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Master Thesis

Carbon dioxide valorization: Continuous production of fine chemicals

ausgeführt am

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BGE	1-butoxy-2,3-epoxypropane
[BHEIM]Br	1,3-bis-(2-hydroxyethyl)imidazolium bromide
BO	butylene oxide
CMC	carboxymethyl cellulose
DCM	dichloromethane
EA	ethyl acetate
[EMIM]Br	1-ethyl-3-methylimidazolium bromide
EO	ethylene oxide
EOPOP	1,2-epoxy-3-phenoxypropane
HCMC	protonated CMC
[HEMIM]Br	1-(2-hydroxyethyl)-3-methylimidazolium bromide
[HPBIM]Cl	1-butyl-3-(3-hydroxypropyl)imidazolium chloride
IL	ionic liquid
IR	infrared spectroscopy
MeOH	methanol
[MOIM]Br	1-methyl-3-octylimidazolium bromide
MTBE	7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene
PC	propylene carbonate
PO	propylene oxide
P_2O_5	phosphorus pentoxide
SILP	supported ionic liquid phase
SO	styrene oxide
[TBA]Br	tetrabutylammonium bromide
[TBHEA]Br	tributyl-(2-hydroxyethyl)ammonium bromide
[TBHEP]I	tributyl-(2-hydroxyethyl)phosphonium iodide
[TBP]Br	tetrabutylphosphonium bromide
TGA	thermal gravimetric analysis
TON	turnover number

1. Abstract

1.1 Short summary

This work focuses on the development of a continuous process for the conversion of carbon dioxide and propylene oxide into propylene carbonate. Processes could be developed which produce pure propylene carbonate in a continuous manner using supercritical carbon dioxide as solvent as well as reagent. Ionic liquids were used as catalysts and were immobilized via the supported ionic liquid phase (SILP) approach. In order to achieve the highest possible production rate, different catalytic systems for this reaction were investigated in a batch process as well as in a continuous flow process. It was shown that the catalytic activity of the reaction system depends on the structure of the ionic liquid as well as on the support material on which it is dispersed. Phosphonium, ammonium and imidazolium (Lewis basic) based ionic liquids, optionally with hydroxyl groups were used. In addition, the influence of different anions, with particular attention to Lewis acidic ones (such as $[ZnBr_4]^{2-}$) was investigated. Their stability, selectivity as well as their interaction with various support materials revealed a significant influence for the catalytic performance. Based on these findings, the most promising system was selected for further optimization of the process parameters in continuous flow.

1.2 Deutsche Kurzfassung

Diese Arbeit setzt sich mit der Umsetzung und Optimierung eines kontinuierlichen Reatkionsprozesses zur Umsetzung von Kohlendioxid und Propylenoxid zu Propylencarbonat auseinander. Dabei spielten ionische Flüssigkeiten als Katalysatoren und für die Umsetzung der „supported ionic liquid phase“-Technologie zur Immobilisierung dieser in einem kontinuierlichen Prozess eine wichtige Rolle. Um eine möglichst hohe Produktionsrate zu erzielen wurden bekannte wie auch einige unbekannte Katalysatorsysteme für diese Reaktion im Batch-Prozess sowie auch im kontinuierlichen Fluss von superkritischem Kohlendioxid untersucht und miteinander verglichen. Es konnte gezeigt werden, dass die Aktivität des katalytischen Systems einerseits vom Aufbau der ionischen Flüssigkeit und andererseits von dem Material auf dem diese fixiert wird, abhängig ist. Dabei konnten bereits aus der Literatur bekannte Einflüsse auf die katalytische Aktivität bestätigt und um weitere Erkenntnisse erweitert werden. So wurden Phosphonium, Ammonium und Imidazolium basierte ionische Flüssigkeiten, mit und ohne Hydroxylgruppen, sowie der Einfluss verschiedener Anionen, mit besonderem Augenmerk auf Lewis-saure Anionen wie $[ZnBr_4]^{2-}$, untersucht. Dabei spielten deren katalytische Aktivität, dessen Stabilität und Selektivität, sowie deren Interaktion mit den Trägermaterialien eine entscheidende Rolle. Darauf aufbauend wurde das vielversprechendste System für die weitere Parameteroptimierung im kontinuierlichen Fluss verwendet.

2. Introduction

2.1 Carbon dioxide as carbon resource

The world's population and therefore its energy demand grows on a daily base. Currently, 80 – 85 % of the world's energy demand is based on fossil fuels.[1] It is fact that the usage of fossil fuels as energy source will not last forever. Similarly, the chemical industry highly depends on fossil fuels as raw material for the production of fine chemicals. Based on these concerns, alternative and renewable carbon resources need to be found, while simultaneously developing new technologies for their efficient valorization.

Carbon dioxide as a feedstock might be a good alternative carbon resource to fossil fuels. Utilizing the green house gas carbon dioxide would be the most direct way to close the anthropogenic carbon cycle by circumventing the use of fossil fuels or biomass in chemical production.[2] Fossil fuels are formed in up to 100 million of years. Carbon dioxide is mostly formed by combustion of organic matter, which is enhanced by human activity causing the man-made climate change. Due to the discussion of the anthropogenic climate change with carbon dioxide as most involved greenhouse gas, strategies to capture carbon dioxide from chemical processes, air and flue gases are recently of great interest. In addition, CO_2 can be directly obtained as by-product from various well developed processes in high amounts.[3] In a fairly pure and concentrated form, CO_2 is formed in a big amount in ammonia synthesis, where at least 120 million tonnes CO_2 per year are available, as well as in ethylene oxide synthesis (5.1 million tonnes per year worldwide). In addition, pure CO_2 is available as a side product of the production of synthesis gas, in refineries or in natural gas purification. Another suitable access to carbon dioxide might be fermentation processes, such as bioethanol production.[4]

Since carbon dioxide is renewable and can be used as recycled waste it is already an economically attractive resource and available in various purities, sufficient for all synthetic purposes.[5] Carbon dioxide is also not flammable and non-toxic. Despite these advantages of carbon dioxide, its chemical utilization suffers from a major drawback, as it is quite stable and unreactive. Carbon dioxide (CO_2) as highest oxidized form of carbon reveals to be also the most stable one. It already

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[1] Aresta, M. *Carbon Dioxide as Chemical Feedstock*; Wiley, 2010

[2] Peters, M.; Köhler, B.; Kuckshinrichs, W.; Leitner, W.; Markewitz, P.; Müller, T. E. *ChemSusChem* **2011**, *4*, 1216–1240

[3] Mertens, J.; Skelland, J. *Hydrocarbon Engineering* **2010**

[4] Ausfelder, F.; Bazzanella, A. *Verwertung und Speicherung von CO_2: Diskusionspapier*; Dechema eV, 2008

[5] Kuckshinrichs, W.; Markewitz, P.; Linssen, J.; Zapp, P.; Peters, M.; Köhler, B.; Müller, T. E.; Leitner, W. *Schriften des Forschungszentrums Jülich Reihe Energie & Umwelt* **2010**, *60*, 139

has relatively low standard Gibbs free energy of formation with -394.39 kJ/mol.[6] To overcome the thermodynamic stability of carbon dioxide, harsh conditions and high energy reaction partners such as hydrogen, unsaturated compounds, or tensed cyclic molecules are required.

Consequently, highly specialized and efficient catalysts are necessary to enable, accelerate and control the conversion of carbon dioxide. The function of the catalyst is usually to form a highly reactive intermediate with those substrates. This so formed intermediate reacts then with the other compound.[2] Economical considerations also pursue low-energy demanding synthetic ways using CO_2 as C_1 building block, and therefore efficient interactions with the specific substrate is required. The low reactivity of CO_2 seems to be the main reason why the usage of carbon dioxide is not already well established in chemical production.

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[6] Housecroft, C. E.; Sharpe, A. G.; Bera, H.; Rompel, A. *Anorganische Chemie*, 2., aktualisierte Aufl.; Chemie; Pearson Studium: München, 2008

3. Theoretical background

3.1 Reactions with carbon dioxide

The idea of using carbon dioxide as a renewable carbon resource already exists for a long time and much research has been already done for the transformation of CO_2 as C_1-building block into useful products.[1] Nowadays, various chemical reactions with carbon dioxide as reagent are known that are summarized in recent reviews by Maeda *et al.*[7] and Peters *et al.*[2] The typical reaction types and transformation principles of carbon dioxide can be divided in different groups. A selection of available transformations and their classification is shown in Figure 1.

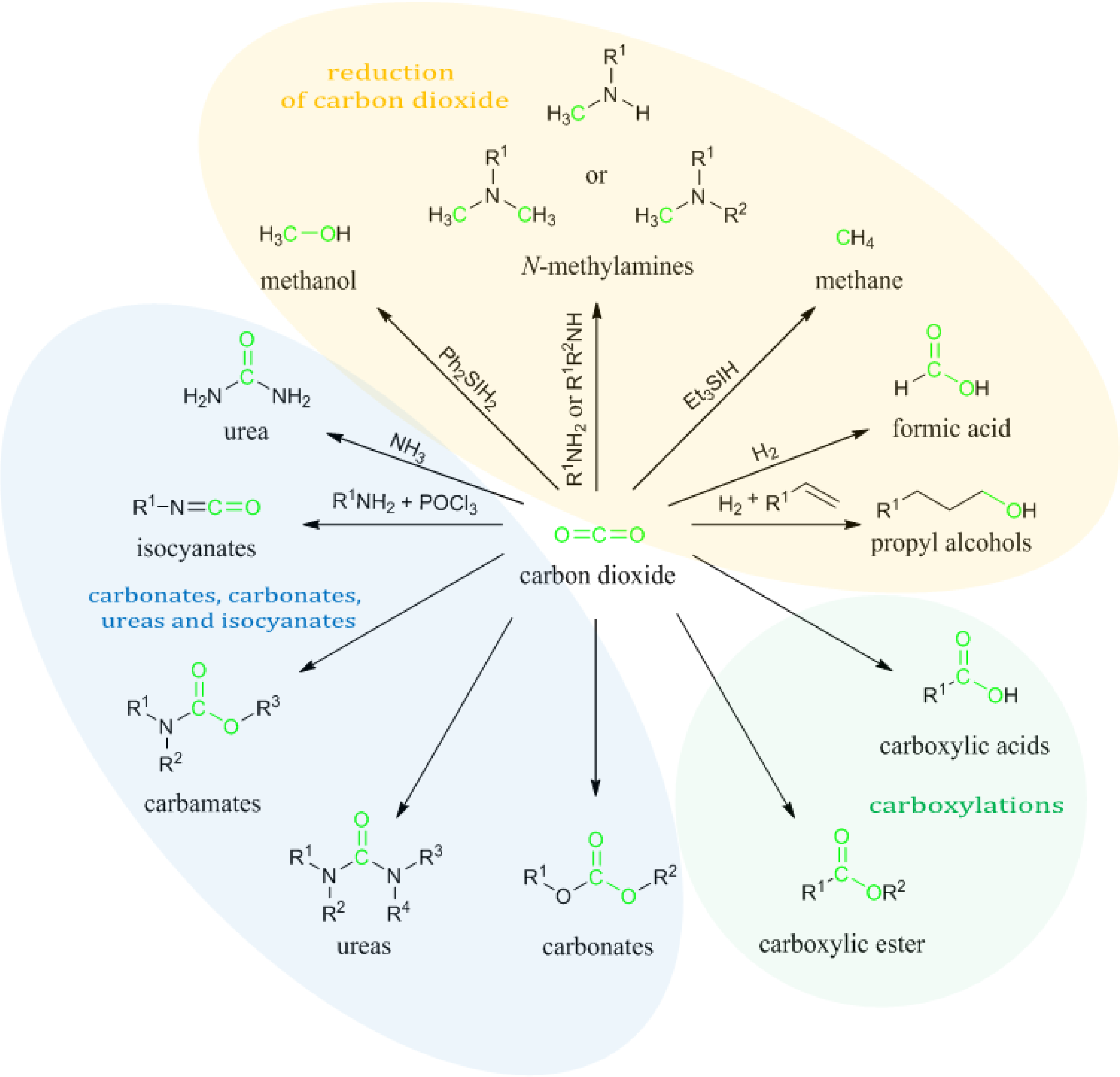

Figure 1: Representative reactions with carbon dioxide as C_1-building block

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[7] Maeda, C.; Miyazaki, Y.; Ema, T. *Catal. Sci. Tech.* **2014**, *4*, 1482–1497

- **Reduction of carbon dioxide**

  Reduction and oxidation are the inseparable parts of a redox reaction. A redox reaction is performed by transferring electrons between two species, which leads to a change in their oxidation numbers. Thereby, one species will be oxidized and another one reduced. Since carbon dioxide is already in a maximum oxidized state of +4, it can only be reduced. Since the carbon within carbon dioxide is already in the highest oxidized state, many synthetic ways lead to a reduced form. Carbon dioxide can be directly reduced to carbon monoxide, formic acid, methanol, and methane by using hydrosilanes or hydrogen as reactant. Nowadays, formic acid is mostly produced in higher amount by the conversion of carbon monoxide with methanol. Since methyl formate is formed by this reaction, the methyl ester has to be cut off by hydrolysis to obtain the acid. Therefore formic acid has to be separated from the aqueous phase, which is quite difficult, since water and formic acid have similar boiling points. The direct reaction of carbon dioxide and hydrogen would be a good alternative way to produce formic acid by avoiding this problem. Formic acid is a commonly used chemical in organic chemistry (solvent, reaction media for transfer hydrogenation, …). Furthermore, this acid and its salts are used as preservatives, aid for thawing, decalcifying agent, mordant and in leather tanning. The worldwide production per year of formic acid is about 0.6 million tonnes.[4]

- **Carboxylations**

  Carboxylations are known to introduce carbon dioxide as C_1-building block as well. Carboxylations are reactions where carboxyl groups are introduced into organic compounds by a nucleophilic attack at carbon dioxide. Carboxylic acids and subsequently even carboxylic esters via esterification are available. A well-known reaction is the Kolbe-Schmitt reaction to synthesize phenolic acids. Beside carbon dioxide as carboxylation agent, metal carbonyls are also known to act in a similar manner.

- **Formation of organic carbonates, carbamates, isocyanates and ureas**

  The formation of organic carbonates, carbamates, isocyanates and ureas are also available reactions using carbon dioxide as substrate. A nucleophilic attack at CO_2 in consequence of a reaction with epoxides and alcohols leads to organic carbonates including poly- and cyclic carbonates. Carbamates, isocyanates and ureas are obtained by using ammonia or amines as nucleophiles. Currently, urea is quantitatively the most important product in industry, where CO_2 is used as C_1-building block. In the year 2011 the annual production of urea was about 153 millions of tonnes. Urea is widely used as fertilizer in agriculture and for the emission control of automotives. In power plants it serves as aid for thawing. In polymer chemistry it is used beside formaldehyde as substrate in high amount for the production of aminoplasts.[2]

3.2 Synthesis of cyclic carbonates from carbon dioxide

An already well-known reaction for the conversion of carbon dioxide into fine chemicals is the formation of cyclic carbonates from epoxides. Due its wide utilization, the reaction shown in Figure 2 is currently performed in industrial scale, but typically runs in batch process mode. The annual production volume of cyclic carbonates worldwide reaches nowadays 80 000 tonnes, and approximately 50% of the total production relies on carbon dioxide as feedstock.[1] Cyclic carbonates can be used as electrolytes in fuel cells and in lithium ion batteries. Furthermore, they have found application as aprotic polar solvent and as intermediates in the production of fine chemicals and pharmaceutical materials. Since they can undergo ring opening polymerization, cyclic carbonates are useful raw materials in polymer chemistry, e.g. for the production of polyurethanes.[8]

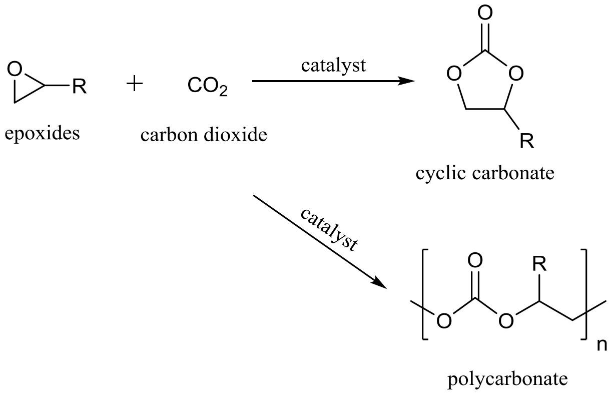

Figure 2: Synthesis of cyclic carbonates and polycarbonates from epoxides and carbon dioxide

Cyclic carbonates are not the only possible products that can be prepared by this substrate combination. Polycarbonates can also be formed, either as desired product or by-product. The selectivity between monomer and polymer can be controlled by choosing a proper catalyst. Nowadays, various catalysts are available to form a mixture or each product selectively. In principle, the formation of cyclic carbonates has been proposed as preferred process rather than polymer formation, related to the thermodynamic stability of five-membered cyclic carbonates. Further catalyst considerations in this work are only related to the formation of cyclic carbonates.[9]

3.2.1 Catalysts for the synthesis of cyclic carbonates

In recent years, various catalysts have been developed for the highly efficient production of cyclic carbonates, such as metal complexes[8,10], alkali metal halides[11], metal oxides[12] or organic bases.[13]

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[8] North, M.; Pasquale, R. *Angew. Chem. Int. Ed.* **2009**, *121*, 2990–2992

[9] Cokoja, M.; Wilhelm, M. E.; Anthofer, M. H.; Herrmann, W. A.; Kuhn, F. E. *ChemSusChem* **2015**, *8*, 2436–2454

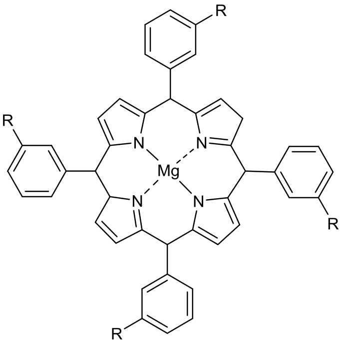
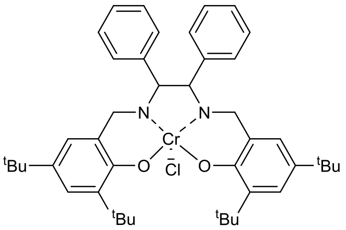
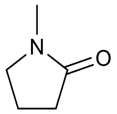
[10] Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nat. Commun.* **2015**, *6*, 5933

[11] Kihara, N.; Hara, N.; Endo, T. *J. Org. Chem.* **1993**, *58*, 6198–6202

[12] Yasuda, H.; He, L.-N.; Takahashi, T.; Sakakura, T. *Appl. Catal., A: General* **2006**, *298*, 177–180

Nishikubo et al. showed that quaternary ammonium and phosphonium salts also have moderate catalytic activity.[14,15] Such organic salts often also referred to as “ionic liquids” and will be discussed in the next chapter in detail. Selected examples of catalytic groups are shown in Table 1.

Table 1: Examples of catalysts for the synthesis of cyclic carbonates

metal complexes		**S**[a]	**conditions**	**results** yield [selectivity] {TON}[b]
Metalloporphyrin catalysts: M(TPP)[c] 16 Mg(TPP) with R=–O(CH_2)$_6$$N^+$$Bu_3$$Br^-$		BO	120 °C, 3 h 15 bar CO_2 0.005 mol%	83% {103000}
Cr(III) salen catalyst with DMAP[d] (co-catalyst)[17]		PO	100 °C; 1.0 h 6.9 bar CO_2 0.075 mol%	{916}
			75 °C; 1.5 h 3.45 bar CO_2 1 mol%	100%
alkali metal halides				
NaBr or LiBr in *N*-methylpyrrolidinone[11]	LiBr or NaBr in 	EOPOP	100 °C; 4 h 1 bar CO_2 5 mol%	100%
metal oxides				
Cs–P–Si oxide mixture[12]	---	PO	200 °C; 8 h 80 bar 1 g/3.3 g PO	94% [96%]

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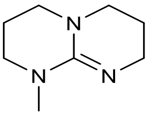
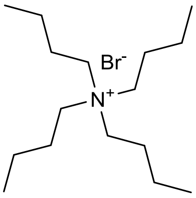
[13] Barbarini, A.; Maggi, R.; Mazzacani, A.; Mori, G.; Sartori, G.; Sartorio, R. *Tetrahedron Lett.* **2003**, *44*, 2931–2934

[14] Nishikubo, T.; Kameyama, A.; Yamashita, J.; Tomoi, M.; Fukuda, W. *J. Polym. Sci. A* **1993**, *31*, 939–947

[15] Yang, Z.-Z.; He, L.-N.; Miao, C.-X.; Chanfreau, S. *Adv. Synth. Catal.* **2010**, *352*, 2233–2240

[16] Ema, T.; Miyazaki, Y.; Koyama, S.; Yano, Y.; Sakai, T. *Chem. Commun.* **2012**, *48*, 4489–4491

[17] Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498–11499

organic bases				
MTBE[e] in acetonitrile[13]		SO	140 °C; 20 h 50 bar 4 mol%	96% [up to 98%]
organic salts				
[TBA]Br[18] tetrabutylammonium bromide		PO	125 °C; 1 h 4 bar CO_2 1.6 mol%	74% [99%]

[a] S = substrate: PO = propylene oxide, BO = butylene oxide, EOPOP = 1,2-epoxy-3-phenoxypropane, SO = styrene oxide; [b] TON = turnover number; [c] TPP = tetraphenylporphyrin; [d] DMAP = 4-(dimethylamino)pyridin; [e] MTBE = 2-methoxy-2-methylpropane

3.2.1.1 Ionic liquids as catalysts

Since 1993 organic salts and subsequently ionic liquids without any additives are known to be able to catalyze this reaction. Ionic liquids are defined as organic salts with a melting point below 100 °C that usually possess a wide liquid range. According to their definition, an ionic liquid consists of an anion and a cation that can be modified to provide the desired properties. Therefore the number and variety of available ionic liquids is extremely large and constantly increases.[19] Some typical cations and anions of common ionic liquids are shown in Figure 3.

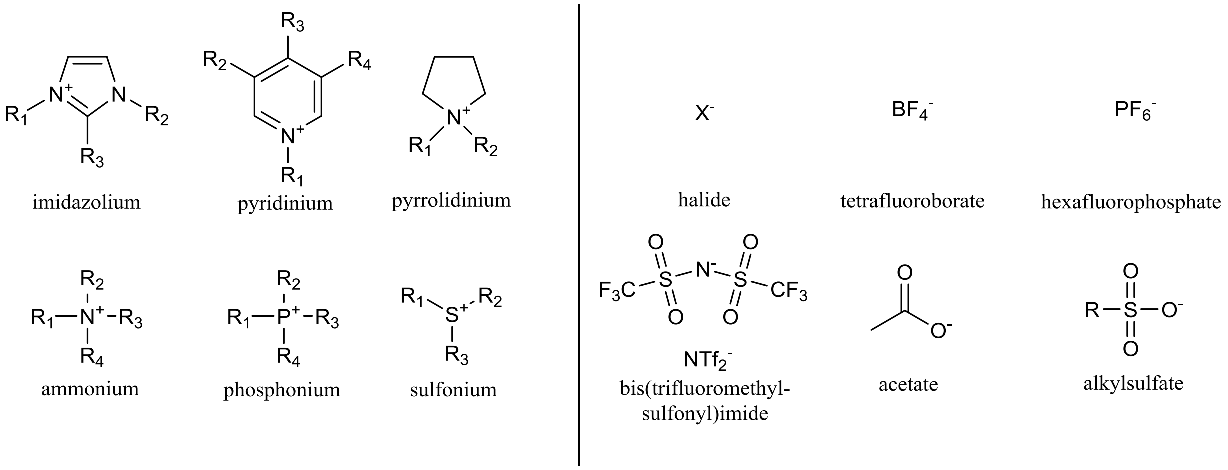


Figure 3: Typical cations (left) and anions (right) of ionic liquids

The popularity of ionic liquids has tremendously increased over the last 20 years, since the area of possible application seems to be unlimited. The physical and chemical properties of ionic liquids can be specifically varied over a wide range by the selection of suitable cations and anions. Especially their reduced vapour pressure, tuneable structure and polarity, high thermal stability and

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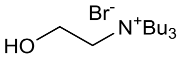
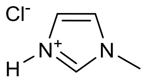
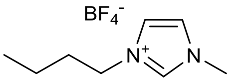
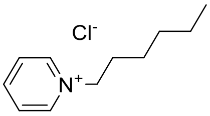
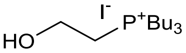
[18] Sun, J.; Zhang, S.; Cheng, W.; Ren, J. *Tetrahedron Lett.* **2008**, *49*, 3588–3591

[19] *Ionic liquids in synthesis;* Wasserscheid, P.; Welton, T., Eds., 2nd, completely rev. and enl. ed.; Wiley-VCH: Weinheim, 2008

electric conductivity make them special.[20] Consequently, ionic liquids are widely used in areas like material synthesis, separation science, synthesis and catalysis. Especially for the valorisations of carbon dioxide, ionic liquids have been heavily investigated and received a lot of attention in the past years. Applications for ionic liquids cover carbon dioxide capture, storage but also the further valorisations of CO_2 toward fine chemicals.

In terms of the conversion of carbon dioxide, ionic liquids can be used as tailored catalysts for the formation of cyclic carbonates from epoxides. According to a recent review by Cokoja et al., the most active ionic liquids can be divided in different groups, based on their cation.9 Ammonium, pyridinium, imidazolium and phosphonium based ionic liquids are known to be highly catalytic active, beside other less intensively investigated ones. Examples are shown in Table 2.

Table 2: Examples of ionic liquids as catalyst for the synthesis of cyclic carbonates

ammonium based IL		**S**[a]	**conditions**	**results** yield [selectivity] {TON}[b]
[TBHEA]Br tributyl-(-2-hydroxyethyl) ammonium bromide[18]		PO	125 °C; 1 h 4 bar CO_2 1.6 mol%	96% [99%]
imidazolium based IL				
[HMIM]Cl 1-H-3-methylimidazolium chloride		PO	140 °C; 2 h 10 bar CO_2 1 mol%	83% [90%]
[BMIM]BF_4 1-butyl-3-methylimidazolium tetrafuoroborate[21]		PO	110 °C; 6 h 25 bar 2 mol%	90% [≥99%] {45}
pyridinium based IL				
[HPy]Cl 1-hexylpyridinium chloride		BGE	100 °C; 6 h 8 bar CO_2 5 mol%	80% conv.
phosphonium based IL				
[TBHEP]I tributyl-(2-hydroxyethyl)-phosphonium iodide[22]		PO	45 °C; 3 h 10 bar CO_2 2 mol%	82 % [≥99 %]

[a] S = substrate: PO = propylene oxide, BGE = 1-butoxy-2,3-epoxypropane; [b] TON = turnover number;

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[20] Mehnert, C. P. *Chem. Eur. J.* **2005**, *11*, 50–56

[21] Peng, J.; Deng, Y. *New J. Chem.* **2001**, *25*, 639–641

[22] Büttner, H.; Steinbauer, J.; Werner, T. *ChemSusChem* **2015**, *8*, 2655–2669

Yang et al. reported that imidazolium based ionic liquids are more effective in the conversion of cyclic epoxides than pyridinium based ionic liquids. The authors also reported that besides the cation, the corresponding anion of an ionic liquid equally affects the catalytic activity in the formation of cyclic carbonates from expoxides and carbon dioxide.[15,23] The most promising ionic liquid so far is the phosphonium based ionic liquid tributyl-(2-hydroxyethyl)phosphonium iodide. The catalyst proved to be very active, selective and is able to catalyse a variety of epoxides as substrate. Even under very mild reaction conditions of 45 °C, excellent yields of different cyclic carbonates were obtained after 18 h.[22] Literature data suggests that the mechanism and interaction of the anion with substrates differs depending on its nature.

