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Synthesis of Cyclic Carbonates from CO_2 and Epoxides Using Ionic Liquids and Related Catalysts Including Choline Chloride-Metal Halide Mixtures

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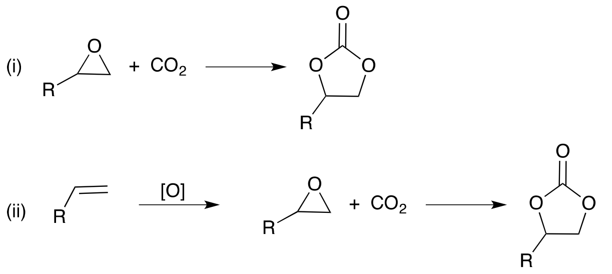
Dedication: This Article is Published in Celebration of the 50th Anniversary of the Opening of the Chemistry Department at the University of York

Contribution for Themed Issue on "Catalytic Conversion and Use of Carbon Dioxide for Value-Added Organics"

Abstract: In this mini-review, progress made in the use of ionic liquid catalysts and related systems for cycloaddition reactions of carbon dioxide with epoxides is described with the primary focus on results from the past eight years. Catalysts described range from simple onium species including tetrabutylammonium bromide, functionalized and simple imidazolium ionic liquids, to a plethora of supported ionic liquid systems. A range of supports including alumina, silica, carbon nanotubes, magnetic nanoparticles, poly(ethyleneglycol), polystyrene, cellulose and chitosan have been used with a variety of ionic groups. These include ammonium, phosphonium and both functionalized and unfunctionalized imidazolium salts. Results have been tabulated to summarize reaction conditions and TONs for styrene oxide, propylene oxide and cyclohexene oxide conversions. It is clear that metal ions used in combination with ionic liquids, particularly $ZnBr_2$, can enhance conversions, and hydroxyl, carboxyl and other functional groups capable of hydrogen-bonding can be incorporated to improve catalysis. Some recent results using flow reactors are highlighted. Examples of ionic catalysts used in the related processes of oxidative carboxylation of alkenes, which also yields cyclic carbonate products, and carbon dioxide-aziridine coupling reactions, which yield oxazolidinone products are described. New data on catalytic styrene carbonate production using choline chloride-transition metal chloride mixtures are presented. For 3*d* metals, the catalytic activity of these mixtures is Cr > Co ≈ Fe ≈ Ni > Mn >> Cu.

Introduction

During the past twenty years, chemists have been widely exploring the chemistry of ionic liquids.[1] These interesting compounds have valuable chemical and physical properties as solvents, reagents and catalysts. A state of the art review on the use of ionic liquids in synthesis and catalysis has been published by Hallett and Welton.[2] It is well-established that carbon dioxide (CO_2) can achieve good levels of solubility in many of these liquids and therefore, it is not surprising that they have become a veritable playground for discovering new chemistry of CO_2. It is over ten years since the first cycloaddition reactions of epoxides with CO_2 using ionic liquids containing imidazolium and pyridinium cations as catalysts.[3] In this report, it was shown that both the cation and anion affects the activity of the ionic liquid. The activity was shown to decrease in the order imidazolium > pyridinium and $BF_4^- > Cl^- > PF_6^-$. These results are also of interest as many metal-containing catalysts for CO_2 activation reactions show enhanced reactivity in the presence of the correct ionic co-catalyst. Therefore, there is the possibility that advances summarized herein may show even greater promise if combined with an exceptional metal complex catalyst. The field of ionic liquid catalyzed reactions towards CO_2 utilization was first reviewed by Arai and co-workers in 2005,[4] and subsequently a review was also published by Zhang and co-workers in 2006.[5] In the latter review, progress made in the area of CO_2 fixation (e.g. separation from flue gases) using ionic liquids is also summarized. More recently, reviews by (i) He and co-workers detailing the use of task-specific ionic liquids for both CO_2 capture and conversion,[6] (ii) Park and co-workers on the use of supported ionic liquids for cyclic carbonate synthesis, [7] and a book chapter on this subject by Arai and co-authors were published.[8] An excellent recent review has been written by North, Pasquale and Young on catalytic conversion of CO_2 to yield cyclic carbonates,[9] and more recently shorter perspectives on this reaction have been published by Whiteoaks and Kleij,[10] and Pescarmona and Taherimehr.[11] The main focus herein will be reports made since 2006 on catalytic CO_2-epoxide cycloaddition reactions, Scheme 1, using ionic catalysts, however, some earlier results will be included for comparative purposes. Data are summarized in Table 1 with some examples discussed more extensively in the text. In this mini-review, we highlight the progress that has been made and recent results from our group using metal-containing eutectics will also be presented. Results concerned with related processes such as coupling reactions with aziridines and two step processes to yield cyclic carbonates *via* initial oxidation of alkenyl-starting materials will also be included. Results concerned with bifunctional catalysts (metal complexes with tethered ionic or neutral co-catalysts)[12, 13,14] will not be discussed nor will those where the ionic liquid acts as a reagent to enhance enantioselectivity.[15] The use of ionic liquids with metal catalysts to produce α-methylene cyclic carbonates and related oxazolidin-2-ones is also not included.[16, 17] The use of electrocatalysis to produce cyclic carbonates from epoxides using ionic liquids,[18] or other ionic materials as supporting electrolytes (e.g. Bu_4NBr) will not be discussed.[19]



Scheme 1. Production of cyclic carbonates *via* (i) cycloaddition of epoxides with CO_2 and (ii) oxidation of alkenes and carboxylation of an intermediate epoxide. [O] = oxidant

In Arai's review,[4] they concluded that "*The activity of ionic liquid is greatly enhanced by the addition of Lewis acidic compounds of metal halides or metal complexes that have no or low activity by themselves*" such as the combination of $ZnBr_2$ with [BMIm]Br,[20] and that ionic liquids greatly aid in product separation and catalyst recycling. These findings have been built on during the last eight years with product separation and recycling being a major focus in this field with significant advances being made on the use of supported ionic liquids in these reactions.[7] Also, ionic liquids functionalized with hydroxyl and carboxyl groups have received significant attention, as such functionalities activate the epoxide towards attack by the nucleophile. A short review on the general use of functionalized ionic liquids in catalysis has been published.[21]

