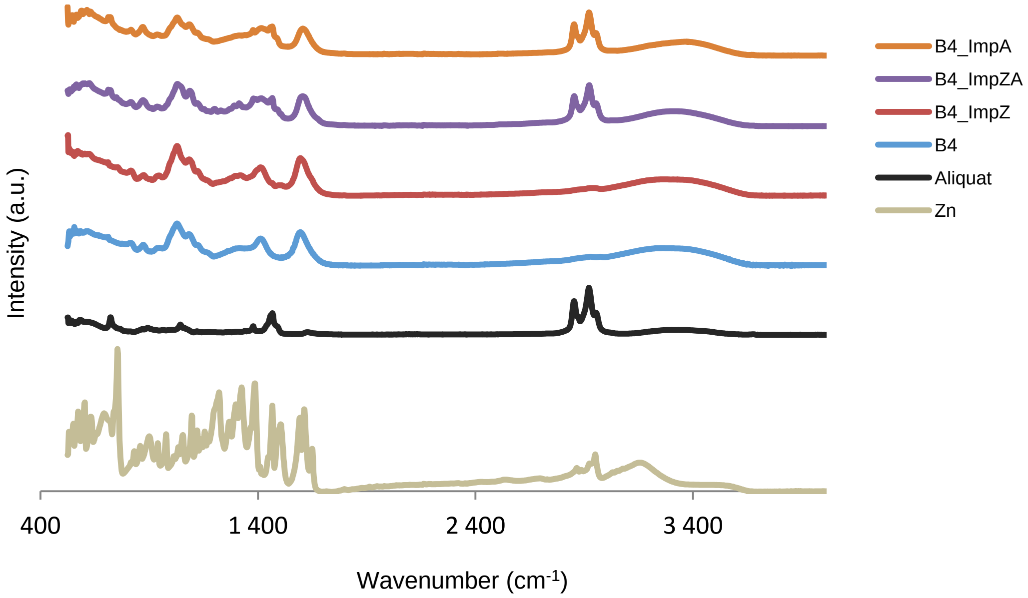


Figure 3. Infrared spectra of pure Zn(II)-AHBD complex 2 catalyst (Zn), pure Aliquat Cl (Aliquat) and Alginate aerogels: blank alginate aerogel (B4), Zn(II)-AHBD complex 2 impregnated aerogel (B4_ImpZ), aerogel impregnated with Zn(II)-AHBD complex 2 and Aliquat Cl (B4_ImpZA) and aerogel impregnated with Aliquat Cl (B4_ImpA).

A similar behaviour of the Zn(II)-AHBD complex 2+Aliquat Cl impregnated silica aerogels was observed as shown in Figure 4 (Silica S3), it was also possible to observed the Aliquat Cl characteristic peaks in the spectrum. In comparison with alginate aerogel, the silica aerogel S3 had weaker absorption bands at 1480 cm^{-1} and between 2800 and 3000 cm^{-1}, which indicates that a fraction of Aliquat Cl was not impregnated into the silica aerogel and was co-extracted with methanol by supercritical CO_2 during the drying process, resulting in a lower Aliquat Cl loading.

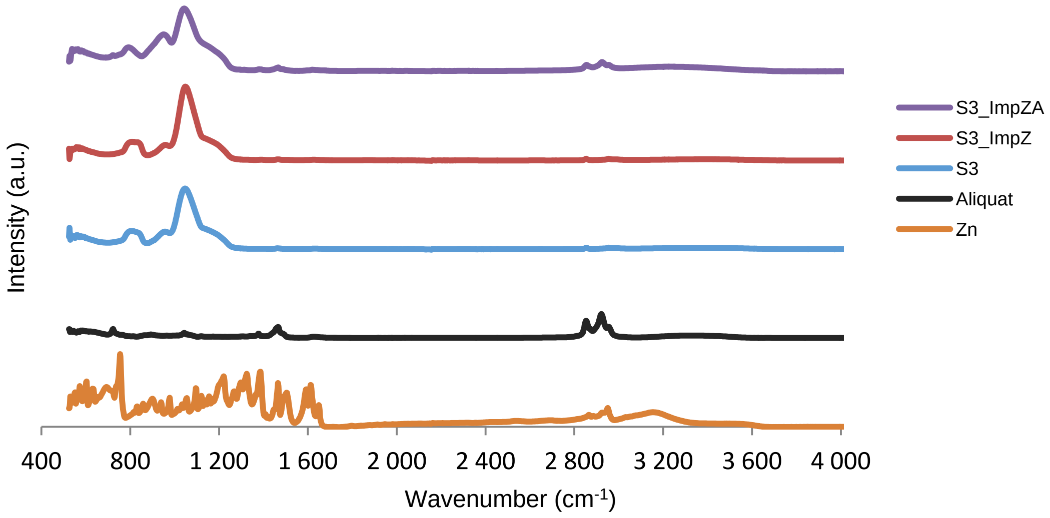


Figure 4. Infrared spectra of pure Zn(II)-AHBD complex 2 catalyst (Zn), pure Aliquat Cl (Aliquat) and silica aerogels: blank silica aerogel (S3), Zn(II)-AHBD complex 2 impregnated aerogel (S3_ImpZ) and aerogel impregnated with Zn(II)-AHBD complex 2 and Aliquat Cl (S3_ImpZA).

For the sample Silica S1 (Figure 5) the characteristic peaks of the Zn(II)-AHBD complex 2 catalyst were not possible to observe, which may indicate that this impregnation was not so successfully made as the previous ones. We did not perform the impregnation with Zn(II)-AHBD complex 2+Aliquat Cl because these type of aerogels was very fragile to perform the high pressure reactions.

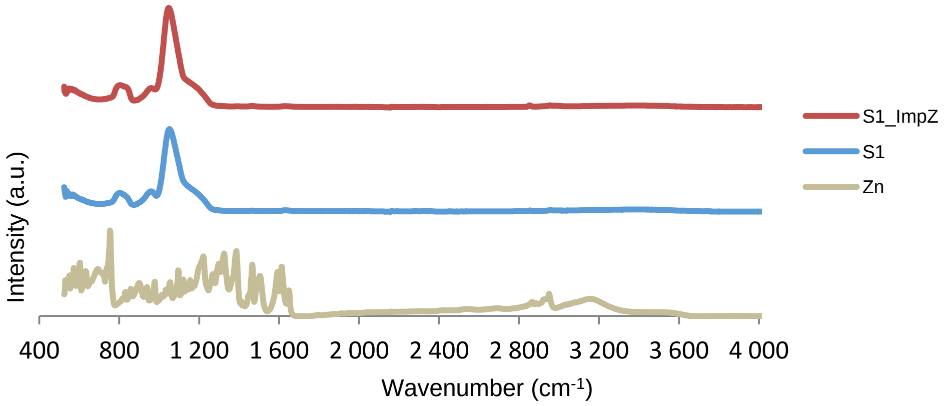


Figure 5. Infrared spectra of pure Zn(II)-AHBD complex 2 catalyst (Zn) and silica aerogels: blank silica aerogel (S1) and Zn(II)-AHBD complex 2 impregnated aerogel (S1_ImpZ).

In the case of the Zn(II)-AHBD complex 2 impregnation, due to the complexity of the structure of the catalyst (Figure 6), the absorption bands appear overlapping and less defined. With this situation is very difficult to analyse the Zn(II)-AHBD complex 2 content in the aerogels, for this purpose other techniques will be use, like for example atomic absorption.

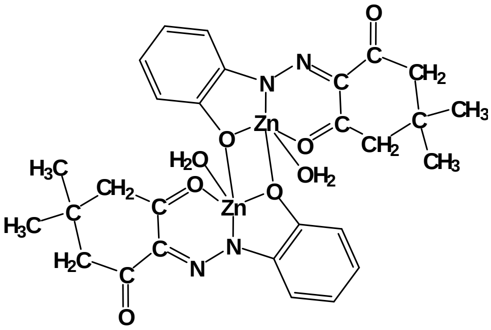


Figure 6. Zn(II)-AHBD complex 2 catalyst structure (zinc(II) complex 2 of arylhydrazones of β-diketones).

4.3.2. Nitrogen physisorption studies

Table 1 shows the porosimetric properties of blank and impregnated alginate and silica aerogels. Regarding the obtained results for the blank aerogels (not impregnated) is was possible to observe that the silica aerogels had a much higher surface area and pore volume if compared with the alginate aerogels, which is in accordance with the bibliography [45, 28b].

Table 1. Porosimetric of blank and impregnated alginate and silica aerogels.

Entry	Aerogel Material	Impregnation[1]	BET surface área (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
1	Alginate (B4)	-	271	2.27	33.56
2	Alginate (B4)	Zn Complex 2	253	2.18	34.46
3	Alginate (B4)	Zn complex 2+ IL	< 1	-	-
4	Alginate (B4_ImpA)	IL	< 1	-	-
5	Silica (S1)	-	882	2.85	12.93
6	Silica (S1)	Zn Complex 2	772	2.96	15.35
7	Silica (S3)	-	1099	2.44	8.912
8	Silica (S3)	Zn Complex 2	258	0.4750	7.363
9	Silica (S3)	Zn complex 2 + IL	245	0.4452	7.253

[1] The ionic liquid used was Aliquat Cl

When the aerogels were impregnated with Zn(II)-AHBD complex 2 a slight decrease of the specific surface area was observed. On the other hand, when impregnated with Aliquat Cl the surface area drastically decreases. The reduction of the specific surface area of the impregnated aerogels indicates that the aerogels pores were filled and partially blocked. This effect is more patent in the alginate aerogels, especially the ones that were impregnated only with Aliquat Cl, where the Bet surface area results was always lower than 1 m^2/g (Entry 4, Table

1). Since the BET surface area lower than 1 m^2/g it was not possible to calculate pore volume and pore diameter of those samples (Entry 3 and 4, Table 1). In the case of silica aerogels this effect was not so visible, some aerogels pores were still free, this may be due the fact that in this case the impregnation was not have so efficient.

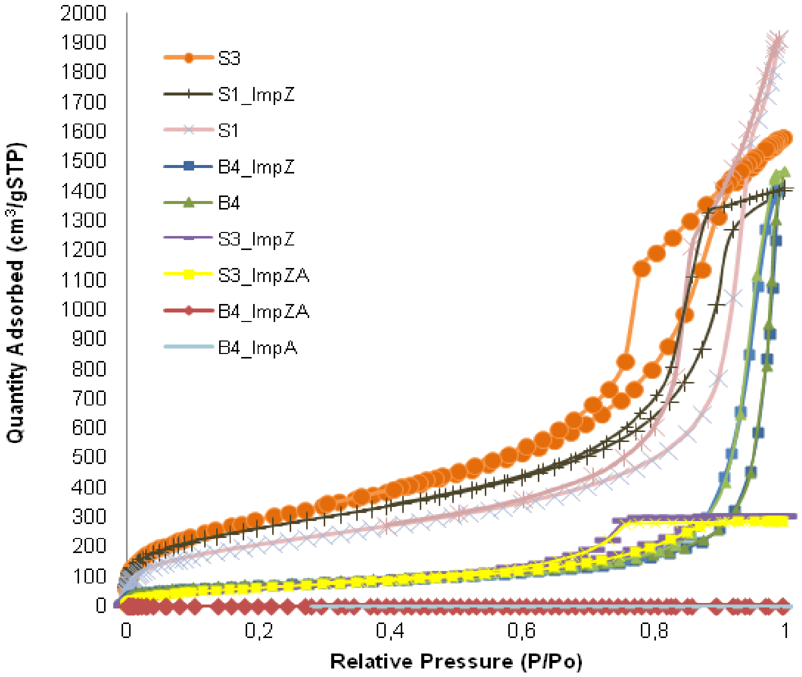


Figure 7. Nitrogen adsorption isotherms of the alginate and silica aerogels.

As a complement to the results reported in the Table 1, Figure 7 shows the Nitrogen adsorption isotherms of the blank and impregnate alginate and silica aerogels. The isotherms belongs to “type IV” which is typical for mesoporous materials. When the impregnation was performed with Aliquat Cl (B4_ImpZA and B4_ImpA, Figure 7) there is no desorption of N_2 from the aerogels, which is in accordance with the Bet surface results.

4.3.3. Powder X-ray diffraction studies

X-ray diffraction patterns for silica and alginate aerogels are shown in the Figure 8 and 9, respectively. Since this technique is to detect the crystallinity of the impregnated Zn(II)-AHBD complex 2 particles only the samples containing only Aliquat Cl were not analyzed here.

The X-ray diffraction patterns for blank silica aerogels (S1 and S3) and Zn(II)-AHBD complex 2 impregnated silica aerogels (S1_ImpZ and S3_ImpZ) are represented in the Figure 8. No changes on crystallinity of impregnated silica aerogels were observed. Therefore, the discussions on the effect of impregnation on surface morphology will be focused only in the alginate aerogels. The diffractogram of alginate consisted of two crystalline peaks around

14 and 23˚ of 2θ which are related to the lateral packing among molecular chains and the layer spacing along the molecular chain direction, respectively [46, 47].

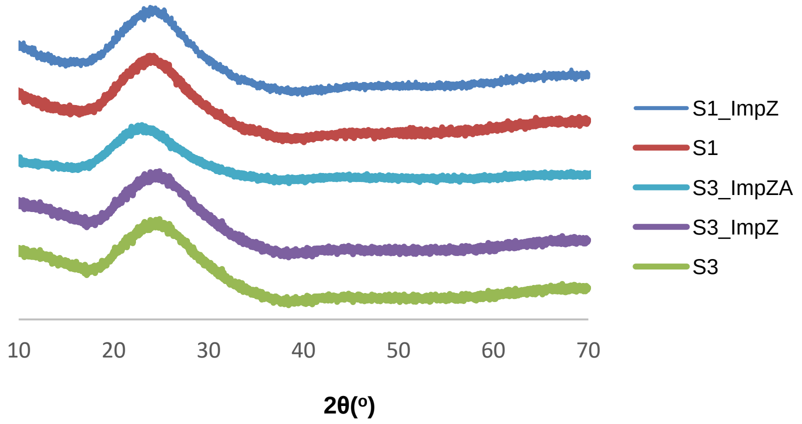


Figure 8. X-ray diffraction patterns of Zn(II)-AHBD complex 2 impregnated silica aerogels and blank silica aerogels.

For the blank alginate aerogel (Figure 9, B4) it was possible to observe several characteristic diffraction peaks, the most intense are 23.3º, 29.6º, 35.9 º, 39.4 º, 42.9 º, 47.1 º and 48.4 º. There is two evident typical diffraction peak of pure Zn(II)-AHBD complex 2 catalyst (Figure 9, Zn29) that can be seen at 7.7º and 25.1º. The spectrum of pure Zn(II)-AHBD complex 2 was compared to the impregnated aerogels (Figure 9, B4_ImpZ) and it is observe that the Zn(II)-AHBD complex 2 characteristic peaks appeared. This indicates that the Zn(II)-AHBD complex 2 was successfully impregnated in the alginate aerogels.

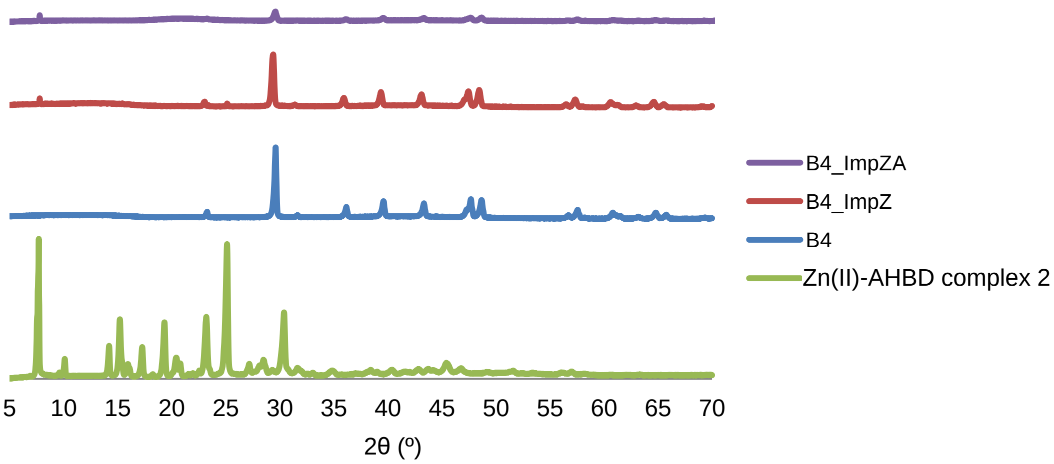


Figure 9. X-ray diffraction patterns of Zn(II)-AHBD complex 2 and Aliquat Cl impregnated alginate aerogels (B4_ImpZA), Zn(II)-AHBD complex 2 impregnated alginate aerogels (B4_ImpZ), blank alginate aerogels (B4) and pure Zn(II)-AHBD complex 2 catalyst, respectively.