3.2.1.2 Mechanism of cyclic carbonate formation with halide based ionic liquids

Halides are small, strongly nucleophilic anions and known to be highly catalytically active in the formation of cyclic carbonates. They are following an in the year 1993 proposed catalytic mechanism which is shown in the following scheme (Figure 4). This mechanism was later on confirmed by density functional theory calculations.[24]

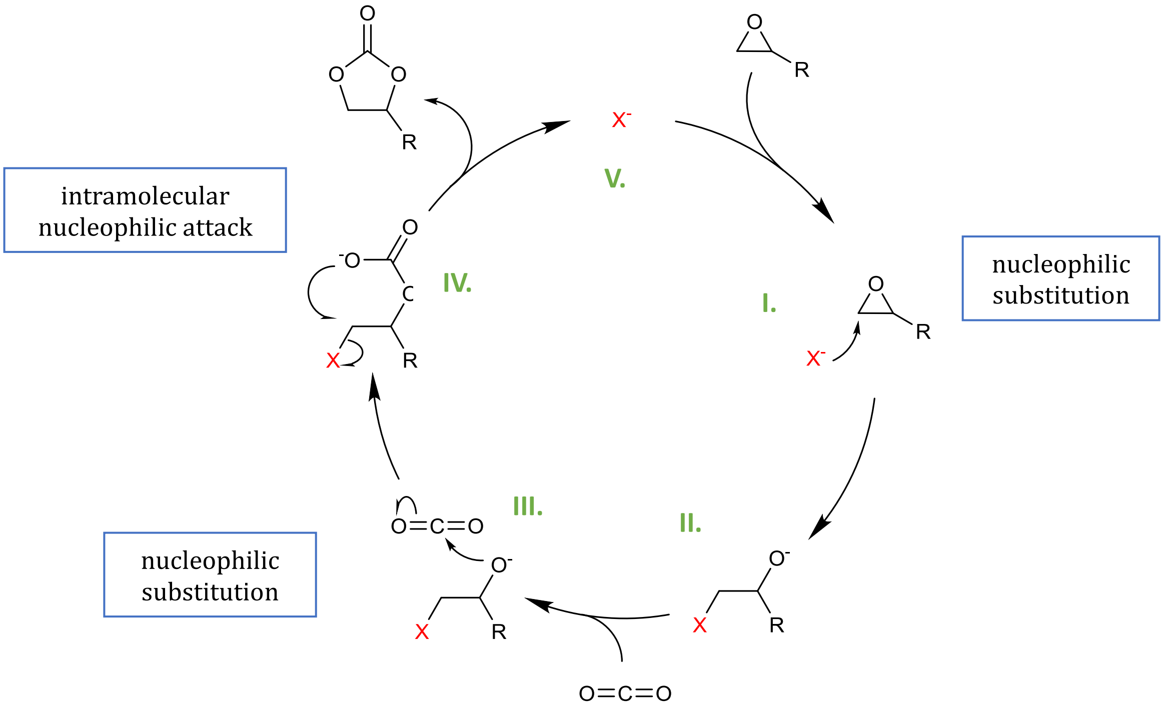

Figure 4: Reaction mechanism for halides

Halides are capable to attack the less hindered carbon of the epoxide (I.) in the first step, opening the ring via nucleophilic substitution. Consequently, the anion needs to be highly nucleophilic. The opening of the strained three-member ring of the epoxide provides the reaction with energy and causes an alkoxide as highly active intermediate (II.). This alkoxide attacks the carbon within the

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[23] Sun, J.; Fujita, S.-i.; Arai, M. *J. Organomet. Chem.* **2005**, *690*, 3490–3497

[24] Wang, J.-Q.; Dong, K.; Cheng, W.-G.; Sun, J.; Zhang, S.-J. *Catal. Sci. Technol.* **2012**, *2*, 1480

carbon dioxide (III.). The following negatively charged carbonate subsequently undergoes an intramolecular nucleophilic attack, closing the five-membered ring by releasing the anion (IV.), which can be re-used. At this stage, the anion has to be also a good leaving group. As a result, the activity of halides usually decreases in the order of $I^- \geq Br^- > Cl^-$, following the influence of nucleophilicity and size.[25]

3.2.1.3 Catalytic mechanism with BF_4^-, PF_6^- and NTf_2^- anions

Ionic liquids with BF_4^-, PF_6^-, NTf_2^- are known to be catalytically active in this reaction.[21,26] Due to non-nucleophilic and bulky nature, such ions are not capable to attack the epoxide in the first place. Therefore T. Seki *et al* proposed a different catalytic pathway for this type of ionic liquids (Figure 5). This mechanism has not been confirmed by DFT (density functional theory) calculations yet but was supported by ATR-IR and X-ray diffraction studies.[26]

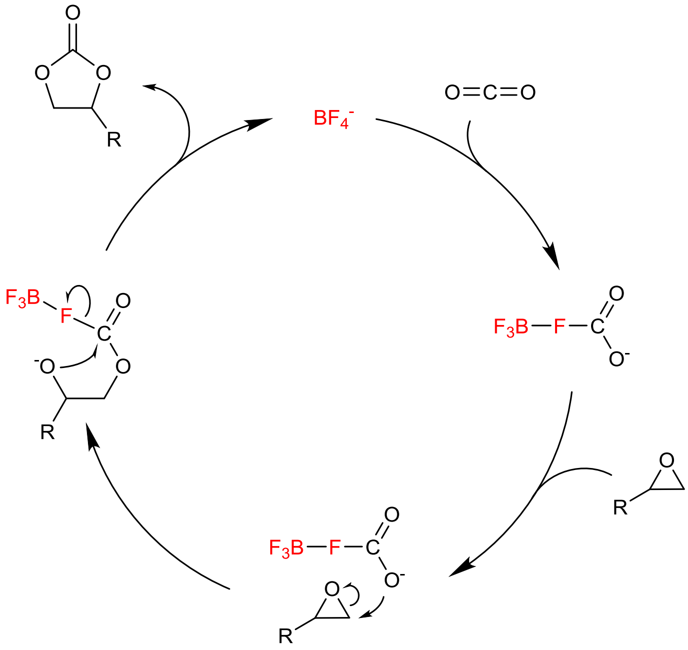

Figure 5: Reaction mechanism for bulky and low nucleophilic anions

The authors suggested that carbon dioxide is highly soluble in ionic liquids with NTf_2^- as anion. Nonetheless, BF_3 is the most catalytically active species, since the CO_2-BF_3 intermediate described in Figure 5 is the most basic and attacks more easily.

3.2.1.4 Halometallate ionic liquids

Xu et al. summarized in a review that ionic liquids with Lewis acidic anions gave improved conversion compared to systems with conventional anions.[27] Authors of various publications have

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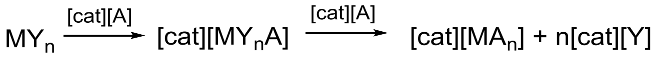
[25] Jutz, F.; Andanson, J.-M.; Baiker, A. *Chem. Rev.* **2011**, *111*, 322–353

[26] Seki, T.; Grunwaldt, J.-D.; Baiker, A. *J. Phys. Chem. B* **2009**, *113*, 114–122

[27] Xu, B.-H.; Wang, J.-Q.; Sun, J.; Huang, Y.; Zhang, J.-P.; Zhang, X.-P.; Zhang, S.-J. *Green Chem.* **2015**, *17*, 108–122

shown that the catalytic activity of known and unfunctionalized ionic liquids can be strongly enhanced by adding Lewis acids such as $ZnBr_2$, $InCl_2$ or $NbCl_5$.[28,29,30,31]

In general, the reaction of a metal halide MY_n with ammonium- or imidazolium halides [cat][A] results in the formation of an ionic liquid with several different anionic species in equilibrium as shown in Figure 6.



$$MY_n \xrightarrow{[cat][A]} [cat][MY_nA] \xrightarrow{[cat][A]} [cat][MA_n] + n[cat][Y]$$

Figure 6: Aspect of the formation of Lewis acidic ionic liquids; adapted from Estager et al.[32]

The formation of the anionic species depends on the molar fraction of MY_n (χ_{MY_n}) as well as on the used metal M and defines the dynamic equilibrium between the existing species. This equilibrium may also contain defined anionic complexes depending on the coordination number of the used metal. The molar fraction of MY_n defines the dominant complex anion species in the equilibrium. In table Table 3 already known dominant anions of widely studied chloroaluminate ionic liquids for given χ_{MY_n} are shown.

Table 3: Known anionic species of chloroaluminate ionic liquids

χ_{MY_n}	0.25	0.33	0.50	0.60	0.67	0.75
Al(III)	Cl^-;$[AlCl_4]^-$		$[AlCl_4]^-$	$[AlCl_4]^-$; $[Al_2Cl_7]^-$	$[Al_2Cl_7]^-$	$[Al_xCl_y]^-$; $AlCl_3\downarrow$
	Lewis basic					Lewis acidic

Analysis methods: ^{27}Al-NMR[33]; Raman[34,35]

The resulting chemical (e.g. Lewis acidity) and physical properties (e.g. state of matter) of the new formed ionic liquid are different from those of the used ionic liquid. The Lewis acidity of such ionic liquids containing halometallate species depends on the metal of the Lewis acid, the ligands which are coordinated around the metal and on the ratio between halide-based ionic liquid and the Lewis acid. In principle, the Lewis acid strength of metal ions is proportional to their electronegativity. In the case of an excess of ionic liquid upon aluminium(III)chloride the increase of more Lewis basic species such as Cl^- makes the dissolution more basic. An increase in the molar fraction of $AlCl_3$ results in an increase of the Lewis acidic strength.[32]

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[28] Sun, J.; Fujita, S.-i.; Zhao, F.; Arai, M. *Appl. Catal., A: General* **2005**, *287*, 221–226

[29] Palgunadi, J.; Kwon, O.-S.; Lee, H.; Bae, J. Y.; Ahn, B. S.; Min, N.-Y.; Kim, H. S. *Catal. Today* **2004**, *98*, 511–514

[30] Li, F.; Xiao, L.; Xia, C.; Hu, B. *Tetrahedron Lett.* **2004**, *45*, 8307–8310

[31] Fujita, S.-i.; Nishiura, M.; Arai, M. *Catal. Lett.* **2010**, *135*, 263–268

[32] Estager, J.; Holbrey, J. D.; Swadzba-Kwasny, M. *Chem. Soc. Rev.* **2014**, *43*, 847–886

[33] Takahashi, S.; Saboungi, M.-L.; Klingler, R. J.; Chen, M. J.; Rathke, J. W. *J. Chem. Soc., Faraday Trans.,* **1993**, *89*, 3591

[34] Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1978**, *17*, 2728–2729

[35] Takahashi, S.; Curtiss, L. A.; Gosztola, D.; Koura, N.; Saboungi, M.-L. *Inorg. Chem.* **1995**, *34*, 2990–2993

In case of zincate-based ionic liquids, a number of anionic zinc-containing species can exist in equilibrium as presented in Table 4.

Table 4: Known anionic species of chlorozincate ionic liquids

χ_{MY_n}	0.25	0.33	0.50	0.60	0.67	0.75
Zn(II)	Cl^-;$[ZnCl_4]^{2-}$	$[ZnCl_4]^{2-}$	$[Zn_2Cl_6]^{2-}$	$[Zn_2Cl_6]^{2-}$; $[Zn_3Cl_8]^{2-}$	$[Zn_3Cl_8]^{2-}$	$[Zn_4Cl_{10}]^{2-}$
	Lewis basic					Lewis acidic

Analysis methods: Raman[36]

This has direct influence on the catalytic properties in the conversion of CO_2. The addition of ZnY_2 results in considerably modified catalytic behaviour as demonstrated by Sun et al. in 2005 with tetrabutylammonium iodide/$ZnBr_2$ for the formation of styrene carbonate.[28] The authors have demonstrated the influence of different tetrabutylammonium iodide/$ZnBr_2$ ratios on the yield for the conversion of styrene oxide as shown in Table 5.[28]

Table 5: Influence of different tetrabutylammonium iodide/$ZnBr_2$ ratios on yield

[TBA]I [mmol]	$ZnBr_2$ [mmol]	yield[a] [%]	TOF[b] [h^{-1}]
0.1	0.1	54	378
0.1	0.05	62	868
0.2	0.1	92	646
0.4	0.1	95	665

[a] Performed with 35 mmol styrene oxide at a CO_2 pressure of 8 MPa for 0.5 h^{-1}
[b] Moles of styrene carbonate produced per mole of metal halide per hour.

A higher ratio (4:1) results in a reduced Lewis acidity and higher yield, whereas a reduced amount of [TBA]I shows lower yield.

Palgunadi et al. synthesised and characterized such compounds based on unfunctionalized imidazolium cations. The authors demonstrated the high activity of such ionic liquid-derived zinc tetrahalide complexes for the conversion of various epoxides with carbon dioxide to the corresponding cyclic carbonate. When investigating the impact of the halides in Lewis acidic tetrahalozincate-based ionic liquids, they used various ionic liquids in combination with $ZnBr_2$ and $ZnCl_2$. The reaction takes place more easily with tetra bromozincate anions due to the higher nucleophilicity, revealing the following activity order: $[ZnBr_4]_2 > [ZnBr_2Cl_2]_2 > [ZnCl_4]_2$.[29]

The effect of different halide combinations on the catalytic activity was also investigated more closely by Fujita and co-workers using propylene oxide as substrate. Their work revealed that the halide choice of the added Lewis acid is more important than the counterion of the ionic liquid. The authors have shown that mixed tetrahalides containing iodide have only slightly higher cata-

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[36] Alves, M. B.; Santos jr., V. O.; Soares, V. C. D.; Suarez, P. A. Z.; Rubim, J. C. *J. Raman Spectrosc.* **2008**, *39*, 1388–1395

lytic activity than tetrahalides containing only bromide. These experiments were carried out with tetrabutylammonium halides and 1-butyl-3-methylimidazolium halides as ionic liquids.[31]

Already since 1986, Lewis-acidic catalysts other than Zinc based systems were known to catalyse the conversion of carbon dioxide with epoxides. Kisch and co-workers investigated various ionic liquids in combination with different Lewis acids and found that zinc as metal is preferable to molybdenum, iron and aluminium.[37]

Monassier et al published in 2012 the impact of Lewis acids based on transition metals of the group 4–6 in the periodic table for the catalytic conversion of carbon dioxide to cyclic epoxides. They came to the conclusion that niobium is the most effective metal within this group.[38] For niobium based ionic compounds, a stoichiometric ratio of at least 1:1 (IL:NbX_5) should be considered, since stable octahedral complexes are known to be formed.

In another work, indium(III)chloride was used in an IL/metallic binary system and revealed to be highly active in combination with 1-butyl-3-methylimidazolium halides.[39]

Unfortunately there is no direct comparison of niobium, zinc and indium-based Lewis acidic ionic liquids used for the conversion of carbon dioxide and epoxides into cyclic carbonates under similar conditions available in literature.

3.2.1.5 Impact of cation structure on the catalytic activity

The catalytic activity of ionic liquids in this reaction can be enhanced by fine-tuning the cation in different ways. The conversion increases when the cation of the ionic liquid has a longer alkyl chain.[23] This effect can be explained by the higher solubility of carbon dioxide in the ionic liquid, resulting in higher mass transfer of carbon dioxide in the catalytic active phase. Independent of the cation structure, the presence of an intramolecular hydrogen bond donor increases the catalytic activity of the ionic liquid. A variety of hydroxyl- and carboxy-functionalized ionic liquids are known to show higher catalytic activity than the unfunctionalized systems.[18,22] Another way to benefit from this effect is to combine the ionic liquids with an intermolecular hydrogen bond donor such as alcohols[40] or materials like silica.[41] Unfunctionalized imidazolium based ionic liquids can already act as hydrogen bond donor themselves due to their proton in position 2, although the catalytic activity can be improved with additional hydrogen bond donors. This synergistic effect can be only achieved when using anions with a strong nucleophilic behaviour, such as halides. The hydrogen bond donor weakens the bond between the oxygen and the carbon within the epoxide

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[37] Kisch, H.; Millini, R.; Wang, I.-J. *Chem. Ber.* **1986**, *119*, 1090–1094

[38] Monassier, A.; D'Elia, V.; Cokoja, M.; Dong, H.; Pelletier, J. D. A.; Basset, J.-M.; Kühn, F. E. *ChemCatChem* **2013**, *5*, 1321–1324

[39] Kim, Y. J.; Varma, R. S. *J. Org. Chem.* **2005**, *70*, 7882–7891

[40] Sun, J.; Ren, J.; Zhang, S.; Cheng, W. *Tetrahedron Lett.* **2009**, *50*, 423–426

[41] Wang, J.-Q.; Yue, X.-D.; Cai, F.; He, L.-N. *Catal. Commun.* **2007**, *8*, 167–172

by drawing electron density from it. This makes the epoxide more vulnerable against nucleophiles. Such situations are demonstrated in Figure 7.

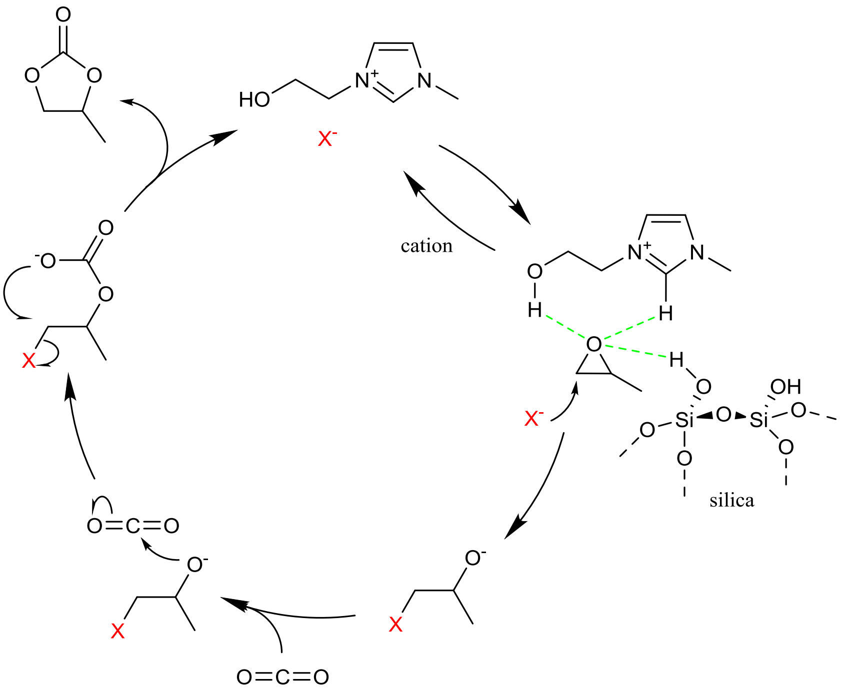

Figure 7: Activation of the epoxide

Only recently, the combination of hydroxyl and carboxyl functionalized imidazolium-based ionic liquids with Lewis acids to combine these effects to achieve higher catalytic activity was published.[42] For imidazolium based ionic liquids high catalytic activity was reported, whereas no data with functionalized phosphonium or ammonium based ionic liquids exists. Moreover, Kim *et al.* used unfunctionalized ionic liquids such as [BMIM]Br and [BPy]Br combined with zinc halides that were subsequently immobilized on silica as hydrogen bond donor via physisorption. Only systems with bromide based IL/silica/$ZnCl_2$ seem to have an additional effect on the conversion, compared to the combination of IL/silica.[43]

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[42] Liu, M.; Wang, F.; Shi, L.; Liang, L.; Sun, J. *RSC Adv.* **2015**, *5*, 14277–14284

[43] Kim, M.-I.; Choi, S.-J.; Kim, D.-W.; Park, D.-W. *Ind. Eng. Chem. Res.* **2014**, *20*, 3102–3107

3.3 Continuous flow conversion of CO_2

Only a few experiments for the formation of cyclic carbonates have been carried out in continuous flow process mode. In 2012, the reaction of carbon dioxide with propylene oxide was carried out under flow conditions in a micro reactor set-up. The ionic liquid catalyst was pumped through the reactor in a solution with the substrate.[44]

Most recently, an example of carboxymethyl cellulose (CMC) supported imidazolium based ionic liquids was used as heterogeneous catalyst for the cycloaddition of CO_2 to cyclic carbonates, allowing to convert CO_2 to cyclic epoxides in continuous flow with high efficiency for the first time.[45] The principles of continuous flow chemistry for the conversion of CO_2 will be discussed in the next chapter.

3.3.1 Principles of continuous flow chemistry

While academic research relied for many years on batch-wise reaction conditions, continuous flow chemistry is attracting more interest over the last few years. The challenge of high investment costs, the lack of suitable equipment and the complexity of optimization kept academics from including this technique in their research.[46] Nevertheless, continuous flow technologies offer a special way to perform synthetic reactions with specific characteristics and undeniable advantages. The most important characteristics for flow reactions in comparison to batch chemistry are shown in Table 6.

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[44] Zhao, Y.; Yao, C.; Chen, G.; Yuan, Q. *Green Chem.* **2013**, *15*, 446–452

[45] Wu, X.; Wang, M.; Xie, Y.; Chen, C.; Li, K.; Yuan, M.; Zhao, X.; Hou, Z. *Appl. Catal., A: General* **2016**, *519*, 146–154

[46] Glasnov, T. *Continuous-Flow Chemistry in the Research Laboratory*; Springer International Publishing: Cham 2016

Table 6: Comparison of the major characteristics of batch and flow reactions

	Batch	**Flow**
Stoichiometry	Ratio of the molar quantities	Ratio of the flow rates
Reaction time	Time spent under defined conditions	Residence time: time spent in the reaction zone
Reaction progress	Time spent under defined conditions	Distance progress under defined conditions within the reaction zone
Steady state characteristics	Uniform concentration/ratio at local positions within the reactor at a particular moment	Steady state but different concentration/ratio at each position throughout the reactor length
Performance specification	in yield and selectivity	in space time yield (STY) and selectivity

Continuous flow chemistry reveals great potential for the optimization of reaction conditions, due to the expanded variation of adjustable factors. All these can improve the performance of a reaction, leading to the possibility to perform even reactions that are impossible under batch conditions. Additionally, reactions under flow conditions are easier to be automated. It is also easier to control heat formation during the reaction, since the heat transfer surface area is large compared to the reactor volume. This efficient heat transfer is particularly explicit in a microflow set-up and of particular importance for highly exothermic or highly endothermic reactions.

Eventually, the higher mass transfer in flow reactions due to continuous flow of solvents, substrates and products leads to a more robust system. Impurities and products are removed more easily from the catalyst surface. Especially for biphasic systems, the higher mass transfer in flow due high interfacial surface interactions is of interest.

The performance of a continuous flow system can be specified by the space time yield.

$$\sigma_P = \frac{m_P}{m_C * t}$$

Equation 1: Space time yield

σ_P......Space time yield (STY) [h^{-1}]

m_P......mass of the produced product [g]

m_C......mass of the used catalyst [g]

t.........reaction time [h]

Instead of using the mass of the catalyst, it is usually common to use the reactor volume, where the catalyst is situated.[47]

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[47] Darvas, F.; Hessel, V.; Dormán, G. *Flow chemistry*; de Gruyter Berlin, 2014

The residence time defines the reaction time in flow reactions, which depends on the flow rate and the size (volume) of the reaction zone. The residence time is described as followed:

$$t_R = \frac{A * L}{100 * \dot{V}}$$

Equation 2: Residence time in flow chemistry

t_R……*residence time [s]*

A……*cross section [mm^2]*

L…….*reactor length [mm]*

$\dot{V}$….. *flow rate [ml/s]*

3.3.1.1 Catalysts in flow chemistry

In any catalytic reaction performed under continuous flow conditions, an efficient immobilization of the catalyst is required.

The most common way in flow chemistry is to use heterogeneous catalysts, which are not soluble in the involved solvents and provide a surface area as high as possible. They are easy to immobilize by using a fixed bed reactor. Therefore heterogeneous catalysis offers the advantage that products are easy to separate from the catalyst. Moreover such catalysts are often more stable and degrade much slower than homogeneous catalysts.

However, heterogeneous catalysis has some disadvantages, since the catalytic activity of such catalysts strongly depends on surface characteristics and phase transfer. Usually, heterogeneous catalysts are quite sensitive against impurities and catalyst poisons and are sometimes difficult to produce. These issues are sometimes difficult to overcome. Homogeneous catalysts circumvent these problems and are soluble in the same phase as the reactants and products. Moreover they can be easier fine-tuned in terms of activity and selectivity. However, at reactions under flow conditions, catalysts have to be immobilized. Otherwise they have to be separated afterwards.[48]

An example for homogeneous catalysis in continuous flow was shown by Zhao et al. for the synthesis of cyclic carbonates catalysed by ionic liquids. This reaction was carried out in a microreactor, where various ionic liquids as catalysts were added. A mixture of reactants and ionic liquids were pumped through the reactor system. In the end, products and the ionic liquids had to be separated for re cycling usage, which is quite difficult to perform automatically. In addition, high amount of catalysts were required.[44]

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[48] Leeuwen, Piet W. N. M. van; Chadwick, J. C. *Homogeneous catalysts*; Wiley: Chichester, 2011

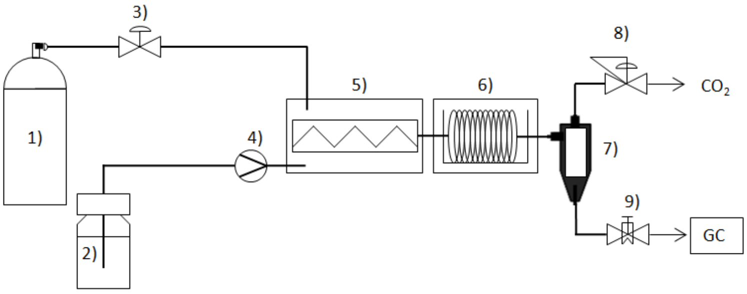

Figure 8: Schematic set up of the microreactor system used by Zhao et al.[44]
1) CO_2 supply bottle; 2) solution of PO and ionic liquid; 3) pressure regulating valve; 4) digital pump; 5) micromixer; 6) spiral capillary in oil bath; 7) gas-liquid separator; 8) back-pressure regulating valve; 9) needle valve

Recently carboxymethyl cellulose (CMC) supported imidazolium based ionic liquids were used as a heterogeneous catalyst for the cycloaddition of CO_2 to cyclic carbonates. More specifically, functionalized ionic liquids in combination with Lewis acids were used as supported catalyst system under continuous flow with a very high carbon dioxide flow rate of 32 ml min^{-1}. By using CMC as support material, they took advantage of the carboxyl groups as co-catalysts. With [HPBIM]Cl + $NbCl_5$ and HCMC, the authors established a catalysis system which showed high activity and catalytic stability in a continuous fixed bed reactor for more than 100 h in flow for the conversion of 2-(chloromethyl)oxirane and CO_2.[45]

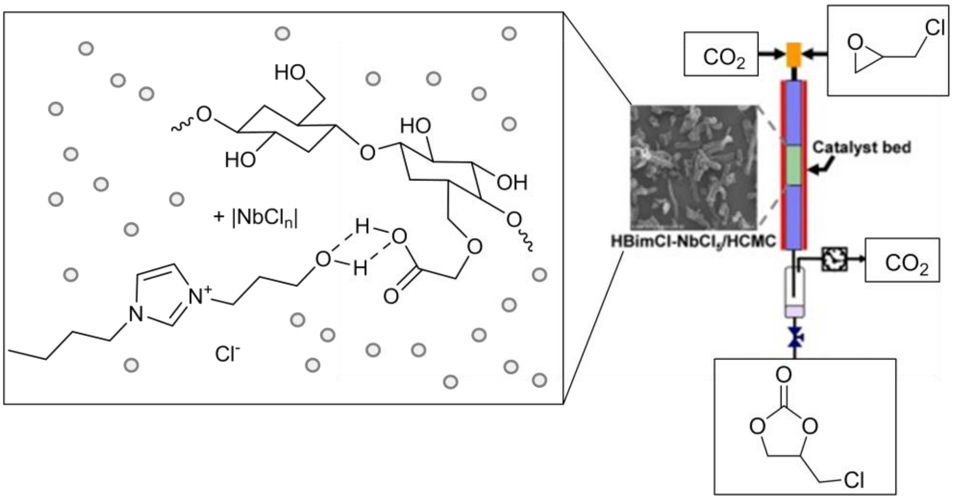

Figure 9: Schematic representation of the continuous conversion of 2-(chloromethyl)oxirane and CO_2; adapted from Wu et al.[45]

3.4 Supercritical fluids

There has been an increase of interest in the use of supercritical fluids as solvent for chemical reactions, particularly in terms of continuous flow processes. Supercritical fluids are especially attractive as a reaction medium for diffusion-controlled reactions involving gaseous reagents. In a flow system the use of supercritical fluids offers various advantages, improves safety and offers the opportunity to replace conventional hazardous organic solvents.

3.4.1 Definition of supercritical fluids

A supercritical fluid is any substance above its critical pressure and critical temperature, but below the pressure required to condense into a solid.

At this state, the interface between gaseous and solid phase disappears and the liquid and gas phase cannot be distinguished anymore. Consequently, a supercritical fluid shows properties from both states of matter.

Table 7: Comparison of gases, liquids and supercritical liquids

	density [kg/m^3]	**viscosity [µPa s]**	**diffusitivity [mm^{2}s^{-1}]**
gases	1	10	1-10
supercritical fluid	100-1000	50-100	0.01-0.1
liquids	1000	500-1000	0.001

A supercritical fluid can have a density like a liquid with adjustable solvent strength and higher mass transfer than a gas. The density and therefore the pressure define the solvent strength of a supercritical fluid. Like a gas, a super critical fluid has low viscosity and high diffusion rates. It fills the whole volume and is also able to interpenetrate other materials.[49] These properties were verified to have a great influence on the performance of a reaction, e.g. for Fischer-Tropsch synthesis or for the hydrogenation of fatty acids.[50]

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[49] Jessop, P. G.; Leitner, W. *Chemical Synthesis Using Supercritical Fluids*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1999

[50] Baiker, A. *Chem. Rev.* **1999**, *99*, 453–474

The existence of the critical point of some liquids has been already discovered in 1822 by Baron Charles Cagniard de la Tour. A few substances and their critical temperature and pressure are listed in Table 8.