Cycloaddition of epoxides and carbon dioxide using ionic catalysts

In terms of catalyst systems considered in this review, perhaps the most simple are quaternary ammonium salts. A detailed, combined experimental and computational study was described by Zhang and co-workers for the conversion of ethylene oxide to ethylene carbonate.[22] In their work, they clearly demonstrated that reactions catalyzed by Bu_4NBr had a lower activation barrier than those catalyzed by Et_4NBr and Et_4NCl. The experimental data showed that the activities of anions increased in the order of $Cl^- > Br^- > I^-$ with the same cation, which is related to stronger nucleophilicity and the smaller steric hindrance of Cl^- than Br^- and I^-. Another computational study, was reported around the same time by Han and co-workers,[23] on the combined efficacy of hydroxyl-containing compounds in combination with KI. They concluded that the "*catalytic essence of KI*" is to provide the I^- anion, which ring-opens the epoxide and that the K^+ cation stabilizes the resultant anionic groups either before or after CO_2 insertion, $(R(CH_2I)CHO)^-$ or $(R(CH_2I)CHO–CO_2)^-$, and that hydroxyl groups of alcohols stabilize transition states and intermediates. The conclusions drawn by the authors of that study will be applicable to catalyst systems presented in Table 1 where hydroxyl- and carboxyl-containing compounds (or polymers) are used in combination with salts. Computational studies have also been performed in detail on imidazolium catalyst systems.[24] The authors identified at least five different pathways *via* which $[C_nMim]Cl$ could facilitate the cycloaddition reaction. For the reaction of PO, cooperativity between the cations and anions was noted that stabilized the intermediates and transition states through hydrogen-bonding, which make the ring opening of the epoxide by the nucleophile easier. The role of hydrogen-bonding has been exploited in many future studies where imidazolium cations bearing hydroxyl or carboxyl functional groups have been employed to enhance such aspects of the cycloaddition mechanism. These include some of the most active supported and easily recyclable ionic liquid catalysts reported to date that are discussed below.[25-27]

In probably the first example of microwave-assisted carboxylation of epoxides, four zinc salts in combination with five ionic compounds were screened for their activity using both conventional and microwave heating.[28] Exceptionally high TON and TOF were achieved for many combinations including a TOF of 6989 h^{-1} for the conversion of PO using zinc phenosulfonate octahydrate in combination with Bu_4NBr. This combination was more active than the same zinc salt with imidazolium ionic liquids or zinc bromide with Bu_4NBr. The conversion of epoxides under microwave irradiation using both supported and unsupported ionic catalysts including Et_4NCl has been reported,[29] and is clearly effective in achieving higher TOF for these reactions. Unfortunately, in the 2010 study, only small amounts of epoxide were converted (low catalyst to epoxide ratio) and therefore, the TON values obtained are meaningless compared with other catalyst systems reported herein including the 2007 microwave-assisted experiments highlighted above. In a related study, using Bu_4NBr as the catalyst, researchers have shown that performing the reaction in dimethylcarbonate as the solvent is beneficial in terms of reaction rates.[30] Reactions performed in this solvent achieved approximately double the conversion in the same amount of time as reactions under neat conditions. It was postulated that the epoxide interacts with the δ^+C of the dimethylcarbonate and this leads to the increased rates. This is an interesting finding as the vast majority of reactions in this field are performed under neat "solvent-free" conditions and therefore, this study highlights the important role that solvent selection could play in enhancing reaction rates.

As highlighted in Arai's review,[4] combinations of metal salts with ionic liquids often show potent reactivity in cycloaddition reactions. In 2007, the catalytic combination of $ZnBr_2$ with phosphonium salts was reported for these reactions.[31] If the phosphonium halide salt was replaced by a phosphine oxide, the catalytic activity was zero. However, excellent TON (>6000) could be achieved for $ZnBr_2$ with PPh_4I, with the chloride and bromide phosphonium analogues being significantly less active (TON 3400 and 5800, respectively). Excellent TONs have also been reported for $ZnCl_2$ used with alkyltriphenylphosphonium chloride and bromide salts.[32]

In 2010, He and co-workers described the reactivity of a range of Lewis basic ionic liquids for these reactions.[33] They found that 1,8-diazabicyclo[5.4.0]undec-7-enium chloride, [HDBU]Cl, Figure 1, gave near quantitative yields of products with related DABCO-derived ionic liquids giving around 80% yield under identical conditions. In some cases, very complex ionic liquids have been prepared and reported for use in these reactions. For example, a tricationic ionic liquid was studied, $[N5]Br_3$, Figure 2.[34] The catalyst could be recycled eight times with less than 2% difference in isolated yields of the cyclic carbonate. However, the high molecular weight of the ionic liquid meant that the catalyst loading used was approximately 50%, which means that TON values are much less than other ionic liquids and salts already explored including commercially available Bu_4NBr and [BMIm] derivatives.

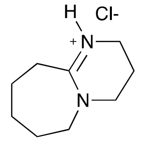


Figure 1 A Lewis basic ionic liquid catalyst, [HDBU]Cl

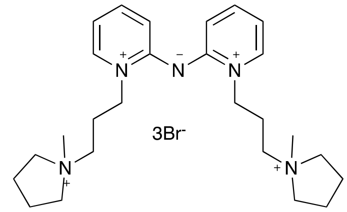


Figure 2 Amino-pyrridinium-pyrrolidinium bromide, [N5]Br_3, ionic liquid

Hydroxyl-functionalized ionic liquids have been studied with 1-(2-hydroxyethyl), 3-methylimidazolium bromide, [HEMIm]Br, being the most active in the first reported cases.[35] 99% yield could be obtained under moderate conditions for a range of epoxides at relatively short reaction times. These studies laid the basis for future research on polymer-supported variants of these ionic liquid catalysts, which are discussed below. Another series of hydroxyl functionalized ionic liquids were very recently reported.[36] These bear a hydroxymethyl group on the carbon 2 of the imidazolium cation, Figure 3. In parallel experiments using BMIm derivatives, these hydroxyl-containing catalysts achieved yields 20-30% higher than their unfunctionalized analogues. Importantly, these ionic liquids are base stable and could therefore be used in the presence of catalytic amounts of base in a two step one pot process to afford transesterification products from epoxides, CO_2 and methanol. In both epoxide carboxylation and transesterification reactions, the ionic liquids could be recycled six times without loss in activity.

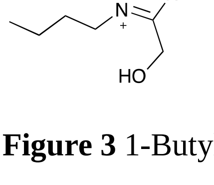


Figure 3 1-Butyl, 2-hydroxymethyl, 3-methylimidazolium bromide, [BHMMIm]Br

Very recently, exciting results have been obtained in terms of maximising reaction efficiency through use of a microflow-reactor.[37] Chen and co-workers used the hydroxyl-functionalized ionic catalyst 2-hydroxyl-ethyl-tributylammonium bromide (HETBAB) and obtained a yield of PC 99.8% with a residence time of 14 s at the moderately low pressure of 35 bar. TOFs of between 3000 and 14 000 h^{-1} were achieved in the flow experiments compared with TOFs of around 60 h^{-1} for the analogous stirred batch reactions. These initial results show that very exciting increases in productivity will be possible in the future by combining the right catalysts with new engineering process design.