4.3.4. Aerogels Images

The images of the impregnated alginate and silica aerogels are present in the Figure 10 and 11, respectively. In the Figure 10a represents the blank alginate aerogel, the Zn(II)-AHBD complex 2 impregnated alginate aerogel and Zn(II)-AHBD complex 2-Aliquat Cl impregnated aerogel, respectively. In the Figure 10b is represented blank alginate aerogel and the Aliquat Cl impregnated aerogels with different impregnation times: A1_24h, A1_48h, A1_72h, A2_24h, A2_48h and A2_72h, respectively (A1 impregnation: 20 mL Aliquat Cl + 10 EtOH, A2 impregnation: 15 mL Aliquat Cl + 15 EtOH).

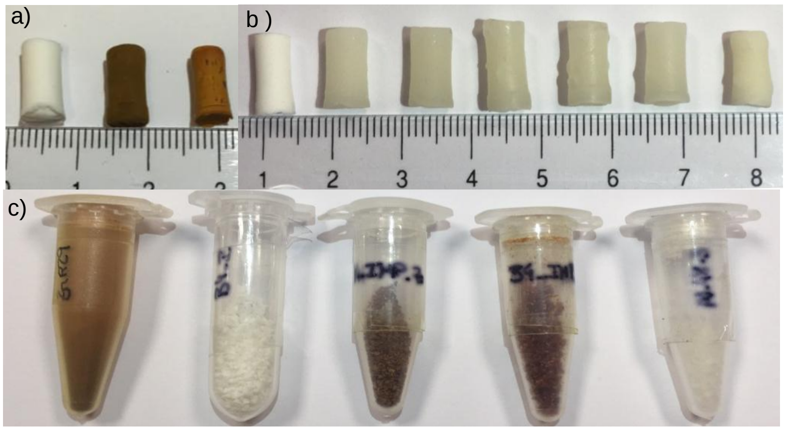


Figure 10. Images of alginate aerogels: Alginate aerogels, a) Blank, Zn(II)-AHBD complex 2 impregnated, Zn(II)-AHBD complex 2 and Aliquat Cl impregnated, respectively; b) Blank and Aliquat Cl impregnated with different impregnation times, respectively; c) Alginate aerogels in small particles.

In the Figure 10c is represented the Zn(II)-AHBD complex 2 catalyst powder and the alginate aerogels destroyed in small particles to see its interior, blank alginate, Zn(II)-AHBD complex 2 impregnated, Zn(II)-AHBD complex 2- Aliquat Cl impregnated and Aliquat Cl impregnated respectively. For the Aliquat Cl impregnated aerogels since all of them have the same visual characteristics we only represented one sample (B4_ImpA1_48h). It was possible to observe that the Zn(II)-AHBD complex 2 impregnated gels have a brown colour which indicates the presence of Zn(II)-AHBD complex 2 catalyst in the aerogels. The same characteristics were observed for the exterior and interior of the impregnated aerogels, indicating a homogeneous loading of the whole aerogel monolith.

Since Aliquat Cl appearance is a yellowish viscous liquid is normal that no big changes were observe visually. However it was possible to observe that the samples are not white anymore and a yellowish appearance is also possible to see. The same colour was observed for the exterior and interior of the impregnated aerogels, indicating a homogeneous loading of the whole aerogel monolith, which may indicate the presence of Aliquat Cl inside the aerogels. No visual differences were observed when different impregnated solutions were used (A1 and A2) and the same when different impregnation time was used (24h, 48h and 72h of impregnation time).

In the Figure 11a and Figure 11b is represented the silica aerogels S1 and S3, first we have a blank aerogel, then Zn(II)-AHBD complex 2-impregnated and in the case of 11b also Zn(II)-AHBD complex 2-Aliquat Cl impregnated silica aerogel. And in the Figure 11c is represented the Zn(II)-AHBD complex 2 catalyst powder and the silica aerogels destroyed in small particles to see its interior, blank silica S1, Zn(II)-AHBD complex 2-impregnated silica S1, blank silica S3, Zn(II)-AHBD complex 2-impregnated silica S3 and Zn(II)-AHBD complex 2-Aliquat Cl silica S3 impregnated, respectively.

Exactly like in the alginate aerogels, in all Zn(II)-AHBD complex 2 impregnated silica aerogels was possible to observe a brown colour responsible for the presence of Zn(II)-AHBD complex 2 catalyst in the aerogels. These characteristics were observed for the exterior and interior of the impregnated aerogels, indicating a homogeneous loading of the whole aerogel monolith.

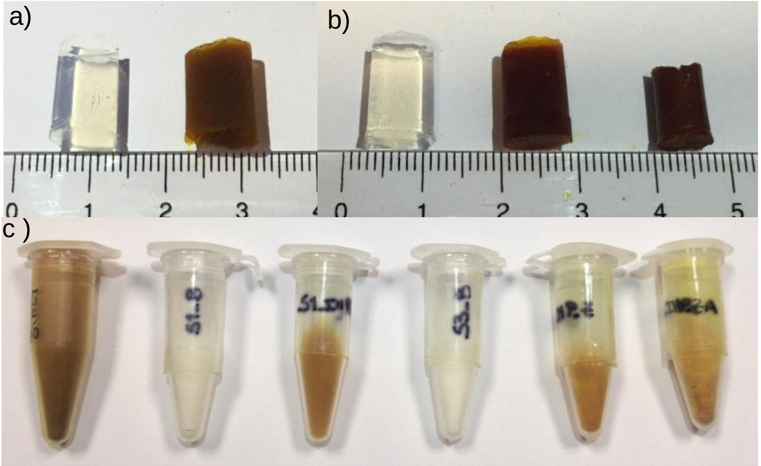


Figure 11. Images of Silica aerogels: a) S1: Blank and Zn(II)-AHBD complex 2 impregnated, respectively; b) S3: Blank, Zn(II)-AHBD complex 2 impregnated and Zn(II)-AHBD complex 2-Aliquat Cl impregnated, respectively; c) Silica aerogels in small particles.

4.3.5. Scanning Electron Microscope

To visualize the changes in the surface morphology of the alginate and silica aerogels we performed scanning analysis microscope (SEM). The SEM micrographs structure of silica and alginate aerogels are presented in the Figure 12 and 13, respectively. Two different magnifications were performed, 5.000 and 30.000, to see different details of the external morphology.

No changes on the surface morphology of silica aerogels after the impregnation were observed (Figure 12). Therefore, the discussions on the effect of impregnation on surface morphology will be focused on the alginate aerogels. We also analyse the SEM images of Silica S1 but since the results were similar to the S3 we did not add these images.

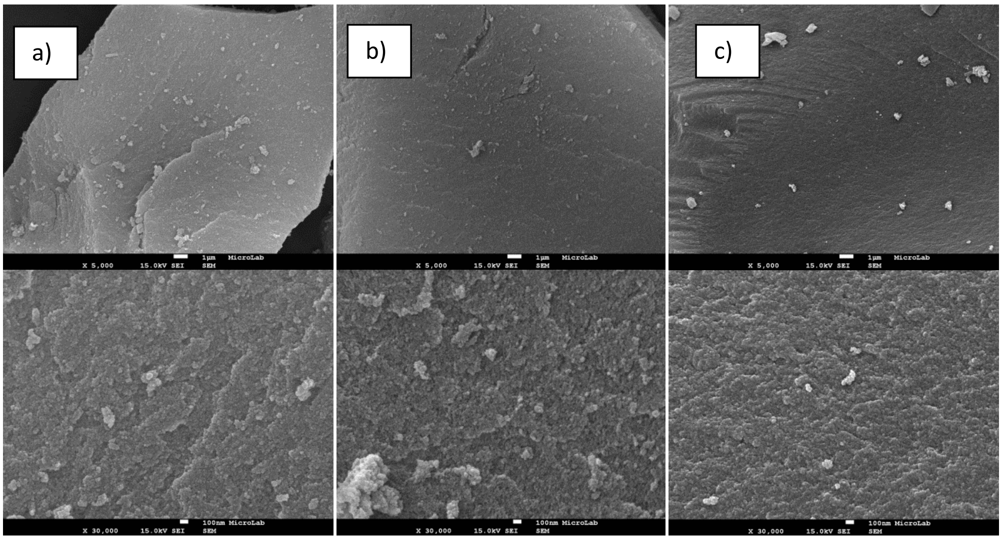


Figure 12. SEM images of silica aerogels (S3): a) blank alginate, b) Zn(II)-AHBD complex 2 impregnation and c) Zn(II)-AHBD complex 2 +Aliquat Cl impregnation. The first line corresponds to a 5.000 magnification and the second line 30.000 magnification.

In the Figure 13 a) it was possible to observe that the blank alginate aerogel have an open pores and a cross-linked structure, typical of the surface morphology of alginate aerogels [40]. On the other hand, the Zn(II)-AHBD complex 2 impregnated alginate aerogels (Figure 13 b) exhibits linkages of granular material, indicating the deposition of Zn(II)-AHBD complex 2 on the surface structure of alginate aerogel.

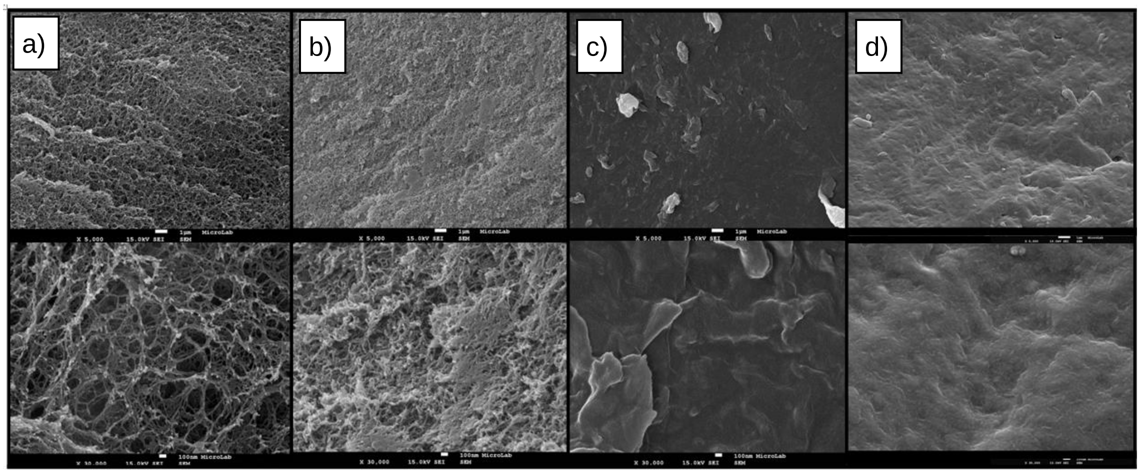


Figure 13. SEM images of alginate aerogels: a) blank, b) Zn(II)-AHBD complex 2 impregnation, c) Zn(II)-AHBD complex 2+Aliquat Cl impregnation and d) Aliquat Cl impregnation. The first line corresponds to a 5.000 magnification and the second line 30.000 magnification.

When we impregnated the alginate aerogels with Zn(II)-AHBD complex 2 and Aliquat Cl (Figure 13 c) the alginate matrix became without pores and more thick. This suggests that the high absorption of Aliquat Cl and Zn(II)-AHBD complex 2 from the ethanol medium has as consequence the change of the pore structure of alginate aerogels. The same result was obtained when only Aliquat Cl was impregnated into the aerogels (Figure 13 d), independent of the impregnation time and impregnated solution. We presented just the SEM images for the sample impregnated during 48h with 20 mL Aliquat Cl and 10 mL of ethanol, however similar results were obtained for the others.

4.3.6. Atomic absorption studies

The metal loading was determined by atomic absorption. We analyze all the samples (except the ones only with Aliquat Cl) but the only one were the Zn(II)-AHBD complex 2 was detected was the alginate aerogel impregnated with Zn(II)-AHBD complex 2 (B4_ImpZ). In the other samples was not possible to quantify the Zn(II)-AHBD complex 2 loading because it was lower than the limit detection. The results obtained for B4_ImpZ was 19883.18 ppm (1.99%), so in this case Zn(II)-AHBD complex 2 was successfully impregnated.

4.3.7. Reactions with aerogels

Impregnated alginate and silica aerogels were evaluated as catalytic systems for the coupling reaction between CO_2 and limonene oxide. Results are summarized in the Table 2. All the reactions were performed during 48 hours, at 353.2 K and 4 MPa, with 1 mL of limonene oxide. It should be noted that to evaluate the capability of using CO_2 as the mobile phase, the aerogel was never used in direct contact with the liquid phase. All reactions took place maintaining the aerogel at the top of the reactor in contact with the gaseous phase as described in the methodology section. The investigated catalytic systems presented near 95% selectivity toward limonene carbonate production.

Table 2. Limonene carbonate formation after 48h at 353.2 K and 4 MPa, using 1 mL of Limonene oxide and aerogels as catalyst support.

Entry	Aerogel Material	Impregnation	Carbonate Formation (%) [a]
1	Silica (S1)	Zn complex	9%
2	Silica (S3)	Zn complex	6%
3	Silica (S3)	Zn complex + Aliquat Cl	< 5
4	Alginate (B4)	Zn complex	< 5
5	Alginate (B4)	Zn complex + Aliquat Cl	35
6	Alginate (B4)	Aliquat Cl	32

[a] Carbonate formation determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture.

Two silica aerogels (S1 and S3) and one alginate aerogel (B4) were investigated. As can be observed from results presented in Table 2, all tested silica aerogels showed practically no activity towards the coupling reaction between CO_2 and limonene oxide (entries 1-3). This result was attributed to the low impregnation efficiency as earlier verified by the FTIR and N_2 adsorption analysis. Curiously, for alginate aerogels, nearly the same activity was observed for the aerogel only impregnated with ionic liquid (entry 6) in comparison with the aerogel impregnated with both Zn(II)-AHBD complex 2 complex and ionic liquid (entry 5).

In fact, aerogels characterization analysis showed that the quantity of Zn(II)-AHBD complex 2 complex impregnated was too low, which is very likely the reason for this result. Finally, as expected alginate aerogel impregnated only with the Zn(II)-AHBD complex 2 complex showed no catalytic activity (entry 4). From our previous studies (Chapter 3), apart from the quantity impregnated in the aerogel, the Zn(II)-AHBD complex 2 complex was not expected to exert any catalytic activity when used alone.

Nevertheless, the fact that an alginate aerogel loaded only with the ionic liquid Aliquat Cl presented around 30% of limonene carbonate formation (Table 2, entry 6) prompted us to further investigate this metal-free catalytic system. In this regard the catalytic activity was studied as a function of different aerogel preparation methods. Results are presented in Table 3.

Table 3. Limonene carbonate formation after 48h at 353.2K and 4 MPa, using 1 mL of limonene oxide and aerogels impregnated with Aliquat Cl.

Entry	Sample	Imp Time (hours)	IL mass (g)	IL load (mass %)	Carbonate Formation (mol %) [a]
1	Blank aerogel	-	-	-	0
2	Imp method 1[b]	72	0,16	81%	42 ± 4
3		48	0,20	82%	32 ± 3
4		24	0,24	83%	33 ± 3
5	Imp method 2[b]	72	0,11	72%	8 ±1
6		48	0,17	79%	31 ± 3
7		24	0,22	84%	46 ± 5

[a] Carbonate formation determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture
[b] Impregnation method 1: impregnation with 20 mL Aliquat Cl + 10 EtOH, Impregnation method 2: impregnation with 15 mL Aliquat Cl + 15 EtOH]

From results obtained and taking into account that the catalytic activity is measured through NMR spectroscopy (with around 10% error), the impregnation method 1 gave rise to very similar aerogels. For the three impregnation times studied around 0.2 g of ionic liquid was impregnated, which corresponds to an ionic liquid loading of 81-83% (w/w) with similar catalytic activities. On the contrary, impregnation method 2, gave rise to aerogels with different catalytic activities. In the wet impregnation process through methodology 2, the volume of the liquid phase (IL+EtOH) was the same of the used in methodology 1, but with different quantities of IL and EtOH. In method 1 a larger amount of IL (20 ml) than ethanol (10 ml) was used, while in method 2, equal amounts of IL (15 ml) and EtOH (15 ml) were used. In this latter, lower and different amounts of ionic liquid were impregnated depending on the time of impregnation. Curiously the quantity of ionic liquid impregnated decreased with time from 24 to 48 and 72 hours.