Table 8: Various supercritical fluids

	critical pressure [bar]	critical temperature [°C]	critical density [g/cm^3]
argon	48.6	-122.5	0.531
water	220	374	0.322
carbon dioxide	73.8	31.1	0.469
propane	42.5	96.6	0.217
methane	45.9	-82.6	0.162
ethene	50.8	9.5	0.215

Further investigations had been done and various applications in industry for supercritical fluids are now well established,[51] e.g. the production of methyl-ethyl-ketone (MEK) using supercritical butene as reactant and solvent.[52]

3.4.2 Supercritical carbon dioxide

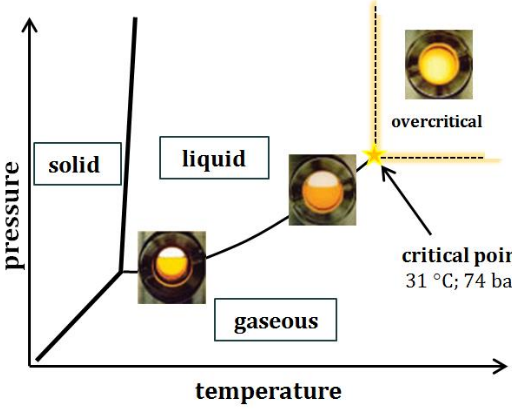

Figure 10: Phase diagram of carbon dioxide; adapted from Leitner

Among all solvents, supercritical carbon dioxide is most frequently used as supercritical fluid in industrial applications. It is well-known as extraction media in food preparation and cleaning processes. The extraction of caffeine from coffee, producing decaffeinated coffee, is the most popular process relying on supercritical carbon dioxide in industrial scale. The most important reason for the interest in using CO_2 as supercritical fluid is that the critical point for CO_2 is very low and therefore, less energy consuming. The supercritical state can be reached under mild conditions at 31 °C and 74 bar. The appropriate phase diagram is shown in Figure 10. In comparison, water has its critical point at 374 °C and 220 bar. Besides the advantages of supercritical fluids, supercritical carbon dioxide is an excellent non-polar solvent and is safer than most other common organic solvents that are otherwise used. Additionally, $scCO_2$ can be considered as a “green solvent”, since it is non-toxic, renewable and environmentally friendly. Used as solvent, CO_2

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[51] Anastas, P. T.; Leitner, W.; Jessop, P. G. *Handbook of Green Chemistry, Green Solvents, Supercritical Solvents*; Handbook of Green Chemistry; Wiley: Hoboken, 2014

[52] Brunner, G. *Annu. Rev. Chem. Biomol. Eng.* **2010**, *1*, 321–342

is easy to remove by relieving the pressure. Therefore pure products without any solvent residues can be collected.[51] The pressure does not have to be completely released to atmospheric state. As soon as it reaches gaseous form and is separated from other substances such as products, it can be directly recycled and re-used in the system, where it can reach super critical state again. In this way, the energy demand of such a system can be reduced.[53] An early example for a commercial plant for heterogeneous catalysis with supercritical carbon dioxide was established by Thomas Swan & Co in 2002. It was first used for the hydrogenation of 3,5,5-trimethyl-2-cyclohexene-1-one to 3,3,5-trimethylcyclohexanone and had a production capacity of ca. 100 kg per hour.[54]

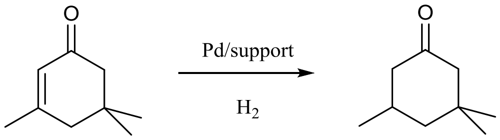

Figure 11: Hydrogenation of 3,5,5-trimethyl-2-cyclohexene-1-one

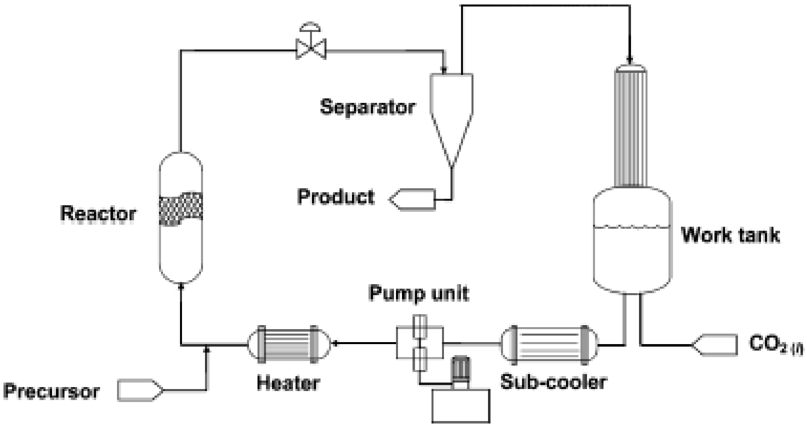

Figure 12: Schematic flow diagram of the supercritical fluid multi-reaction plant; adapted from Licence et al.[54]

During the last years, more reactions including $scCO_2$ as reactant or solvent were published.[55] Several reaction types, such as Diels-Alder reactions have been intensively investigated on the influence of $scCO_2$ as reaction media.[50]

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[53] Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789

[54] Licence, P.; Ke, J.; Sokolova, M.; Ross, S. K.; Poliakoff, M. *Green Chem.* **2003**, *5*, 99–104

[55] Leitner, W. *Erdöl, Erdgas, Kohle* **2000**, *116*, 137–140

3.5 Supported ionic liquid phase

Ionic liquids have the ability to form a second phase with organic solvents or even with aqueous media. This can be used to perform liquid-liquid biphasic catalysis, a special form of homogeneous catalysis particularly suited for hardly soluble metal catalysts.

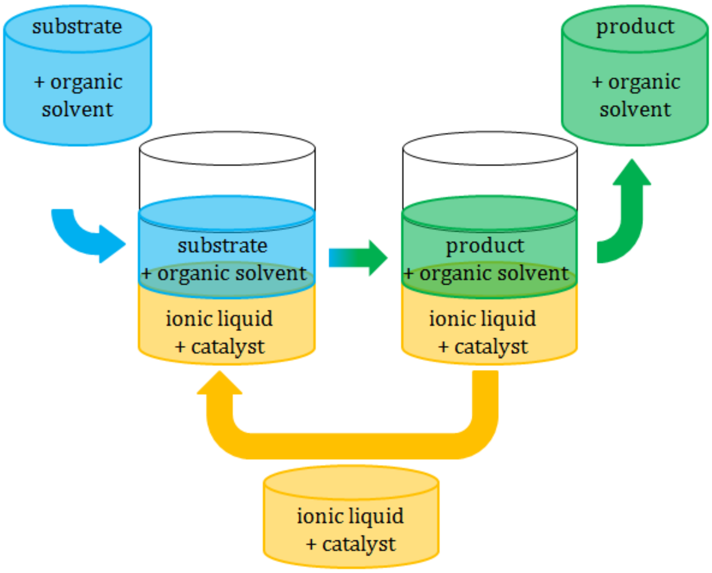

Figure 13: Concept of liquid-liquid biphasic catalysis with ionic liquids

The almost unlimited possibilities to combine cation and anion allow the synthesis of suitable ionic liquids that can stabilise the catalytic species. Thereby, an active catalyst is dissolved in an ionic liquid phase. The substrate may be miscible with the ionic liquid, but the product which is formed should be hardly soluble in it. Therefore, the product can be easily removed through the second phase while the catalyst can be recovered.[53] Some ionic liquids are even known to form triphasic systems for catalytic applications.[56] However, in any liquid-liquid biphasic catalysis, the high viscosity of ionic liquids can induce mass transfer limitations, especially when the reaction is fast. Moreover, the relatively high amount of ionic liquids required is a disadvantage, since ionic liquids can still be expensive.[57]

Eventually, the immobilization of catalysts for continuous-flow processes is difficult to realize in liquid-liquid biphasic systems. One relatively novel approach to circumvent these problems is known as “supported ionic liquid phases (=SILPs)”, where ionic liquids are immobilized on solid support materials. This strategy circumvents the problems of common biphasic systems and can drastically reduce the required amount of ionic liquid since just a thin layer of ionic liquid is required. Additionally high surface area can be achieved by using high porous support materials and less mass transfer limitations caused by the high viscosity of the ionic liquids, occur.

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[56] Hejazifar, M.; Earle, M.; Seddon, K. R.; Weber, S.; Zirbs, R.; Bica, K. *J. Org. Chem.* **2016**, *81*, 12332–12339

[57] Riisager, A.; Fehrmann, R.; Haumann, M.; Wasserscheid, P. *Eur. J. Inorg. Chem.* **2006**, *2006*, 695–706

A classical SILP catalyst, as it is shown in Figure 14[58], is defined as a porous solid support material, e.g. silica with a thin film of ionic liquid on its surface. The ionic liquid remains on the solid surface due to physisorption or by covalent bonding. The first SILP catalysts were made by immobilization of pre-formed ionic liquids, such as chloroferrate based ionic liquids on silica. These catalysts were well investigated for Friedel-Crafts reactions. In these reactions, the ionic liquid itself was the catalytic active species and was immobilized on silica and charcoal via physisorption.

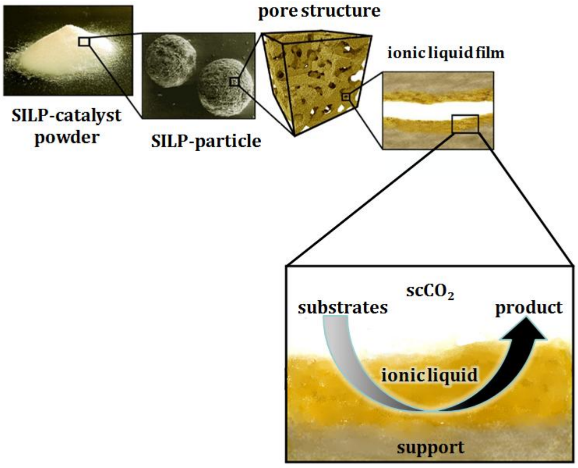

Figure 14: SILP-catalyst; adapted from Wölfel et al.[58]

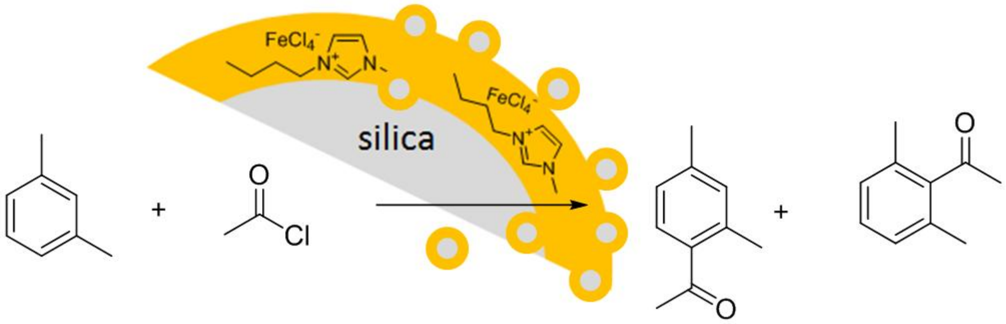

Figure 15: SILPs used in Friedel-Crafts acylation

In this way, the ionic liquid on silica was more selective for the desired product, but less active compared to using the ionic liquid without a support under batch conditions as well as under flow conditions.[59]

If the ionic liquid itself does not have catalytic activity, other catalysts can be dissolved in the ionic liquid phase, providing a liquid and catalytically active surface film on the support material. The reaction takes place in the ionic liquid and it can be consequently considered as homogenous catalysis, corresponding to a liquid-liquid biphasic system while simultaneously providing the advantages of improved handling and immobilization of heterogeneous catalysts.

3.5.1 SILP-concept in continuous flow

Outstanding examples for the use of SILP-catalysts in continuous flow are gas phase hydroformylation processes, well described by Riisager and co-workers. Rh-complexes dissolved in a thin

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[58] R. Wölfel. Ionic Liquid materials as engineering fluids and novel catalysts. https://www.crt.cbi.uni-erlangen.de/research/silp/index.shtml (accessed March 5, 2017)

[59] Valkenberg, M.; deCastro, C.; Hölderich, W. *Appl. Catal., A.* **2001**, *215*, 185–190

layer of 1-butyl-3-methylimidazolium hexafluorophosphate on silica are suitable as catalyst for the hydroformulation of propene with hydrogen and carbon monoxide in flow process mode.[60] A further example, given by Riisager et al. is the application for methanol carbonylation in continuous process mode[61] and the hydroformulation of 1-butene.[62]

While catalyst immobilization via the SILP strategy is already well-established for gas-phase reaction, e.g. via fixed-bed reactors, the implementation for liquid phase continuous processing is more difficult. Leaching of the ionic liquid from the surface can occur quite easily in liquid state, resulting in catalyst losses and product contamination.

A careful selection of the ionic liquid, support material, immobilization strategy and solvent for continuous flow processes can solve this issue to some extend.[20] A particularly attractive strategy in this regard is the use of supercritical carbon dioxide as solvent in combination with SILP catalysts. In principle, the combination of an apolar solvent such as $scCO_2$ and a polar ionic liquid leads to a biphasic system. It has been reported that CO_2 can significantly dissolve in an ionic liquid phase, which facilitates the in the catalytically active ionic liquid layer. The choice of the cation and anion of an ionic liquid dictates the solubility of carbon dioxide.[63] In contrast, ionic liquids are hardly soluble in carbon dioxide, which circumvents leaching of the catalytically active ionic liquid phase in the product.

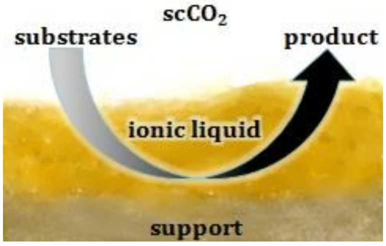

Figure 16: Biphasic system of $scCO_2$ and ionic liquid

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[60] Riisager, A. *J. Catal.* **2003**, *219*, 452–455

[61] Riisager, A.; Jorgensen, B.; Wasserscheid, P.; Fehrmann, R. *Chem. Commun.* **2006**, 994–996

[62] Haumann, M.; Dentler, K.; Joni, J.; Riisager, A.; Wasserscheid, P. *Adv. Synth. Catal.* **2007**, *349*, 425–431

[63] Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* **1999**, *399*, 28–29

4. Aim of thesis

This master thesis focuses on the development of a continuous process for the conversion of carbon dioxide as C_1-building block into fine chemicals. Supercritical carbon dioxide ($scCO_2$) should act as solvent and reactant, allowing to directly react with epoxides toward high-valuable cyclic carbonates (Figure 17). The required catalysts should be immobilized via SILP (=supported ionic liquid phase)-approach, allowing to collect the product in pure form, as carbon dioxide is removed by releasing the pressure.

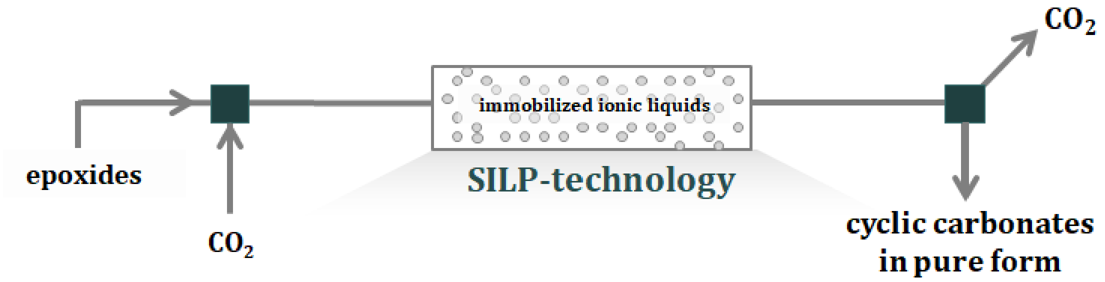


Figure 17: Schematic representation of the continuous flow process for the conversion of epoxides and carbon dioxide into cyclic carbonates

A number of critical steps had to be realized to enable the efficient conversion of CO_2 towards cyclic epoxides: After the selection of suitable catalysts, several catalytically active ionic liquids as well as similar compounds with a Lewis acidic anion should be synthesized. These catalysts should be initially evaluated for the formation of propylene carbonate in a batch process. After pre-selection of ionic liquids and suitable support materials, supported ionic liquid catalysts should be prepared and investigated under flow conditions. Eventually, the best performing catalytic system should be selected and further optimized for the efficient continuous flow production of propylene carbonate.

5. Results and discussion

5.1 Choice of the reaction

The first step of this work was to choose a suitable reaction for the conversion of carbon dioxide into valuable chemicals. The choice of the reaction was affected by several aspects as requirements had to be fulfilled, including

1) absence of solid products
2) non-gaseous products and substrates
3) reasonable low toxicity of all involved reagents
4) reasonable cost of all involved starting materials and catalysts
5) continuous flow mode not yet established

Consequently, the formation of cyclic carbonates from carbon dioxide and epoxides has been chosen, as it fulfils the required criteria (Figure 18).

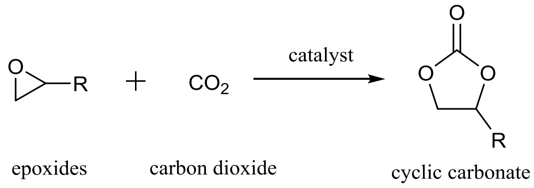


Figure 18: Synthesis of cyclic carbonates from epoxides and carbon dioxide

Moreover, a number of aspects were considered as advantageous, such as the availability of a large set of potential catalysts based on literature. Even pure ionic liquids are known to catalyse this reaction; however, to date, this reaction has been rarely performed in continuous flow mode.

Eventually, propylene oxide (PO) was selected as model substrate for the formation of cyclic carbonates, since it is most frequently used in literature, thereby allowing a comparison to existing systems. Further advantages are that both PO and the product propylene carbonate are liquid at room temperature with a reasonable boiling point and considered as harmless.

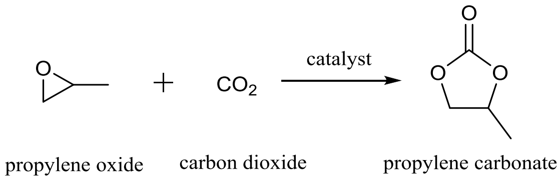
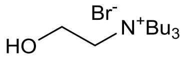
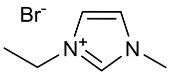
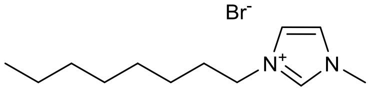
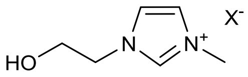
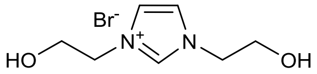
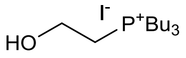


Figure 19: Synthesis of propylene carbonate

5.2 Selection of ionic liquids

Based on literature data, a set of suitable and catalytically active ionic liquids for the selective conversion of propylene oxide to propylene carbonate was chosen as shown the following table (Table 9).

Table 9: Selection of ionic liquids for the conversion of propylene oxide to propylene carbonate

ammonium based		**acronym**
$N^+Bu_4\ Br^-$ tetrabutylammonium bromide TBAB		**[TBA]Br**
 tributyl-(2-hydroxyethyl)ammonium bromide		**[TBHEA]Br**
imidazolium based		
 1-ethyl-3-methylimidazolium bromide		**[EMIM]Br**
 1-methyl-3-octylimidazolium bromide		**[C₈MIM]Br**
 1-(2-hydroxyethyl)-3-methylimidazolium halide	Cl^-	**[HEMIM]Cl**
	Br^-	**[HEMIM]Br**
 1,3-bis(2-hydroxyethyl)imidazolium bromide		**[BHEIM]Br**
phosphonium based		
$P^+Bu_4\ Br^-$ tetrabutylphosphonium bromide		**[TBP]Br**
 tributyl-(2-hydroxyethyl)phosphonium iodide		**[TBHEP]I**

Based on the variety of known catalytically active ionic liquids in literature, ammonium, imidazolium and phosphonium based ionic liquids with similar structure were chosen. Optionally, these ionic liquids were functionalized with an intramolecular hydroxyl group. Since imidazolium based ionic liquids are the best studied ionic liquids for this reaction, an additional hydroxyl group, a small variety of counter ions and longer alkyl chains were introduced. According to literature data, the ionic liquid [TBHEP]I seems to be the most effective catalyst within this selection, as it is capable to catalyze this reaction in high conversion even at low temperatures of 45 °C.[22]

Several cations within this selection were also used for the formation of Lewis-acidic ionic liquids as efficient catalytic systems. For example, the ammonium-based salt [TBAB]Br is known to form Lewis acidic tetrahalides as anion with Lewis acids like ZnX_2. Thereby, the catalytic activity increases drastically.[31] In the same way [EMIM]Br and even [HEMIM]Br with $ZnBr_2$ could catalyse the conversion of propylene oxide with higher yield compared to the catalytic system without $ZnBr_2$.[42] To our best knowledge, the substance [BHEIM] has never been investigated for this reaction.

With the exception of [TBA]Br that is commercially available, all ionic liquids were synthesized via alkylation of amine or phosphine precursors with the corresponding alkyl halides that act as electrophilic alkylation agents.

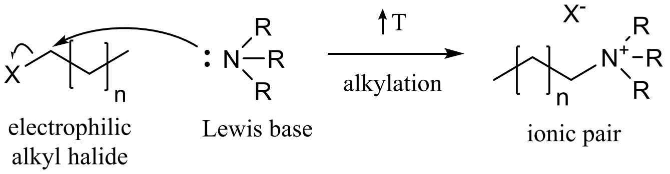


Figure 20: Alkylation

Although such alkylations can be sometimes exothermic, they are typically performed with moderate heating to facilitate full conversion, as reactions can be quite slow – particularly when chloroalkanes are used as alkyl halides. However, the temperature should be kept reasonable low to avoid discoloration of the obtained ionic liquids. To prevent other by-products and water, argon as inert gas was used, since ionic liquids are hydroscopic.

In general, the synthesis of ionic liquids was performed with equivalent amounts of both reagents. Conversion was monitored via ^{1}H NMR spectroscopy. In the case of alkyl halides with low boiling point, an excess of alkylating reagent was used to ensure complete conversion, since it could be easily removed in vacuo. In any case, the crude products were washed with n-hexane or diethyl ether and were dried 24 h or 48 h under high vacuum. Every substance was obtained in high yields ranging from 80% to >99% and in spectroscopically pure form. [HEMIM]Cl was already available in the laboratory from previous experiments and only had to be dried under high-vacuum before use.

Table 10: Results of ionic liquid synthesis

	[TBHEA]Br	[EMIM]Br	[MOIM]Br	[HEMIM]Br	[BHEIM]Br	[TBP]Br	[TBHEP]I
yield [%]	80	99	93	85	97	86	91

In case of the ionic liquid [BHEIM]Br a modified procedure was developed, as it was difficult to prepare the precursor, 1-(2-hydroxyethyl)imidazole, in satisfying yield and purity. A one pot reaction using imidazole, 2-bromoethanol and 1,3-dioxolan-2-one was found to be a suitable way to synthesize 1,3-bis-(2-hydroxyethyl)imidazolium bromide. Dioxane or toluene was used as solvent, allowing to isolate the product in 97% yield and high purity.

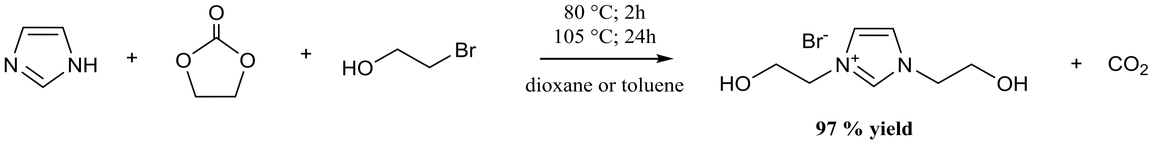


Figure 21: Synthesis of 1,3-bis-(2-hydroxyethyl)imidazolium bromide; [BHEIM]Br

All ionic liquids synthesized as described above were stored either in sealed round bottom flasks filled with argon as liquids or in an exicator over phosphorus pentoxide as solid crystals.

5.2.1 Synthesis of ionic liquids with Lewis acidic anions

Literature suggested that the catalytic activity of known and unfunctionalized ionic liquids can be strongly enhanced by adding Lewis acids. Therefore, $ZnBr_2$ was added to selected ionic liquids in different ratios varying from a ratio 1:1 to 4:1 (IL/$ZnBr_2$). This was done in a glove box under inert-gas atmosphere, since $ZnBr_2$ is highly hygroscopic. The mixtures were heated to 120 °C under vigorous stirring for 24 h to obtain Lewis acidic ionic liquids.

5.3 Synthesis of propylene carbonate under batch process mode

5.3.1 Investigations on the catalytic activity of conventional ionic liquids

After successful synthesis of the selected ionic liquids, their catalytic activity in the conversion of propylene oxide with carbon dioxide was evaluated.

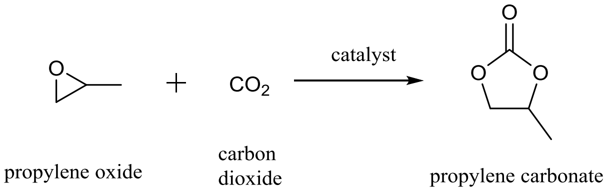


Figure 22: Synthesis of propylene carbonate

This was done initially in batch process mode. Consequently, an autoclave was charged with 2 g propylene oxide, 5 mol% ionic liquid as catalyst and pressurized to 40 bar carbon dioxide. Since a common carbon dioxide flask is filled with a maximum pressure of 50-60 bar, it was not possible to reach supercritical conditions, even with a reaction temperature of 70 °C. Experiments were stopped after 18 h. The reactions were performed at 45 °C and 70 °C respectively, and the results are summarized in Figure 23.

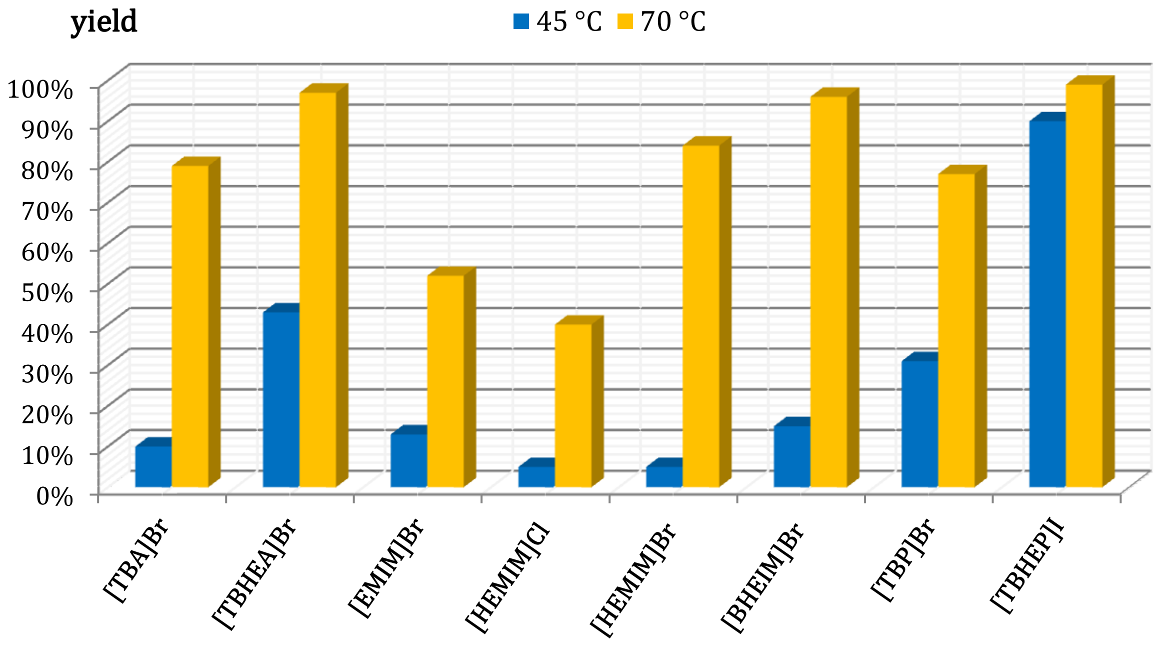


Figure 23: Catalytic activity of conventional ionic liquids at 45 °C and 70 °C

As to be expected from literature data, all ionic liquids with a hydroxyl group as substituent revealed to have higher reactivity than those without. The ionic liquid, [BHEIM]Br with two intramolecular hydroxyl groups is even more effective than [HEMIM]Br.

In a similar way, the influence of the anion could be confirmed as ionic liquids with bromide as anion showed higher reaction rates. The most promising phosphonium based IL, [TBHEP]I, exhibits the highest catalytic activity. Even with 45 °C temperature, the results were outstanding compared to the other ionic liquids.

5.3.2 Investigations on the catalytic activity of Lewis acidic ionic liquids

After evaluating the catalytic performance of unfunctionalized ionic liquids, the impact of $ZnBr_2$ to form Lewis acidic ionic liquids was further investigated in the same reaction. After addition of $ZnBr_2$, Lewis acidic tetrahalide anions were formed. The formation of the highly catalytically active species has already been reported in literature for some ionic liquids shown in Table 9. Other ionic liquids such as [TBHEP]I in combination with a Lewis acid as catalyst have not been used before for the conversion of CO_2 with epoxides. All reactions with Lewis acidic ionic liquids were carried out only at the lower temperature (45 °C) for a better insight in the catalytic activities. A similar molar ratio (5 mol%) of ionic liquid was used, and experiments were running for 18 h as before. An overview about the results with and without $ZnBr_2$ at 45 °C is shown in Figure 24.