Betaine-based catalysts, $[Me_3NCH_2COOH]X$ (X = Cl, Br, I, BF_4, PF_6), have been studied in cycloaddition reactions.[38] They were made by protonation of betaine (which can be naturally sourced). In most cases, the activity of these catalysts in a standard reaction (carboxylation of PO) were comparable with choline chloride or Et_4NBr as catalysts. However, the iodide containing betaine catalyst (X = I) showed superior reactivity and outperformed all the others studied. It could also be recycled and maintained its activity. Similar reactivity (e.g. TON) were also observed recently for quaternized glycine (prepared by addition of MeI to the amino acid glycine).[39] In support of their experiments, DFT studies were also undertaken and provided additional support for a synergistic mechanism utilizing both the -COOH group and the halide ions. In related research, twenty naturally occurring α-amino acids were studied for activity in these reactions and were found to possess moderate to excellent activity.[40] It was suggested that the zwitterionic form of the amino acid is active in the catalysis and therefore, they are included in this review.

Bifunctional acid-base ionic catalysts based on imidazolium and pyridinium cores have been prepared and studied in cycloaddition reactions.[41] In general, those containing imidazolium ions were more reactive than the pyridinium analogues, and a comparison of methylene (CH_2) and propyl- ($CH_2CH_2CH_2$) groups separating the carboxylic acid moiety from the core found that longer chain separation afforded more active catalysts with the most active compound shown in Figure 4. In general, the bromide salts were four times more active than the related chlorides.

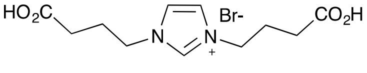


Figure 4 Example bifunctional acid-base catalyst, $[Im(C_3H_6COOH)_2]Br$

Zwitterionic materials containing no halide counterions have been used as bifunctional organocatalysts in cycloaddition reactions.[42] A range of aromatic zwitterions were studied with 3-(trimethylammonio)phenolate, Figure 5, found to be the most effective. Interestingly, they were able to isolate and characterize a CO_2-adduct of the zwitterion and use this as a synthon with the epoxide to generate the cyclic carbonate product. Thereby, they identified one of the intermediates in their catalytic cycle.

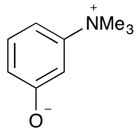


Figure 5 Example bifunctional ammonium betaine catalyst, 3-(trimethylammonio)phenolate

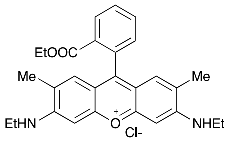
Table 1. Summary of data for cycloaddition reactions between carbon dioxide and the epoxides employing ionic catalyts (styrene oxide (SO), propylene oxide (PO) and cyclohexene oxide (CHO)).

Reference	**Catalyst**	**Epoxide**	**Reaction Conditions**	**Yield (Conv.)**	**TON**
Wang *et al.* 2012 [22]	Bu_4NCl	PO	14.3 mmol epoxide, 100 °C, 30 bar, 2 h PO:Cat 100:1	72% (73%)	72
	Bu_4NBr	PO	14.3 mmol epoxide, 100 °C, 30 bar, 2 h PO:Cat 100:1	56% (56%)	56
Mamparambath *et al.* 2010 [29]	Bu_4NCl	SO	37.4 mmol epoxide, Temperature not reported, MW power = 200 W, 9.7 bar, 30 min Epoxide:Cat 37.4:1	97.9%	37
		PO		91.4%	34
		CHO		41%	15

Kumar *et al.* [30]	Bu_4NBr	SO	10 mmol epoxide, 10 mL dimethylcarbonate (DMC), 100 °C, 21 bar Epoxide:Cat 100:1 6.5 h	96% *Note: without DMC, 45% yield*	96
		PO	2.5 h	98%	98
Ono *et al.* 2007 [28]	Zn phenosulfonate/ Bu_4NBr	SO	29.9 mmol epoxide, 30 bar, MW power = 300 W, 15 min Epoxide:Zn:BuN_4Br 2300:1:46 120 °C	62.5%	1747
		PO	100 °C	76%	1440
Yang *et al.* 2010 [33]	Lewis basic ionic liquid, HDBU.Cl	SO	10 mmol epoxide, 10 bar Epoxide:cat 100:1 140 °C, 2 h	81%	81
		PO	140 °C, 2 h	97%	97
		CHO	140 °C, 10 h	19%	19
Peng *et al.* 2001 [3]	$BMImBF_4$	PO	PO:CO_2:IL 21000:660:1 140 °C, 20 bar, 6 h	90%	450
Kim *et al.* 2003 [20]	$(EMIm)_2ZnBr_2Cl_2$	EO	EO:Zn 5000:1 120 °C, 34 bar, 1 h	-	4270
		PO	PO:Zn 2000:1 120 °C, 34 bar, 1 h	-	1960

Sun *et al.* 2004 [43]	$(BMIm)_2ZnBr_2Cl_2$	SO	SO:Zn 88:1 80 °C, 40 bar, 1 h	-	81
Li *et al.* 2004 [44]	BMImBr + 15% $ZnCl_2$	PO	BMIm:Zn 6:1 in 20 mL epoxide 100 °C, 15 bar, 1 h	98%	5580
		SO	BMIm:Zn 6:1 in 20 mL epoxide 100 °C, 15 bar, 1 h	86%	3015
		CHO	BMIm:Zn 6:1 in 20 mL epoxide 100 °C, 15 bar, 1 h	34%	1205
Lee *et al.* 2012 [45]	$[DMIm]_2[Br_2Zn(Me_2PO_4)_2]$	PO	PO:IL 1000:1 100 °C, 35 bar, 1 h	94.4%	944
Kossev *et al.* 2003 [46]	$[TEBA]_2CaCl_4$	PO	PO:Ca 430:1 170 °C, 40 bar, 4 h	97%	417
	$[Ph_3PMe]CaICl_2$	PO	PO:Ca 430:1 170 °C, 40 bar, 4 h	87.5%	376
Wu *et al.* 2008 [31]	$ZnBr_2$-Ph_4PI	SO	105 mmol epoxide, 120 °C, 25 bar Epoxide:Zn:P 7000:1:6 2 h	(86.6%)	6062
		PO	1 h	(89.6%)	6272
Sun *et al.* 2006 [32]	$ZnCl_2$-$PPh_3C_6H_{13}Br$	SO	120 °C, 15 bar, 1 h Epoxide:Zn:P 5000:1:6 0.175 mol SO	(81%)	2464