It should be noted that aerogels loadings obtained in this work are quite high in comparison with those reported in the literature for supported ionic liquid catalysts. These loadings of around 80% of ionic liquid onto the solid matrix are more likely to be observed in supported ionic liquid membranes [48]. Reproducibility experiments were further performed to evaluate the efficiency of different aerogels prepared with the same methodology.

Three reactions were performed with different aerogels prepared by impregnation method 1 (20 ml IL + 10 ml EtOH) during 72h. Results are presented in Table 4.

Table 4. Reproducibility experiments for three reactions performed at 353.2 K and 4 MPa during 48 hours, , using 1 mL of limonene oxide and aerogels impregnated with Aliquat Cl.

Reaction	Carbonate Formation (% mol) [a]
1	46
2	43
3	42

[a] Carbonate formation determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture

Nearly the same limonene carbonate formations were achieved using similar but different aerogels. Furthermore, the possibility of reusing the aerogel was also evaluated by performing three reaction cycles using the same aerogel. Results are presented in Table 5.

Table 5. Reutilization experiments for three cycles at 403.2 K and 4 MPa, during 3 hours, using 1 mL of limonene oxide and aerogels impregnated with Aliquat Cl.

Reaction	Cycle Number	CC Formation (%) [a]
1	1	15
2	2	7
3	3	3

[a] Carbonate formation determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture

Results observed show how the aerogel catalytic activity significantly decreased, which could be caused by the leaching of the ionic liquid from the aerogel into the liquid phase. The peaks of Aliquat Cl were detected in the liquid phase by ^{1}H-NMR spectroscopy. Furthermore, in an attempt to increase the aerogel performance, the effect of the reactor volume for the same reaction conditions was assessed.

As can be observed in Table 6, cyclic carbonate formation decreased with the increase of the volume of the reactor, which was expected and results from a dilution effect on the epoxide (substrate) concentration. However this dilution effect did not avoid the leaching of the catalyst from the aerogel matrix, which was still detected in the reaction mixture by ^{1}H-NMR analysis (supplementary information).

Table 6. Cyclic Carbonate formation using different volume reactors. The reactions were performed at 353.2 K and 4 MPa during 48 hours, using 1 mL of limonene oxide and aerogels impregnated with Aliquat Cl.

Reaction	Reactor Volume (mL)	mi SILP (g)	mf SILP (g)	CC formation (%) [a]
1	11	0.267	0.218	43
2	11	0.267	0.319	35
3	33	0.238	0.272	20

[a] Carbonate formation determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture

4.5. Conclusions

Alginate and Silica aerogels were prepared and explored as supports for ionic liquids (Aliquat Cl) and applied as catalysts in the cycloaddition reaction between limonene oxide and CO_2. As catalysts, alginate impregnated aerogel materials presented much higher activities in comparison with silica aerogels. Physical characterizations showed differences on the impregnation efficiency of Aliquat Cl onto alginate and silica aerogels, very likely due to significant differences on the size of the pores. High ionic liquid loadings (of around 80% wt.) were obtained for alginate aerogels, although an attempt to simultaneously impregnate a Zn(II) complex failed. The inefficient Zn(II) complex impregnation was due to high losses of the complex on the solvent used during wet impregnation. Although the prepared materials presented moderate catalytic activity, their reutilization was not possible due to the leaching of the ionic liquid from the solid support and product accumulation inside the aerogel matrix during the reaction. Aerogels are very interesting materials since they can uptake high quantities of ionic liquid, but on the other hand they are formed by open structures which facilitate the leaching of the catalyst. To improve its performance a covalent linking between the ionic liquid and the support is required. Alternatively the selection of an ionic liquid with very low affinity for both substrate and product might considerably improve it final performance.

4.6. References

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4.7. Supplementary information

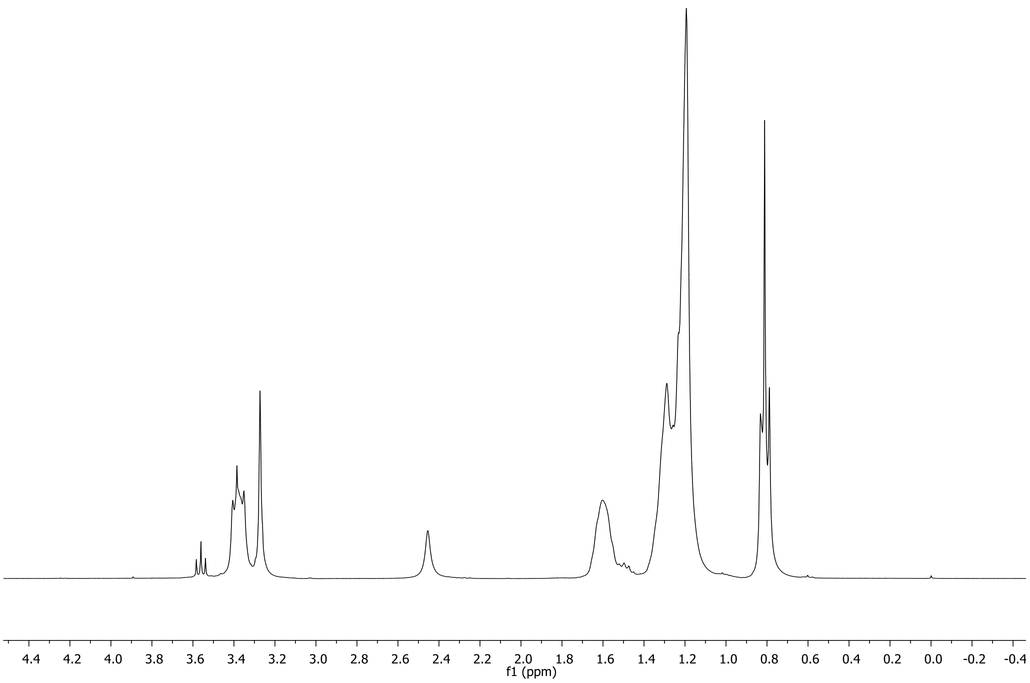


Figure 14. ^{1}H-NMR spectrum of Trioctylmethylammonium Chloride (Aliquat Cl) in $CDCl_3$.

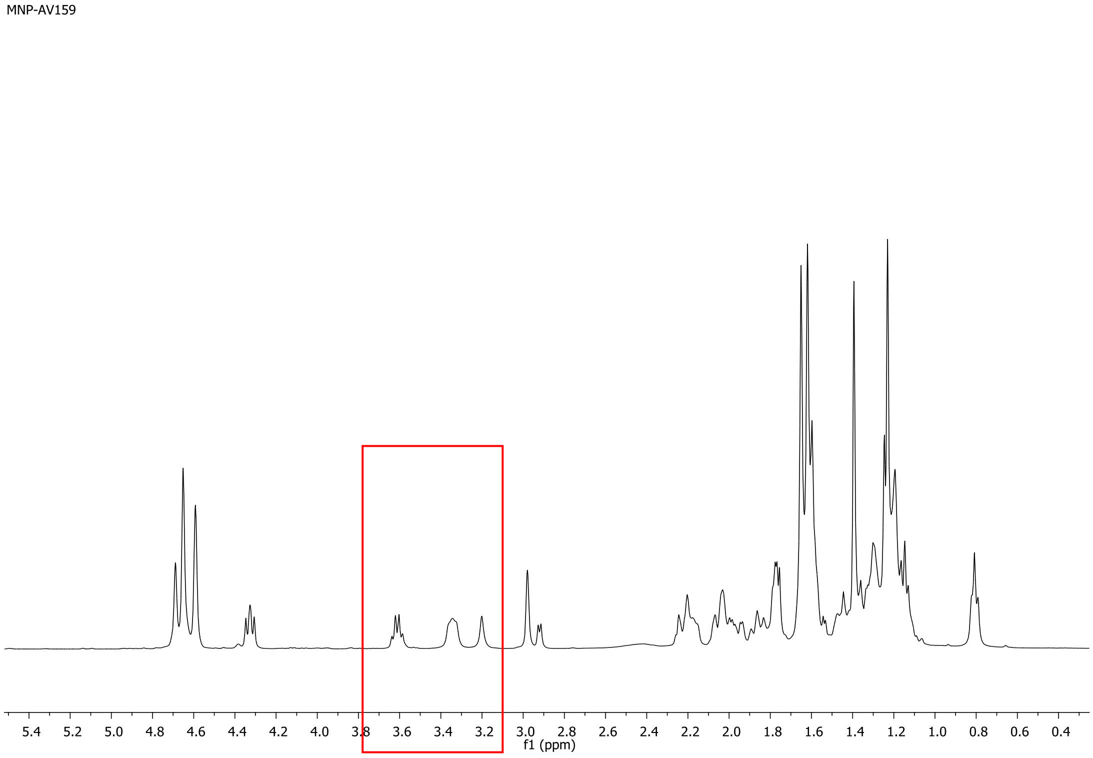


Figure 16. ^{1}H-NMR spectrum from the reaction mixture AV159 in $CDCl_3$.

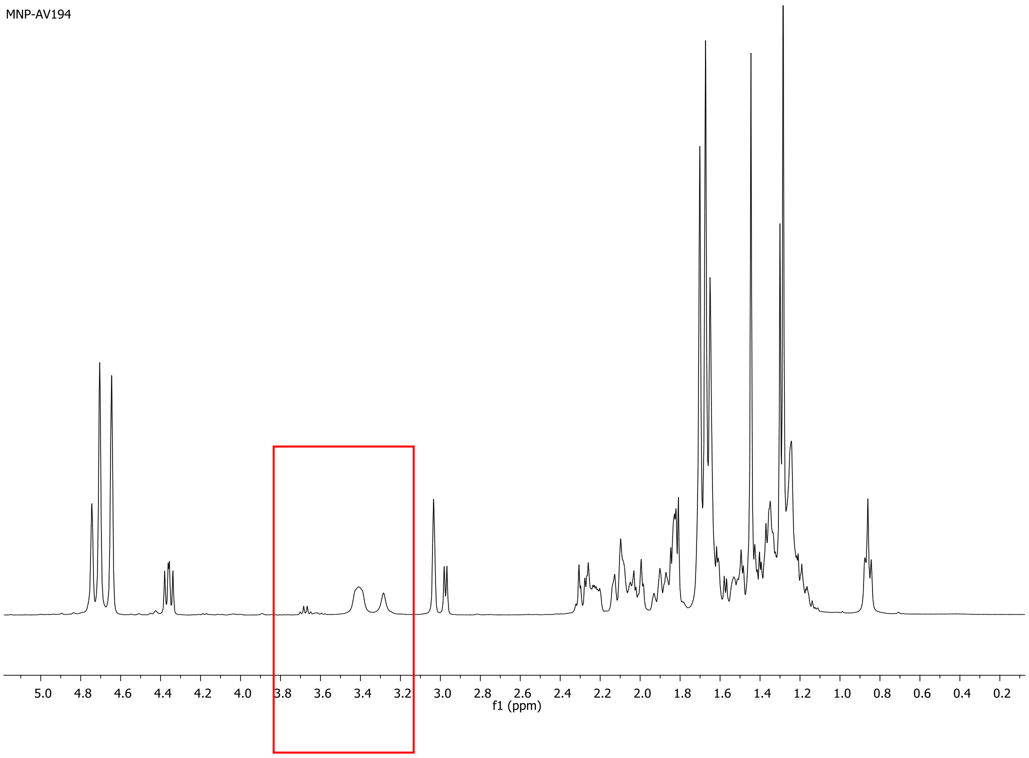


Figure 17. ^{1}H-NMR spectrum from the reaction mixture AV194 in $CDCl_3$.

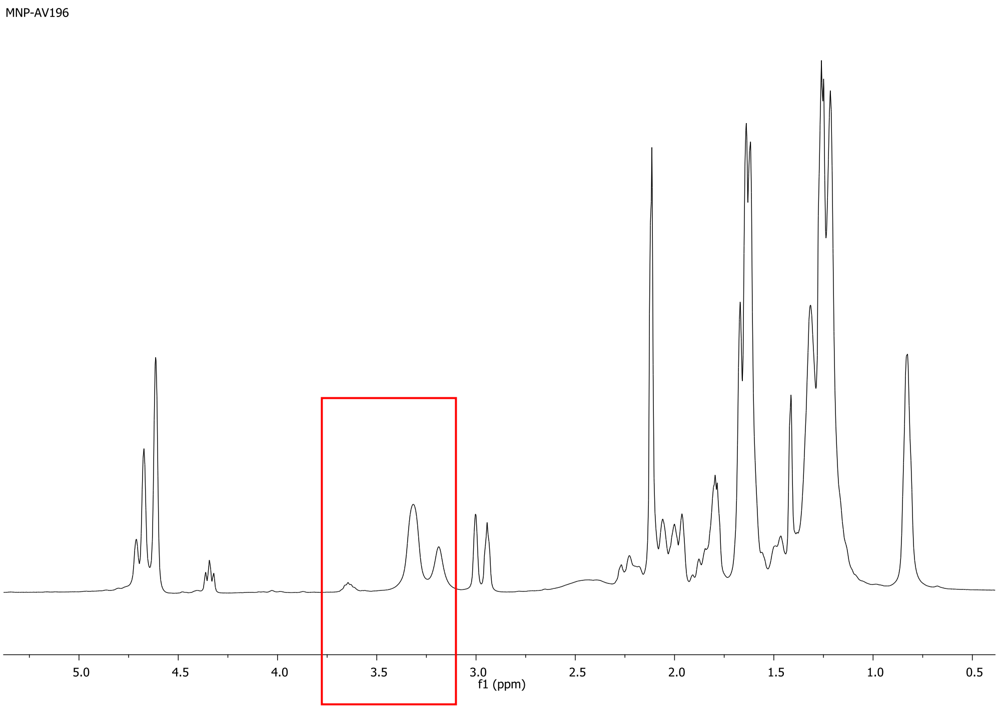
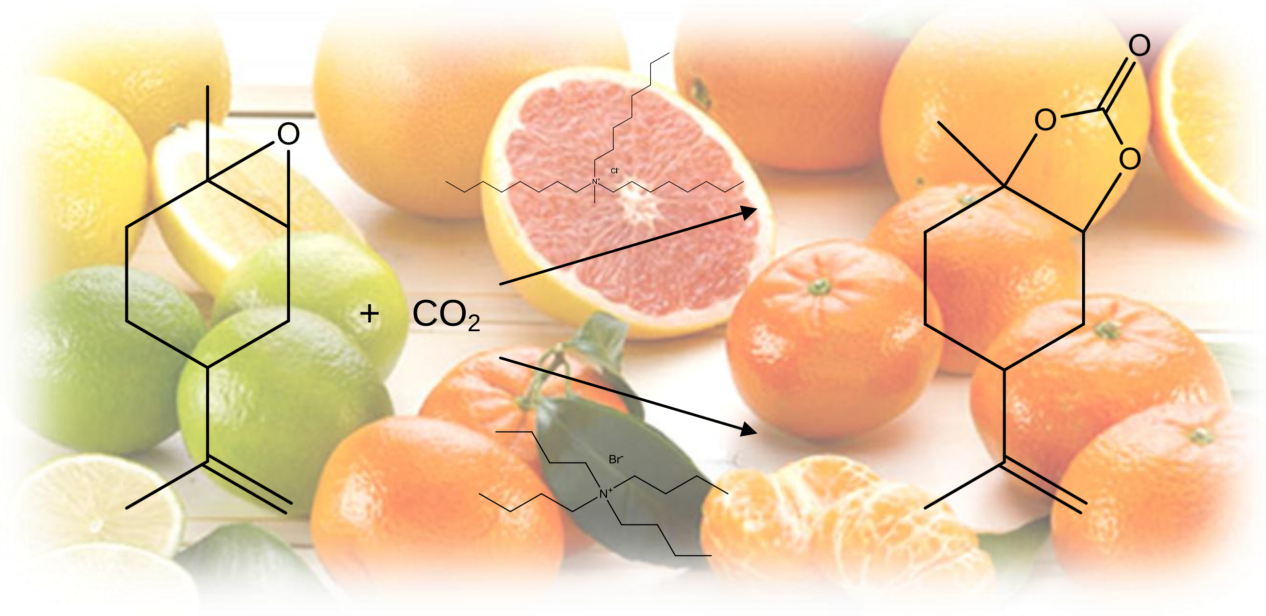


Figure 18. ^{1}H-NMR spectrum from the reaction mixture AV196 in $CDCl_3$.