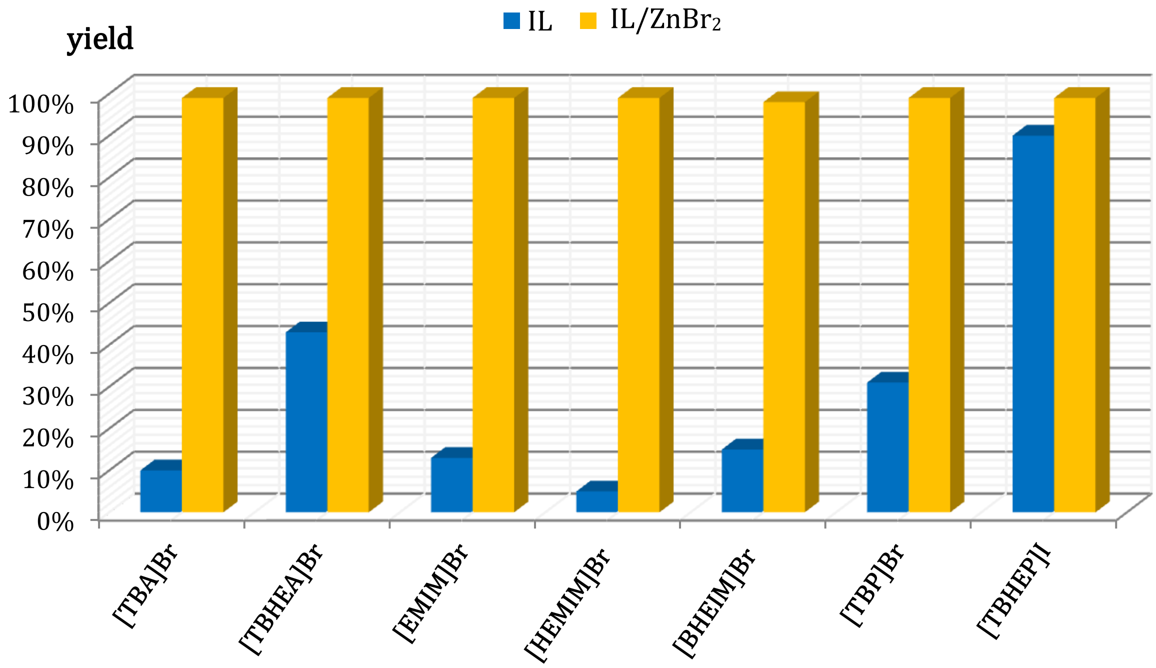


Figure 24: Catalytic activity of selected ionic liquids in combination with $ZnBr_2$ (4:1) at 45 °C

As can be seen from Figure 24 the catalytic activity for every ionic liquid increased drastically by the addition of $ZnBr_2$. Even at a low temperature of 45 °C, quantitative conversion and high yields of approx. 100% were reached with every Lewis acidic ionic liquid. When comparing the results of all batch experiments as listed in Table 11 it is obvious that the impact of Lewis acidic anion on the catalytic activity outperforms the impact of side chain functionalization. At 45 °C, only the phosphonium based hydroxyl functionalized ionic liquid [TBHEPI can compete with Lewis acidic species and reaches a yield >90%.

Table 11: Summing up the results from batch process mode with ionic liquids

	[TBA]Br	[TBHEA]Br	[EMIM]Br	[HEMIM]Cl	[HEMIM]Br	[BHEIM]Br	[TBP]Br	[TBHEP]I
45 °C	10%	43%	13%	< 5%	< 5 %	15%	31%	90%
70 °C	79%	97%	52%	40%	84%	96%	77%	>99%
45 °C $ZnBr_2$	>99%	>99%	99%	---	>99%	98%	>99%	>99%

Conditions: 34.4 mmol propylene oxide; 5 mol% ionic liquid; 4 MPa CO_2 pressure; 18 h; Analysis was done via ^{1}H NMR and GC

5.3.3 Influence of silica in batch process mode

The influence of silica as SILP-material was also investigated under batch conditions in small scope to further evaluate the impact of silica as support material for future use in supported catalysts. Especially the influence of silica on hydroxyl-functionalized ionic liquids was of interest. Supported catalysts were prepared with [EMIM]Br and [HEMIM]Br via physisorption (10 w%). The obtained SILP materials were used as catalyst under batch conditions at 70 °C; however, in comparison to the other batch reactions, a large quantity of SILP-material (3-4 g) was required to work under identical molar catalyst ratios.

Table 12: Comparison of batch experiments with and without silica stated by yields

	without silica		**with silica**			
			without $ZnBr_2$	**$ZnBr_2$/IL 1:4**	**$ZnBr_2$/IL 1:2**	**$ZnBr_2$/IL 1:1**
	45 °C	**70 °C**	**70 °C**	**70 °C**	**70 °C**	**70 °C**
[EMIM]Br	13%	52%	81%	72%	74%	73%
[HEMIM]Br	< 5%	84%	74%			

Conditions: 34.4 mmol propylene oxide; 5 mol% ionic liquid; 4 MPa CO_2 pressure; 18 h; Analysis was done via ^{1}H NMR and GC

The comparingly large amount of SILP catalyst transformed the reaction mixture into a slurry, which was poorly mixed during the reaction. For that reason, these results have to be regarded with caution. Nevertheless, the yield with [EMIM]Br increases from 52% to 81% by the addition of silica. This indicates that the addition of intermolecular hydroxyl groups improves the catalytic activity of [EMIM]Br in a synergistic way. In contrast, a small decrease in yield was observed with [HEMIM]Br. It can be assumed that intramolecular and intermolecular hydroxyl groups are incompatible and cannot further improve the catalytic activity. In addition, the combination of silica and $ZnBr_2$ with [EMIM]Br was investigated, as well as the influence of different $ZnBr_2$/ionic liquid ratios on silica. The addition of $ZnBr_2$ decreased the yield around 10 %, independent of the ratio which was used. However, the increase of yield after addition of silica remains drastically below the strong improvements that were observed for unsupported ionic liquids, indicating that the presence of silica also inhibits the catalytic effect of Lewis acidic ionic liquids in this reaction.

5.4 Continuous conversion of $scCO_2$ with epoxides

After evaluation of different ionic liquids under batch conditions in an autoclave, the conversion of propylene oxide with carbon dioxide was further studied in continuous flow.

5.4.1 Setup for flow experiments

The organization of the $scCO_2$-device which was used for all experiments in flow process mode is shown in Figure 25.

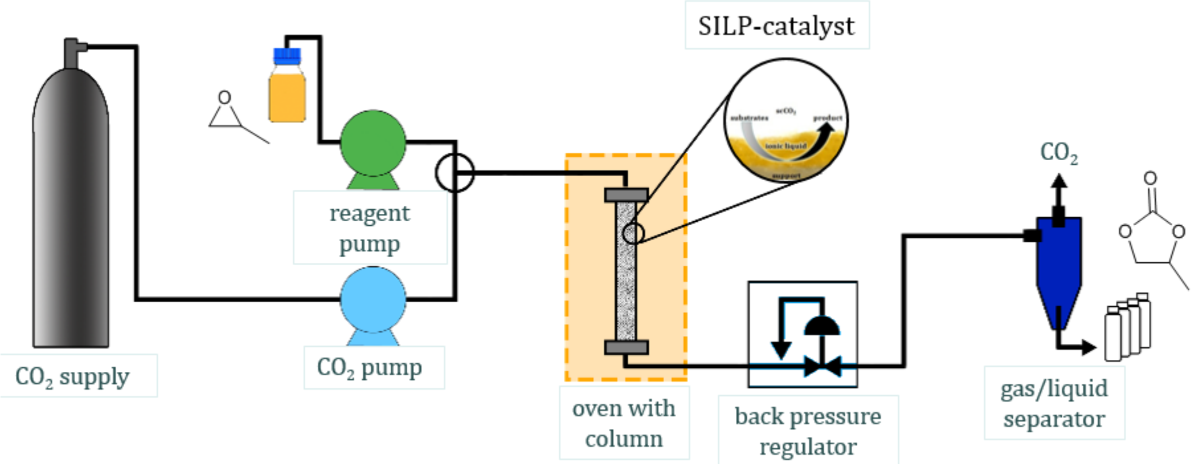


Figure 25: Set-up of continuous-flow conversion of CO_2 adapted from S. Kampichler

A liquid carbon dioxide cylinder with an ascending pipe serves as CO_2 supply. Liquid carbon dioxide can be pumped through the system with adjustable flow rate and was pressurized to the desired pressure by two pumps. Other reagents or their solutions can be added with an additional HPLC pump. After preheating in a coil, the reaction mixture in supercritical carbon dioxide passes through a catalyst cartridge placed in an oven for temperature control. For this purpose, used HPLC-columns were emptied and filled with SILP material. After this thermostated reaction unit, the reaction mixture in $scCO_2$ is decompressed in a back pressure regulator, followed by a gas/liquid separator and a fraction collector.

A flow experiment is affected by many parameters. In the first part, some pre-experiments had to be done and decisions had to be made to establish a suitable setting for following flow experiments. Initially, 10 w% [TBHEP]I on silica was selected as SILP catalyst. Silica as support material was chosen, since it is the most commonly used support material. The phosphonium based ionic liquid [TBHEP]I was selected as it gave the best results under batch experiments. The following settings and system parameters for various test series with (Table 13) were established in these first experiments.

Table 13: System parameters under standard conditions

System-parameter	**value**
Oven temperature	80 °C
Temperature at the back pressure regulator	60 °C
IL on support-material (SILP)	10 w% IL
Pressure	100 bar
Column length	4.6 x 150 mm
CO_2-flow rate	2 x 0.99 ml/min
Substrate flow rate (1:1 PO in *n*-hexane)	0.02 ml/min
Residence time	75 s

Due to system limitations, an oven temperature of 80 °C was used, since it is the highest adjustable temperature possible. The pressure was set at 100 bar to ensure supercritical conditions.

When selecting flow rate and substrate mixture, some consideration regarding the boiling point of the starting materials had to be taken into account, since a solvent with a low boiling point such as propylene oxide (bp. 34 °C) can cause issues with incorrect flow rate. Consequently a substrate mixture with *n*-hexane as solvent was used to insure a correct substrate flow rate. For the first experiments the use of a 1:1 mixture seemed to be reasonable, since similar results were obtained in the same experiment without a co-solvent. Other co-solvents such as methyl tertbutyl ether (MTBE) were used instead of *n*-hexane resulted in lower yields.

After depressurization, unreacted PO as well as the co-solvent n-hexane were automatically evaporated at the back pressure regulator set at 60 °C before collecting the product. Consequently, the product could be collected in pure form without any other compounds. This allowed directly determining the yield gravimetrically, and eventually, calculating the space-time yield (STY).

$$\sigma_P = \frac{m_P}{m_C * t}$$

Equation 3: Space time yield

σ_P......Space time yield (STY) [h^{-1}]

m_P......mass of the produced product [g]

m_C......mass of the used catalyst [g]

t.........reaction time [h]

5.4.2 Impact of support material

In order to identify suitable support materials for catalyst immobilization, different materials were investigated. The support material also might influence the catalytic activity of the SILP-catalyst, due different porosity and surface area as well as functional groups on its surface. Silica, calcinated silica, charcoal, cellulose and aluminium oxide were used as support material for [EMIM]Br. In any case, 10 w% ionic liquid was dispersed on the surface of the support materials. Briefly, the ionic liquid was dissolved in methanol or dichloromethane, the support material was added, and the solvent was slowly evaporated. After removing solvent traces under high vacuum, all SILP catalyst were obtained as free flowing powders. Characteristics of used materials are represented in Table 14.

Table 14: Support material characteristics

	size[a] [µm]	**specific surface area[a] [m²/g]**	**water content[b] [w%]**	**pH (suspension)**
Silica 60[d]	40 - 60	480 - 540	6.0	6.7
charcoal[e]	300 - 500	---	5.4	3.8
cellulose[d]	40 - 250	---	5.1	3.9
aluminium oxide 60[c]	50 - 200	135 - 165	4.5	6.5

[a]data provided by the supplier; [b]determined via TGA before drying at 110 °C; [c]purchased from Acros Organics, [d]Merck, [e]Fluka

According to thermal gravimetric analysis (TGA), all support materials revealed to have some water content, ranging from 4 to 6%. Since water has a great influence on the catalysis in this reaction, all materials were dried before use at 110 °C for at least for 24 h in an oven under vacuo, aiming to reduce the water content before the preparation of supported ionic liquid catalysts. The obtained SILP materials were further evaluated in the conversion of propylene oxide with supercritical CO_2 under standard conditions, and the results of those flow experiments are presented in Figure 26.

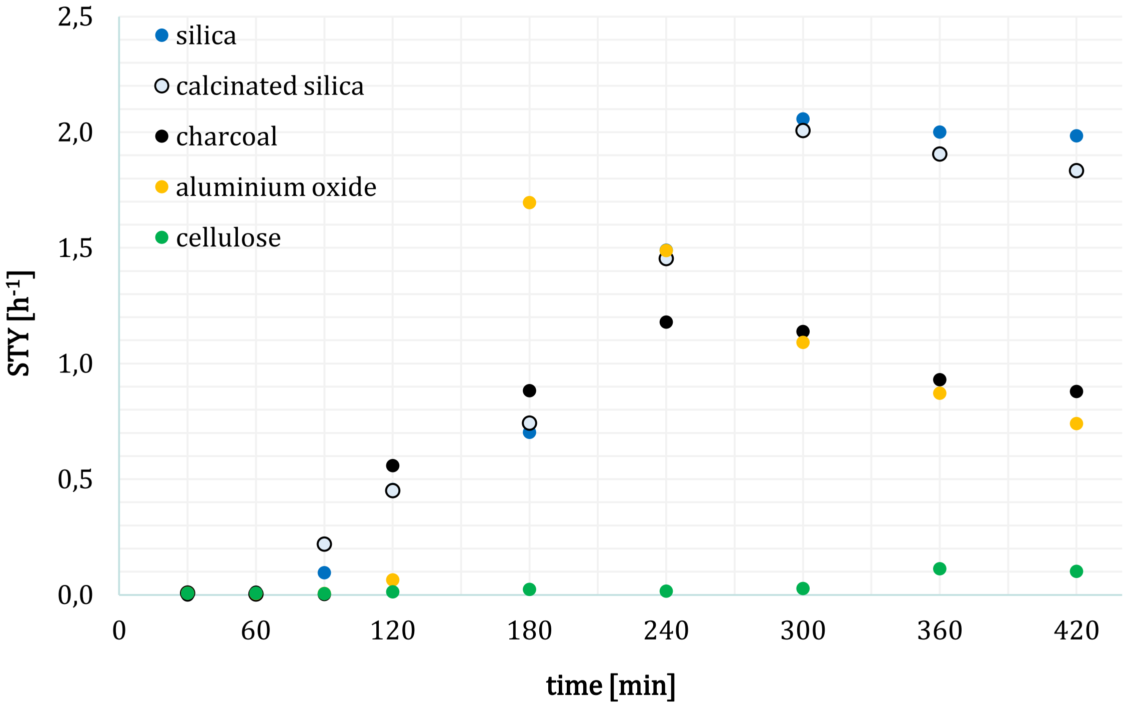


Figure 26: Investigation of different support materials with [EMIM]Br

At 420 min, a stable product output over at least 2 h was observed for every investigated support material, except for aluminium oxide. In this case, the ionic liquid was leaching from the material surface. Cellulose as support material showed stabilized space time yield over time after 360 min, however the STY did not rise above 0.1 h^{-1}. The product output was low despite the presence of intermolecular hydroxyl groups, suggesting that the low STY is due to the low porosity of the material. The result for charcoal showed a STY maximum and decreased afterwards. At 420 min the product output stabilized at least for 2 h. Interestingly, no leaching of ionic liquid in the product phase was detected according to ^{1}H NMR analysis for all support materials except alumina oxide, indicating that the SILP approach provides a suitable technique for the fast and efficient catalyst immobilization on solid support.

The best results with a space time yield of 2.0 h^{-1} could be observed using silica as support material. The combination of surface-located hydroxyl groups, high surface area and high porosity seemed to have a great influence on the catalytic activity. For further investigations on the influence of surface hydroxyl groups, silica was calcinated to reduce surface hydroxyl groups by heating it to 540 °C. This process is demonstrated in Figure 27.

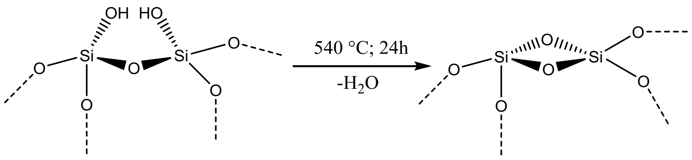


Figure 27: Calcination of silica

Calcinated silica as support material showed slightly lower space time yield than conventional silica. This result supports the co-catalytic effect of surface hydroxyl groups, suggesting that a removal of hydroxyl groups lead to reduced catalytic activity.

5.4.2.1 Influence of different ionic liquids on silica as support material

After establishing pre-dried silica a most suitable support material, all ionic liquids were evaluated under flow conditions. Consequently SILP-catalysts were prepared with all ionic liquids shown in Table 9 and used for the formation of propylene carbonate. The results are shown in Figure 28.

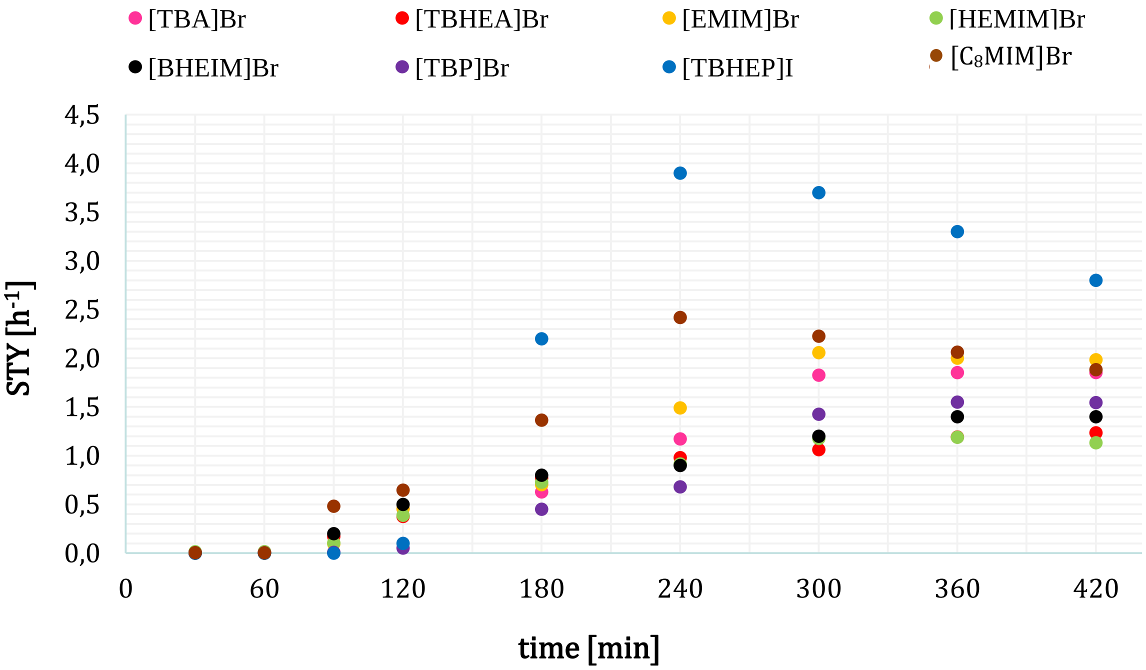


Figure 28: Influence of different ionic liquids on silica

In any case no leaching of catalyst was observed for any ionic liquid on silica. As to be expected from batch experiments, the phosphonium based ionic liquid [TBHEP]I also seems the most active catalyst under continuous flow (Figure 29). However, the product output and STY did not stabilize over time. This effect is even more pronounced in a long-time stability experiment shown in Figure 29, were a constant decrease of STY is visible over time.

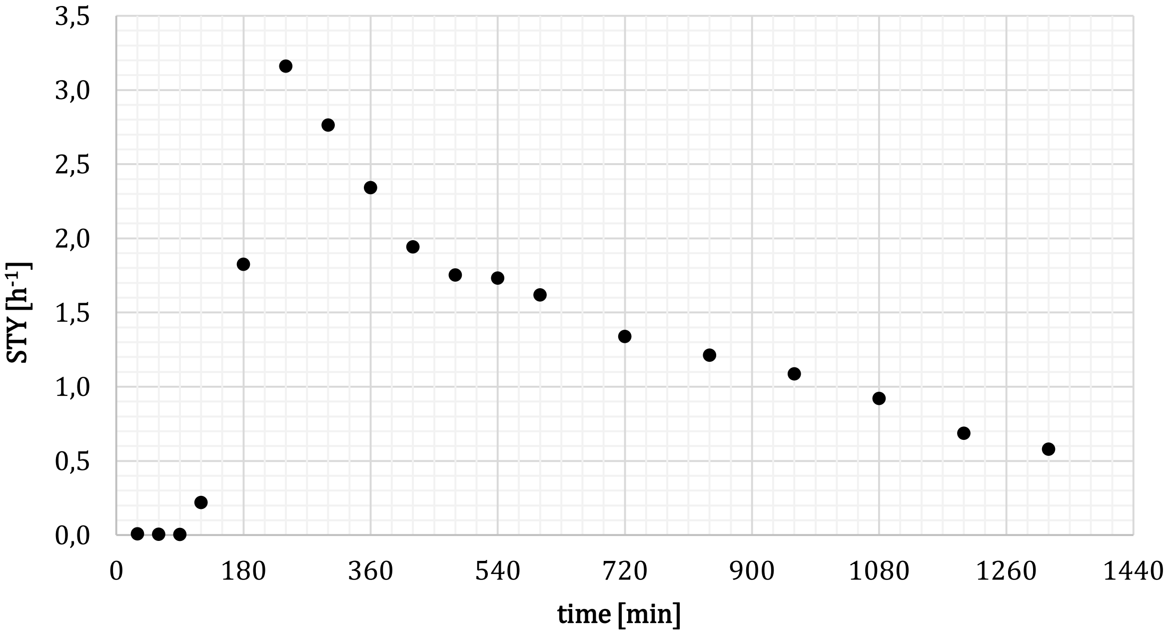


Figure 29: Long time stability of [TBHEP]I on silica

After reaching a maximum of a space time yield of 3.2 h^{-1} at 240 min, a decrease to 0.9 h^{-1} was observed after 1320 min, corresponding to a yield of only 11%. Further investigations showed that the catalyst was decomposing on silica during the reaction. This is in contrast to the unsupported material, since [TBHEP]I without silica as support did not decompose under batch conditions.

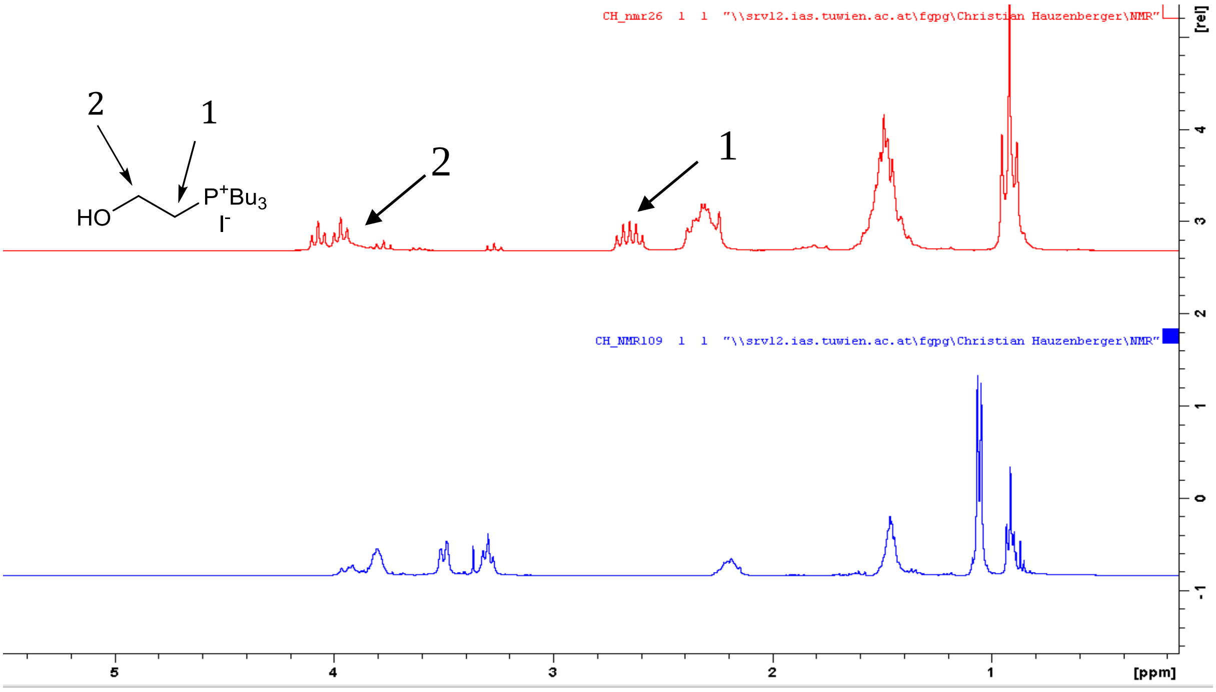


Figure 30: ^{1}H NMR spectrum of [TBHEP]I before use (top) and after use (bottom)

The decomposition of the phosphonium based catalyst is visible in ^{1}H NMR spectra of native and used [TBHEP]I. Beside the signals of polypropylene glycol at 1.0 ppm (d) and 3.4 ppm (m), which is formed to small extend with every ionic liquid on silica, it is obvious that the signals of the hydroxyl-functionalized side chain have disappeared. This indicates a degradation of the hydroxyethyl chain in the phosphonium salt as main reason for the decrease of catalytic activity over time. The problem of catalyst deactivation was not observed for any other ionic liquid, were reasonably stable product output was observed over time for 420 min. However, a different order of catalytic activity of all ILs on silica in flow was observed compared to batch conditions. Interestingly, [EMIM]Br without any intermolecular hydroxyl groups seemed to be the most efficient ionic liquid on silica based on all tested ionic liquids under flow conditions.

The pool of ionic liquids was further widened to include [C_8MIM]Br, allowing to investigate the influence of a longer alkyl chain. This should enable a higher CO_2 solubility in the ionic liquid layer on the SILP catalyst, but also a lower viscosity and higher mass transfer. The product output reached its maximum already at 240 min and gave higher yields compared to [EMIM]Br with a shorter chain. However, space time yield was slowly decreasing and did not stabilize over time. Eventually [EMIM]Br with a high and stable STY over at least 2 h was considered as most suitable catalyst.

Based on all tested systems, the combination of [EMIM]Br and untreated silica as support material revealed to be the best working system for the formation of propylene carbonate. Without process optimization, a STY of 2.5 h^{-1} was achieved by this system, which means a stabilized production rate of 0.34 ml PC per hour for at least for 2 hrs. This corresponds to 43% yield based on the substrate input.

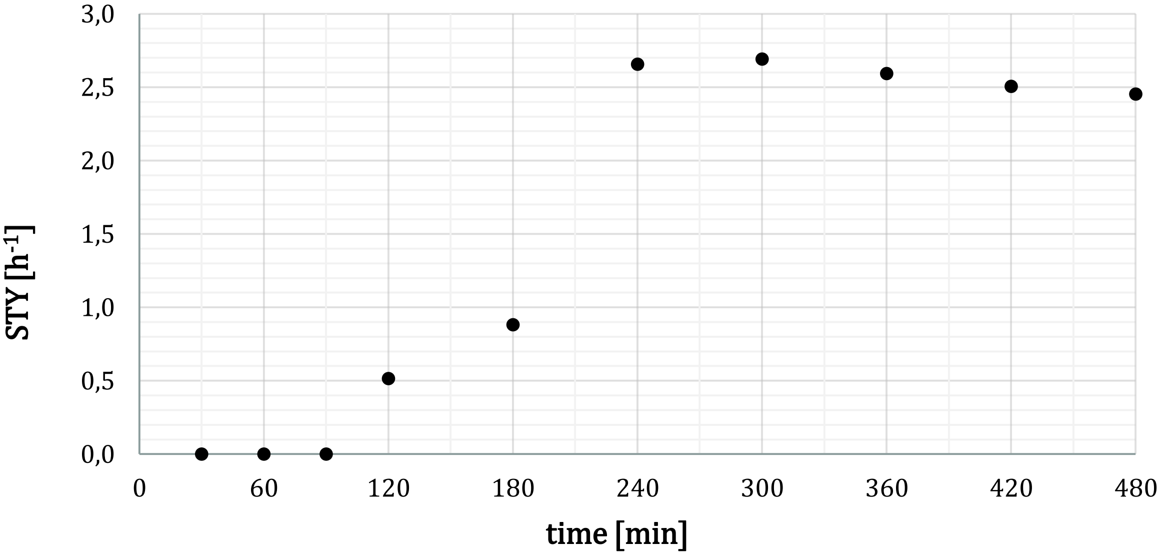


Figure 31: [EMIM]Br on silica

The product could be directly collected without solvent contamination in high purity, since *n*-hexane as well as the unconverted PO evaporated together with carbon dioxide. In addition, no leaching of catalyst could be observed. Traces of the by-product, polypropylene glycol, remained on the silica support. A typically ^{1}H NMR spectrum of a collected fraction is shown in Figure 32 and confirms the purity of the obtained product.