		PO	0.29 mol PO	(96%)	4718
Kilic *et al.* 2013 [47]	Ni(dioxime)$_2$/BMImPF$_6$	SO	11 mmol epoxide, 100 °C, 15 bar, 2 h Epoxide:Ni:BMImPF$_6$ 1000:1:2	91%	910
		PO		65%	650
Wong *et al.* 2008 [34]	Amino-pyridinium-pyrrolidinium bromide, [N5]Br$_3$	SO	8 mmol epoxide, 2.7 g [N5]Br$_3$ (4.06 mmol), water 60 μL, 80 °C Epoxide:[N5]Br$_3$ 1.97:1 15 bar, 2 h	85%	1.7
		PO	40 bar, 3 h	99%	1.95
Sun *et al.* 2008 [35]	1-(2-hydroxylethyl), 3-methylimidazol-ium bromide, [HEMIm]Br	SO	0.2 mmol epoxide, 125 °C, 20 bar Epoxide:Cat 62.5:1 1 h	99%	62
		PO	1 h	99%	62
		CHO	5 h	99%	62
Wang *et al.* 2013 [36]	1-Butyl, 2-hydroxymethyl, 3-methylimidazolium bromide, [BHMMIm]Br	SO	14.3 mmol epoxide, 120 °C, 20 bar Epoxide:Cat 100:1 2 h	90%	90
		PO	1 h	98%	98
		CHO	6 h	89%	89
Zhou *et al.* 2008 [38]		SO	10 mmol epoxide, 80 bar Epoxide:cat 40:1	96%	38

	Betaine-based catalysts, $[Me_3NCH_2COOH]I$		140 °C, 8 h		
		PO		98%	39
		CHO		34%	14
Tharun *et al.* 2013 [39]	Quaternized glycine, $(HO_2CCH_2NMeH)I$	SO	18.6 mmol epoxide, 120 °C, 12 bar, 2 h SO:Cat 46.5:1	79% (80%)	37
		PO	PO:Cat 46.5:1	84% (86%)	39
		CHO	CHO:Cat 46.5:1	51% (55%)	24
Sun *et al.* 2011 [41]	Acid-base bifunctional ionic liquid, $[Im(C_3H_6COOH)_2]Br$	SO	200 mmol epoxide, 20 bar Epoxide:cat 100:1 125 °C, 1 h	95%	95
		PO	100 °C, 1 h	99%	99
		CHO	125 °C, 15 h	85%	85
Tsutsumi *et al.* 2010 [42]	Bifunctional ammonium betaine catalyst, 3-(trimethylammonio) phenolate	SO	10 mmol epoxide, 10 bar, 120 °C, 24 h Epoxide:cat 33.3:1	98%	32
		PO		99%	33
Yu *et al.* 2012 [48]	Amidinium carbamate IL/ amidinium halide mixtures	SO	50 °C, 25 bar, 8 h Epoxide:C6-HBr 50:1	99%	49.5
		CHO		91%	45.5
Gong *et al.* 2012 [49]	Rhodamine 6G  	SO	16 mmol SO, 90 °C, 1 atm, 24 h SO:Rh6G:DBU 100:1:1	94%	94

Chatelet *et al.* 2013 [50]	Azaphosphatrane chlorides	SO	5.0 mmol SO, 1 mL toluene, 100 °C, 1 atm, 7 h SO:cat 100:1	50%	50
			100 h		*500-600*
Foltran *et al.* 2013 [51]	1,5,7-triaza-bicyclo[4.4.0]dec-5-enium bromide (TBD.HBr)	SO	80 °C, 80 bar, 20 h Epoxide:TBD.HBr 100:1	88%	88
		PO		81%	81
Dai et al 2013 [52]	Amine-guanidium bromide ($[TMGC_2H_4NH_2]Br$)	SO	35.7 mmol epoxide, 130 °C, 25 bar Epoxide: $[TMGC_2H_4NH_2]Br$ 200:1 3 h	99%	198
		PO	2 h	95%	190
		CHO	20 h	83%	166
Zheng *et al.* [53]	Magnetic nanoparticle supported ionic liquid, MNP-1	SO	10 mmol epoxide, 140 °C, 10 bar Epoxide:Cat 100:1 12 h	93%	93
		PO	4 h	99%	99
		CHO	72 h	98%	98
Sakai *et al.* [54]	Silica grafted phosphonium catalysts, $Si\text{-}PPh_3Br$	SO	10 mmol epoxide, 90 °C, 10 bar Epoxide:Cat 100:1 6 h	86%	86
		PO	6 h	99%	99

		CHO	24 h	21%	21
Han *et al.* 2012 [55]	Silica grafted imidazolium ionic liquid with metal ions (Si-IL-Zn)	SO	40 mmol epoxide, 120 °C, 18 bar, 0.5 g catalyst (0.29 mmol Zn) Epoxide:Zn 138:1 6 h	96%	132
		PO	2 h	98%	135
		CHO	24 h	80%	110
Han *et al.* 2011 [56]	Silica grafted imidazolium ionic liquid with carboxyl group (Si-CIL-Br)	SO	40 mmol epoxide, 16 bar, 0.5 g catalyst (0.18 mmol Br) Epoxide:Br 222:1 115 °C, 5 h	96%	213
		PO	110 °C, 3 h	99%	220
		CHO	115 °C, 24 h	82%	182
Aprile *et al.* 2-11 [57]	Multilayered supported ionic liquid catalyst, mlc-SILP, SBA-15-Br	SO	46 mmol epoxide, 100 bar, 150 °C, 3 h Epoxide:cat 100:1	(55%)	55
		PO		(84%)	84
		CHO		(6.4%)	6.4
Xie *et al.* 2010 [58]	Silica supported Glycidyl-BImCl, SBA15-NH$_2$-IL	PO	6.2 mmol PO, 60 bar, 130 °C, 11 h PO:cat 333:1	95%	316
Xie *et al.* 2010 [58]	Polymer supported Glycidyl-BImCl, P-NH$_2$-IL	PO	6.2 mmol epoxide, 60 bar, 130 °C Epoxide:cat 14258:1	95%	13973