Chapter 5

Limonene carbonate synthesis from CO_2: continuous flow catalysis with integrated product separation



Recent developments comprise the replacement of fossil-based epoxides by bio-derived epoxides for the production of entirely renewable cyclic carbonates. Bio-derived epoxides are however, less reactive and, thus, more challenging substrates due to their complex structure and substitution patterns. In this context, process intensification strategies are particularly important in view of future large-scale industrial applications.

Limonene epoxide is a bio-derived building block obtained from the epoxidation of limonene, a natural compound widely available as by-product of the citrus industry. In this chapter, the continuous flow production of limonene carbonate from limonene epoxide and CO_2 was explored using a biphasic reaction system composed of CO_2 and an ionic liquid (IL) in a high-pressure set-up apparatus. The working principle of CO_2/IL biphasic systems is based on the fact that supercritical CO_2, used as the carrier, has high solubility in ILs, while ILs have no measurable solubility in CO_2 and cross-contamination is avoided [3]. The IL phase (Aliquat Cl and TBABr) was used as the catalyst, while supercritical CO_2 was used as the reactant and mobile phase. Phase behaviour studies both for the reagent and the product were first performed to identify suitable operating conditions for the flow-system. Continuous-flow experiments were then conducted using a continuous stirred tank reactor. The results under continuous-flow conditions will be discussed and compared with those obtained for reactions operated at batch conditions.

Chapter 5

5.1. Introduction

A direct and straightforward use of CO_2 as a C_1 building block for chemical synthesis is the cycloaddition reaction between CO_2 and epoxides to obtain cyclic carbonates [1]. This reaction has been object of intensive studies as reflected by the growing number of publications in the last three decades [2-4]. Most investigations, however, just focused on the reaction under batch conditions between CO_2 and benchmark oil-derived epoxides such as propylene oxide, styrene oxide and cyclohexene oxide [5].

In respect to continuous flow operation, some works have reported the immobilization of coordinated metal complexes catalysts onto solid supports like silica-based [6], activated carbon [7] and polymers [8]. North and co-workers reported the utilization of a flow reactor containing aluminium(salen) complex and tetrabutylammonium bromide immobilised into silica supports for the production of ethylene carbonate from CO_2 [9]. Zhang et al. described the cycloaddition of CO_2 to epichlorohydrin under continuous flow conditions in packed bed reactor using carbon tethered ionic liquids as catalysts [10]. In both cases, the starting materials as well the resulting products are very volatile and therefore the reactions have been performed under gas-phase conditions.

A different approach that has gained attention as an alternative to solid support immobilization of homogeneous catalysts is the exploitation of biphasic systems formed by ionic liquids (ILs) and supercritical CO_2 ($scCO_2$). It consists in dissolving the homogeneous catalyst in a stationary phase formed by an adequate IL and use a $scCO_2$ mobile phase for delivering the substrate into the IL phase. At the same time, as it passes through the reactor, the $scCO_2$ mobile phase continuously extracts the reaction product, which is then recovered (with high purity) by simple depressurization [11, 12]. The working principle of this system is based on the fact that $scCO_2$ has high solubility in ionic liquids, while ILs have no measurable solubility in CO_2, combining rapid mass transfer with minimum cross-contamination between phases. This allows an effective integration of catalytic reaction and product separation in a single-step process [13].

Pioneering works in this area were reported by the groups of Jessop [14], Tumas [15] Cole-Hamilton [16] and Leitner [17]. In 2012, Wesselbaum *et al.* [18] have successfully demonstrated a continuous flow method that allows the hydrogenation of $scCO_2$ to pure formic acid in a single processing unit. The $scCO_2$ phase is used both as reactant feeding and extractive phase, resulting in the continuous removal of the product based on the negligible vapour pressure of the ruthenium catalyst in the IL phase [EMIm][NTf_2]. This approach is also attractive for reactions in which one of the reactants is a gas and especially when CO_2 can be used both as the reagent and as the mobile phase as is the case in the cyclic carbonates synthesis from CO_2 [19].

Recently, cyclic carbonates coming from bio renewable sources increase their importance namely through its application as building blocks in non-isocyanate polyurethanes [20]. In particular, commercially available and inexpensive limonene oxide has been documented as an attractive, available and renewable epoxide monomer and its use as polycarbonate material development is steadily increasing [21]. In order to address advantages of continuous flow processing, a low reactive compound, limonene oxide, was selected as substrate. Limonene oxide is a bio-based substrate derived from the abundant natural occurring terpene (limonene) [22], it is a tri-substituted epoxide and for that reason considerably more reluctant to react [23].

The literature for the cycloaddition reaction between CO_2 and limonene oxide is still limited [24] and the issue of continuous flow processing has not yet been addressed for this specific epoxide [25-27]. Nevertheless tetrabutylammonium halide is known as an efficient catalyst for the synthesis of cyclic carbonates [28]. Newly Morikawa *et al.* publishes a work using tetrabutylammonium chloride as catalyst for the production of cyclic limonene carbonate from limonene oxide and CO_2 [26]. They found that increasing the temperature enhanced the carbonate formation, the best yield was at 413.2 K but unknown by-products were detected. In terms of pressure, under ambient CO_2 pressure the reaction barely proceeded and beyond 5 MPa the carbonate formation decreased by increasing the pressure. Regarding the reaction time, the prolongation from 48 to 72h did not improve the carbonate formation considerably, which was 65% and 69%, respectively.

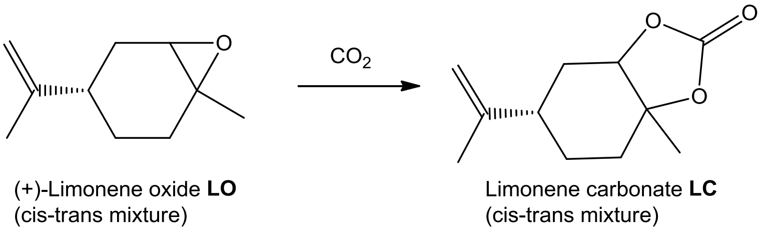


Figure 1. Synthesis of cyclic limonene carbonate (LC) from CO_2 and limonene oxide (LO).

In this work, the biphasic system $scCO_2$+IL was explored for the continuous flow production of cyclic carbonates from CO_2 and limonene oxide (Figure 1). To the best of our knowledge, it is the first time that this biphasic system is applied to cyclic carbonates production.

5.2. Experimental Section

5.2.1. Materials

All chemicals and solvents were used as received without further purification. Carbon dioxide (> 99.9 mol % purity) was supplied by Air Liquide (Portugal) or by Westfalen AG (Germany). Limonene oxide (97 mol % purity), chloroform, deuterated chloroform, deuterated ethanol, pentane, ethyl acetate and mesitylene were purchased from Sigma-Aldrich.

5.2.2. Batch reactions

The reactions between CO_2 and epoxides were performed in high-pressure reactors at two different institutions: Faculdade Ciências e Tecnologia- Universidade Nova de Lisboa (FCT-UNL), Portugal and at Institut für Technische und Makromolekulare Chemie of RTWH Aachen University (ITMC-RWTH), Germany.

The high pressure reactor used at FCT-UNL is a stainless steel cylindrical cell with two sapphire windows with an internal volume of approximately 11 cm^3 equipped with a pressure transducer (204 Setra with a ± 0,073% full scale accuracy) and a magnetic stirring bar [29]. The reactor was first loaded with the substrate limonene oxide and the catalyst and then immersed in a thermostated water bath (±0.1 °C). CO_2 was introduced by means of a compressor until the desired pressure was reached. At the end of the reaction, the reactor was cooled down to room temperature and slowly depressurized through an ice-cooled glass trap to atmospheric pressure. Afterwards, the cell was opened and the contents collected. The content of the cell and of the glass trap were mixed and analysed via NMR spectroscopy.

Batch reactions at ITMC were conducted in a similar way using a stainless steel high pressure reactor with an internal volume of approximately 11 cm^3 equipped with thick-glass windows, a pressure transducer, a thermocouple, and a magnetic stirring bar. Prior to use, the reactor was dried at 60 °C in laboratory oven and repeatedly filled with argon. After charging the catalyst and substrate, the reactor was closed and heated to desired temperature on a hot stirring plate. Then, CO_2 was introduced from a high pressure ring line and the pressure adjusted at desired value by means of a pressure reducer. Gas uptake curves were recorded via an electronic pressure reader (WIKA) connected to LabVIEW (National Instruments). At the end of the reaction, the autoclave was cooled, carefully vented, and an aliquot of the content analysed via NMR spectroscopy.

5.2.3. NMR Measurements

At FCT-UNL ^{1}H-NMR spectra were recorded on Bruker 500 MHz type (400 MHz). At IMTC-RWTH ^{1}H-NMR spectra were recorded on Bruker Avance-300 or 400 MHz. In both cases the chemical shifts were also recorded in parts per million (ppm) and peak frequencies were compared against solvent, deuterated chloroform at 7.26 ppm.

For the batch reactions the carbonate formation was determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture. The calculations were made using the signals from the epoxy groups of limonene oxide (δ=2.9-3.1 ppm) and from the cyclic carbonate groups (δ=4.3- 4.5 ppm) [30]. Errors in the carbonate formation measurements were estimated by comparing the results of at least 3 integrations of each spectrum. The error introduced into the final results was lower than 10%. For continuous flow reactions an aliquot of the solution was analysed by means of ^{1}H-NMR spectroscopy using deuterated chloroform as the solvent, and the yield was determined using mesitylene as the internal standard. Please note that the selectivity for cyclic carbonate products in all cases was determined to be >99%. The mass balance of the experiments was also performed by ^{1}H-NMR spectroscopy using deuterated chloroform as the solvent and mesitylene as the internal standard.

5.2.4. Phase Behaviour Studies

Limonene carbonate is not commercially available and the amounts required for these measurements were isolated from reaction mixtures and purified by flash chromatography on silica gel by using n-pentane/ethyl acetate (10:1) as the eluent (Figure 2). Separation was monitored by thin layer chromatography over silica gel coated TLC plates (Polygram Sil G/UV 254, Macherey-Nagel). Spots were visualized by UV lamp or stained using aqueous potassium permanganate ($KMnO_4$).

Phase behaviour measurements were carried out at ITMC in the same high pressure reactor used in the batch experiments (see above). All measurements have been carried out at 373.2 K. After loading a known amount of a pure sample (substrate or product), the reactor was closed and placed on the heating plate. After attaining the desired temperature, the system was progressively pressurized with CO_2 until a fully homogeneous phase was visually observed (method of the last liquid drop).

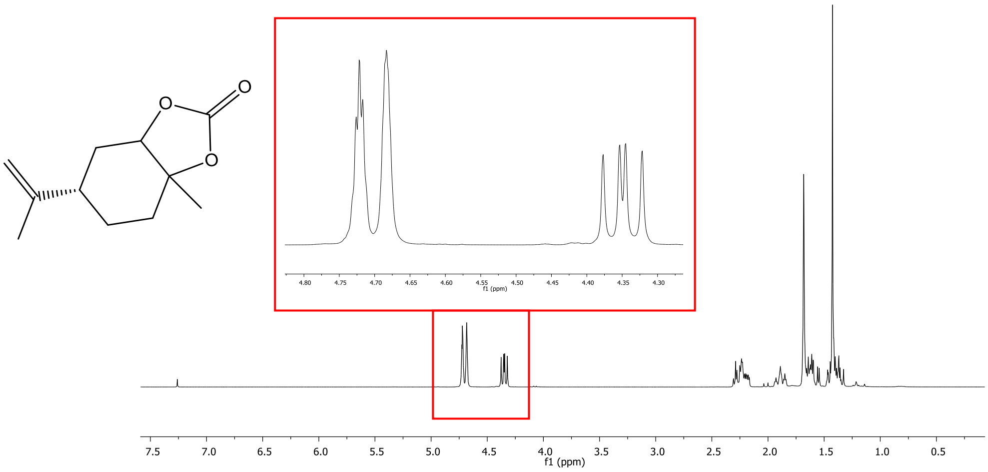


Figure 2. ^{1}H-NMR spectrum of the limonene carbonate produced.

5.2.5. Continuous-flow reactions procedure

A series of continuous flow experiments was carried out at the ITMC-RWTH using a computer-controlled in-house built setup based on [31]. It was used the same reactor as in batch and phase behaviour experiments, however an inlet deep tube was added, allowing the introduction of the reagents at the bottom of the reactor i.e. directly into the catalyst liquid phase (Figure 3).

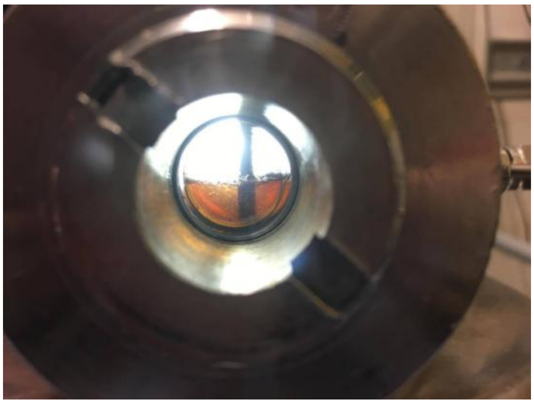


Figure 3. Detail of the deep tube inside the high pressure reactor used for the continuous mode reactions.

A picture and a schematic illustration of the apparatus used are shown in Figure 4 and Figure 5, respectively. First the reactor was filled with the catalyst, sealed and placed in the heating plate. When the desired temperature was achieved, the reactor was pressurized with CO_2 until a pressure of 30 MPa was attained. A flow rate of 40 mL/min was settled and the system was allowed to equilibrate for 30 min.

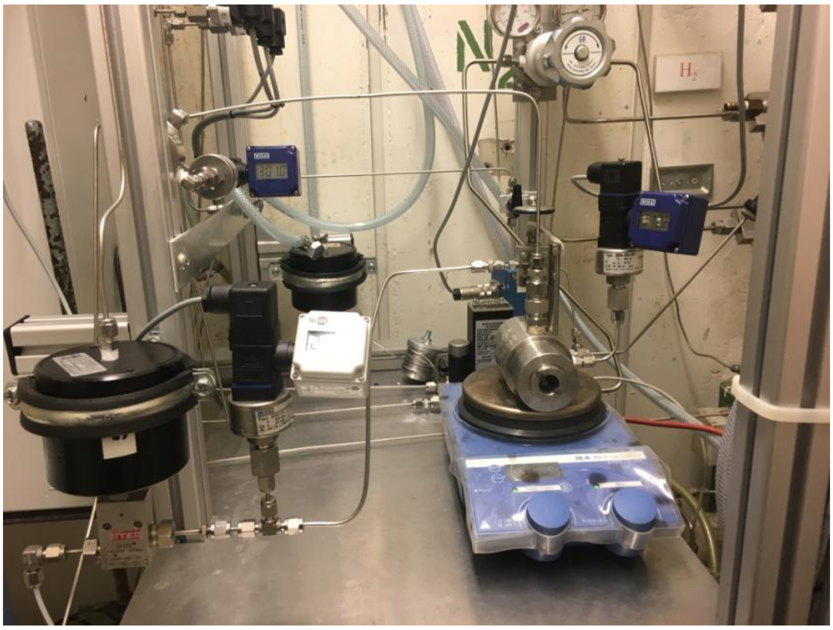


Figure 4. Experimental apparatus used for the continuous mode of the coupling reactions between limonene oxide and CO_2.

Then limonene oxide (substrate) was introduced into the CO_2 stream using an Isco Syringe Pump. The feed line of the pump was first purged with a few millilitres of fresh liquid substrate to flush out potential gas bubbles from the line and the valves in the pump head. The line was closed and the pump started at 1 mL/min until 30 MPa pressure had been built up and remained stable after pump stop. The flow was lowered stepwise to 0.5, 0.1, and 0.05 mL/min to ensure steady pressure build-up also at low piston velocities. When the pump was able to build up pressure at the desired reaction flow rate it was kept under overpressure ready for application.