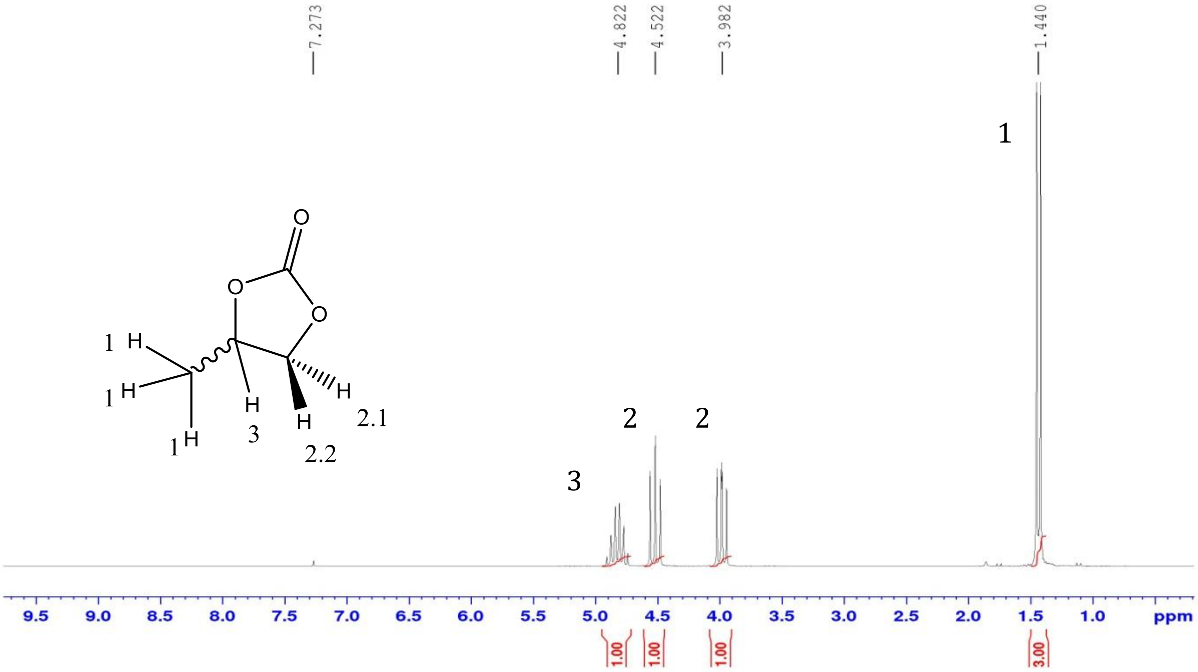


Figure 32: ^{1}H NMR spectrum of a typical product fraction

5.4.2.1.1 Influence caused by the addition of $ZnBr_2$

After investigating of the selected ionic liquids, the impact of the Lewis acid $ZnBr_2$ was further investigated. In the following diagram (Figure 33) the results of selected ionic liquids on silica with the optional addition of $ZnBr_2$ in a ratio 4:1 are shown. Space time yields were reported after 420 min, as this corresponds to a stable product output.

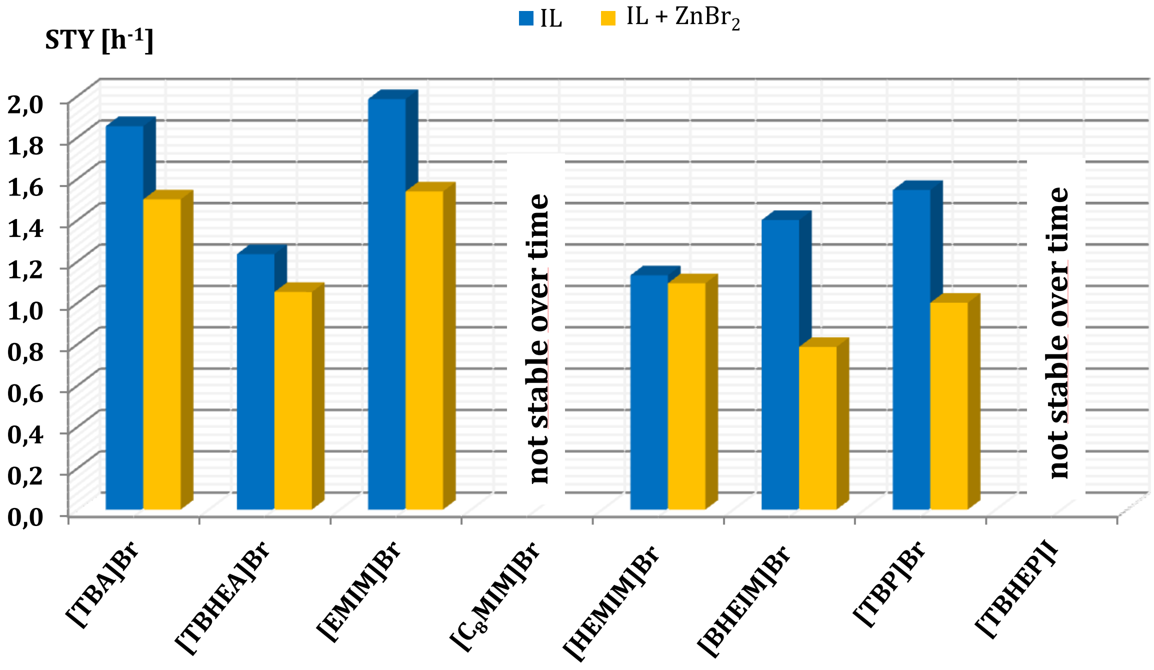


Figure 33: Comparison between IL and IL + $ZnBr_2$ (4:1) on silica in continuous mode

Figure 33 reveals that the supported Lewis acidic ionic liquids on silica are less catalytically active in continuous flow than conventional supported ionic liquids on silica. The effect was contrary to the results in 5.3.2 under batch conditions, were a strong improvement of catalytic activity was observed in the presence of a Lewis acid. It seems that the Lewis acid and hydroxyl groups on the support counteract each other. Again, traces of polypropylene glycol were formed as side product, which remained on the support material.

Since [EMIM]Br revealed to be the most active ionic liquid even with $ZnBr_2$, the influence on the catalytic activity of different [EMIM]Br/$ZnBr_2$ ratios was investigated. Therefore, the ratios of 1:1, 2:1 and 4:1 were used. The direct comparison of the results is shown in Figure 34.

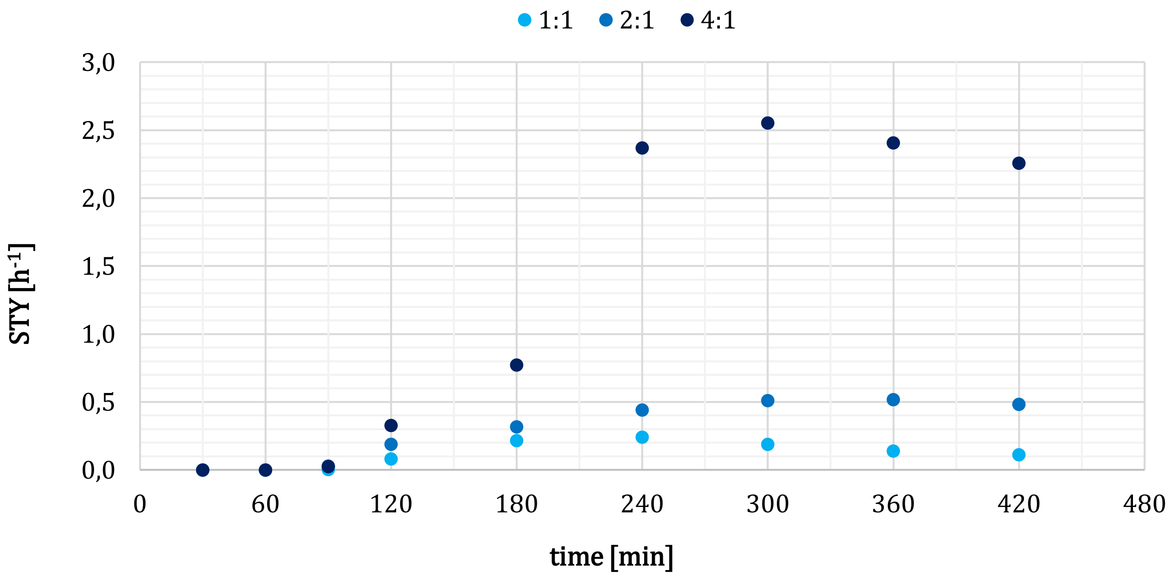


Figure 34: Influence of [EMIM]Br/ZnBr$_2$ ratio

These results showed that an increase of ZnBr$_2$ from a ratio 4:1 to 1:1 drastically reduced the activity. At this point it was clear that ionic liquids on silica are not compatible with ZnBr$_2$ to reach higher catalytic activity. To further exclude any problems during the production of silica-supported Lewis acidic ionic liquids, the preparation of SILP materials was modified and dichloromethane was used as solvent instead of methanol. Results showed that methanol as solvent had indeed a negative influence on the catalytic activity of the produced SILP-catalyst. In the following graph, the results of a SILP-catalyst made with methanol and in comparison with dichloromethane as solvent are shown.

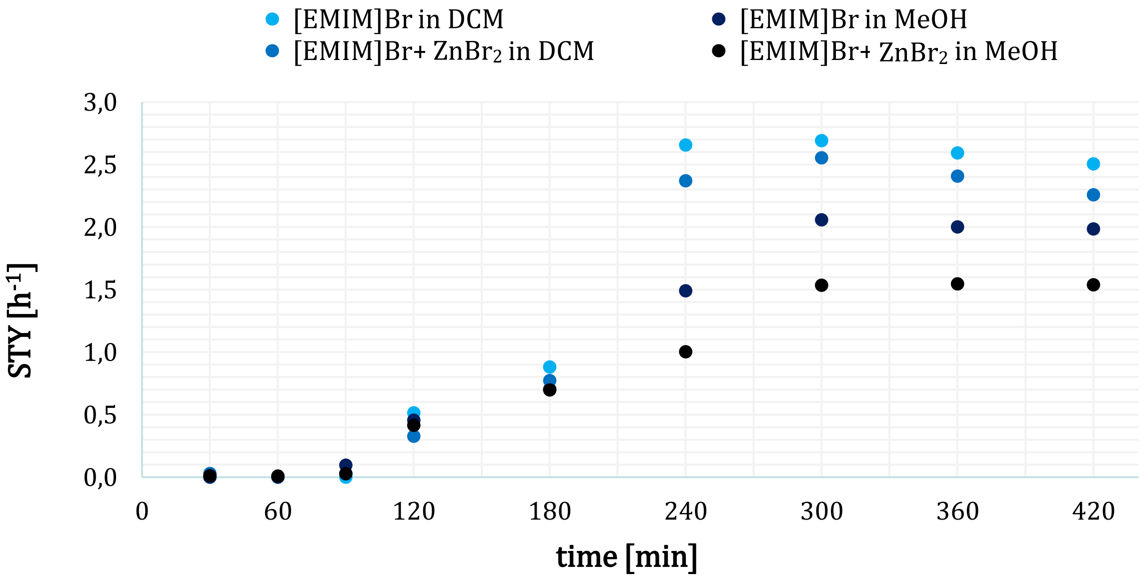


Figure 35: Influence of the solvent at the SILP-production on catalytic activity based on silica

Experiments showed that SILP-catalysts made with methanol are less catalytically active than SILP-catalysts made with dichloromethane. The reason for that might be that methanol, which is able to partially dissolve silica, alters the high porous surface of silica and reduces the specific surface area. However, in any case results with Lewis acidic supported ionic liquids remained below the values with conventional ionic liquids, showing that the mode of preparation is not responsible for the limited influence of Lewis acid under continuous flow conditions.

5.4.2.2 Influence of $ZnBr_2$ on other support materials

Since the addition of $ZnBr_2$ gave no improvement with silica as support (in 5.4.2.1.1), other support materials including charcoal and cellulose were investigated as support material for Lewis acidic ionic liquids. Again, a loading of 10 w% ionic liquid in a ratio [EMIM]Br/$ZnBr_2$ 4:1 was chosen. In Figure 36 results of those experiments and a comparison with silica is shown.

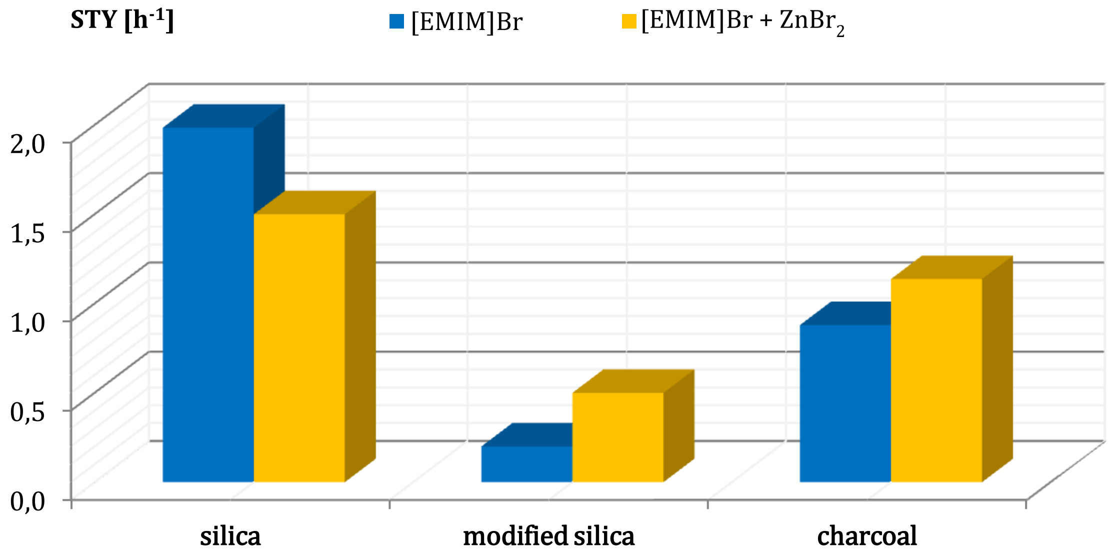


Figure 36: Comparison of [EMIM]Br with [EMIM]Br + $ZnBr_2$ on different support materials. Results for STY are reported after 420 min.

In Figure 36, the space time yield using charcoal and cellulose as support material compared to silica is reported. In contrast to previous experiments, an increase in space time yield after addition of $ZnBr_2$. could be observed on charcoal or cellulose. However, the effect was small and values could not reach the yields obtained with [EMIM]Br on silica without $ZnBr_2$.

5.4.2.3 Impact of surface-modificated silica

While silica revealed to be a suitable support to improve the catalytic activity, problems with long –term stability of the supported ionic liquids and with incompatibility of $ZnBr_2$ limited its application. Since further improvements were desirable, silica was further modified with a covalently bond monolayer of an ionic liquid as a novel support material. Due to its inherent catalytic acivity, an imidazolium based ionic liquid was chosen. Organosilanes are commonly used for silica surface modifications, as methoxy or ethoxy silane groups as anchor groups are known to react with the hydroxyl groups of silica.[64] The following compound (Figure 37) was chosen for the modification of silica.

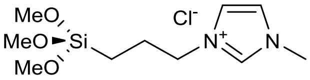


Figure 37: 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride

The ionic liquid was reacted with the hydroxyl groups on the surface of silica. The reaction is demonstrated in Figure 38.

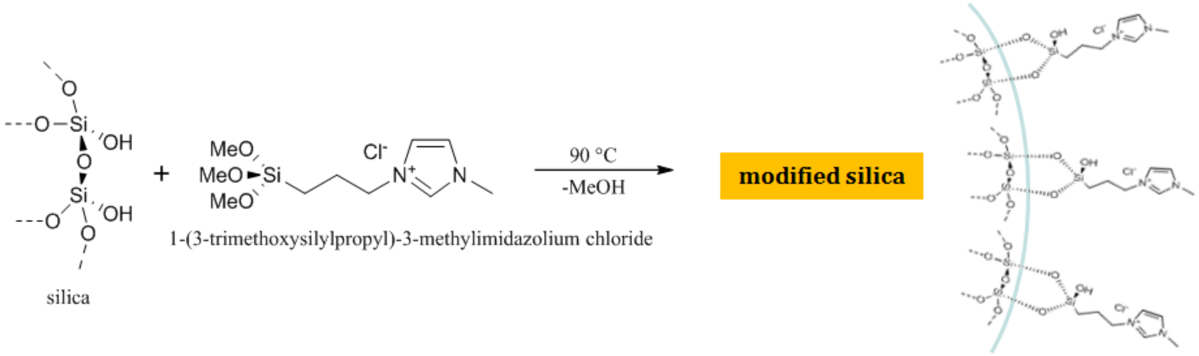


Figure 38: Modification of silica

In order to ensure the maximum loading of ionic liquids on the silica surface, the reaction was conducted twice with a large excess of ionic liquid. The reaction time was at least 48 h and the excess of ionic liquid was removed after every process. Analysis via ATR-IR spectra showed the disappearance of the silica hydroxyl groups, confirming the successful surface modification of silica with a monolayer of imidazolium-based ionic liquid. The spectra are shown in Figure 67 (see experimental section). After modifying silica, the broad band of the hydroxyl stretching vibrations visible at 3372 cm^{-1} has mostly disappeared. Instead C-H stretching vibrations from methyl and methylene groups at 3068 became visible.

5.4.2.4 Influence of $ZnBr_2$ on modified silica

After preparation of surface-functionalized silica, its catalytic properties were investigated, optionally with 10 w% [EMIM]Br dispersed on its surface. Additionally, the impact of $ZnBr_2$ was investigated in the same manner as for the other support materials. The results and the direct comparison to unmodified silica are shown in Figure 39.

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[64] Goerl, U.; Hunsche, A.; Mueller, A.; Koban, H. G. *Rubber Chem. Technol* **1997**, *70*, 608–623

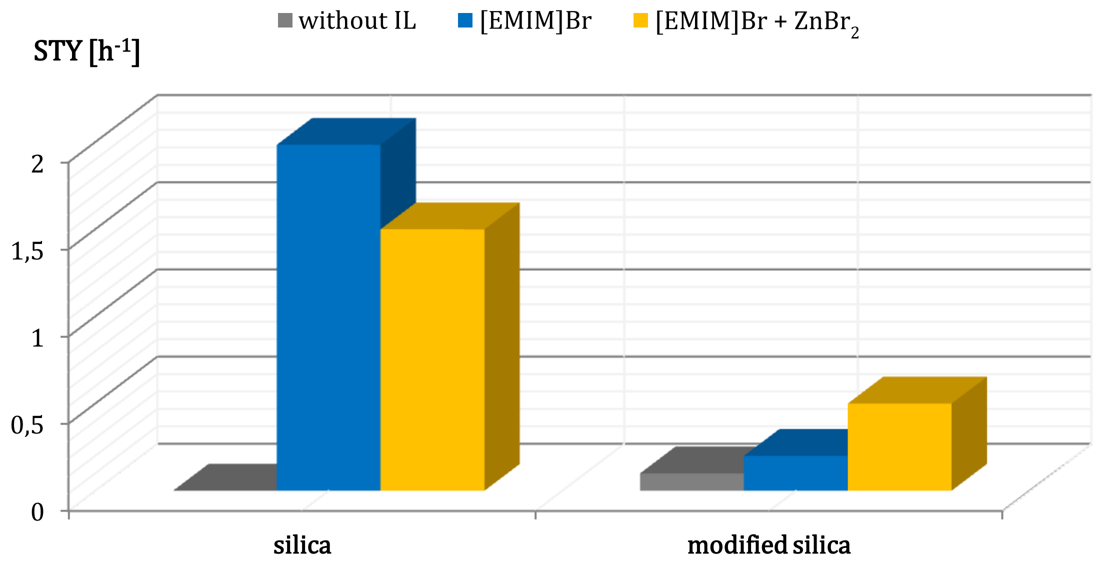

Figure 39: Comparison of silica to modified silica as support in continuous flow

The comparison is based on the maximum stabilized space time yield observed during the flow experiments. While no product formation was observed with unmodified silica, the modified silica instead revealed to be catalytically active. The additional loading with 10 w% [EMIM]Br via physisorption increased the space time yield. Even for modified silica, no leaching of the ionic liquid was observed, as the excess ionic liquid remains on the modified silica surface due the ionic interactions with the covalently bond ionic liquid. Unfortunately, the improvement of the STY with additional ionic liquid was much lower in case of modified silica compared to common silica. The further addition of $ZnBr_2$ gave a small improvement; however, results remained again below the values obtained with [EMIM]Br on normal silica. It seems that the positive effect of silica hydroxyl groups is more important for the catalytic activity than the addition of $ZnBr_2$ in case of supported catalyst systems under continuous flow.

5.4.3 Optimization of the continuous flow process

Since all previous experiments revealed [EMIM]Br on silica as most efficient catalytic system, the process parameters were further optimized to improve the overall yield of 43%. A number of system parameters can be modified and are listed below.

1) temperature (> 80 °C)
2) SILP-loading (> 10 w% >)
3) pressure (> 100 bar >)
4) flow rate (> 2 ml/min >)
5) column length (> 150 mm)

All optimization experiments were carried out at least for 420 min, allowing to studying long-term stability under optimized conditions.

5.4.3.1 Impact of reaction temperature

Initially, the impact of increased temperature on the conversion of propylene oxide with $scCO_2$ was investigated. Since the oven temperature in the commercial $scCO_2$ plant was not able to reach temperatures over 80 °C, the set-up had to be modified. Consequently, the catalyst cartridge with the SILP catalyst was transferred to an external glycerin heating bath. This set-up allowed pre-heating the reaction mixture to 80 °C and further conducting the catalytic process at considerably higher reaction temperatures. In this way, the reaction was performed at 100 °C and 120 °C and results are shown in Figure 40.

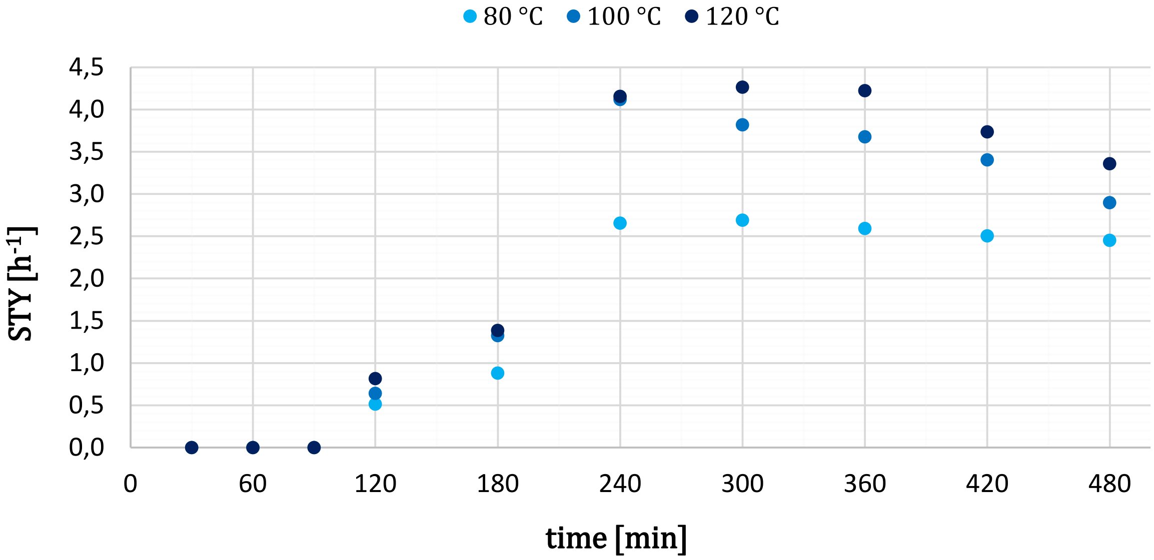

Figure 40: Influence of temperature on STY

As to be expected, a higher temperature resulted also in higher space time yield. Even at this elevated temperature, no leaching of ionic liquid catalyst was observed. Although a maximum of 74% yield was achieved corresponding to a STY of 4.3 h^{-1}. The product output decreased at 120 °C after 3 h quite rapidly (Figure 41). This decrease of STY is more rapid at a higher temperature.

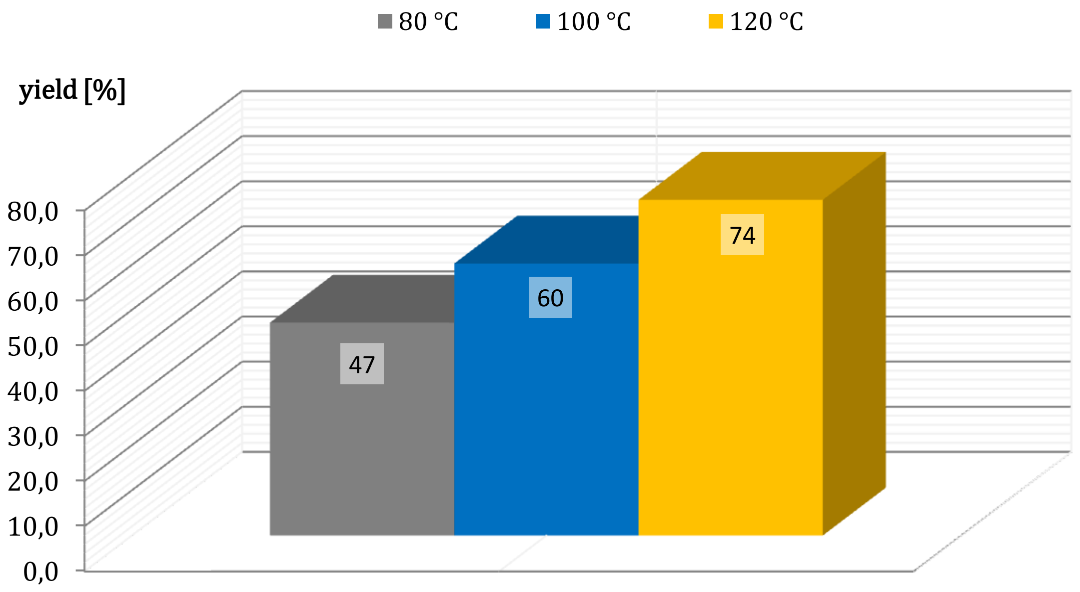

Figure 41: Influence of temperature on yield

In Figure 41 the yields at 300 min of each experiment are compared.

5.4.3.2 Influence of SILP-loading

To investigate the effect of different amounts of ionic liquid dispersed on silica, SILP-catalysts with 5 w%, 10 w% and 20 w% were tested. The results are shown in Figure 42.

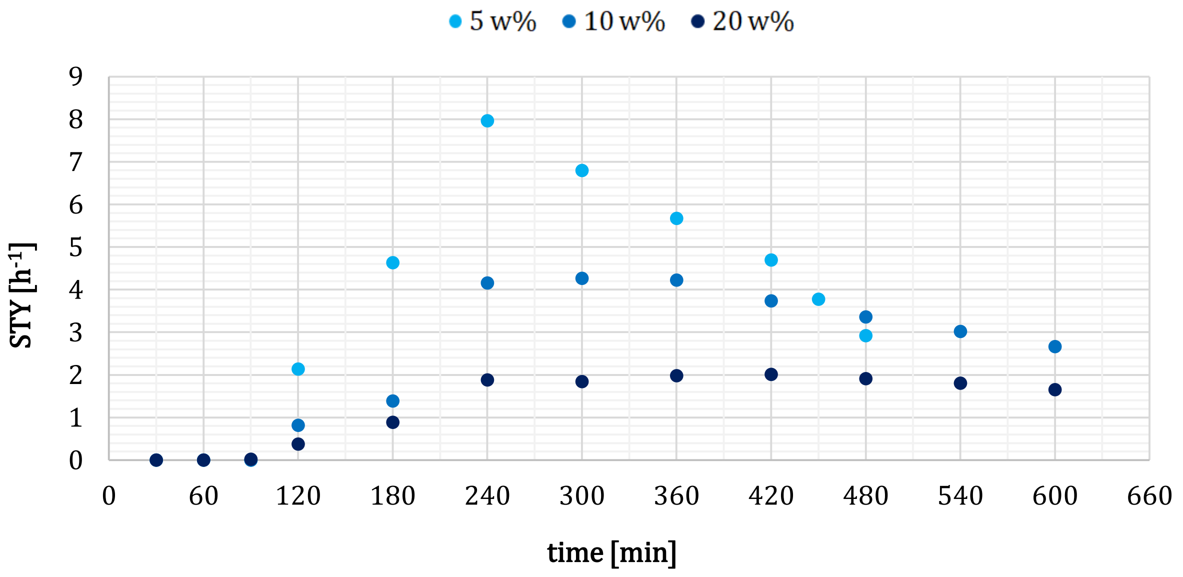

Figure 42: Influence of SILP-loading on STY at 120 °C

As can be seen from Figure 42, a lower loading of ionic liquid results in a higher STY, but also in a fast decrease of the catalytic performance. The reason for the lower STY at higher loading might be the reduction of specific surface area due higher amount of ionic liquid, filling the whole volume of small pores. Therefore, less catalytically active surface is available.