			8 h		
		SO	6 h	91%	12975
Dou *et al.* [59]	PEG-supported guanidium bromide, $BrGPEG_{6000}GBr$	SO	15.8 mmol epoxide, 40 bar, 110 °C, 4 h Epoxide:cat 200:1	97%	194
		PO		99%	198
Yang *et al.* 2012 [60]	PEG-supported basic ionic liquid, $BrTBDPEG_{150}TBDBr$	SO	10 mmol epoxide, 120 °C Epoxide:Cat 100:1 1 bar, 8 h	93%	93
		PO	10 bar, 3 h	99%	99
		CHO	10 bar, 20 h	95%[a]	95
Yao *et al.* 2012 [61]	PEG-supported acidic ionic liquid, PEG_{400}-MIM-HSO_4	PO	120 °C, 30 bar, 4 h PO:MIM 17:1	95%	16
Tian *et al.* [62]	PEG-Supported Phosphonium salt, $PEG_{2000}(PBu_3Br)_2$	PO	28.6 mmol PO, 80 bar, 120 °C, 6 h PO:PR_4Br 100:1	99%	99
Gao *et al.* 2012 [63]	Polystyrene-supported Fe(III) containing ionic liquid, PS-MIm $FeCl_4$	SO	10 mmol epoxide, 80 bar Epoxide:Fe 100:1 120 °C, 12 h	84%	84
		PO	100 °C, 6 h	88%	88
		CHO	120 °C, 24 h	7%	7
Zhang *et al.* 2012 [64]	Polystyrene-supported carboxyethylimidazoli	SO	28.6 mmol epoxide, 140 °C, 20 bar Epoxide:CEIMBr 230:1	94%	216

	um bromide, PDVB-CEIMBr		4 h		
		PO	4 h	96%	221
		CHO	24 h	70%	161
Zhang *et al.* 2012 [27]	Polystyrene-supported N,N-dimethylglycinium chloride salt, PS-CQNS	SO	28.6 mmol, 150 °C, 20 bar, 5 h Epoxide:glycinium 100:1	93%	93
		PO		96%	96
Xiong *et al.* 2012 [65]	Cross-linked poly(ionic liquid) gel catalyst	SO	3 mL epoxide, CLPN 0.1 g (10.8% N), 140 °C, 30 bar 24 h	87%	-
		PO	5 h	95%	-
Xie *et al.* 2007 [66]	Polydivinylbenzene-BVImCl copolymer (PSIL)	SO	14.8 mmol, 0.100 g PSIL (0.200 mmol), 110 °C, 60 bar Epoxide:Imid 74:1 7 h	79%	58
		PO	7 h	97%	72
		CHO	72 h	93%	69
Ghazali-Esfahani *et al.* 2013 [67]	Polymeric imidazolium ionic liquid, poly[bisVBIm]Cl	SO	7.4 mmol epoxide, 140 °C, 50 bar Epoxide:Imid 100:1 24 h	67%	67
		CHO	5 days	42%	42
Sun *et al.* 2009 [68]	Polymer supported hydroxylethyl functionalized ionic liquids	SO	0.1 mol, 25 bar Epoxide:OH 62.5:1 120 °C, 6 h	93%	58
		PO	120 °C, 2.5 h	98%	61

		CHO	125 °C, 20 h	80%	50
Dai *et al.* 2010 [25]	Polydivinylbenzene supported hydroxylethyl functionalized ionic liquid	SO	28.6 mmol epoxide, 140 °C, 20 bar Epoxide:Diol 227:1 4 h	99.5%	226
	PDVB-HEImBr	PO	4 h	97.6%	222
		CHO	24 h	72.9%	165
Watile *et al.* 2012 [26]	Polymer supported diol functionalized ionic liquids	SO	25 mmol epoxide, 130 °C, 20 bar Epoxide:Diol 375:1 (based on 3 mmol/g diol in polymer) 1 h	98%	368
		PO	3 h	97%	364
		CHO	15 h	85%	319
Shi *et al.* 2013 [69]	Polymer supported IL (R = CH_2CO_2H)	SO	14.3 mmol epoxide, 130 °C, 25 bar Epoxide:Cat 100:1 6 h	90%	90
		PO	4 h	99%	99
		CHO	18 h	80%	80
Song *et al.* 2013 [70]	Fluorous polymer supported phosphonium catalyst	SO	28.6 mmol epoxide, 150 °C, 80 bar, 8 h Epoxide:Cat 100:1	91%	91
		PO		98%	98
Han *et al.* 2012 [55]	Imidazolium ionic liquid grafted on	SO	40 mmol epoxide, 115 °C, 18 bar	97%	-

	carbon nanotube (CNT-HMImI)		6 h		
		CHO	24 h	83%	-
Roshan *et al.* 2012 [71]	Carboxymethyl cellulose supported butylimidazolium iodide (CMIL-4-I)	SO	42.8 mmol epoxide, 110 °C, 18 bar Epoxide:IL 83:1 4 h	92%	76
		PO	2 h	98%	81
		CHO	8 h	68%	56
Roshan *et al.* 2013 [72]	Quaternized cellulose	SO	42.8 mmol epoxide, 120 °C, 12 bar Epoxide:Cat 250:1 4 h	93%	233
		PO	3 h	97%	243
		CHO	8 h	39%	98
Xiao *et al.* 2005 [73]	Chitosan supported $ZnCl_2$ with [BMIm]Br	PO	143 mmol PO, 110 °C, 15 bar, 1 h PO:Zn:BMIm 2860:1:6 4 h	95%	2717
Sun *et al.* 2012 [74]	Chitosan supported ionic liquid (CS-EMImBr)	SO	120 °C, 20 bar, 4 h Epoxide:Cat 100:1	85%	85
		PO		96%	96
Tharun *et al.* 2013 [75]	Quaternized chitosan	SO	18.6 mmol epoxide, 120 °C, 11.7 bar Epoxide:Cat 62.5:1 6 h	88-89%	55

		PO	6 h	88-89%	55
		CHO	24 h	66%	41
Liang *et al.* 2011 [76]	Cellulose with KI (66:34 wt%)	SO	20 mmol epoxide, 110 °C, 20 bar, 9 h SO:KI 50:1	98	49
Song *et al.* 2012 [77]	Soybean lecithin with KI	SO	20 mmol epoxide, 100 °C, 20 bar Epoxide:KI 80:1 6 h	94%	75
		PO	4 h	98%	78
Song *et al.* 2008 [78]	β-cyclodextrin with KI	SO	20 mmol epoxide, 120 °C, 60 bar Epoxide:KI 40:1 12 h	94%	38
		PO	4 h	98%	39
		CHO	24 h	<3%	-

[a] NMR yield

Amidinium bromides have been successfully used as catalysts in *in situ* prepared ionic liquids (amidinium carbamates) or in acetonitrile.[48] The TONs achieved in this study (e.g. 49.5 for SO to SC) were significantly higher than those obtained in a related study using amidinium bromide and iodides for related reactions in neat epoxide or THF solution, where a maximum TON of 19 was obtained.[79] However, this could be partially due to the different pressures of CO_2 used (25 atm in the first case and 1 atm in the latter). Recently, a very detailed study using *in situ* FT-IR and Raman spectroscopy on similar ionic catalysts for these cycloaddition reactions has been reported.[51] 1,5,7-triaza-bicyclo[4.4.0]dec-5-enium bromide (TBD.HBr) and

1-methyl-3-methylimidazolium iodide ([MMIm]I) were highlighted as being more efficient than Bu_4NBr under identical conditions for the conversion of SO to SC. They noted that (i) the guanidinium cation, $TBDH^+$, was highly active due to its ability to stabilize intermediates *via* hydrogen-bonding and (ii) TBD.HBr is easily prepared compared with imidazolium salts and is therefore an environmentally-friendly catalyst. In a related study a series of substituted acyclic guanidinium salts were studied, where the most active system therein was the one bearing a pendant $-NH_2$ group.[52] Presumably, this increased activity may also be ascribed to the hydrogen-bonding ability of the amine functionality.