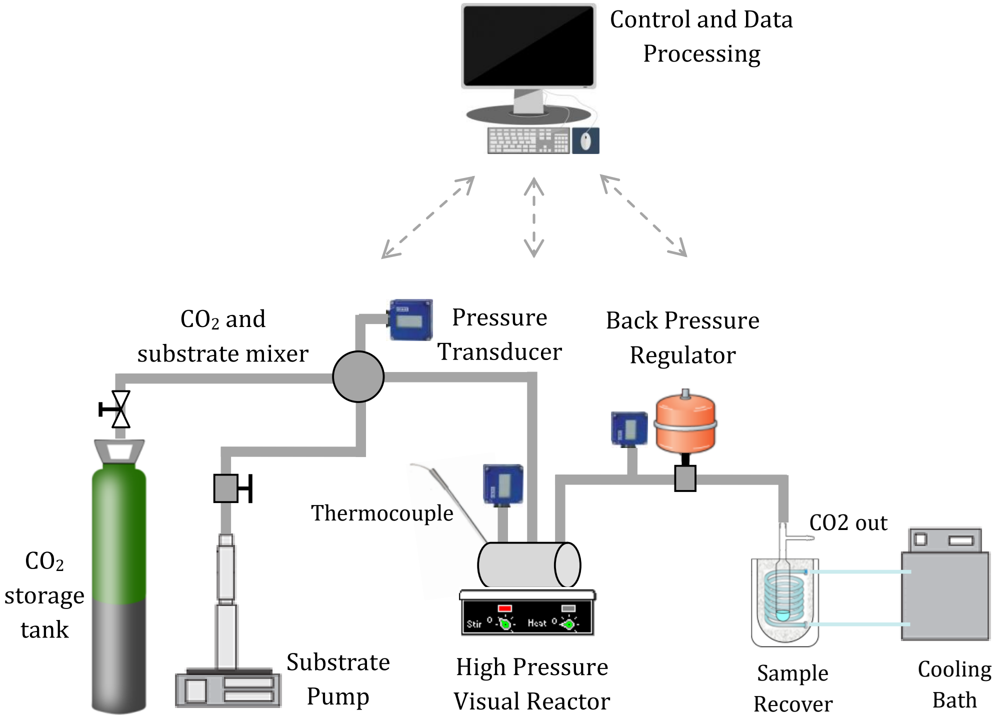


Figure 5. Schematic representation of the full continuous flow set-up.

The reaction was started by switching on the pump and opening the ball valve to the equilibrated supercritical fluid flow, always with an overpressure of liquid substrate to avoid gas intrusion. During the experiment the reaction mixture inside the high pressure reactor was stirred at 500 rpm. The product was collected in a cold trap filled with deuterated ethanol and weighted amounts of mesitylene (internal standard).

To avoid any evaporation of the sample, the glass traps were surrounded by a serpentine with a cooling liquid at -20°C, cooled by means of a cryostat bath. While the system was running, the cold traps were changed periodically and the contents analysed by ^{1}H-NMR spectroscopy. The reaction was stopped by closing substrate feeds. The system was purged with CO_2 for at least a further hour to extract residual substrate/product from the catalyst phase. In the end we stopped it by switching off the CO_2 flow and settling the back pressure regulator (BPR) valve to atmospheric pressure using a depressurization ramp of 0.3 MPa/min.

5.3. Results and Discussion

In this work the possibility of setting a continuous flow process for the synthesis of limonene carbonate (LC) from CO_2 and limonene oxide (LO) was investigated. Following our previous studies on the utilization of $scCO_2$ not only as a C_1 building block, but also as a green solvent for product separation from the reaction mixture [29, 32], a proof-of-concept of the continuous flow process was carried out. The ionic liquid Aliquat Cl was selected as liquid catalyst phase and LO as a challenging and bio-based renewable substrate. Preliminary batch reactions and phase behaviour studies were performed. Results obtained for high pressure batch reactions using different operating conditions are presented in Table 1. All reactions were performed under solvent-free conditions.

The low reactivity of LO is evident when comparing results obtained in entries 1 and 2. In fact, LO is an internal, trisubstituted epoxide and the kinetic barrier for its activation is significantly higher than for terminal epoxides. Furthermore, both time and temperature increase presented positive effects on LC formation (entries 2, 4, 5 and 6), while a pressure increase from 4 to 20 MPa resulted in a slight negative effect (entry 7). Lower carbonate formations at higher densities of the gas phase, are very likely due to the substrate partition preferentially in the $scCO_2$ rather than in the ionic liquid phase. However and since the aim of the work is to use CO_2 as reactant and solvent for final product separation, high pressure conditions are required to achieve an efficient extraction of the final product. In this context, an increase in LC formation to 70% was achieved by following the increase in the reaction pressure, with an increase in the reaction temperature, up to 373.2 K (entry 8). In entry 9 it was possible to observe that also at 373.2 K an increase in reaction pressure results a negative effective in the carbonate formation.

Table 1.Cyclic carbonate (CC) formation from epoxide and carbon dioxide

Entry [a]	Substrate(mmol)	P_{CO2} (MPa)	T (K)	t (h)	CC formation [b]
1	PO (14.3)	4	333.2	3	30%
2	LO (6.10)	4	353.2	3	< 5%
3	LO (6.10)	4	373.2	3	10%
4	LO (6.10)	4	403.2	3	65%
5	LO (6.10)	4	353.2	24	40
6	LO (6.10)	4	353.2	48	65%
7	LO (6.10)	20	353.2	48	60%
8	LO (6.10)	20	373.2	48	75%
9	LO (6.10)	30	373.2	48	70%

[a] All reactions were performed using 1 mL of substrate and 1 g of Aliquat Cl as the catalyst

[b] Carbonate formation determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture

The activity of the selected ammonium-based ionic liquid (Aliquat Cl) used by us in previous studies [29] as liquid phase and reaction catalyst was compared with the activity of the most reported ionic liquid tetrabutylammonium bromide (TBABr) and also with Aliquat Br, in order to compare the effect of the chloride and bromide anions. Results are presented in Figure 6.

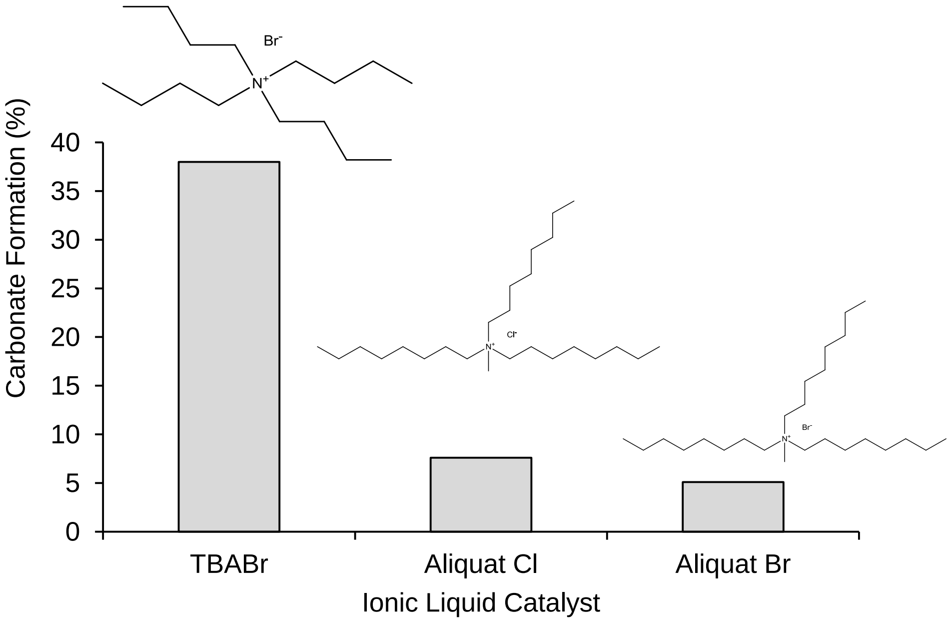


Figure 6. Carbonate formations obtained for batch reactions using different ionic liquids as catalyst for limonene oxide coupling reaction with CO_2. Reactions were performed for 3 h, 373.2 K and 4 MPa, using 1 mL of limonene oxide (6.10 mmol) and 1g of ionic liquid catalyst.

Although TBABr is solid until around 373.2 K (Melting Point = 376.2 K), it is a liquid under the reaction conditions. This is due to the melting point depression caused by the CO_2 and the high temperature.

Regarding the activity of bromide versus chloride anion, bromide is often reported as being the more efficient anion for the ring opening step, due to stronger nucleophilicity. However, in this case that difference was not verified, probably due to the fact that being LO a sterically crowded epoxide, the size of the nucleophile stands as an additional factor to be considered, as reported by Rintjema *et al.* [33].

In order to determine the suitable conditions for integrating reaction and separation steps, high pressure phase behaviour studies of the binary mixtures CO_2+LO and CO_2+LC were performed. Ideally to have an efficient continuous flow process the substrate should be more soluble in the stationary catalytic phase, whereas the product should preferentially dissolves in the $scCO_2$ mobile phase.

LO and LC solubility's in $scCO_2$ were estimated from phase behaviour studies at 373.2 K. Figure 7 and 8, shows images taken at different pressures for mixtures of CO_2 with pure LO and

LC, respectively. Visual observations, allowed us to conclude that as expected the solubility of both compounds rises with increasing CO_2 pressures. Although the carbonate functionality is considered a "CO_2-philic" substituent, the solubility trend rather follow the volatility of LO and LC. In fact, as CO_2 pressure increases, the formation of a homogeneous supercritical phase was observed.

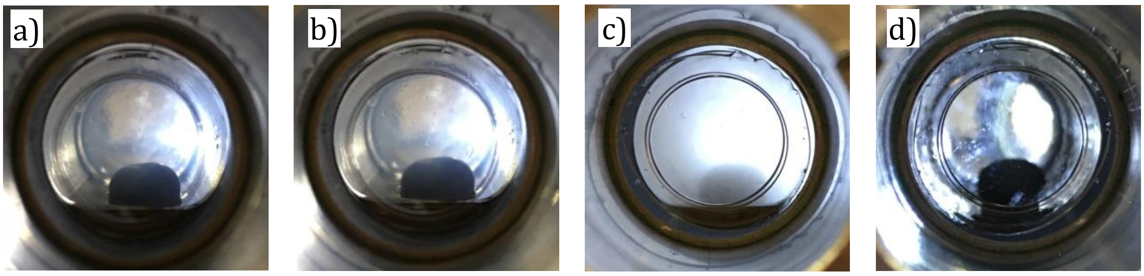


Figure 7. Images of the interior of the high pressure reactor at 373.2 K and different pressures showing the progressive dissolution of the LO in the $scCO_2$: (a) 10, (b) 15, (c) 17.5, and (d) 19.5 MPa.

At 19.5 MPa, LO was completely solubilised in the CO_2 phase (Figure 7d). The system transition from two phases (gas+liquid) to a single supercritical phase was observed at 17.5 MPa of CO_2 (Figure 7c). In the case of LC, the phase transition was observed at 24.5 MPa (Figure 8c) and a complete dissolution of the solute was observed at 25.5 MPa (Figure 8d).

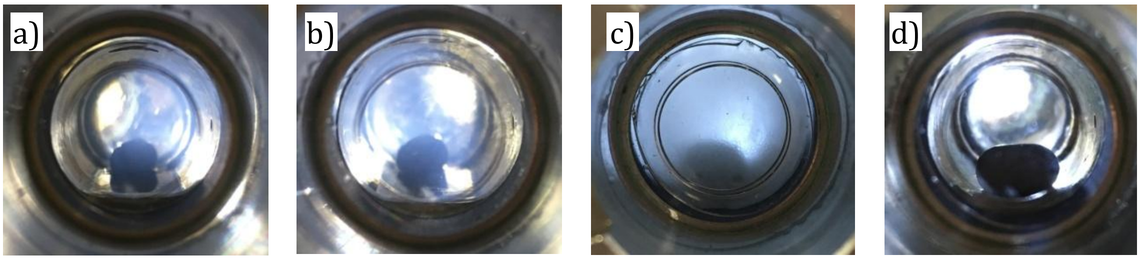


Figure 8. Images of the interior of the high pressure reactor at 373.2 K and different pressures showing the progressive dissolution of the LC in the $scCO_2$: (a) 10, (b) 20, (c) 24.5, and (d) 25.5 MPa.

Analysing phase behaviour results obtained, it is possible to conclude that for this particular reaction system, the reaction substrate (LO) is more soluble in the supercritical phase than the reaction product (LC). As mentioned before, this is exactly the opposite of an ideal system, in which the product should be more soluble than the substrate in the mobile phase. Another additional important factor that has not been considered in these phase behaviour studies is the presence of the ionic liquid phase, which will influence the partition coefficient of both substrate and product between phases. Nevertheless, based on results obtained for high pressure phase behaviour, operational conditions for which both substrate and product were soluble, a pressure of 30 MPa and temperature of 373.2 K were selected.

These high pressure and temperature conditions were selected in order to prevent the accumulation of the product inside the reactor. On the other hand, to achieve high carbonate formations, a high residence time was assured by selecting a low substrate flow of 0.005mL/min. Finally, after preliminary experiments a CO_2 flow rate of 40 mL/min was selected.

The continuous flow process was investigated using TBABr as the catalytic phase and testing three different temperatures (in the same experiment). Unexpectedly the initial conversion at 373.2 K was significantly lower than that obtained for preliminary batch reactions, with LC formation percentages achieving only ca.10% as shown in Figure 9.

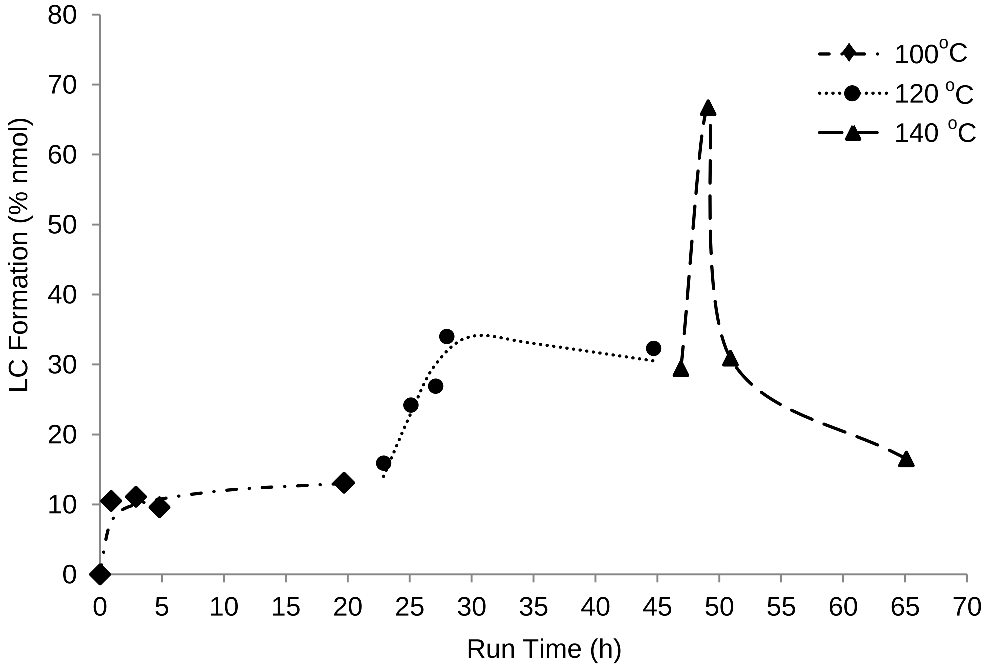


Figure 9. LC formation from cycloaddition reaction of CO_2 and LO in continuous flow mode. Reactions were performed sequentially at 30 MPa and different temperatures in a high pressure cell with 1 g of TBABr. A LO flow of 0.005mL/min and CO_2 flow of 40 ml/min was used. Note that the dashed line is just showing the tendency of the obtained data.

Moreover, as can be observed, by increasing the temperature from 373.2 to 393.2 K, it was possible to increase the LC formation to ca. 35%. A further temperature increase to 413.2 K, significantly increased LC mol% recovered in the cold trap. This increase should be related with the temperature increase, however, after 65 h, there was no observation of LC formation increase, which result, actually seems to indicate a slight conversion fall. The explanation for these results at 413.2 K is possibly a more efficient product extraction from the reactor due to temperature increase, which however rapidly levelled off.