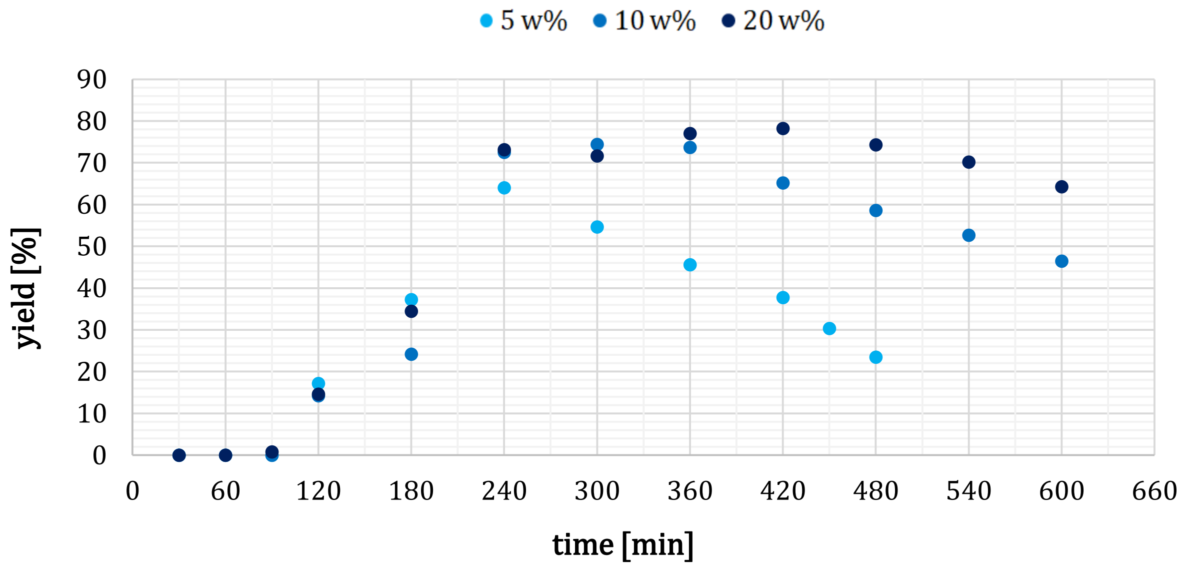

Figure 43: Influence of SILP-loading on yield

The difference of the maximum yield at 240 min varied about 15% for different ionic liquid loadings. A higher amount of ionic liquid resulted in increased the yields and a longer stable state. However, with 20 w% loading and 120 °C leaching of the ionic liquid was observed. The leaching intensity against time is shown in Figure 44.

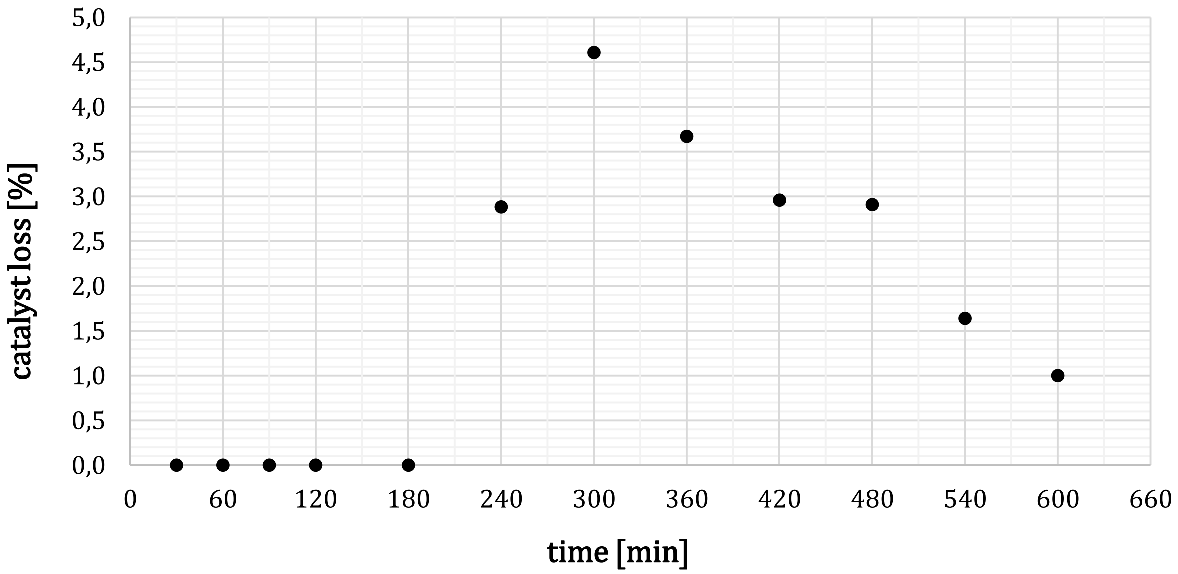

Figure 44: Intensity of catalyst leaching with 20 w% loading at 120 °C

The catalyst leaching started after 180 min and reached its maximum at 300 min with almost 5% of ionic liquid loss within one hour. Afterwards it decreases continuously. The intensity of leaching was estimated by ^{1}H NMR. Based on this estimation the amount of [EMIM]Br on silica should be reduced to less than 15 w% to avoid leaching at 120 °C.

5.4.3.3 Influence of pressure

According to literature for batch-wise processes, the reaction rate should be only weakly influenced by pressure modifications. As this might differ under continuous flow conditions two further experiments were carried out at 60 bar and 160 bar. The low pressure of 60 bar was deliberately chosen to test conditions below the supercritical state. The maximum yields of every experiment are compared in Figure 45.

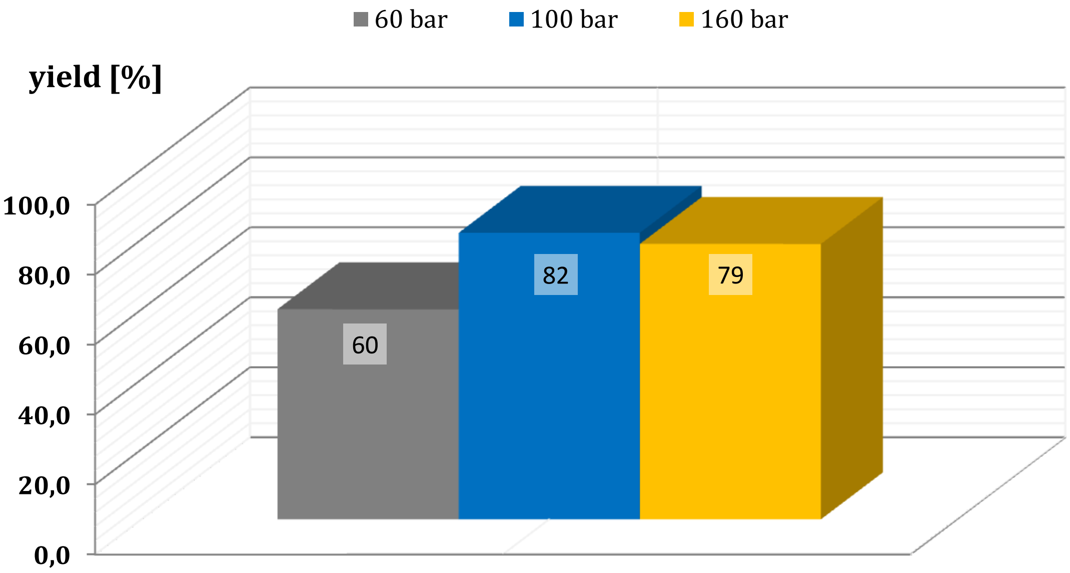

Figure 45: Influence of pressure on yield

Table 15: Influence of pressure on STY

	STY [h^{-1}] at maxima
60 bar	3.8
100 bar	5.2
160 bar	5.1

As can be seen from Figure 45 and Table 15, the change from 60 bar to supercritical conditions (>74 bar) caused higher product yield and STY. A further increase did not have a significant influence. In terms of energy consumption, the lowest pressure required for supercritical conditions should be desirable. Therefore, a pressure of 100 bar was used for further experiments.

5.4.3.4 Increase of carbon dioxide flow rate and column length

To demonstrate the influence of a higher flow rate on the system, the carbon dioxide flow rate was increased to a total flow rate of 10 ml/min. In this case, the experiments were carried out without *n*-hexane as co-solvent. The results are shown in Figure 46.

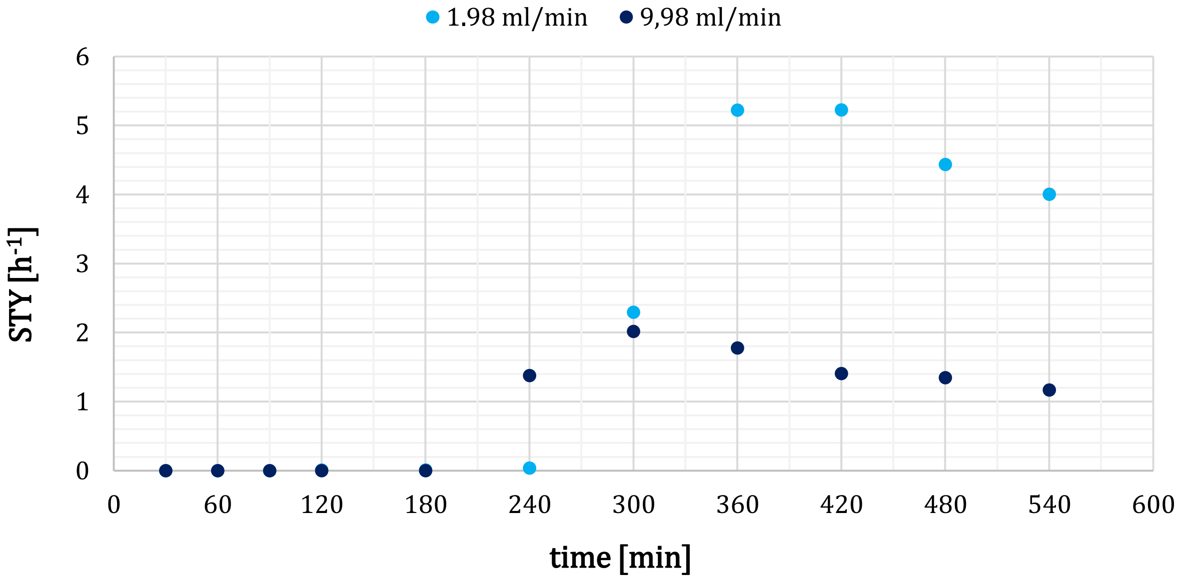

Figure 46: Increase of the carbon dioxide flow rate

According to Figure 46 a higher flow rate resulted in an earlier product output due to a shortened residence time from 75 s to 15 s. Consequently, a lower space time yield was observed. Since the residence time strongly depends on the length of the column (Equation 2), the column length was increased from 150 mm to 250 mm..

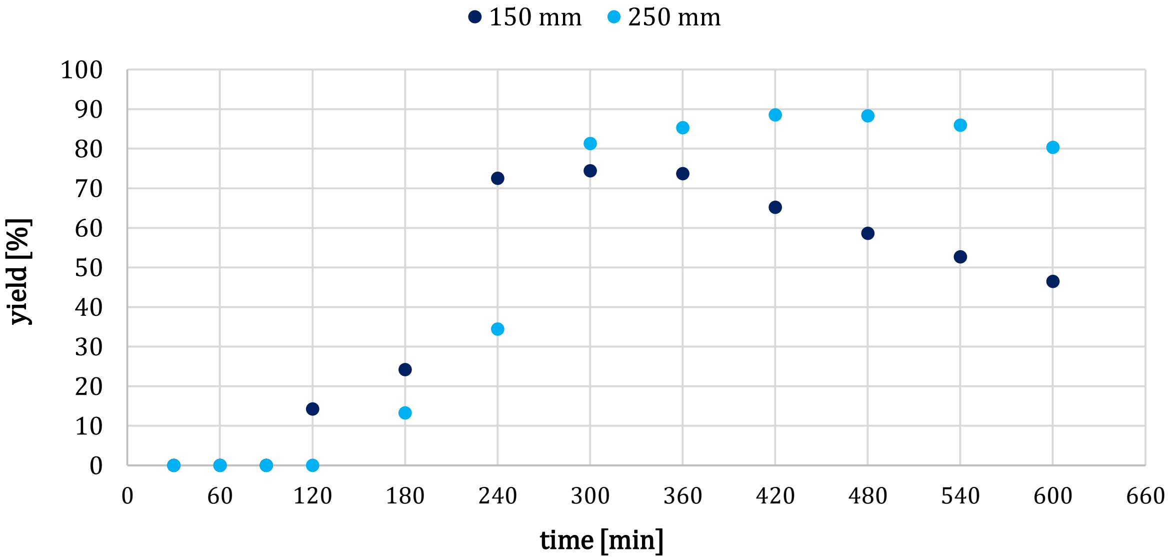

Figure 47: Influence of the column length on yield

Figure 47 shows the influence of a different column length on the product yield. The residence time increased from 75 seconds to 125 second when using a 250 mm column instead of a 150 mm column. According to a longer residence time the yield increased and product output was observed earlier. The product collection started 60 min earlier than with the shorter column. Additionally, the state of stabilization lasted longer with the longer column.

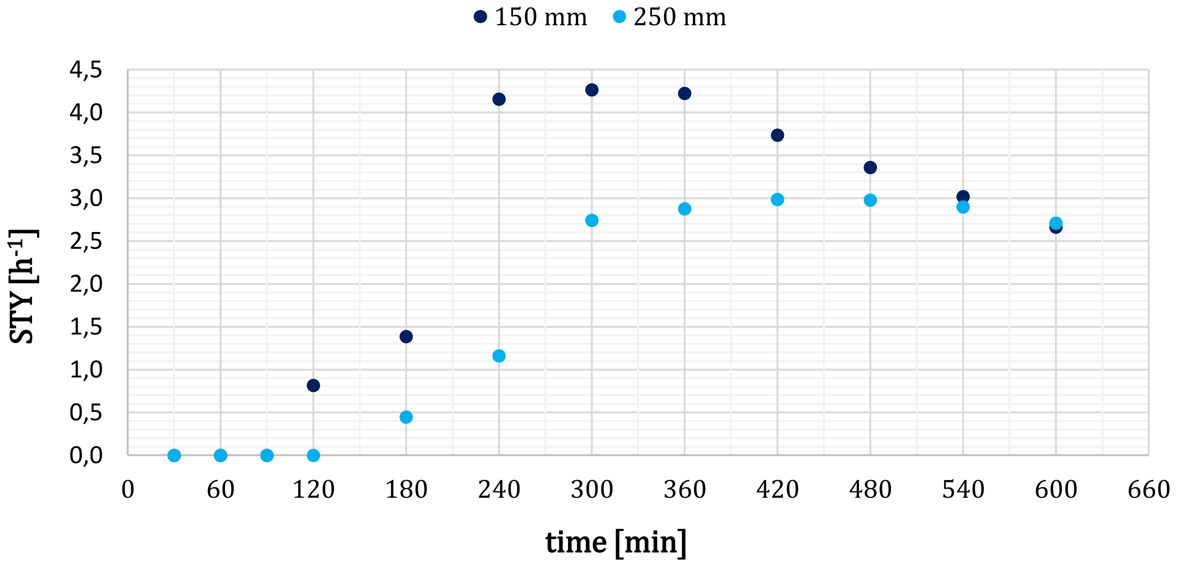

Figure 48: Influence of the column length on STY

Due to the higher amount of catalyst used with a longer column, the STY was lower (see Table 16).

Table 16: Catalyst-cartridge characteristics

HPLC-column	**volume [cm^3]**	**capacity [g]**	**amount of ionic liquid [g]**
4.6 x 150 mm	2.5	1.3 g	0.13
4.6 x 250 mm	4.2	2.3 g	0.23

In case of 250 mm column length the product yield increased to 88%. Since the system loss of propylene carbonate is approximately 10%, the conversion can be considered as quantitative. This state was stable for 5 h until the product output started to decrease.

5.4.4 Optimized processes

After evaluation of all system parameters as discussed above, the optimized parameters were identified and are summarized in Table 17.

Table 17: Optimized system for the conversion of propylene carbonate

catalysis system [EMIM]Br on silica	
system-parameter	**value**
temperature	120 °C
temperature at the back pressure regulator	45 °C
IL on silica (SILP)	10 w% IL max. 15 w%
pressure	100 bar
column length	4.6 x 250 mm
CO_2-flow rate	2 x 0,99 ml/min
substrate flow rate (1:1 PO in n-hexane)	0.02 ml/min
residence time	125 s

The experiment under optimized conditions is shown in Figure 49.

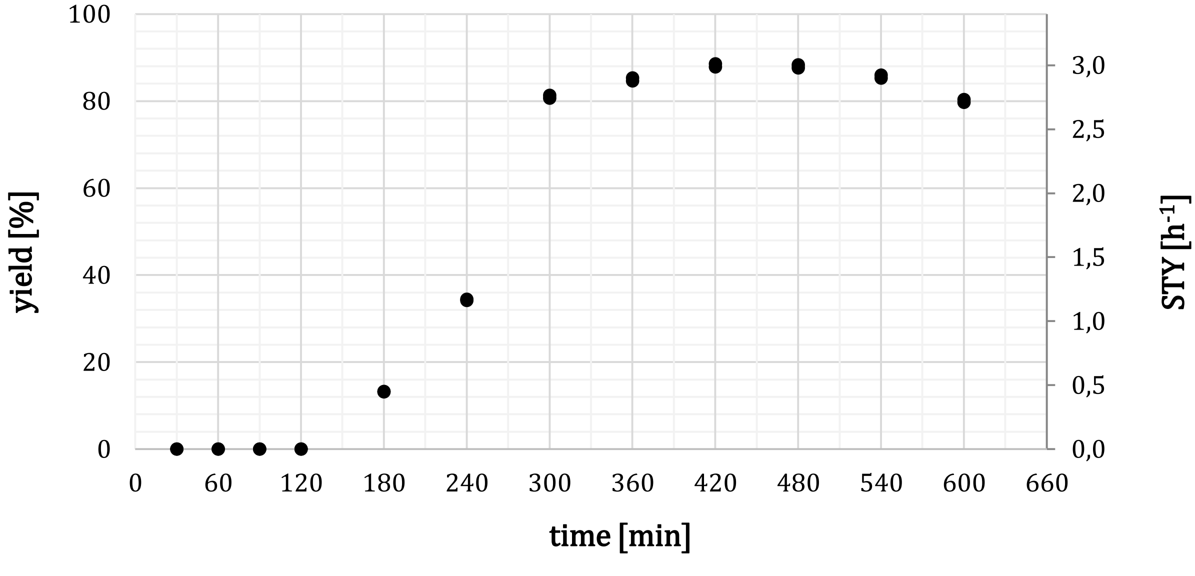

Figure 49: [EMIM]Br on silica under optimized conditions

Under these parameters, the process reached a maximum yield of 89% at 420 min. This corresponds to a STY of 3.0 h^{-1}. At this point a production rate of PC in high purity of 0.6 ml/h could be achieved. In the product fractions, no traces of leached ionic liquid or other additional compounds was observed as demonstrated in Figure 50.

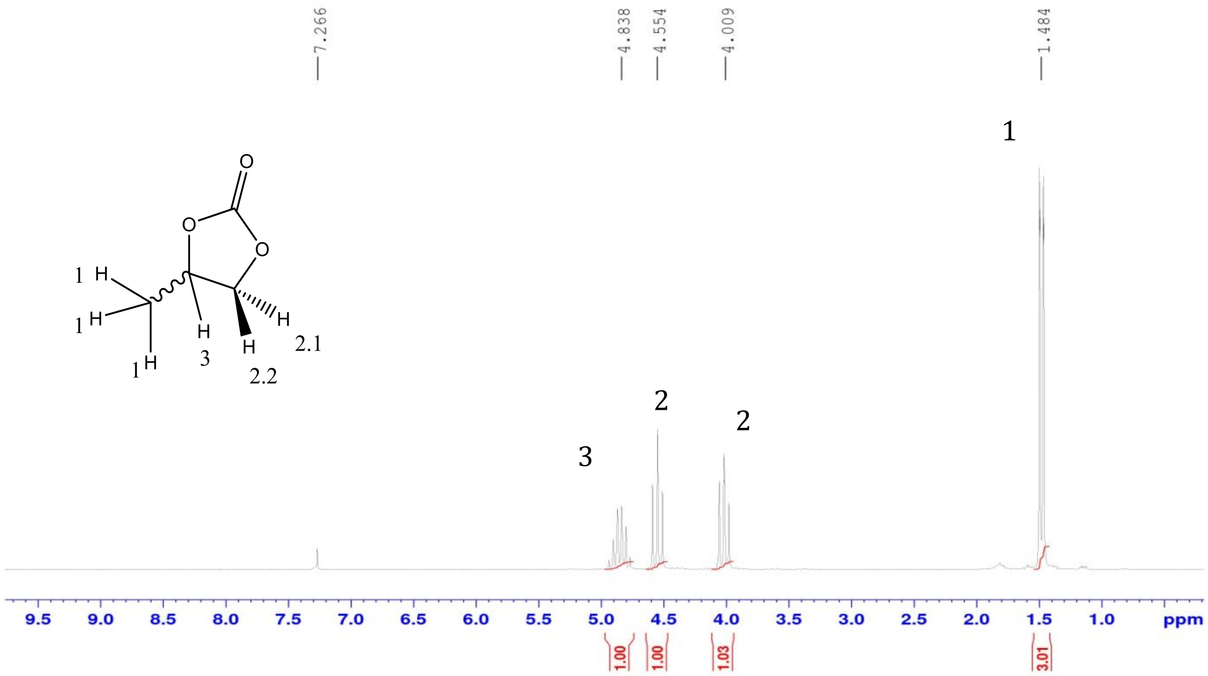

Figure 50: ^{1}H NMR-spectrum of the fraction 12
[EMIM]Br under optimized conditions

Yet after 540 min the production rate slowly decreased. This might be caused by the formation of a by-product that remained on the SILP catalysts. The decrease of the catalytic activity was observed with several SILP catalysts on silica. Further studies showed that small traces of polypropylene glycol or oligomers of PO formed by polymerisation of PO were indeed responsible for the reduced long term stability

In order to prove this, used SILP-catalysts were investigated by NMR analysis. All residues from the catalysis process were removed separately. Propylene carbonate, the product of the reaction process, should be easily removed by washing the catalyst 3 times with DCM. The by-product polypropylene glycol should be successively removed using ethyl acetate instead. With MeOH most of the ionic liquid should be eventually recovered. ^{1}H NMR-spectra of each fraction collected from a previously prepared model SILP catalyst ([EMIM]Br on silica) doped with product and by-product are shown in Figure 51.

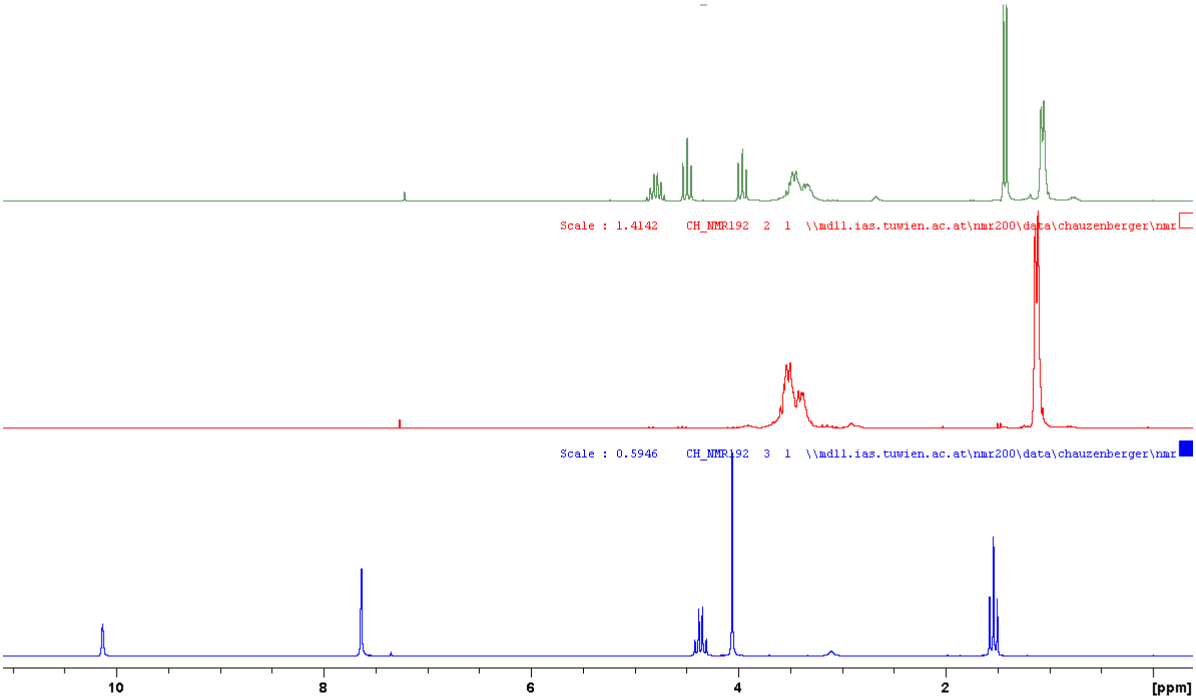

Figure 51: ^{1}H NMR spectra of a model SILP catalyst: DCM- (top), EA- (middle) and MeOH-fraction (bottom)

NMR analysis showed that parts of the undesired PPG oligomers were already removed with DCM (Figure 51, top). The remaining part could be removed by EA without taking off the ionic liquid. When repeating these extraction steps with an authentic SILP catalyst, the initial washing step with dichloromethane showed only the presence of product accumulated in the ionic liquid layer. However, when the spent catalyst material was further treated with methanol, a mixture of ionic liquid contaminated with polypropylene glycol was found. This clearly supports the theory that the oligomers and polymers formed as by-product are deposited in the ionic liquid layer over time, and consequently responsible for the decreasing long-term activity. Figure 52 shows the MeOH fraction without using EA before.

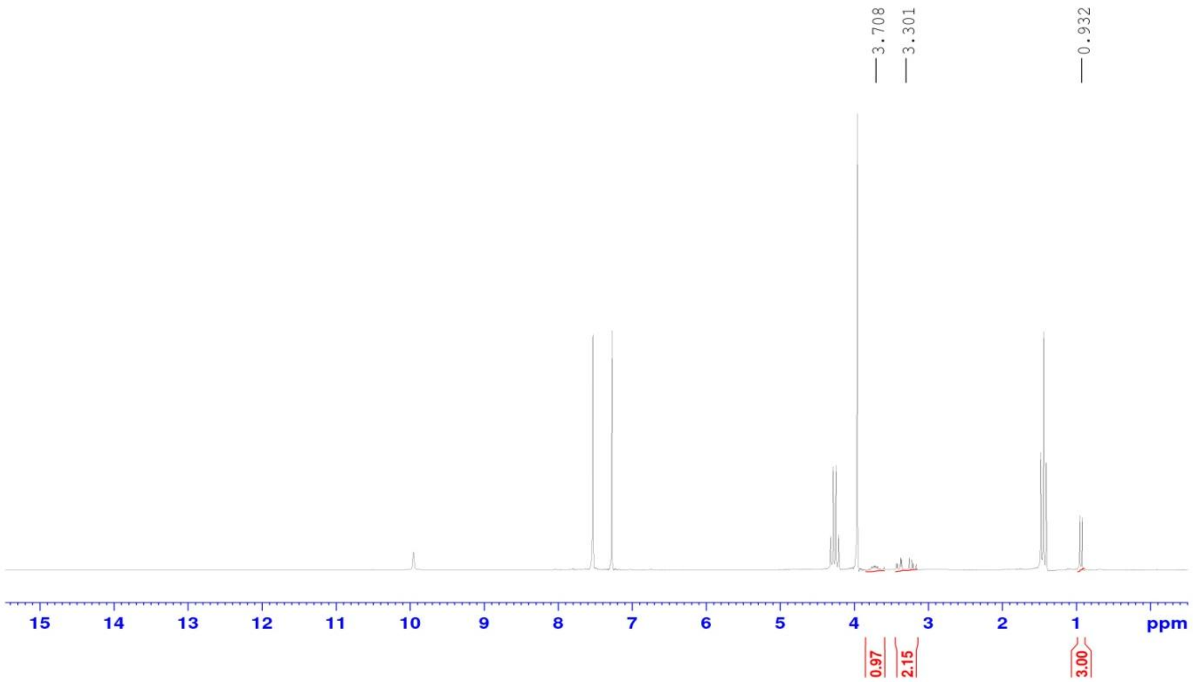

Figure 52: ^{1}H NMR spectra: MeOH-fraction of used [EMIM]Br on silica

Despite the lower catalytic activity, the reaction catalysed by modified silica revealed almost no by-product formation and a stable product output for 600 min. In the following ^{1}H NMR spectrum the MeOH fraction (without using EA before) of the used SILP-catalyst with modified silica is shown, demonstrating that no detectable amount of polypropylene glycol remained in the ionic liquid. Interestingly, a small amount of ionic liquid (and almost undetectable traces of the polymer/oligomer) was already removed via DCM, indicating, that the ionic liquid is easier to remove from modified silica surface than from common silica.