Both organic (synthetic polymer and biopolymer) and inorganic (silica, alumina, magnetic nanoparticle) supported ionic liquids have been used as catalysts for these reactions. From the data presented in Table 1 and the discussion below, it is clear that we are still learning about which supports will work best in these reactions and there have been excellent results with both mesoporous silicas and cross-linked polymers. Until support effects are fully understood in this field, it is likely that researchers will continue to learn *via* a trial and error approach. In most cases, recycling studies showed that the catalysts could be re-used at least five times without significant reductions in activities. In terms of man-made support materials for catalysts, imidazolium ionic liquids have been grafted onto carbon nanotubes (CNT-HMImI),[55] and as expected, these materials showed good activity in these reactions. However, cheaper supports such as silicas and polymers are more likely to find widespread use.

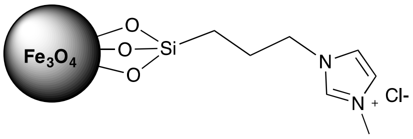


Figure 6 Example magnetic nanoparticle supported ionic liquid catalyst (MNP-1)

In 2009, magnetic nanoparticles were reported as supports for ILs and for MNP-1, Figure 6, conversions of SO were comparable with BMImCl.[53] In some of the earliest studies of silica supported-ionic liquids for cycloaddition reactions, the materials were prepared by simply stirring ammonium or imidazolium salts in a dispersion of silica particles, followed by removal of the solvent under vacuum.[80, 81] As the ionic catalyst was not covalently bound or grafted to the silica surface, it is not surprising that the activity of such catalysts was identical to unsupported analogues as presumably catalysis occurred under homogeneous rather than heterogeneous conditions. At the same time, Sakakura and co-workers first reported the immobilization of phosphonium catalysts on polystyrene (PS) and silica supports.[82] A surprising synergistic, promotional effect was noted for the combination of phosphonium salts with a silica support. Silica alone did not show any catalytic ability for the cycloaddition reactions but the supported catalyst SiO_2-C_3H_6-P(*n*-Bu)$_3$I exhibited reaction rates (normalized per phosphorus atom) 300 times greater than its homogeneous analogue P(*n*-Bu)$_4$I. The bromide version of the supported catalyst was employed in a fixed-bed flow reactor for the conversion of PO. Conversions >80% (99.9% selectivity) for over 1000 h were achieved, which corresponded to a total productivity equivalent to 580 ton PC per month per ton of catalyst. In a related study, phosphonium catalysts grafted onto silica or alumina were screened for catalytic activity.[54] The triphenylphosphonium bromide derivative, Figure 7, supported on mesoporous silica (Si-PPh_3Br) showed the highest activity and could be recycled ten times without significant losses in activity. Imidazolium ionic liquids grafted on silica as catalysts for this reaction were first reported by Han *et al.* in 2009. For allyl glycidyl ether, TON of between 20 and 50 were obtained at 110 °C and 7.5 bar CO_2 pressure in 3 h.[83] In later studies, ionic liquids grafted with silica were used in combination with metal ions with the highest TON (232) for allyl glycidyl ether conversion achieved using Ni salts.[55] A general trend related to the Lewis acidity of the metal centre was ascribed. However, for studying the variation in yield with different epoxides, the Zn containing material (Si-IL-Zn) was used.

Ionic liquids containing acidic carboxyl groups have also been grafted onto silica, with the bromide derivative (Si-CIL-Br), Figure 7, showing good reactivity and achieving a TON four times greater than analogous silica supported ILs with no carboxyl groups.[56] Ionic liquids functionalized with glycidyl groups have been prepared and reacted with amino (NH_2) and carboxyl (COOH) functionalized inorganic and polymer supports.[58] The silica supported materials (SBA15-NH_2-IL) possessed similar activities to the homogeneous glycidyl functionalized ionic liquids. Surprisingly, the polymer-supported analogues (P-NH_2-IL) showed significantly enhanced reactivity with TOF approximately 40 times greater than the homogeneous ionic liquid. It was proposed that this was due to the polymer-based catalyst being more easily dispersed in the epoxide and thus having increased opportunity to interact with the substrate leading to an increased reaction rate compared with the homogeneous and silica-supported versions of this catalyst.

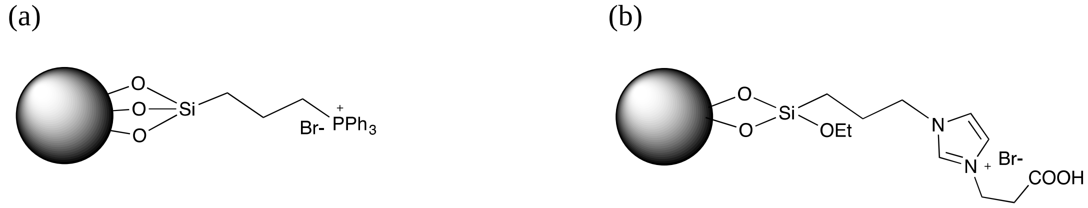


Figure 7 Examples of silica supported (a) phosphonium catalyst, Si-PPh_3Br, (b) carboxyl containing ionic liquid, Si-CIL-Br

Attempts have been made to prepare inorganic-organic composite catalysts. Multilayered covalently supported ionic liquid phases (mlc-SILP) were prepared *via* reaction of bis-vinylimidazolium salts with mercaptopropyl-modified silicas (amorphous or ordered SBA-15) using a thiol-ene reaction (free-radical "click" process).[57] This led to cross-linking of the silica phases with organic, imidazolium salt phases. Analogous organic materials were also prepared using thiol-modified polystyrene (PS). Conversions for the reactions of a range of epoxides were only moderate even with their best catalyst (SBA-15-Br) but were nearly double those achieved using the PS analogues. Disappointedly, significantly higher temperatures and pressures (150 °C, 100 bar) were used in this study compared with other data summarized herein and this may be due to poor accessibility to the active centres by the substrates under more reasonable (lower temperature and pressure) conditions.