The same process was repeated using Aliquat Cl as the catalytic liquid phase. Three different temperatures were investigated, this time in independent experiments. Results are presented in Figure 10.

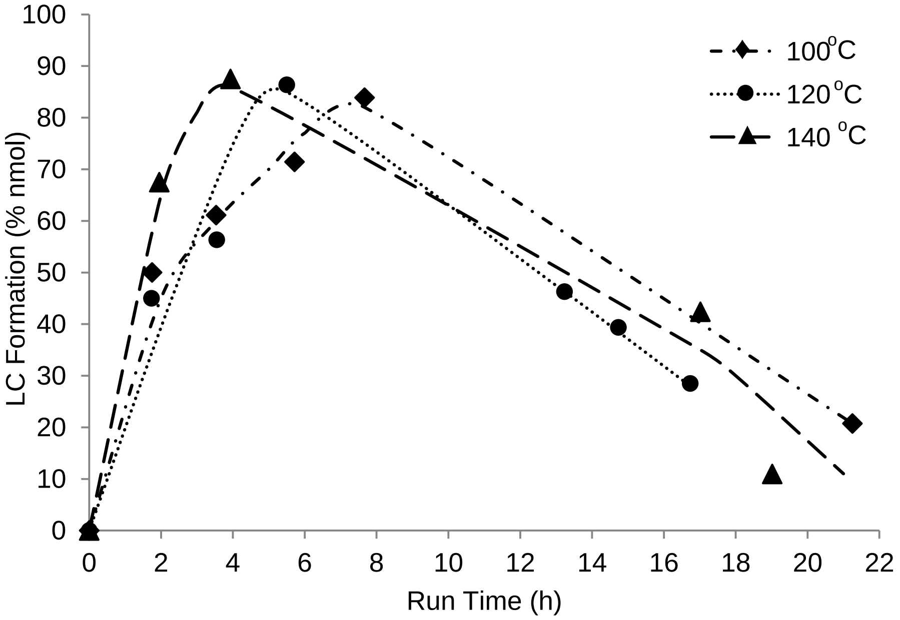


Figure 10. LC formation from cycloaddition reaction of CO_2 and LO in continuous flow mode. Reactions were performed at 30 MPa and different temperatures in a high pressure cell with 1.4 g of Aliquat Cl. LO flow of 0.005mL/min and CO_2 flow of 40 ml/min was used. Note that the dashed line is just showing the tendency of the obtained data.

Contrary to what was expected, Aliquat Cl proved to be a much more effective catalytic phase, with LC formation percentages achieving 90%. The fact that Aliquat Cl is a liquid at room temperature, makes it very likely a less viscous liquid than TBABr at the reaction conditions. This difference in viscosities affects mass transfer and the reaction kinetics, resulting in lower conversions in the flow operation in contrast to what was earlier verified for batch reactions. In addition, when Aliquat Cl was used as the catalytic liquid phase, a strong unexpected carbonate formation decay was observed at around 12 hours of reaction, for all studied temperatures (Figure 10). This sharp decrease resulted in a total carbonate formation of only 18% after near 20 hours of reaction.

Table 2. Mole Balance for the LC formation from cycloaddition reaction of CO_2 and LO in continuous flow mode for the experiments shown in Figure 9 and 10, using Aliquat Cl and TBABr, respectively, as catalyst.

Catalyst	T (K)	LO pumped (nmol)	LO recovered (nmol)	LC formation (nmol)	Molar Balance (%)
Aliquat Cl	373.2	49.4	30.6	12.6	87.5
Aliquat Cl	393.2	30.6	13.7	13.8	89.8
Aliquat Cl	413.2	37.1	27.2	6.1	89.8
TBABr	373.2, 393.2, 413.2	119.2	83.3	18.3	85.2

The possibility of being a result of product retention inside of the reactor was excluded after proper molar balances calculations. Results are presented in Table 2. For all the experiments a molar balance higher than 85% was obtained. Therefore, the observed reaction conversion decay must be due to catalyst deactivation probably due to the effect of such high temperatures during larger periods of time. In Table 3, a direct comparison of results obtained for batch and continuous flow experiments is presented.

Table 3. Summary of process intensification using continuous flow technology for the coupling reactions between limonene oxide and CO_2 for the production of cyclic carbonates. Conditions for comparable batch reactions are also given. For flow reactions it was selected the total TON (tTON), the maximum TOF (TOF max) and the total STY (tSTY).

Entry	T (K)	Catalyst	Reaction Type [a]	tTON [b]	TOF max [b]	tSTY (g/h L) [b]
1	413.2	Aliquat Cl	Flow	1.73	0.18	5.92
2		TBABr	Flow [c]	5.88	0.10	5.50
3	393.2	Aliquat Cl	Batch	1.46	0.03	2.94
4			Flow	4.08	0.16	16.2
5		TBABr	Batch	0.81	0.02	2.14
6			Flow [c]	5.88	0.10	5.50
7	373.2	Aliquat Cl	Batch	1.43	0.02	2.17
8			Flow	2.92	0.08	7.94
9		TBABr	Batch	1.28	0.03	3.39
10			Flow [c]	5.88	0.10	5.50

[a] batch reactions were performed at 4 MPa for 48h and 1 g of catalyst and 1 mL of LO (6.10mmol); flow reactions with TBABr were performed sequentially at 30 MPa and different temperatures in a high pressure cell with 1 g of TBABr; flow reactions with Aliquat Cl were performed at 30 MPa and different temperatures in a high pressure cell with 1.4 g of Aliquat Cl. In both flow experiments LO flow of 0.005mL/min and CO_2 flow of 40 ml/min was used.

[b] these results were calculated based on the carbonate formation

[c] these three temperatures were investigated in the same experiment

Although these results are not optimized, it is possible to observe an increase in the TON, TOF and STY for all the flow experiments over the batch experiments. These results demonstrate significant improvements in process intensity for the coupling reactions between epoxides and CO_2. Additionally, the flow setup offers high accuracy of process control in continuous operation mode over a wide range of conditions. Besides that, it allows automated experimentation and monitoring and recording all the process conditions.

5.4. Conclusions

A continuous flow process based on a CO_2/ionic liquid biphasic mixture was explored to carry out the cycloaddition reaction between CO_2 and limonene oxide. High pressure solubility measurements revealed a non-optimal behaviour, with the substrate (limonene oxide) presenting a higher solubility in the supercritical phase, than the product (limonene carbonate). For Aliquat Cl, carbonate formations of 90% (never attained in the batch process) were observed followed however by an abrupt carbonate formation decrease. For the case of TBABr, carbonate formations were much more moderate. However, it was possible to conduct the reaction for around 20 hours and working temperatures of 373.2 K and 393.2 K. TBABr revealed to be a much more stable catalytic liquid phase for the continuous flow process, when compared with ALIQUAT Cl.

5.5. References

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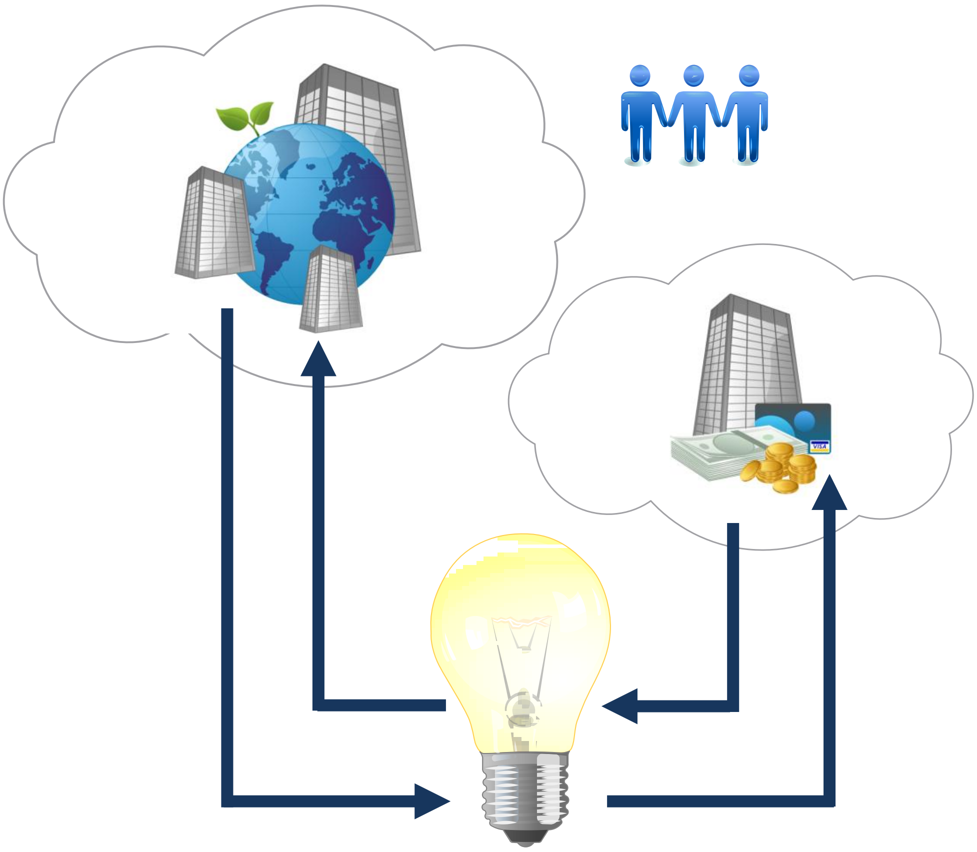
Chapter 6

Concluding Remarks and Future Perspectives



Conclusions and Future work

The production of cyclic carbonates from CO_2 and epoxides is one of the most promising strategies to rapidly introduce significant amounts of CO_2 into the chemical value chain. This thesis addressed two main challenges in this context, which relates with the necessity to expand the type of epoxides to be used as substrates, namely by exploiting bio-based epoxides, and the development of more sustainable chemical processes which can preferentially operate in continuous flow.

Homogeneous metal complexes are still among the most effective catalytic systems explored as they significantly decrease the energy barrier of the reaction by coordinating with the epoxide. In this work, Zinc(II)-complexes of arylhydrazones of ß-diketones were used for the first time in this application and although the catalytic activity observed was around the same activity of other complexes reported in literature, their very high stability and solubility in polar solvents may bring considerable advantages to large scale industrial processes. It should be noted that also as many metal complexes reported in the literature, Zn(II)-AHBD did not presented any catalytic activity when used alone, whereas a nucleophile (as TBABr) has always to be used. In fact TBABr, which is still considered an ionic liquid (Tm~373.2 K), also exhibited catalytic activity when used alone.

Towards these results, the effect of other ionic liquids (in catalytic quantities) was studied with bulkier cations (as tetrabutylammonium) and highly nucleophilic anions (as chloride and bromide) presenting the best results and standing as the best combination. Actually, among several effects studied, the bulkiness of the cation was the more important factor affecting the reaction kinetics. Furthermore, trioctylmethylammonium chloride (Aliquat Cl) due to lower melting point (253.2 K) was for the first time explored as solvent in this reaction, efficiently dissolving Zn(II)-AHBD complexes and also showing to act as catalyst during the reaction. This system was effectively applied to catalyse the reaction between CO_2 and limonene oxide, a bio-based epoxide that due sterically hindrance presented much lower reactivities in comparison with fossil-derived epoxides.

An important issue, since CO_2 has always to be present in the process, is the possibility of taking advantage of it peculiar properties at high pressures, which is particular relevant and has been disregarded by scientists in the field. Two different high pressure CO_2/ ionic liquid biphasic systems were explored in order to develop continuous flow operations with integrated product separation. This concept intends to take advantage of the possibility of using CO_2 as reactant and solvent to separate the final product (limonene carbonate) out of the reaction mixture. An ionic liquid was used as catalyst either supported onto an alginate aerogel (SILP process) or as bulk liquid phase inside a continuous flow reactor (BULK process).

In the SILP process, an alginate aerogel was used for the first time as a support for an ionic liquid (Aliquat Cl) phase and although really high loadings were attained, results showed that the ionic liquid was very easily leaching out of the support. This effect led to the impossibility of reusing the catalyst, which occurred very likely due to the aerogel highly opened porous structure. In this way if one wants to take advantage of aerogel technology high loadings and light material, the ionic liquid phase probably has to be covalently attached to the support.

Regarding the BULK process, a continuous flow operation was carried out for several hours using TBABr as the catalyst liquid phase. High-pressure CO_2 was successfully used as reactant and solvent for final product (limonene carbonate) separation. However for 413.2 K an abrupt decay of the catalytic activity was observed very likely due to TBABr degradation with temperature. When Aliquat Cl was used this effect was even more pronounced, with deactivation occurring for all temperatures studied. Future perspectives clearly indicate the necessity of a joint effect among ionic liquids and metal homogeneous catalysts in order to considerably increase the catalytic activity of the system and allow a substantial reduction of the reaction temperature.

In conclusion, this work provides new opportunities in terms of process engineering for the development of continuous flow processes for cyclic carbonates production from CO_2 and epoxides. Although still higher catalytic activities have to be found, high-pressure CO_2/ ionic liquid biphasic system showed a promising potential in order to develop a continuous flow process for this particular application.

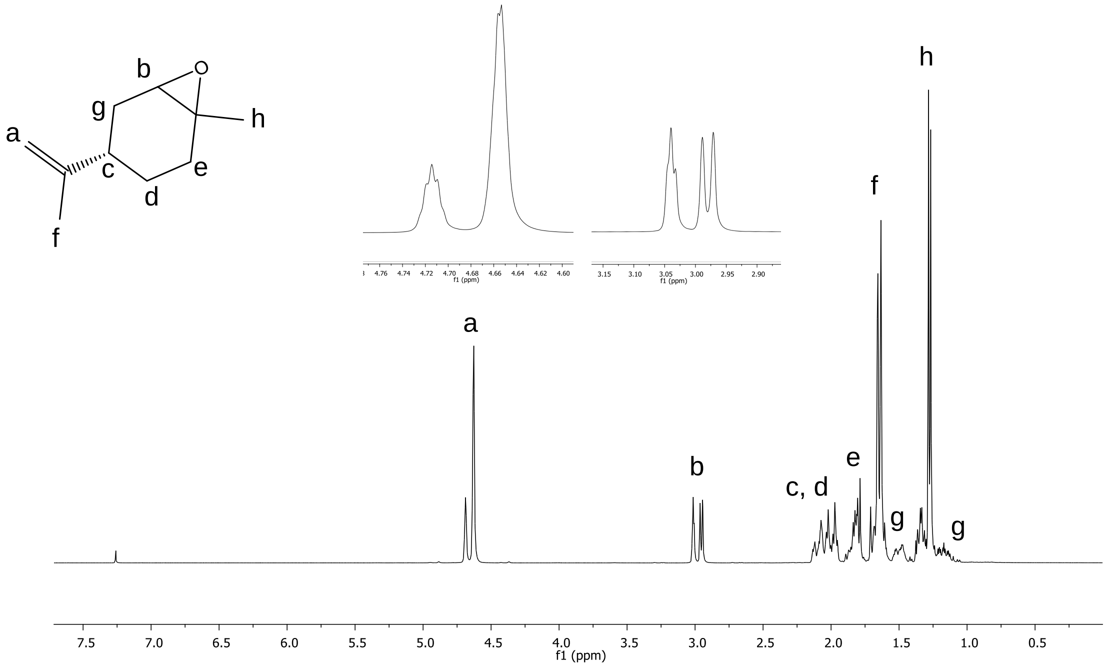


Figure A1. ^{1}H-NMR spectrum of limonene oxide (δ=3.0 ppm), mixture of cis and trans in CDCl$_3$.