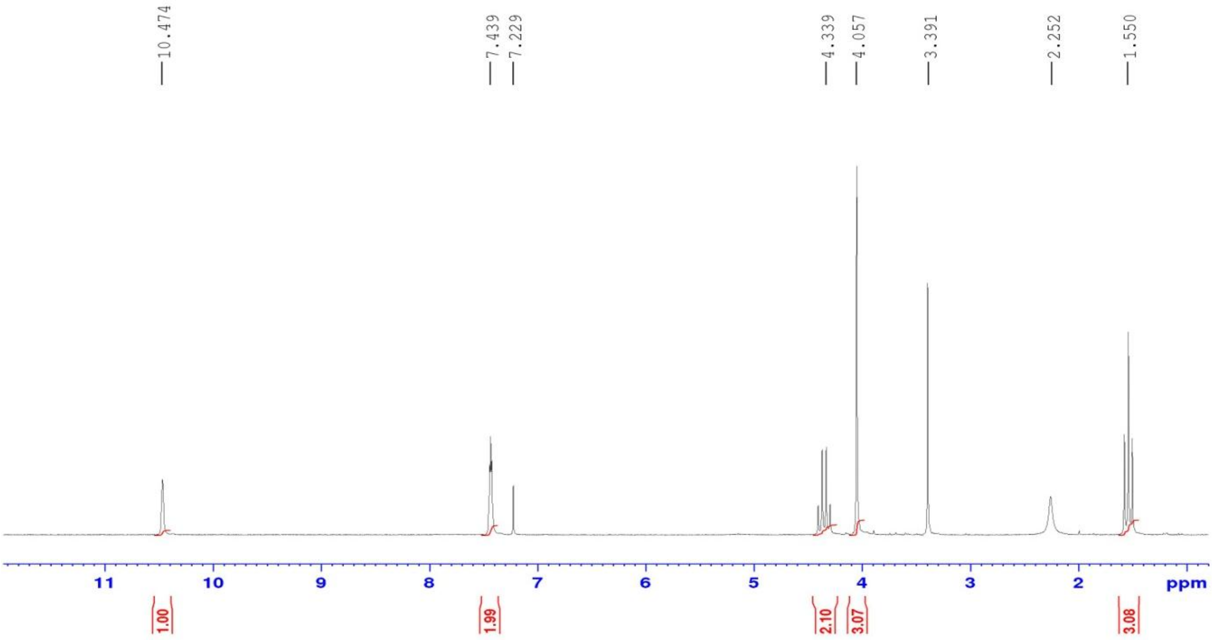

Figure 53: ^{1}H NMR spectra of the MeOH of used [EMIM]Br on modified silica

Consequently, no decrease in catalytic performance and no leaching was observed when the reaction was performed under optimized conditions (Table 17) with surface-modified silica as support material.

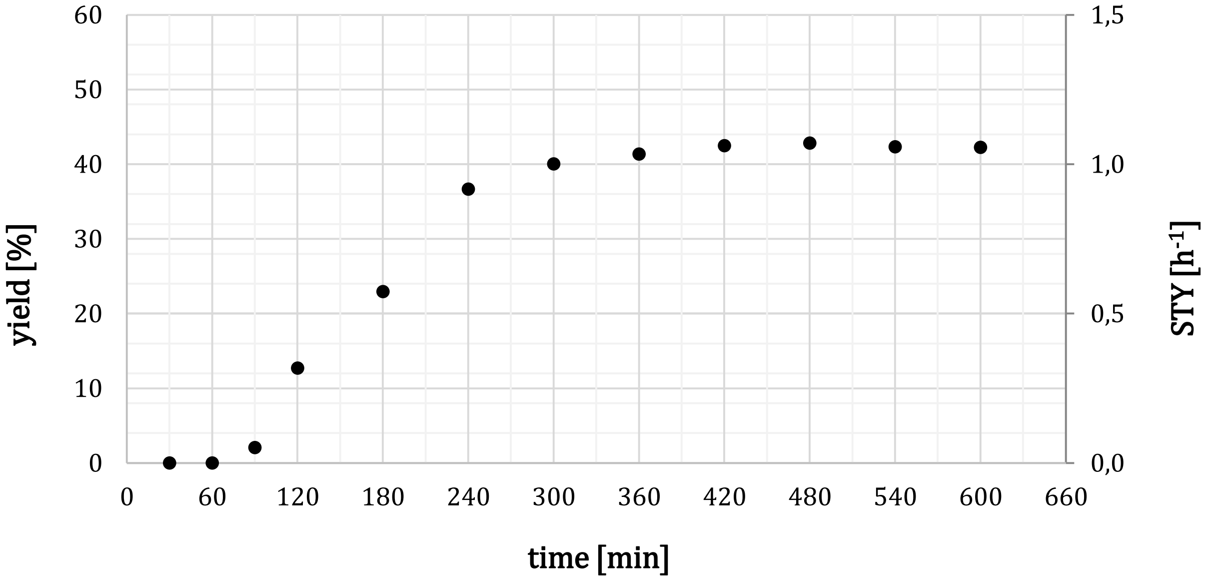

Figure 54: [EMIM]Br on modified silica under optimized conditions

The experiment showed a stable state for at least 600 min. This is in contrast to all SILP-catalysts with unmodified silica that slowly lost their catalytic activity over time. The production rate in the process shown in Figure 54 corresponds to 0.3 ml PC per hour obtained in pure form.

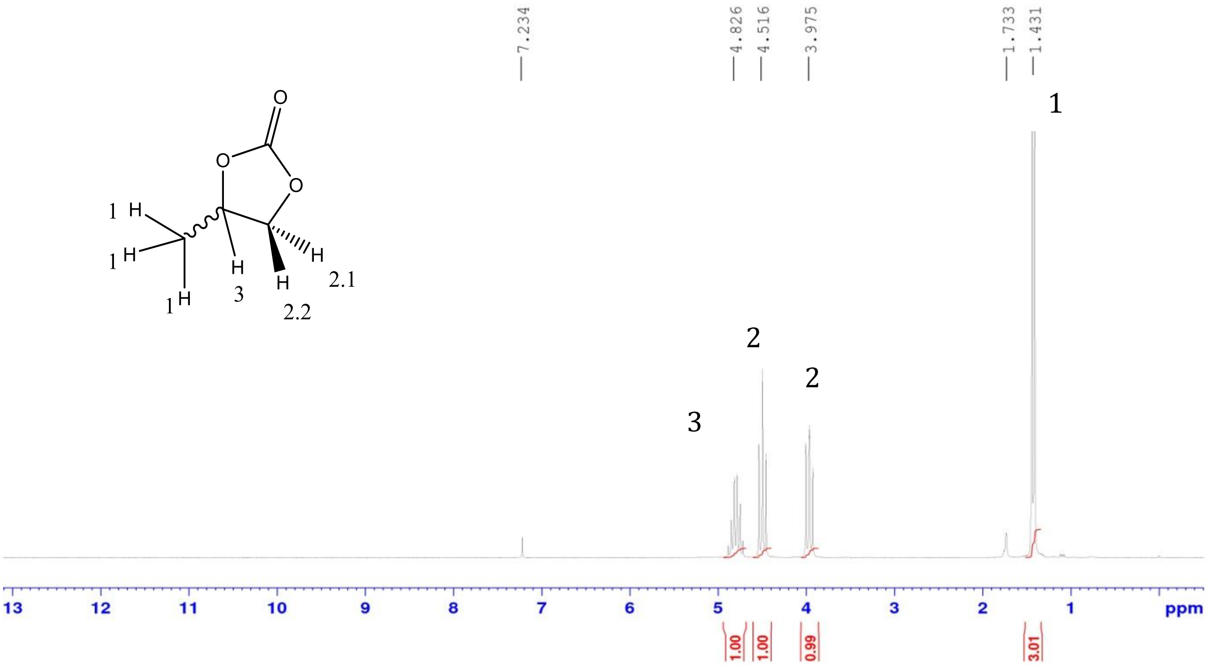

Figure 55: ^{1}**H NMR of fraction 10 with [EMIM]Br on modified silica**

Eventually, this provides a sensible compromise between catalytic activity and long-term stability: Although the values remain below these obtained with unmodified silica, the constant and stable performance opens the field for continuous production of propylene carbonate and seems particularly promising for further applications in continuous flow.

6. Conclusion

In the present work, a continuous flow process for the conversion of carbon dioxide and propylene oxide into propylene carbonate was developed, relying on the simultaneous use of supercritical carbon dioxide as solvent and reagent. Cheap and easy producible ionic liquids were used as catalysts for this reaction. A set of various ionic liquids including Lewis acidic species and functionalized ionic liquids with side chain modification were synthesized and initially evaluated as catalyst under batch conditions.

For the further development of a continuous flow process selected ionic liquids were immobilized via physisorption on various support materials ("supported ionic liquid phases", SILPs). Considerable differences between the catalytic activity of supported and unsupported ionic liquids were observed. Silica revealed to be the most suitable support material, resulting in high catalytic activity of supported ionic liquids due to synergistic effects with the hydroxyl groups on the silica surface. Moreover, the use of $scCO_2$ as solvent and reagent could avoid any leaching of the ionic liquid catalyst, resulting in an efficient continuous flow process. Among all ionic liquids tested, the imidazolium derivative 1-ethyl-3-methylimidazolium bromide supported on silica showed the highest catalytic activity. Under optimized conditions up to 0.6 ml propylene carbonate per hour could be obtained in pure form.

Problems with a loss of catalytic activity over time due by-product formation could be improved via surface modification of silica with 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride. Although a lower overall production rate of 0.3 ml PC per hour was obtained, this catalytic system can be considered as basis for further development in continuous flow process mode for similar or different reaction systems, as it showed a stable performance over a longer period of time.

7. Experimental part

7.1 Materials and methods

All reagents were purchased from commercial suppliers and were used without further purification unless it is described otherwise. Anhydrous solvents such as dichloromethane, methanol, dioxane, tetrahydrofuran and toluene were pre-distilled and desiccated on Al_2O_3 columns (PURESOLV, Innovative Technology) if not otherwise noted.

^1H and ^{13}C NMR spectra were measured on a Bruker AC 200 (200 MHz) or Bruker Advance UltraShield 400 (400 MHz) spectrometer and chemical shifts (δ) are reported in ppm using tetramethylsilane as internal standard. Coupling constants (J) are described in Hertz (Hz). Multiplicities were reported as following: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintett, sex = sextet, m = multiplet, br = broad. NMR spectra were recorded from $CDCl_3$, DMSO-d_6 or MeOD solutions.

Gas chromatography (GC) was recorded by a GC Thermo Scientific Focus with a FID detector. The column used was a BGB-5 (3 m x 0.32 mm ID; 0.25 µm film) with the temperature program indicated in Table 18. *N*-Hexadecane was used as internal standard.

Table 18: Method for GC measurements

temperature program		
first step	second step	third step
60 °C up to 170 °C with 15 °C/min	170 °C up to 300 °C with 50 °C/min	300 °C for 5 min
15 min		

All IR-spectra were recorded with a Perkin Elmer Spectrum 65 FTIR (PerkinElmer, Waltham; USA) as ATR-FTIR spectra. The ATR part is defined as Specac 'Golden Gate' with a diamond as ATR-crystal. The software spectrum (PerkinElmer, Waltham; USA) was used for recording the spectra. Bands were reported as followed: vw = very weak, w = weak, m = medium, s = strong, vs = very strong, br = broad.

The water content of the support materials was determined via TGA on a Netzsch STA 449 F1 (Simultaneous Thermal Analysis) system. The temperature was increasing to 600 °C with a rate of 10 °C/min. The helium inert gas flow was set to 20 ml/min.

7.2 Preparation of catalysts

7.2.1 Synthesis of ionic liquids

7.2.1.1 Synthesis of 2-iodoethanol

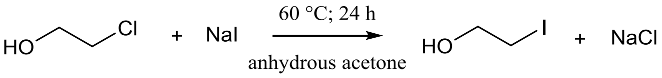

Figure 56: Synthesis of 2-iodoethanol

2-Chloroethanol was distilled at 72 °C and 120 mbar for purification.

A one neck round bottom flask with a condenser and a magnetic stirring bar was charged with 2-chloroethanol (1.0 eq; 99.8 mmol; 8.04 g), sodium iodide (1.0 eq; 99.7 mmol; 14.94 g) and 50 ml anhydrous acetone. The mixture was stirred at 60 °C for 24 h under nitrogen atmosphere. Sodium chloride as colourless crystalline solid precipitated over time. After removing acetone reduced pressure, a small amount of distilled water was added to the reaction mixture until the solid was dissolved. The aqueous mixture was extracted five times with dichloromethane (30 ml each time). The combined organic layers were dried over sodium sulphate, and the solvent was removed under reduced pressure. 2-Iodoethanol (12.86 g) was obtained as colourless liquid in 75% yield.

The product was stored in the refrigerator stabilized with copper chips.

^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ [ppm] = 3.78 (t, 2H, J = 6 Hz, *I-CH*$_2$*-*); 3.27 (t, 2H, J = 6 Hz, *-CH*$_2$-OH); 2.22 (s, 1H, -CH$_2$-*OH*)

Analytical data was in accordance with literature.[22]

7.2.1.2 Synthesis of tributyl-(2-hydroxyethyl)phosphonium iodide

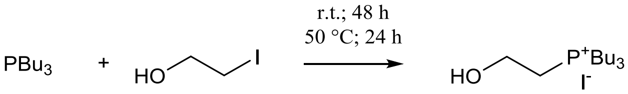

Figure 57: Synthesis of tributyl-(2-hydroxyethyl)phosphonium iodide; [TBHEP]I

Tributylphosphine was distilled at 112 °C and 10 mbar for purification.

A one neck round bottom flask with a magnetic stirring bar was charged with 2-iodoethanol (1.0 eq; 71.3 mmol; 10.43 g) and sealed with a septum. Tributylphosphine (1.0 eq; 60.6 mmol; 12.27 g) was slowly added with a syringe. After complete addition, the mixture was stirred at room temperature for 48 h. For completion, the temperature was increased to 50 °C for further 24 h. Subsequently, the highly viscous liquid was washed 3 times with a small amount of diethyl ether to remove impurities. Remaining volatile materials were removed under high vacuum to obtain the product as a highly viscous colourless liquid in 91% yield.

^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ [ppm] = 4.05 (dt, 2H, J = 20 Hz, -CH_2-OH); 3.78 (s,1H, -CH_2-*OH*); 2.68 (dt, 2H, J = 12 Hz, -P^+-CH_2-CH_2-OH); 2.32 (m, 6H, -P^+(-CH_2-CH_2-CH_2-CH_3)$_3$); 1.50 (m, 12H, -P^+(-CH_2-CH_2-CH_2-CH_3)$_3$); 0.91 (t, 9H, -P^+(-CH_2-CH_2-CH_2-CH_3)$_3$)

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ [ppm] = 54.8 (d, 1C, J_{CP} = 7 Hz, -CH_2-CH_2-OH); 24.0 (d, 3C, J_{CP} = 15 Hz, -P^+(-CH_2-CH_2-CH_2-CH_3)$_3$); 23.7 (d, 3C, J_{CP} = 5 Hz, -P^+(-CH_2-CH_2-CH_2-CH_3)$_3$; 22.9 (d, 1C, J_{CP} = 49 Hz, -CH_2-CH_2-OH); 19.9 (d, 3C, J_{CP} = 47 Hz, -P^+(-CH_2-CH_2-CH_2-CH_3)$_3$); 13.5 (s, 3C, -P^+(-CH_2-CH_2-CH_2-CH_3)$_3$)

Analytical data corresponds to literature data.[22]

7.2.1.3 Synthesis of 1-(2-hydroxyethyl)-3-methylimidazolium bromide

The compound was prepared in accordance to literature.[42]

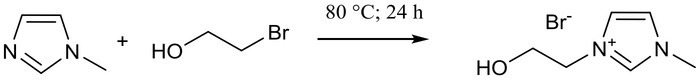

Figure 58: Synthesis of 1-(2-hydroxyethyl)-3-methylimidazolium bromide; [HEMIM]Br

1-Methylimidazole was distilled at 72 °C and 8 mbar for purification.

A one neck round bottom flask with a magnetic stirring bar was charged with 1-methylimidazole (1.0 eq; 49.5 mmol; 4.06 g) and 30 ml dry toluene. The flask was sealed with a septum and flooded with argon. 2-Bromoethanol (1.02 eq; 50.5 mmol; 6.31 g) was slowly added with a syringe. After complete addition the mixture was stirred over 24 h at 80 °C. A second more viscous and colourless liquid appeared. After the reaction time the mixture cooled down, whereby the new phase crystallized. Remaining volatile substances were removed under high vacuum to obtain the product as colourless crystalline solid in 84% yield. It was stored in a 50 °C vacuum oven.

^{1}H-NMR (200 MHz, DMSO-d_6, 25 °C): δ [ppm] = 9.17 (s, 1H, -N=*CH*-N-); 7.73 (dd, 2H, -N-*CH*=*CH*-N-); 5.09 (br s, 1H, -N-CH_2-CH_2-*OH*); 4.22 (t, 2H, -N-CH_2-CH_2-OH); 3.88 (s, 3H, -N-CH_3); 3.70 (t, 2H, -N-CH_2-CH_2-OH);

Analytical data corresponds to literature data.[18]

7.2.1.4 Synthesis of 1,3-bis-(2-hydroxyethyl)imidazolium bromide

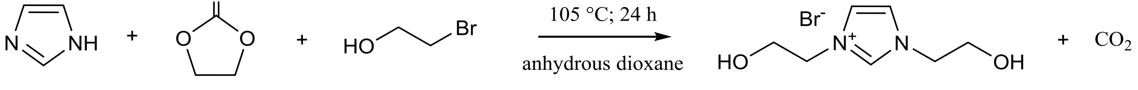

Figure 59: Synthesis of 1,3-bis-(2-hydroxyethyl)imidazolium bromide; [BHEIM]Br

A three-neck round bottom flask with a magnetic stirring bar was charged with imidazole (1.0 eq; 35.4 mmol; 2.41 g) and 1,3-dioxolan-2-one (1.02 eq; 36.1 mmol; 3.18 g), in addition with 30 ml dioxane. The mixture was stirring for 2 h at 80 °C. After 2 h, 2-bromoethanol (1.0 eq; 35.5 mmol; 4.43 g) was slowly added with a syringe at 80 °C.

After complete addition the mixture was stirred over 24 h at 105 °C. A second yellowish viscous phase appeared. The dioxane phase was removed with a pipette. The viscous phase was washed with diethyl ether and acetone. Solvent traces were removed under vacuum (0.01 mbar, 50 °C) with stirring for 24 hrs to obtain the ionic liquid as a yellowish viscous liquid in 97% yield.

^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C): δ [ppm] = 9.15 (s, 1H, -N=*CH*-N-); 7.78 (s, 2H, -N-*CH*=*CH*-N-); 5.16 (br s, 2H, -N-CH$_2$-CH$_2$-*OH*); 4.25 (t, 4H, -N-CH$_2$-*CH*$_2$-OH); 3.72 (t, 4H, -N-*CH*$_2$-CH$_2$-OH)

Analytical data corresponds to literature data.[65]

7.2.1.5 Synthesis of tributyl-(2-hydroxyethyl)ammonium bromide

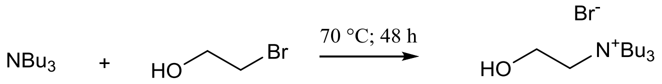

Figure 60: Synthesis of tributyl-(2-hydroxyethyl)ammonium bromide; [TBHEA]Br

Tributylamine was distilled at 117 °C and 25 mbar for purification.

A one neck round bottom flask with a magnetic stirring bar was charged with tributylamine (1.0 eq; 32.1 mmol; 5.96 g). The flask was sealed with a septum and flooded with argon. 2-Bromoethanol (1.02 eq; 32.8 mmol; 4.10 g) was slowly added with a syringe while stirring. After complete addition the mixture was stirred over 10 h at 70 °C. Due to incomplete reaction additional 2-bromoethanol (0.06 eq; 2.0 mmol; 0.25 g) was added until ^{1}H-NMR analysis indicated complete conversion. The viscous and yellow liquid was washed with diethyl ether and remaining volatile substances were removed under vacuum (0.1 mbar, 50 °C) for 24 h to obtain the ionic liquid as viscous yellow liquid in 79% yield.

^{1}H NMR (200 MHz, DMSO-d$_6$, 25 °C): δ [ppm] = 5.26 (br s, 1H, -CH$_2$-CH$_2$-*OH*); 3.78 (t, 2H, -$^+$N-CH$_2$-*CH*$_2$-OH); 3.34 (t, 2H, -$^+$N-*CH*$_2$-CH$_2$-OH); 3.24 (t, 6H, -N$^+$(-*CH*$_2$-CH$_2$-CH$_2$-CH$_3$)$_3$); 1.57 (quin, 6H, -N$^+$(-CH$_2$-*CH*$_2$-CH$_2$-CH$_3$)$_3$); 1.27 (sex, 6H, -N$^+$(-CH$_2$-CH$_2$-*CH*$_2$-CH$_3$)$_3$); 0.90 (t, 9H, -N$^+$(-CH$_2$-CH$_2$-CH$_2$-*CH*$_3$)$_3$)

Analytical data corresponds to literature data.[18]

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[65] Deng, F.; Reeder, Z. K.; Miller, K. M. *J. Phys. Org. Chem.* **2014**, *27*, 2–9

7.2.1.6 Synthesis of tributylphosphonium bromide

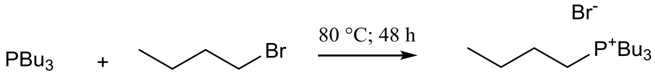

Figure 61: Synthesis of tributylphosphonium bromide; [TBP]Br

Tributylphosphine was distilled at 115 °C and 13 mbar for purification.

A one neck round bottom flask with a magnetic stirring bar inside was charged with tributyphosphine (1.0 eq; 29.7 mmol; 6.01 g). The flask was sealed with a septum and flooded with argon. 1-bromobutane (1.0 eq; 32.8 mmol; 4.11 g) was slowly added with a syringe. After complete addition the mixture was stirred for 48 h at 80 °C. The product crystallized during this time and a colourless crystalline solid was achieved. The product was recrystallized in a mixture of toluene and n-hexane. Obtained crystals were washed with n-hexane and the organic solvent was removed under reduced pressure. The ionic liquid was obtained as a colourless crystalline solid in 86% yield.

^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ [ppm] = 2.42 (m, 8H, $P^+(-\mathit{CH_2}-CH_2-CH_2-CH_3)_4$); 1.48 (m, 16H, $P^+(-CH_2-\mathit{CH_2}-\mathit{CH_2}-CH_3)_4$); 0.92 (t, 12H, $P^+(-CH_2-CH_2-CH_2-\mathit{CH_3})_4$)

Analytical data corresponds to literature data.[22]

7.2.1.7 Synthesis of 1-ethyl-3-methylimidazolium bromide

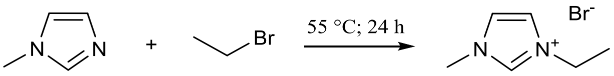

Figure 62: Synthesis of 1-ethyl-3-methylimidazolium bromide; [EMIM]Br

Bromoethane was distilled at 42.5 °C and 850 mbar for purification.

A one neck round bottom flask with a magnetic stirring bar was charged with 1-methylimidazole (1.0 eq; 100.2 mmol; 8.2 g). The flask was sealed with a septum and flooded with argon. Bromoethane (1.1 eq; 110.2 mmol; 12.0 g) was slowly added with a syringe at room temperature. After complete addition of bromoethane the mixture was stirred over 12 h at 55 °C. Due to incomplete reaction additional bromoethane (0.02 eq; 2.2 mmol; 0.2 g) was added until ^{1}H NMR analysis indicated complete conversion. The product appeared as a viscous and slightly brownish liquid. This viscous liquid was washed 3 times with 15 ml dry diethyl ether. Remaining volatile traces were removed under high vacuum. Thus, the product crystallized as white crystalline solid and was obtained in 99% yield. Since the product is highly hygroscopic it was stored over phosphorus pentoxide in an exicator.

^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ [ppm] = 10.26 (s, 1H, $-N=\mathit{CH}-N-$); 7.59 (s, 2H, $-N-\mathit{CH}=\mathit{CH}-N-$); 4.37 (q, 2H, $-N-\mathit{CH_2}-CH_3$); 4.08 (s, 3H, $-N-\mathit{CH_3}$); 1.54 (t, 3H, $-N-CH_2-\mathit{CH_3}$)

Analytical data corresponds to literature data.[66]

7.2.1.8 Synthesis of 1-methyl-3-octylimidazolium bromide

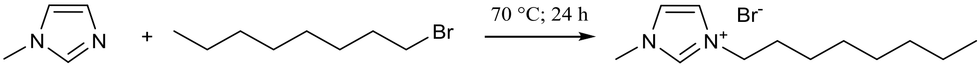

Figure 63: Synthesis of 1-methyl-3-octylimidazolium bromide; [C$_8$MIM]Br

A one neck round bottom flask with a magnetic stirring bar inside was charged with 1-methylimidazole (1.0 eq; 36.4 mmol; 2.99 g). The flask was sealed with a septum and flushed with argon. 1-Bromooctane (1.0 eq; 36.4 mmol; 7.02 g) was slowly added with a syringe at room temperature. After complete addition the mixture was stirred for 24 h at 70 °C. The product appeared as a viscous and slightly yellow liquid. This viscous liquid was washed 3 times with 15 ml anhydrous diethyl ether. Remaining volatile solvent traces were removed under high vacuum (0.1 mbar, 50 °C). The ionic liquid was obtained as slightly yellow viscous liquid in 92% yield.

^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ [ppm] = 10.35 (s, 1H, -N=*CH*-N-); 7.62 (s, 1H, -N-*CH*=CH-N-); 7.42 (s, 1H, -N-CH=*CH*-N-); 4.28 (t, 2H, -N-CH_2-(CH$_2$)$_6$-); 4.09 (s, 3H, -N-CH_3); 1.87 (t, 3H, -N-CH$_2$-CH_2-(CH$_2$)$_5$-CH$_3$); 1.24 (m, 10H, -N-CH$_2$-CH$_2$-$(CH_2)_5$-CH$_3$); 0.81 (t, 3H, -N-(CH$_2$)$_7$-CH_3)

Analytical data corresponds to literature data.[67]

7.2.1.9 Synthesis of 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride

The synthesis procedure was adapted from literature.[68]

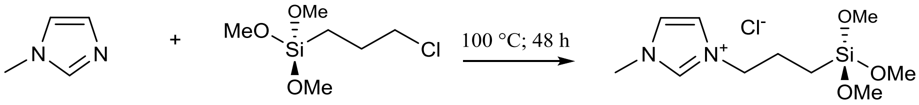

Figure 64: Synthesis of 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride

A one neck round bottom flask with a magnetic stirring bar inside was charged with 1-methylimidazole (1.0 eq; 36.4 mmol; 2.99 g). The flask was sealed with a septum and flooded with argon. (3-Chloropropyl)trimethoxysilane (1.0 eq; 36.6 mmol; 7.28 g) was slowly added with a syringe. The mixture was stirred over 28 h at 100 °C. The product appeared as a viscous and slightly yellow liquid. This viscous liquid was washed with anhydrous diethyl ether. Remaining volatile solvent traces were removed under high vacuum. The product was obtained as slightly yellow viscous liquid in 98% yield.

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[66] Bresien, J.; Ellinger, S.; Harloff, J.; Schulz, A.; Sievert, K.; Stoffers, A.; Taschler, C.; Villinger, A.; Zur Taschler, C. *Angew. Chem. Int. Ed.* **2015**, *54*, 4474–4477

[67] Keaveney, S. T.; Greaves, T. L.; Kennedy, D. F.; Harper, J. B. *J. Phys. Chem. B* **2016**, *120*, 12687–12699

[68] Valizadeh, H.; Amiri, M.; Shomali, A.; Hosseinzadeh, F. *J. Iran. Chem. Soc.* **2011**, *8*, 495–501

^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ [ppm] = 10.58 (s, 1H, -N=*CH*-N-); 7.67 (s, 1H, -N-*CH*=CH-N-); 7.39 (s, 1H, -N-CH=*CH*-N-); 4.27 (t, 2H, -N-CH_2-CH_2-); 4.08 (s, 3H, -N-CH_3); 3.50 (s, 9H, -Si-(O-CH_3)$_3$); 1.95 (quint, 2H, -N-CH_2-CH_2-); 0.58 (t, 2H, -CH_2-CH_2-Si-)

Analytical data corresponds to literature data.[68]

7.2.2 Preparation of mixtures with ionic liquids and zinc bromide

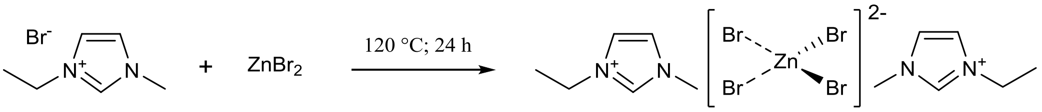

Figure 65: Preparation of mixtures with ionic liquids and zinc bromide

A 8 ml screw-cap flask was charged with [EMIM]Br (4.0 eq; 15.7 mmol; 3.00 g) and $ZnBr_2$ (1.0 eq; 3.9 mmol; 0.88 g) under inert gas atmosphere (glove box). The mixture was stirred for at least 24 h at 120 °C. Afterwards the liquid mixture was stored in an exicator over phosphorus pentoxide. Mixtures in ratios of 2:1 and 1:1 with [EMIM]Br and $ZnBr_2$ were prepared in the same manner whereby crystalline solids were obtained.

The preparation of Lewis acidic ionic liquids corresponds to this procedure.