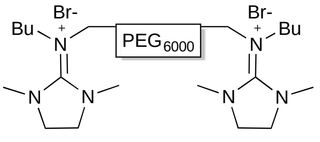


Figure 8 PEG-supported guanidinium ionic catalyst, $BrGPEG_{6000}GBr$

Guanidinium bromide has been supported on polyethyleneglycol (PEG) with a molecular weight of 6000 ($BrGPEG_{6000}GBr$), Figure 8. It was used as a catalyst for the conversion of six different epoxides and could be used for four consecutive reactions with <10% decrease in yields. PEG-supported basic ionic liquids, including $BrTBDPEG_{150}TBDBr$ (TBD = 1,5,7-triazabicyclo[4.4.0]dec-5-ene), have also been used in these reactions.[60] Good TON were obtained even at low pressures of CO_2 and the catalyst could be re-used at least five times. Through NMR and IR studies, it was shown that carbamic acid groups form through reaction of the NH groups and CO_2. Related supported ionic liquids have also been used in aziridine-CO_2 coupling reactions, see below. PEG-supported imidazolium ILs containing an acidic counterion have been used in PO to PC conversion. Although TON for one reaction was relatively low (16), the catalyst could be re-used 9 times maintaining 75-80% yield, which would lead to a total TON over 100.[61] By comparing these results for PEG-supported ionic liquids with N-centered (basic) cations, it is clear that bromide counter ions offer optimum activity for these reactions.

A range of phosphonium salts including the PEG-supported phosphonium bromide $PEG_{2000}(PBu_3Br)_2$ and its PEG-supported ammonium analogue were screened for activity in the carboxylation of PO.[62] Although recycling studies were not reported, the authors state that the polymer could be precipitated upon the addition of ether and this would facilitate any recycling process. In related studies, it was shown that when a lower molecular weight tether was used (PEG_{600}) with PPh_3Br end groups, the catalyst could be used in the sequential synthesis of 2-oxazolidinones/2-imidazolidinones from CO_2, epoxides and either amino alcohols or alkylene diamines.[84] PEG-supported phosphonium halides have also been used with K_2CO_3 in a two step catalytic process of (i) cycloaddition of PO and CO_2 followed by (ii) transesterification with methanol to give dimethylcarbonate (DMC) in up to 99% yield.[85] Yields were improved in the last step by simultaneously removing the DMC *via* distillation. In the same paper, it was reported that $PEG_{6000}(PBu_3Br)_2$ produced 89-99% cyclic carbonate for a range of epoxide/CO_2 cycloaddition reactions.

Commercially available resins based on polystyrene (PS) have been used as a starting point for preparing a wide range of materials including the synthesis of supported ionic liquids. Imidazolium ionic liquids with a $FeCl_4^-$ anion have been supported on PS and the materials showed significantly higher activity compared with the parent chloride ion containing materials, and showed near identical activity to the homogeneous analogue ($[BMIm]FeCl_4$).[63] They were also active in aziridine-CO_2 couplings, see below. Hydroxyl and diol functionalized polymer supported ionic liquids have been prepared *via* grafting imidazolium salts onto Merrifield (PS) resin, Figure 9.[26, 68] Higher yields and shorter reaction times were achieved using the diol-functionalized material. In both studies, the materials could be re-used at least 5 times whilst maintaining >95% yields. Hydroxyl and carboxylic acid functionalized polymer-supported ionic liquids have also been prepared *via* radical polymerization of vinyl substituted imidazolium ionic liquids with divinylbenzene (DVB) as a crosslinking monomer.[69] The resulting polymer-supported ionic liquids were found to be efficient catalysts for cyclic carbonate formation and the catalysts could be re-used five times without any significant loss in reactivity. Hydroxyl-functionalized supported ionic liquids have also been prepared *via* grafting onto cross-linked polydivinylbenzene that was pre-functionalized with amino-propyl imidazole groups at a loading of 1.5 mmol/g.[25] These materials achieved higher TON (165-226) than the hydroxyl functionalized ILs prepared *via* reaction with Merrifield resin but were still significantly less active than the supported diol-functionalized ionic liquids. In related studies, Zhang and co-workers incorporated pyridine moieties into the polymeric support and found that, compared with polymer supported ionic liquids without pyridine groups present, reactivity was enhanced (76% yield compared with 64% under identical conditions).[86] In this same report, computational studies on the role of hydrogen-bond donors within catalyst systems for promoting these cycloaddition reactions were discussed.

An imidazolium ionic liquid covalently supported on a divinylbenzene-crosslinked polymer has been prepared *via* copolymerization of 3-butyl-1-vinylimidazolium chloride (VBImCl) with DVB to give the catalyst PSIL.[66] Good yields for a range of epoxides were seen and these were over double those obtained with a homopolymer catalyst prepared from VBImCl. PSIL could be readily re-used at least four times and SEM images of the polymer showed no changes in morphology upon repeated use. The authors highlighted that the catalyst although insoluble maintains high activity. Imidazolium containing cross-linked polymers have also been prepared *via* a grafting method.[64] The most active catalyst containing a carboxyethyl ($-CH_2CH_2CO_2H$) showed good activity and stability – it could be recycled five times without losses and thus its TON would increase from just over 200 to over 1000. The authors propose that there is synergistic effect between the Brønsted acidic carboxylic acid group and the imidazolium's anion in this case Lewis basic Br^-. Activities for single reactions were not dissimilar to analogous unsupported bifunctional catalysts discussed above.[41] Cross-linked poly(ionic liquid) gels have been prepared from di-imidazolium ionic liquids bearing vinyl groups and cross-linking agents such as ethylene glycol dimethacrylate.[65] They were briefly studied as catalysts for cyclic carbonate formation and exhibited activity similar to other polymer-supported catalysts. A range of vinyl substituted imidazolium ionic liquids were prepared and used as monomers to give polymer-supported ionic liquids, which were used as catalysts in the cycloaddition of CO_2 with electron-deficient epoxides.[67] For the carboxylation of epichlorohydrin, the polymeric catalyst, poly[bisVBIm]Cl (bisVBIm = 1,3-bis(4-vinylbenzyl)imidazolium), could be re-used ten times with only a slight loss in activity.