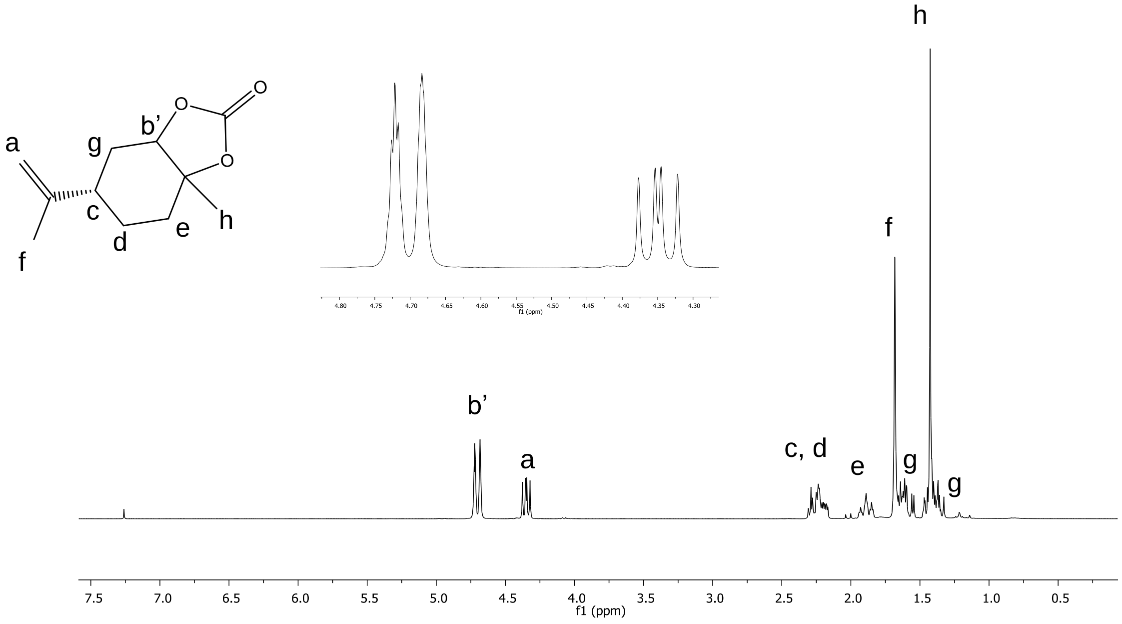


Figure A2. ^{1}H-NMR spectrum of limonene carbonate (δ=4.4 ppm) purified by flash chromatography on silica gel by using n-pentane/ethyl acetate (10:1) as the eluent in CDCl$_3$.

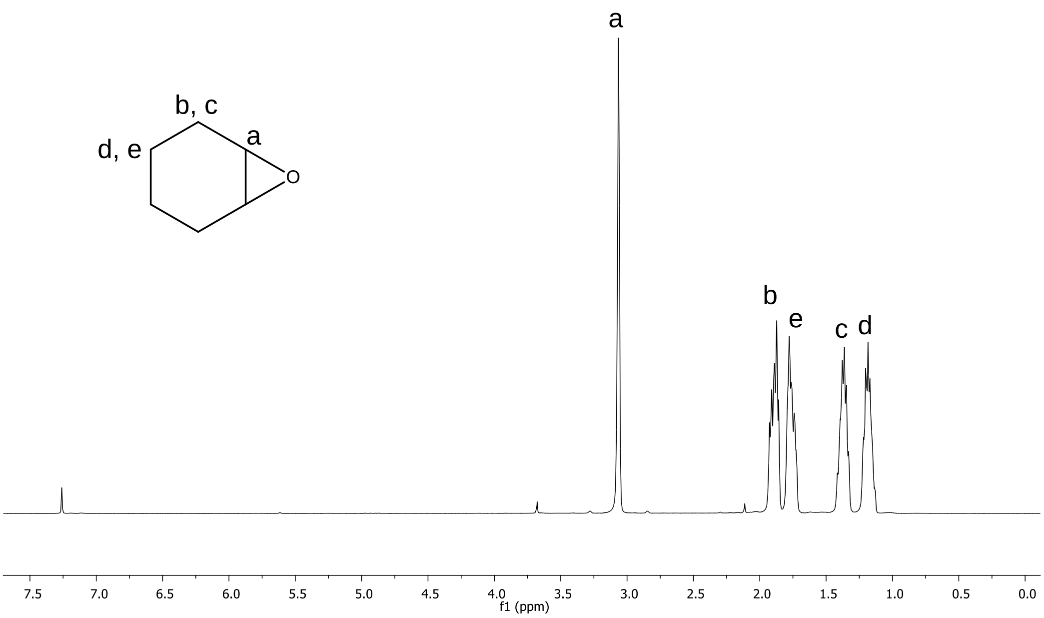


Figure A3. ^{1}H-NMR spectrum of cyclohexene oxide (δ=3.0 ppm) in CDCl3.

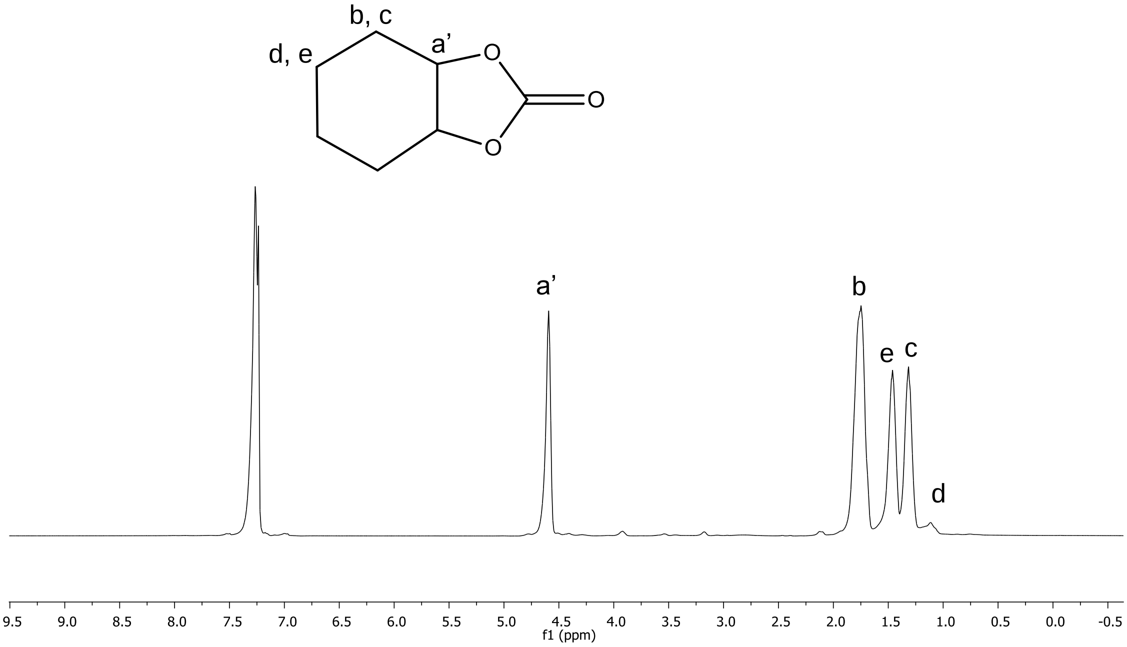


Figure A4. ^{1}H-NMR spectrum of cyclohexene carbonate (δ=4.6 ppm) from the reaction mixture in $CDCl_3$.

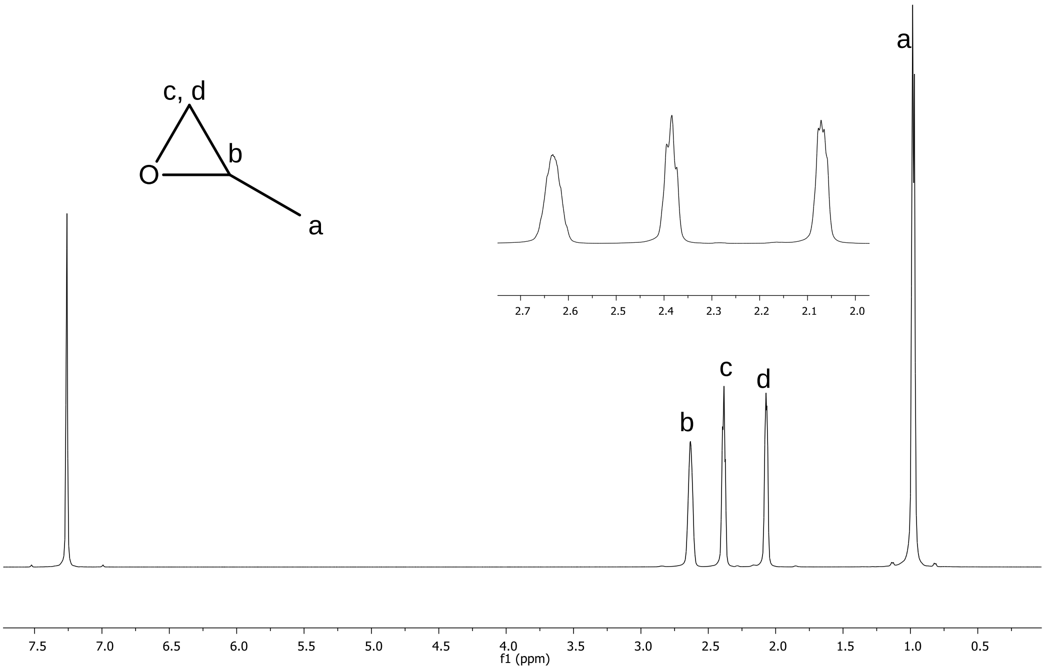


Figure A5. ^{1}H-NMR spectrum of propylene oxide (δ=2.9 ppm) in CDCl$_3$.

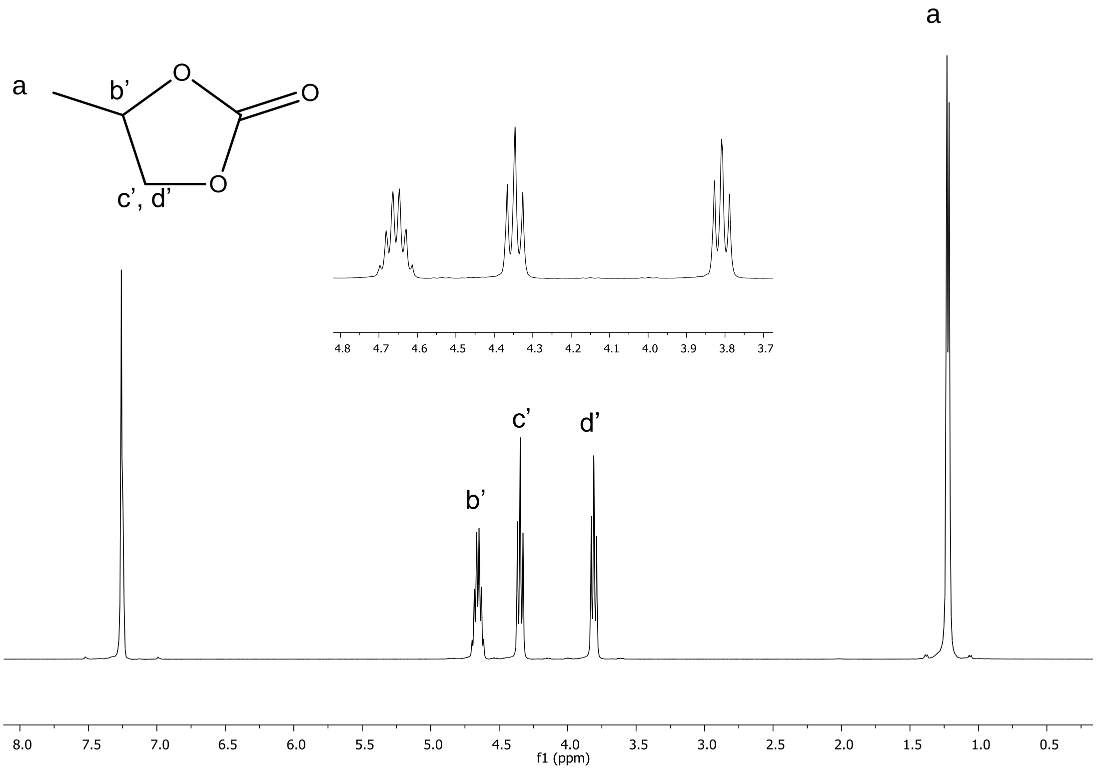


Figure A6. ^{1}H-NMR spectrum of propylene carbonate (δ=4.8 ppm) in CDCl$_3$.

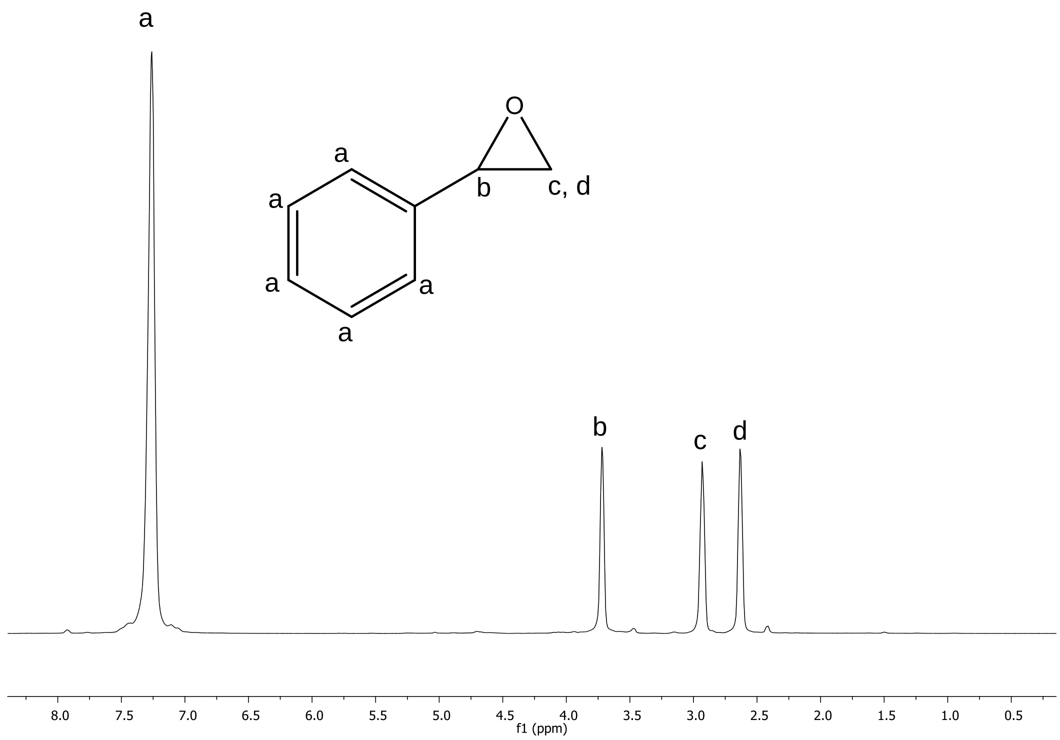


Figure A7. ^{1}H-NMR spectrum of styrene oxide (δ=3.8, 2.9 and 2.7 ppm) in $CDCl_3$.

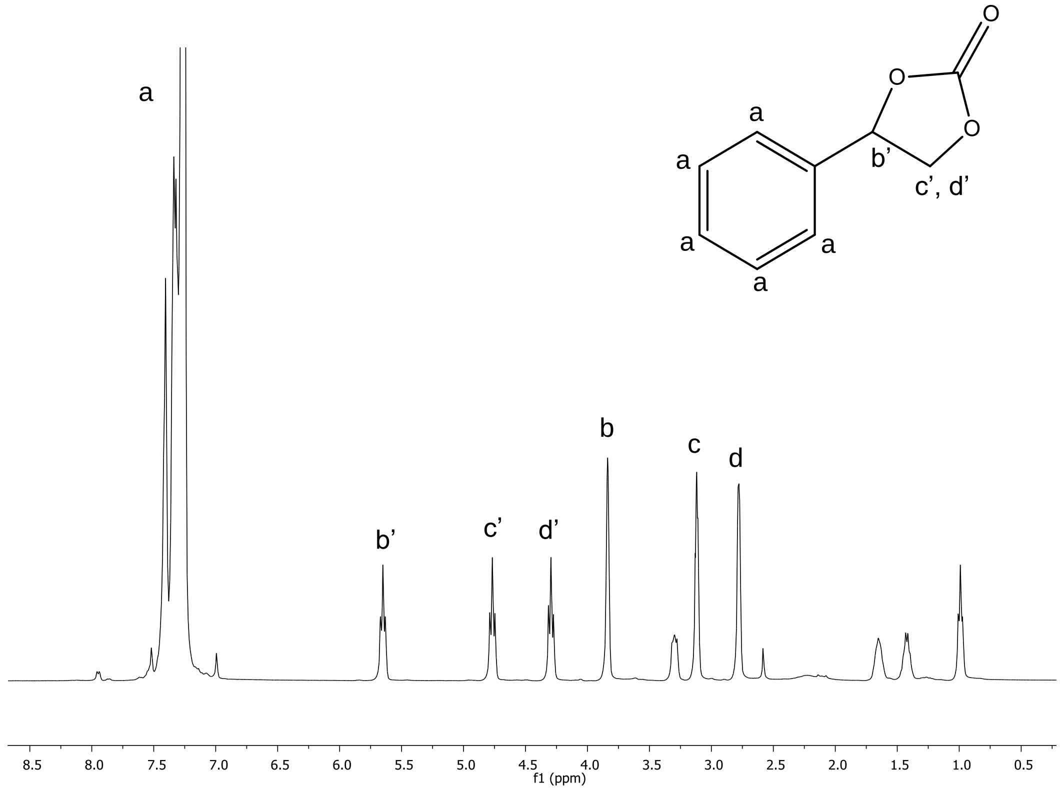


Figure A8. ^{1}H-NMR spectrum of styrene carbonate (δ=5.6, 4.8 and 4.3ppm) from the reaction mixture in $CDCl_3$.