7.2.3 Preparation of modified silica

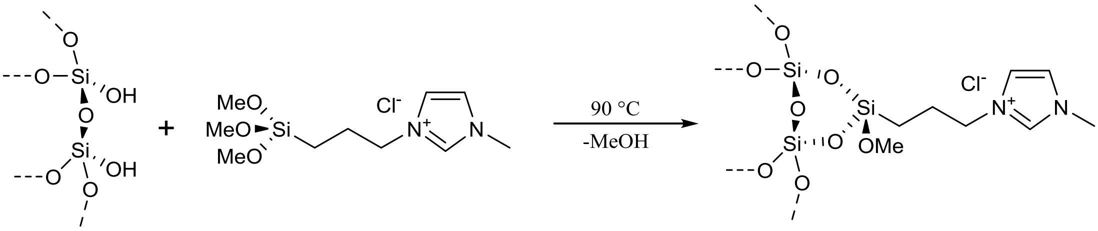

Figure 66: Preparation of modified silica

A 250 ml round bottom flask was filled with dried silica (10 g; vacuum oven at 50 °C; 24 h) and 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride (6 g). A mixture of anhydrous chloroform (50 ml) and 1,4-dioxane methane (50 ml) was added. Under vigorous stirring the suspension was refluxed for 48 h at 90 °C until a complete disappearance of the OH-band (silica) recorded via IR-spectroscopy was observed. Subsequently, the solvent and the excess of ionic liquid were removed by washing the colourless product 3 times in a glass suction filter with DCM. Remaining volatile traces were removed under reduced pressure and the product was dried under high vacuum. This procedure was repeated two times. Modified silica was achieved as colourless powder. The excess of ionic liquid was recovered by removing the volatile solvents at reduced pressure for re-use.

FTIR-ATR (blue) λ_{max} [cm^{-1}]: 3372 (br; -O-H stretching vibration), 1633 (w; -Si-H_2O), 1051 (vs, -Si-O-Si- asymmetric bond stretching vibration), 800 (m; network -Si-O-Si- symmetric bond stretching vibration)

FTIR-ATR (red) λ_{max} [cm^{-1}]: 3068 (br; -C-H stretching vibration), 1575 (w; -Si-H_2O), 1061 (vs, -Si-O-Si- asymmetric bond stretching vibration), 798 (m; network Si-O-Si symmetric bond stretching vibration)

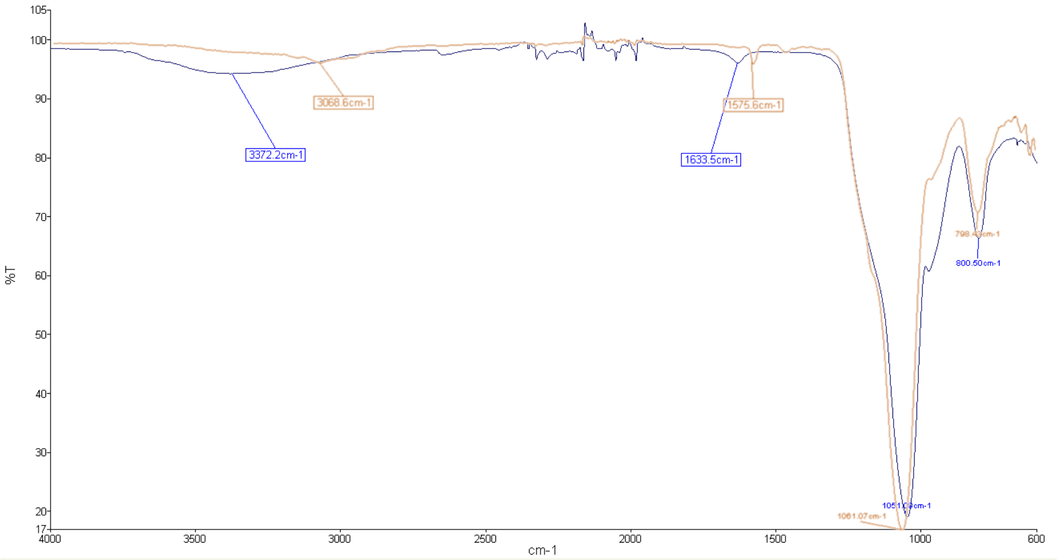

Figure 67: FTIR-ATR spectra of silica (blue) and modified silica (red)

7.2.4 Preparation of SILP-catalysts

The supported ionic liquid phase catalysts were prepared by impregnation of various support materials, following an in literature known procedure.[69]

For the preparation of a SILP-catalyst with 10 w% [EMIM]Br on silica, a 250 ml round bottom mixture was suspended in 22.8 g dried silica (vacuum oven at 50 °C; 24 h) and 2.3 g [EMIM]Br. The flask was charged with 100 ml DCM and shaken at room temperature until the complete amount of ionic liquid was dissolved. The solvent was removed carefully by reduced pressure. Remaining solvent traces were removed via high vacuum for 24 h. SILP-catalysts were stored in an excicator over P_2O_5.

Other SILP-catalysts were prepared according to this procedure.

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[69] van Doorslaer, C.; Wahlen, J.; Mertens, P.; Binnemans, K.; Vos, D. de. *Dalton Trans.* **2010**, *39*, 8377–8390

7.3 Formation of cyclic carbonates in batch process mode

7.3.1 Synthesis of propylene carbonate with 1-ethyl-3-methylimidazolium bromide

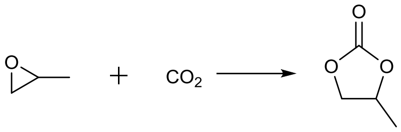

Figure 68: Synthesis of propylene carbonate

A 40 cm^3 stainless steel autoclave was charged with propylene oxide (1.0 eq; 34.4 mmol; 2.0 g) and 5 mol% [EMIM]Br (4.9 eq; 1.7 mmol; 0.3 g). After adding a stirring bar (15 x 6 mm) the autoclave was tightly closed. Attached to the autoclave station with temperature control and manometer the autoclave was filled with approximately 40 bar carbon dioxide. The temperature was set to 45 °C. The temperature was decreased automatically as soon as the reaction was finished after 18 h. At room temperature, carbon dioxide was released and the product was separated from the catalyst by flash chromatography with DCM as solvent. Substrate and solvent were removed under reduced pressure. The product as colourless liquid was obtained and analysed by ^{1}H NMR.

^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ [ppm] = 4.84 (sex, 1H,) 4.49 (t, 1H,); 3.97 (t, 2H,); 1.43 (d, 3H,)

In addition, the quality and yield were determined by GC-FID and *n*-hexadecane was used as internal standard. The retention time of propylene carbonate was 5.0 min. Other batch experiments were carried out following the same procedure. For experiments with support material, the required amount of SILP-catalyst was used to reach the same amount ionic liquid.

Table 19: Results of batch experiments with ionic liquids[a]

	[TBA]Br	[TBHEA]Br	[EMIM]Br	[HEMIM]Cl	[HEMIM]Br	[BHEIM]Br	[TBP]Br	[TBHEP]I
45 °C	10%	43%	13%	< 5%	< 5 %	15%	31%	90%
70 °C	79%	97%	52%	40%	84%	96%	77%	>99%
45 °C $ZnBr_2$	>99%	>99%	99%	---	>99%	98%	>99%	>99%

[a] Conditions: 34.4 mmol propylene oxide; 5 mol% ionic liquid; 4 MPa CO_2 pressure; 18 h; Analysis was done via ^{1}H NMR and GC

Table 20: Results of batch experiments with SILP-catalysts[a]

	silica			
	without $ZnBr_2$	**$ZnBr_2$/IL 1:4**	**$ZnBr_2$/IL 1:2**	**$ZnBr_2$/IL 1:1**
[EMIM]Br	81%	72%	74%	73%
[HEMIM]Br	74%			

[a] Conditions: 34.4 mmol propylene oxide; 5 mol% ionic liquid; 4 MPa CO_2 pressure; 18 h; Analysis was done via ^{1}H NMR and GC

7.4 Experiments in continuous flow process mode

All flow experiments were carried out with a $scCO_2$ extraction device. Every part was produced by Jasco (Jasco Corporation, Tokyo, Japan), if not otherwise noted. Liquid CO_2 (> 99,995 % purity; with ascension pipe; Messer Austria GmbH) was cooled by a recirculating cooler (FL300, JULABO GmbH) to prevent it from gasification and was introduced by two CO_2-pumps (PU2086Plus) with cooled heads. An HPLC-pump (PU2082Plus) delivered substrates and solvents. HPLC-columns (50 mm, 150 mm and 250 mm x 4.5 mm ID) were attached in a thermostated oven (CO-2060Plus) with a temperature of 80 °C. A back pressure regulator (BP-2080Plus), gas/liquid separator (HC-2086-01) and a product collector (SCF-Vch-Bp) were also included.

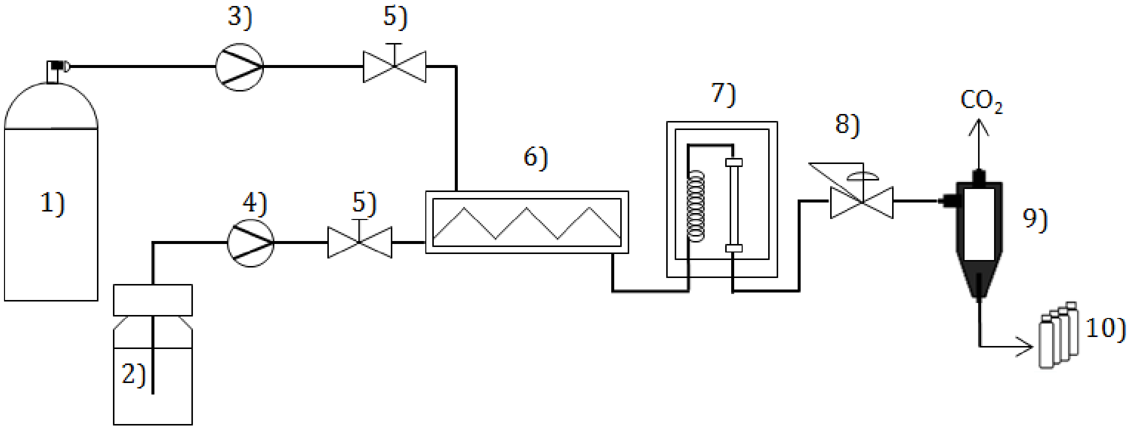

Figure 69: Schematic representation of the $scCO_2$ device

1) liquid CO_2 supply; 2) solution supply; 3) CO_2 pump; 4) solvent pump; 5) hand operated valve; 6) inline mixer; 7) oven and catalyst cartridge; 8) back pressure regulator; 9) gas-liquid separator; 10) product collector

7.4.1 Representing procedure for continuous flow experiments

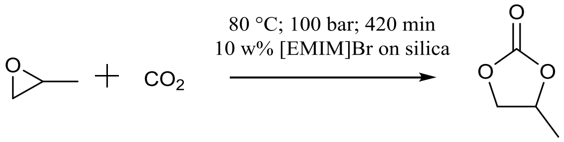

Figure 70: Synthesis of propylene carbonate

An empty HPLC column (150 mm x 4.5 mm ID) was filled with SILP-catalyst (10 w% [EMIM]Br on silica; 1.36 g) and connected to the $scCO_2$-device in an preheated oven (80 °C). A substrate solution of *n*-hexane and propylene oxide cooled in an external ice bath was used as substrate supply. After the pressure reached 100 bar, the process was started by adding the substrate solution. The product was collected as colourless liquid in 30 ml vials at different fractions. The collection time for each flask was set to 30 min for 2 hours and the remaining time to 60 min until the process ended after 420 min.

The output was weighted after 1 hour and a ^{1}H NMR-spectrum was recorded of every collected fraction to determine the yield and quality. Other batch experiments were carried out following the same procedure. Every flow experiment was carried out at least for 420 min and thereby at least 6 fractions (with 30 or 60 min between each fraction) were collected. For each fraction a ^{1}H-NMR 200 MHz spectrum was recorded and optionally a GC chromatogram was measured to determine the quality of the product. The yield was determined by the product output (weight) depending on the reactor substrate input. All calculations to determine the yield in flow are described in the following equations.

$$\phi_{PO} = \frac{V_{PO}}{(V_{PO} + V_{cs})}$$

Equation 4: Volume fraction of PO in substrate solution

ϕ_{PO}................ *volume fraction of PO in solution [ml]*
V_{PO}................ *volume of PO in solution [ml]*
V_{cs}................. *volume of co-solvent in solution [ml]*

$$PO_{input} = \dot{V}_{ss} * \phi_{PO} * t_{fr} * \rho_{PO}$$

Equation 5: Input of PO related to a period of time

PO_{input}.......... *input of PO [g]*
$\mathring{V}ss$................. *flow rate of the substrate solution [ml/min]*
ϕ_{PO}................ *volume fraction of PO in solution*
t_{fr}.................. *time of a fraction [min]*
ρ_{PO}................. *density of PO [g/ml]*

$$PC_{theo} = \frac{PO_{input}}{M_{PO}} * M_{PC}$$

Equation 6: Theorectical output of the product PO

PC_{theo}............ *max. theoretical output of the product PO [g]*
PO_{input}.......... *input of PO [g]*
M_{PO}............... *molar mass of PO [g/mol]*
M_{PC}................ *molar mass of PC [g/mol]*

$$yield_{PC} = \frac{PC_{output}}{PC_{theo}} * 100$$

Equation 7: Yield of PC per fraction in flow

$yield_{PC}$.......... *yield of PC in one fraction [%]*
PC_{theo}............ *max. theoretical output of the product PO [g]*
PO_{output}........ *actual output of PC [g]*

To specify every specific catalyst system, the space time yield (Equation 1) was determined. Therefore, it was possible to compare different catalyst systems with each other.

References

[1] Aresta, M. *Carbon Dioxide as Chemical Feedstock*; Wiley, 2010.

[2] Peters, M.; Köhler, B.; Kuckshinrichs, W.; Leitner, W.; Markewitz, P.; Müller, T. E. Chemical technologies for exploiting and recycling carbon dioxide into the value chain. *ChemSusChem* **2011**, *4*, 1216–1240.

[3] Mertens, J.; Skelland, J. Rising to the CO_2 challenge, Part 3: CO_2 emissions reduction options in refineries. *Hydrocarbon Engineering* **2010**.

[4] Ausfelder, F.; Bazzanella, A. *Verwertung und Speicherung von CO_2: Diskusionspapier*; Dechema eV, 2008.

[5] Kuckshinrichs, W.; Markewitz, P.; Linssen, J.; Zapp, P.; Peters, M.; Köhler, B.; Müller, T. E.; Leitner, W. Weltweite Innovationen bei der Entwicklung von CCS-Technologien und Möglichkeiten der Nutzung und des Recyclings von CO_2. *Schriften des Forschungszentrums Jülich Reihe Energie & Umwelt* **2010**, *60*, 139.

[6] Housecroft, C. E.; Sharpe, A. G.; Bera, H.; Rompel, A. *Anorganische Chemie*, 2., aktualisierte Aufl.; Chemie; Pearson Studium: München, 2008.

[7] Maeda, C.; Miyazaki, Y.; Ema, T. Recent progress in catalytic conversions of carbon dioxide. *Catal. Sci. Tech.* **2014**, *4*, 1482–1497.

[8] North, M.; Pasquale, R. Mechanism of cyclic carbonate synthesis from epoxides and CO_2. *Angew. Chem. Int. Ed.* **2009**, *121*, 2990–2992.

[9] Cokoja, M.; Wilhelm, M. E.; Anthofer, M. H.; Herrmann, W. A.; Kuhn, F. E. Synthesis of cyclic carbonates from epoxides and carbon dioxide by using organocatalysts. *ChemSusChem* **2015**, *8*, 2436–2454.

[10] Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using carbon dioxide as a building block in organic synthesis. *Nat. Commun.* **2015**, *6*, 5933.

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

[12] Yasuda, H.; He, L.-N.; Takahashi, T.; Sakakura, T. Non-halogen catalysts for propylene carbonate synthesis from CO_2 under supercritical conditions. *Appl. Catal., A: General* **2006**, *298*, 177–180.

[13] Barbarini, A.; Maggi, R.; Mazzacani, A.; Mori, G.; Sartori, G.; Sartorio, R. Cycloaddition of CO_2 to epoxides over both homogeneous and silica-supported guanidine catalysts. *Tetrahedron Lett.* **2003**, *44*, 2931–2934.

[14] Nishikubo, T.; Kameyama, A.; Yamashita, J.; Tomoi, M.; Fukuda, W. Insoluble polystyrene - bound quaternary onium salt catalysts for the synthesis of cyclic carbonates by the reaction of oxiranes with carbon dioxide. *J. Polym. Sci. A* **1993**, *31*, 939–947.

[15] Yang, Z.-Z.; He, L.-N.; Miao, C.-X.; Chanfreau, S. Lewis Basic Ionic Liquids-Catalyzed Conversion of Carbon Dioxide to Cyclic Carbonates. *Adv. Synth. Catal.* **2010**, *352*, 2233–2240.

[16] Ema, T.; Miyazaki, Y.; Koyama, S.; Yano, Y.; Sakai, T. A bifunctional catalyst for carbon dioxide fixation: cooperative double activation of epoxides for the synthesis of cyclic carbonates. *Chem. Commun.* **2012**, *48*, 4489–4491.

[17] Paddock, R. L.; Nguyen, S. T. Chemical CO 2 Fixation: Cr(III) Salen Complexes as Highly Efficient Catalysts for the Coupling of CO 2 and Epoxides. *J. Am. Chem. Soc.* **2001**, *123*, 11498–11499.

[18] Sun, J.; Zhang, S.; Cheng, W.; Ren, J. Hydroxyl-functionalized ionic liquid: A novel efficient catalyst for chemical fixation of CO2 to cyclic carbonate. *Tetrahedron Lett.* **2008**, *49*, 3588–3591.

[19] *Ionic liquids in synthesis;* Wasserscheid, P.; Welton, T., Eds., 2nd, completely rev. and enl. ed.; Wiley-VCH: Weinheim, 2008.

[20] Mehnert, C. P. Supported ionic liquid catalysis. *Chem. Eur. J.* **2005**, *11*, 50–56.

[21] Peng, J.; Deng, Y. Cycloaddition of carbon dioxide to propylene oxide catalyzed by ionic liquids. *New J. Chem.* **2001**, *25*, 639–641.

[22] Büttner, H.; Steinbauer, J.; Werner, T. Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Bifunctional One-Component Phosphorus-Based Organocatalysts. *ChemSusChem* **2015**, *8*, 2655–2669.

[23] Sun, J.; Fujita, S.-i.; Arai, M. Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids. *J. Organomet. Chem.* **2005**, *690*, 3490–3497.

[24] Wang, J.-Q.; Dong, K.; Cheng, W.-G.; Sun, J.; Zhang, S.-J. Insights into quaternary ammonium salts-catalyzed fixation carbon dioxide with epoxides. *Catal. Sci. Technol.* **2012**, *2*, 1480.

[25] Jutz, F.; Andanson, J.-M.; Baiker, A. Ionic liquids and dense carbon dioxide: a beneficial biphasic system for catalysis. *Chem. Rev.* **2011**, *111*, 322–353.

[26] Seki, T.; Grunwaldt, J.-D.; Baiker, A. In situ attenuated total reflection infrared spectroscopy of imidazolium-based room-temperature ionic liquids under "supercritical" CO_2. *J. Phys. Chem. B* **2009**, *113*, 114–122.

[27] Xu, B.-H.; Wang, J.-Q.; Sun, J.; Huang, Y.; Zhang, J.-P.; Zhang, X.-P.; Zhang, S.-J. Fixation of CO 2 into cyclic carbonates catalyzed by ionic liquids: A multi-scale approach. *Green Chem.* **2015**, *17*, 108–122.

[28] Sun, J.; Fujita, S.-i.; Zhao, F.; Arai, M. A highly efficient catalyst system of ZnBr2/n-Bu4NI for the synthesis of styrene carbonate from styrene oxide and supercritical carbon dioxide. *Appl. Catal., A: General* **2005**, *287*, 221–226.

[29] Palgunadi, J.; Kwon, O.-S.; Lee, H.; Bae, J. Y.; Ahn, B. S.; Min, N.-Y.; Kim, H. S. Ionic liquid-derived zinc tetrahalide complexes: Structure and application to the coupling reactions of alkylene oxides and CO_2. *Catal. Today* **2004**, *98*, 511–514.

[30] Li, F.; Xiao, L.; Xia, C.; Hu, B. Chemical fixation of CO_2 with highly efficient $ZnCl_2$/[BMIm]Br catalyst system. *Tetrahedron Lett.* **2004**, *45*, 8307–8310.

[31] Fujita, S.-i.; Nishiura, M.; Arai, M. Synthesis of Styrene Carbonate from Carbon Dioxide and Styrene Oxide with Various Zinc Halide-Based Ionic Liquids. *Catal. Lett.* **2010**, *135*, 263–268.

[32] Estager, J.; Holbrey, J. D.; Swadzba-Kwasny, M. Halometallate ionic liquids. *Chem. Soc. Rev.* **2014**, *43*, 847–886.

[33] Takahashi, S.; Saboungi, M.-L.; Klingler, R. J.; Chen, M. J.; Rathke, J. W. Dynamics of room-temperature melts: Nuclear magnetic resonance measurements of dialkylimidazolium haloaluminates. *J. Chem. Soc., Faraday Trans.,* **1993**, *89*, 3591.

[34] Gale, R. J.; Gilbert, B.; Osteryoung, R. A. Raman spectra of molten aluminum chloride: 1-butylpyridinium chloride systems at ambient temperatures. *Inorg. Chem.* **1978**, *17*, 2728–2729.

[35] Takahashi, S.; Curtiss, L. A.; Gosztola, D.; Koura, N.; Saboungi, M.-L. Molecular Orbital Calculations and Raman Measurements for 1-Ethyl-3-methylimidazolium Chloroaluminates. *Inorg. Chem.* **1995**, *34*, 2990–2993.

[36] Alves, M. B.; Santos jr., V. O.; Soares, V. C. D.; Suarez, P. A. Z.; Rubim, J. C. Raman spectroscopy of ionic liquids derived from 1-n-butyl-3-methylimidazolium chloride and niobium chloride or zinc chloride mixtures. *J. Raman Spectrosc.* **2008**, *39*, 1388–1395.

[37] Kisch, H.; Millini, R.; Wang, I.-J. Bifunktionelle Katalysatoren zur Synthese cyclischer Carbonate aus Oxiranen und Kohlendioxid. *Chem. Ber.* **1986**, *119*, 1090–1094.

[38] Monassier, A.; D'Elia, V.; Cokoja, M.; Dong, H.; Pelletier, J. D. A.; Basset, J.-M.; Kühn, F. E. Synthesis of Cyclic Carbonates from Epoxides and CO 2 under Mild Conditions Using a Simple, Highly Efficient Niobium-Based Catalyst. *ChemCatChem* **2013**, *5*, 1321–1324.

[39] Kim, Y. J.; Varma, R. S. Tetrahaloindate(III)-based ionic liquids in the coupling reaction of carbon dioxide and epoxides to generate cyclic carbonates: H-bonding and mechanistic studies. *J. Org. Chem.* **2005**, *70*, 7882–7891.

[40] Sun, J.; Ren, J.; Zhang, S.; Cheng, W. Water as an efficient medium for the synthesis of cyclic carbonate. *Tetrahedron Lett.* **2009**, *50*, 423–426.

[41] Wang, J.-Q.; Yue, X.-D.; Cai, F.; He, L.-N. Solventless synthesis of cyclic carbonates from carbon dioxide and epoxides catalyzed by silica-supported ionic liquids under supercritical conditions. *Catal. Commun.* **2007**, *8*, 167–172.

[42] Liu, M.; Wang, F.; Shi, L.; Liang, L.; Sun, J. Zn-based ionic liquids as highly efficient catalysts for chemical fixation of carbon dioxide to epoxides. *RSC Adv.* **2015**, *5*, 14277–14284.

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

[44] Zhao, Y.; Yao, C.; Chen, G.; Yuan, Q. Highly efficient synthesis of cyclic carbonate with CO 2 catalyzed by ionic liquid in a microreactor. *Green Chem.* **2013**, *15*, 446–452.

[45] Wu, X.; Wang, M.; Xie, Y.; Chen, C.; Li, K.; Yuan, M.; Zhao, X.; Hou, Z. Carboxymethyl cellulose supported ionic liquid as a heterogeneous catalyst for the cycloaddition of CO2 to cyclic carbonate. *Appl. Catal., A: General* **2016**, *519*, 146–154.

[46] Glasnov, T. *Continuous-Flow Chemistry in the Research Laboratory: Modern Organic Chemistry in Dedicated Reactors at the Dawn of the 21st Century*; Springer International Publishing: Cham, s.l., 2016.

[47] Darvas, F.; Hessel, V.; Dormán, G. *Flow chemistry*; de Gruyter Berlin, 2014.

[48] Leeuwen, Piet W. N. M. van; Chadwick, J. C. *Homogeneous catalysts*; Wiley: Chichester, 2011.

[49] Jessop, P. G.; Leitner, W. *Chemical Synthesis Using Supercritical Fluids*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1999.

[50] Baiker, A. Supercritical fluids in heterogeneous catalysis. *Chem. Rev.* **1999**, *99*, 453–474.

[51] Anastas, P. T.; Leitner, W.; Jessop, P. G. *Handbook of Green Chemistry, Green Solvents, Supercritical Solvents*; Handbook of Green Chemistry; Wiley: Hoboken, 2014.

[52] Brunner, G. Applications of supercritical fluids. *Annu. Rev. Chem. Biomol. Eng.* **2010**, *1*, 321–342.

[53] Wasserscheid, P.; Keim, W. Ionic Liquids—New “Solutions” for Transition Metal Catalysis. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789.

[54] Licence, P.; Ke, J.; Sokolova, M.; Ross, S. K.; Poliakoff, M. Chemical reactions in supercritical carbon dioxide: From laboratory to commercial plantThis work was presented at the Green Solvents for Catalysis Meeting held in Bruchsal, Germany, 13–16th October 2002. *Green Chem.* **2003**, *5*, 99–104.

[55] Leitner, W. Chemische Synthese in überkritischem Kohlendioxid. *Erdöl, Erdgas, Kohle* **2000**, *116*, 137–140.

[56] Hejazifar, M.; Earle, M.; Seddon, K. R.; Weber, S.; Zirbs, R.; Bica, K. Ionic Liquid-Based Microemulsions in Catalysis. *J. Org. Chem.* **2016**, *81*, 12332–12339.

[57] Riisager, A.; Fehrmann, R.; Haumann, M.; Wasserscheid, P. Supported Ionic Liquid Phase (SILP) Catalysis: An Innovative Concept for Homogeneous Catalysis in Continuous Fixed-Bed Reactors. *Eur. J. Inorg. Chem.* **2006**, *2006*, 695–706.

[58] R. Wölfel. Ionic Liquid materials as engineering fluids and novel catalysts. https://www.crt.cbi.uni-erlangen.de/research/silp/index.shtml (accessed March 5, 2017).

[59] Valkenberg, M.; deCastro, C.; Hölderich, W. Friedel-Crafts acylation of aromatics catalysed by supported ionic liquids. *Appl. Catal., A.* **2001**, *215*, 185–190.

[60] Riisager, A. Continuous fixed-bed gas-phase hydroformylation using supported ionic liquid-phase (SILP) Rh catalysts. *J. Catal.* **2003**, *219*, 452–455.

[61] Riisager, A.; Jorgensen, B.; Wasserscheid, P.; Fehrmann, R. First application of supported ionic liquid phase (SILP) catalysis for continuous methanol carbonylation. *Chem. Commun.* **2006**, 994–996.

[62] Haumann, M.; Dentler, K.; Joni, J.; Riisager, A.; Wasserscheid, P. Continuous Gas-Phase Hydroformylation of 1-Butene using Supported Ionic Liquid Phase (SILP) Catalysts. *Adv. Synth. Catal.* **2007**, *349*, 425–431.

[63] Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. Green processing using ionic liquids and CO_2. *Nature* **1999**, *399*, 28–29.

[64] Goerl, U.; Hunsche, A.; Mueller, A.; Koban, H. G. Investigations into the Silica/Silane Reaction System. *Rubber Chem. Technol* **1997**, *70*, 608–623.

[65] Deng, F.; Reeder, Z. K.; Miller, K. M. 1,3-Bis(2′-hydroxyethyl)imidazolium ionic liquids: Correlating structure and properties with anion hydrogen bonding ability. *J. Phys. Org. Chem.* **2014**, *27*, 2–9.

[66] Bresien, J.; Ellinger, S.; Harloff, J.; Schulz, A.; Sievert, K.; Stoffers, A.; Taschler, C.; Villinger, A.; Zur Taschler, C. Tetracyanido(difluorido)phosphates M(+) PF2 (CN)4 (.). *Angew. Chem. Int. Ed.* **2015**, *54*, 4474–4477.

[67] Keaveney, S. T.; Greaves, T. L.; Kennedy, D. F.; Harper, J. B. Understanding the Effect of Solvent Structure on Organic Reaction Outcomes When Using Ionic Liquid/Acetonitrile Mixtures. *J. Phys. Chem. B* **2016**, *120*, 12687–12699.

[68] Valizadeh, H.; Amiri, M.; Shomali, A.; Hosseinzadeh, F. Ionic liquid 1-(3-Trimethoxysilylpropyl)-3-methylimidazolium nitrite as a new reagent for the efficient diazotization of aniline derivatives and in situ synthesis of azo dyes. *J. Iran. Chem. Soc.* **2011**, *8*, 495–501.

[69] van Doorslaer, C.; Wahlen, J.; Mertens, P.; Binnemans, K.; Vos, D. de. Immobilization of molecular catalysts in supported ionic liquid phases. *Dalton Trans.* **2010**, *39*, 8377–8390.