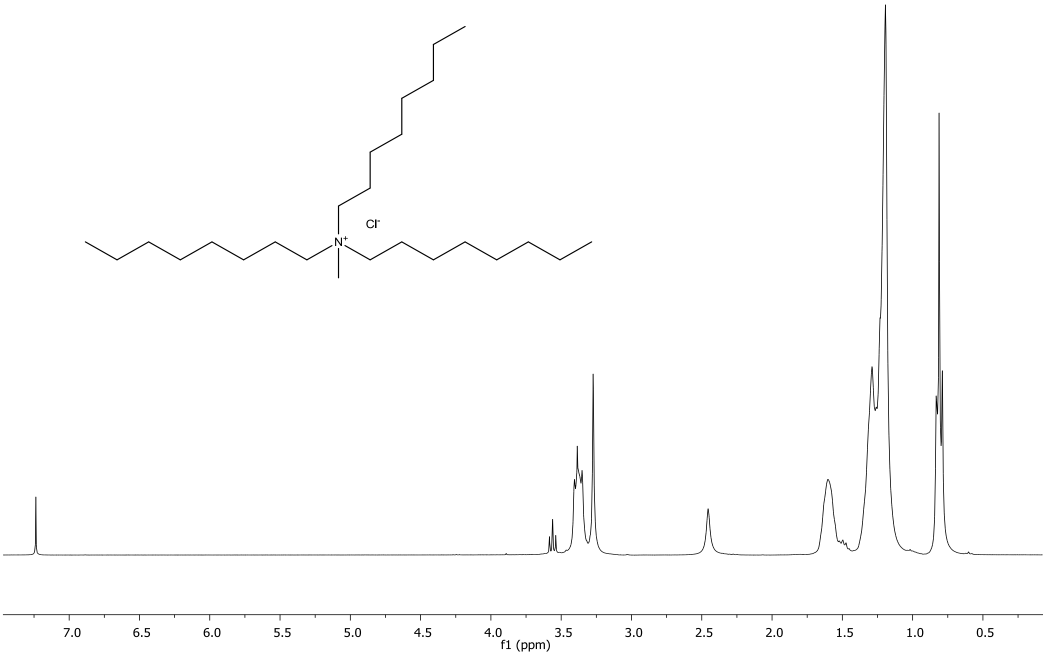


Figure A9. ^{1}H-NMR spectrum of Trioctylmethylammonium Chloride (Aliquat Cl) in $CDCl_3$.

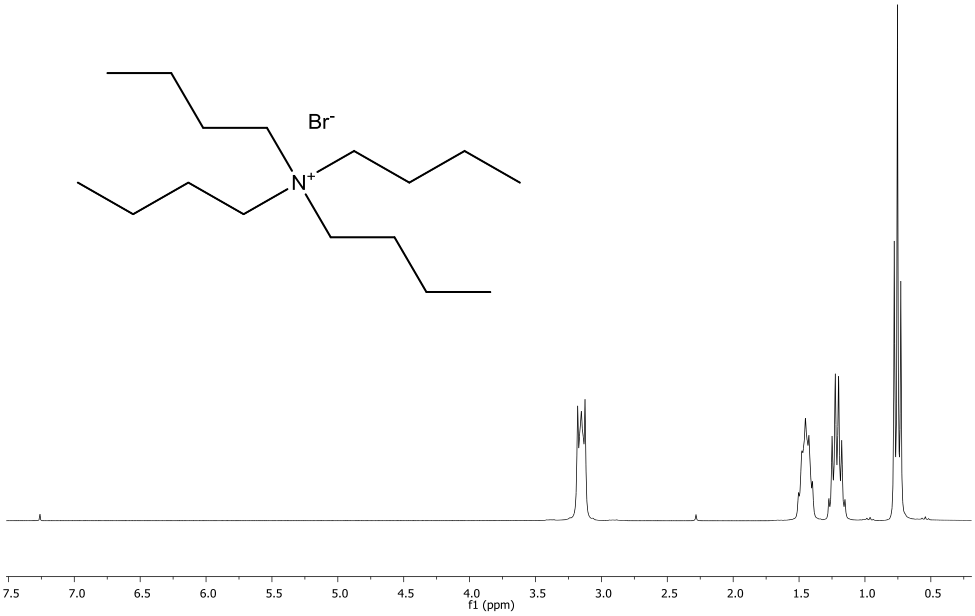


Figure A10. ^{1}H-NMR spectrum of Tetrabutylammonium Bromide (TBABr) in $CDCl_3$.

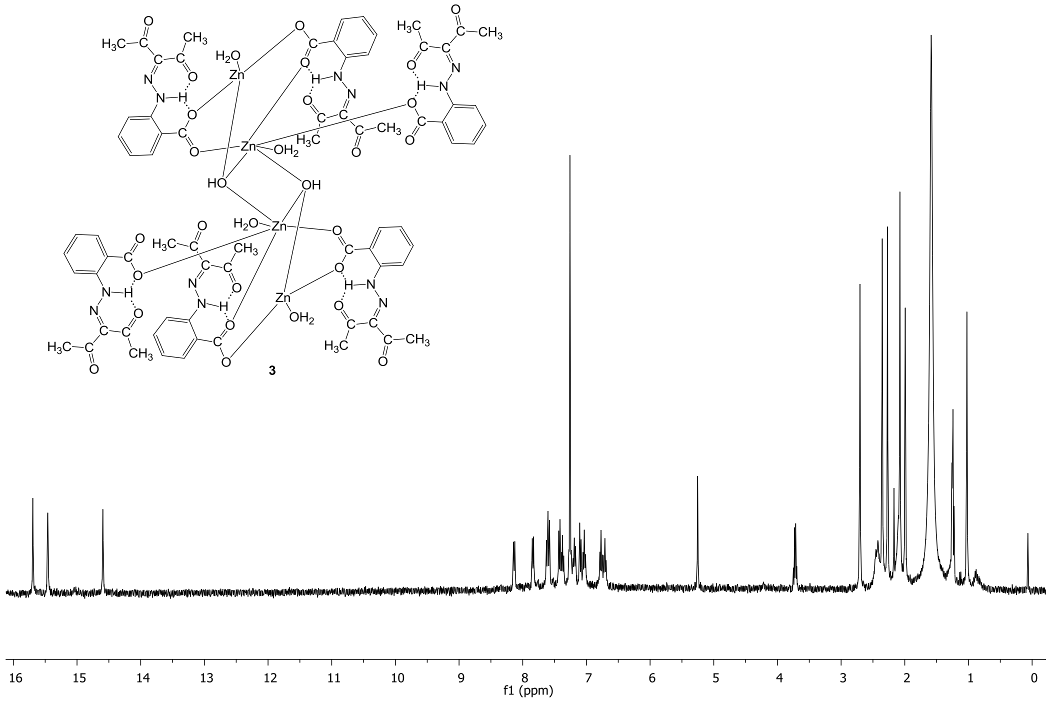


Figure A11. ^{1}H-NMR spectrum of Zinc II Complex 3 in $CDCl_3$.

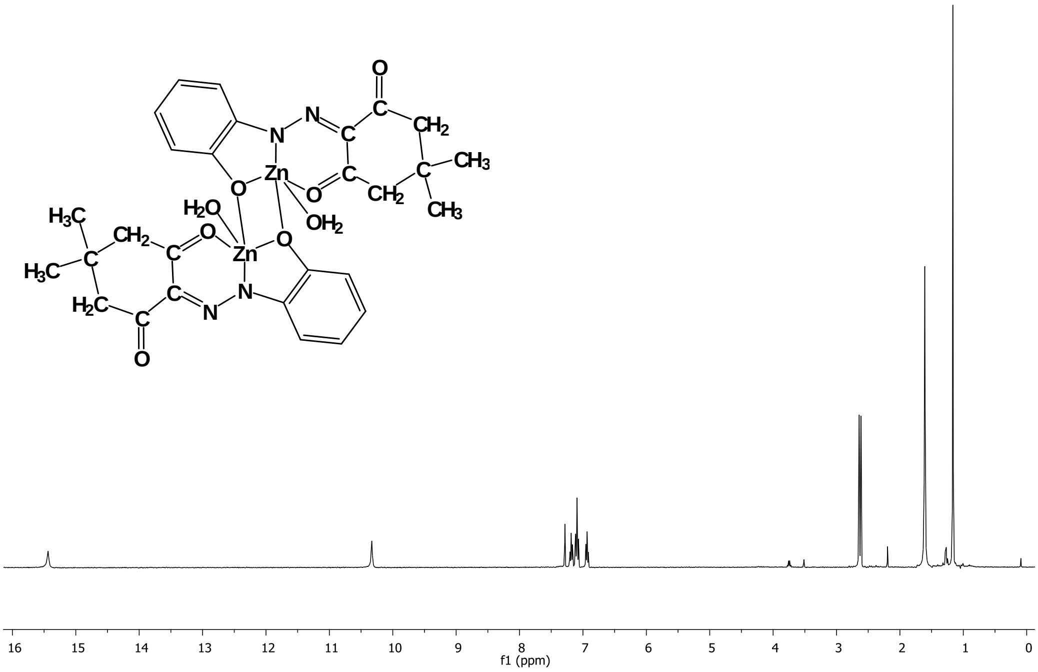


Figure A12. ^{1}H-NMR spectrum of Zinc II Complex 2 in $CDCl_3$.

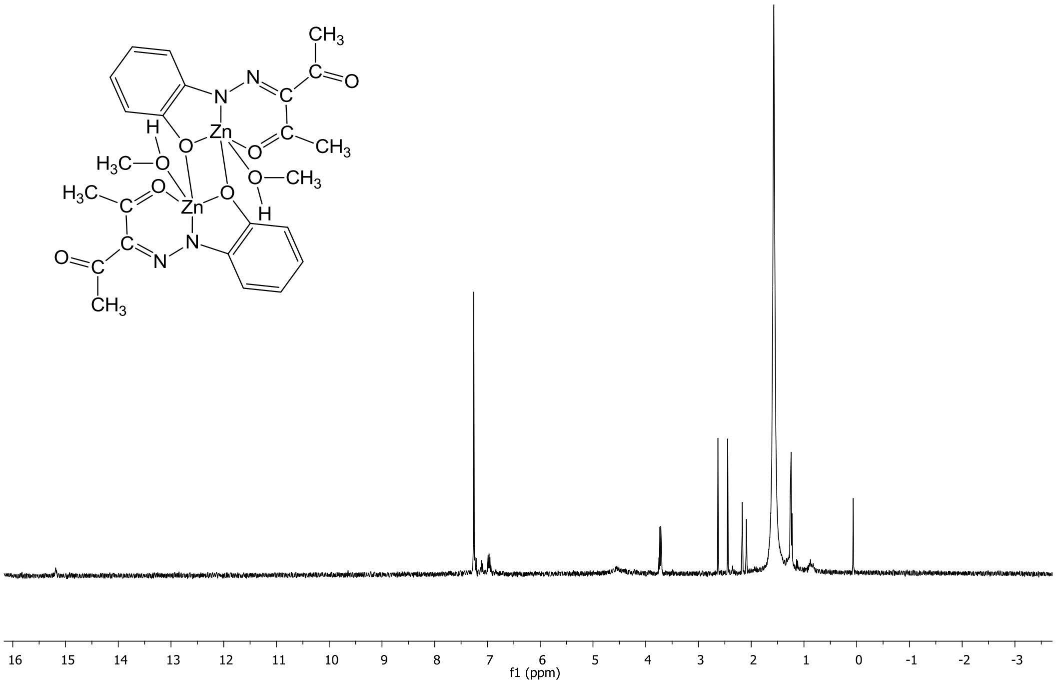


Figure A13. ^{1}H-NMR spectrum of Zinc II Complex 1 in $CDCl_3$.

Scientific Contributions

List of Publications

CO_2 + ionic liquid biphasic system for reaction/product separation in the synthesis of cyclic carbonates, Ana B. Paninho, Alexandre Ventura, Luís C. Branco, Armando J. L. Pombeiro, M. Fátima C. Guedes da Silva, Manuel Nunes da Ponte, Kamran T. Mahmudov, Ana V. M. Nunes, J. Supercrit. Fluids, 2018, 132, 71 (DOI:10.1016/j.supflu.2017.07.039);

Carmen A. Montoya, Clara F. Gómez, Ana B. Paninho, *et al.*, Cyclic carbonate synthesis from CO_2 and epoxides using zinc(II) complexes of arylhydrazones of β-diketones, J. Catal., 2016, 335, 135 (DOI:10.1016/j.jcat.2015.12.027);

Ventura, Marcia; Paninho, Ana; Nunes, Ana; Fonseca, Isabel; Branco, Luis; Aerogels of locust bean gum prepared by Ionic Liquids and $scCO_2$ sustainable system, RSC Advances, 2015, 5, 107700 (DOI: 10.1039/C5RA17314K);

Montoya C.A., Paninho A. B., Felix P., Zakrzewska M.E., Vital J. Najdanovic-Visak V and Nunes A.V.M, Styrene carbonate synthesis from CO_2 using tetrabutylammonium bromide as a non-supported heterogeneous catalyst phase, J. Supercrit. Fluids, 2015, 100, 155 (DOI:10.1016/j.supflu.2015.01.027);

List of Communications

Cyclic Carbonate Synthesis from CO_2 and Epoxides: Sustainable Intensification, Works4u @Nova – Bridging Academia & Industry in Chemistry and Life Sciences, Lisbon – Portugal, 29-30 May 2018 (Oral Communication).

Limonene carbonate synthesis from CO_2: Continuous flow catalysis with integrated product separation, 12th International Symposium on Supercritical Fluids, Antibes – France, 22-25 April 2018 (Oral Communication)

Coupling Reactions between CO_2 and Epoxides Using Aerogels as Supporting Metal-Ionic Liquid Phase, 16th European Meeting on Supercritical Fluids, Lisbon- Portugal, 25-28 April 2017 (Oral Communication)

Impregnation of zinc catalyst into aerogels as catalytic system for coupling reaction between CO_2 and epoxides, COST Meeting - Action CM1206, Lyon – France, 30-31 March 2017 (Oral Communication)

Separation Process Integrated in the Production of Cyclic Carbonates from High-Pressure CO_2, 1st Scientific Meeting of the Doctoral Programme in Sustainable Chemistry, Aveiro- Portugal, 26th September 2016 (Poster Communication Award)

Reaction-Separation Process Integration In the Production of Cyclic Carbonates From High-Pressure CO_2, 15th European Meeting on Supercritical Fluids, Essen-Germany, 8-11 May 2016 (Oral Communication)

Differences in reactivity of propylene oxide versus cyclohexene oxide on the production of cyclic carbonates from CO_2 using zinc(II) complexes, 2nd EuCheMS Congress on Green and Sustainable Chemistry, Lisbon-Portugal, 4- 7 October 2015 (Poster Communication)

Styrene carbonate production from CO_2 using zinc(II) complexes of arylhydrazones of β-diketones, 2nd EuCheMS Congress on Green and Sustainable Chemistry, Lisbon-Portugal, 4-7 October 2015 (Poster Communication)

Boosting CO_2 conversion through phase behaviour manipulation at high pressures, Large Volume CO_2 Utilization: Enabling Technologies for Energy and Resource Efficiency, International Scientific Forum on CO_2 chemistry and biochemistry, Lyon-France, 25-26 September 2014 (Oral Communication).

Boosting CO_2 as a renewable carbon source: new opportunities provided by high pressure conditions, 14th European Meeting on Supercritical Fluids, Marseille-France, 18-21 May 2014 (Poster Communication)