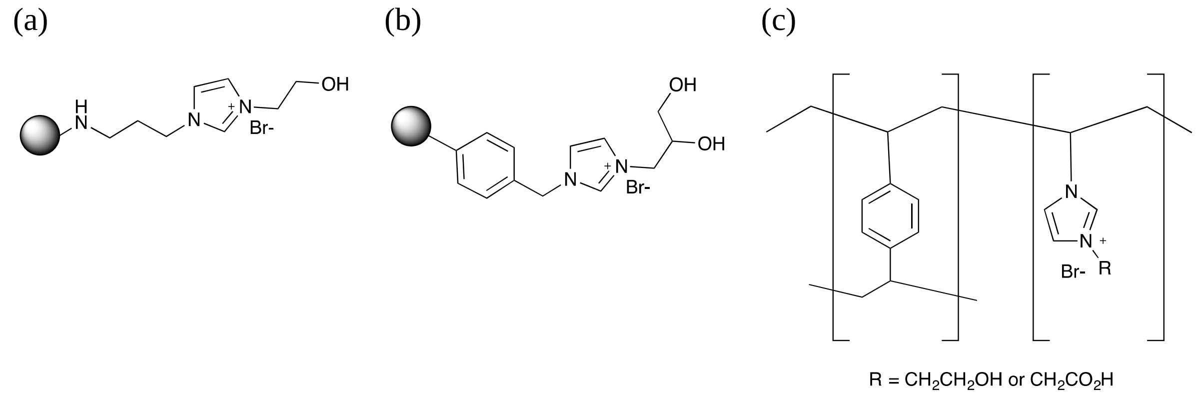


Figure 9 Polymer-supported ionic liquids, (a) hydroxyl functionalized prepared by grafting onto polydivinylbenzene (PDVB-HEImBr), (b) diol functionalized prepared *via* grafting to Merrifield resin,[26] and (c) hydroxyl and carboxyl functionalized prepared *via* copolymerization of vinyl substituted imidazolium salts.[69]

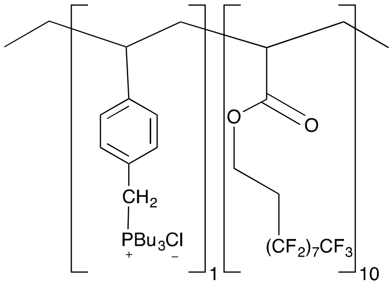


Figure 10 Fluorous polymer-supported phosphonium catalyst

Fluorous polymer supported phosphonium catalysts have also been studied, and could be re-used seven times without any significant loss in activity.[70]

A broad range of catalyst systems for cycloaddition have been developed based on carbohydrates and other natural materials. Chitosan (an -NH_2 containing polysaccharide) has been widely used as a support for metal-containing catalysts.[87] Therefore, it comes as no surprise that it has been used to support $ZnCl_2$ and that this supported zinc complex has been used as a catalyst for cycloaddition reactions in combination with a range of salts as co-catalysts.[73] For PO conversion, the order of reactivity in terms of ionic co-catalyst was [BMIm]Br > Bu_4NBr > [BuPy]Br > [BMIm]Cl, demonstrating that both the cation and anion affect reactivity. Excellent TON and TOF were obtained e.g. PO 2717 h^{-1}, SO 1454 h^{-1} and

CHO 532 h^{-1}. The biopolymer was also found to yield more active catalysts than a synthetic polymer support, poly(*N*-vinyl-2-pyrrolidone) (PVP) and this might be due to interactions of the epoxide with hydroxyl residues within the biopolymer that are absent in PVP. Chitosan has also been reacted with 1-(2-bromoethyl)-3-methylimidazolium bromide and to give CS-EMImBr, which exhibited similar reactivity to related PS supported ionic liquids.[74] It was also more active than quaternized chitosan (chitosan reacted directly with methyl iodide and used as a catalyst) having approximately double the TON in half the time. In another recent study, modified chitosan prepared *via* quaternization reactions using a variety of haloalkanes was used as a catalyst for cycloaddition reactions with a range of epoxides.[75] Initial studies were performed using allyl glycidyl ether and the catalyst prepared using methyl iodide gave the highest product yields (94%), which had also been reported earlier.[88] Unfortunately, in catalyst recycling studies, the yield dropped to 74% by the fourth run. However, for modified cellulose catalysts no such loss in reactivity (re-used 6 times whilst maintaining activity) was observed,[72] perhaps indicating that if a biopolymer supported catalyst is desired in this area maybe cellulose is the one to choose. Although one should note that recycling studies with the former catalyst were performed using allyl glycidyl ether as the epoxide whereas in the latter study propylene oxide was used.

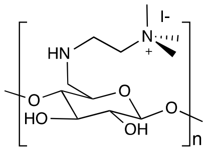


Figure 11 Quaternized cellulose catalyst.

Imidazolium ionic liquids supported on carboxymethylcellulose (CMC) have been prepared *via* the reaction of triethoxysilyl-containing ionic liquids with the carboxylic acid residue of CMC. Of a series of such materials, those containing iodide anions showed the greater reactivity towards CO_2/epoxide cycloaddition reactions. Later results from the same group using quaternized cellulose,[72] Figure 11, showed that greater TONs could be obtained using the simple ammonium containing materials compared to the imidazolium-modified celluloses. TON for reactions using quaternized cellulose were also significantly higher than the simple combination of KI with cellulose.[76] In such catalyst systems, the -OH groups hydrogen-bond with the epoxide prior to ring-opening induced by the iodide ion. In related studies, soybean lecithin (phospholipid) has been used with KI to afford a promising and simple catalyst for cycloaddition reactions.[77] Unfortunately, combinations of lecithin with salts containing other halide anions (Cl^- and Br^-) possessed very little activity for these reactions. In an earlier study, KI was used with β-cyclodextrin as a catalyst system and the catalyst could be effectively recycled five times without loss.[78] Interestingly, the catalyst activity reached a maximum at 60 bar and decreased significantly at higher pressures. This was possibly due to reduced contact between the catalyst and the epoxide in the presence of such a high concentration of CO_2 at elevated pressures. It is also worth noting that this system is more significantly affected by the sterics of the substrate with exceedingly poor conversions obtained for CHO.

Results for cycloaddition reactions using choline chloride-transition metal chloride mixtures

Given the excellent results obtained using hydroxyl-functionalized ionic liquids, we decided to look at choline chloride (ChCl = $[Me_3NCH_2CH_2OH]Cl$) - metal chloride mixtures as catalysts for cycloaddition reactions. These combinations form a class of ionic liquids known as deep eutectic solvents (DES).[89, 90] ChCl can be obtained naturally but is also manufactured on a large scale and is non-toxic. The solubility of CO_2 in choline chloride/urea eutectic mixtures has been studied in detail,[91] and we assumed that CO_2 would also be miscible with the metal-containing mixtures. The syntheses, properties and applications of this class of ionic material has recently been reviewed.[92] During the course of our research, it was shown that $ZnBr_2$ in combination with ChCl could be used as a catalyst for cycloaddition reactions and excellent TONs were obtained.[93] Data for this is shown in Table 3. Five equivalents of ChCl were used per Zn centre. In this report, combinations with $CuCl_2 \cdot 2H_2O$ and $FeCl_3$ gave 5% and 14% yields of propylene carbonate respectively, and in control reactions trace product was obtained with ChCl and 1% yield with $ZnBr_2$ alone. In the study of betaine-derived catalysts described in the earlier section of this review,[38] ChCl was also studied and found to have moderate activity for cycloaddition reactions at higher temperatures and pressures compared with those used in the $ZnBr_2$/ChCl study. It has also been shown that a ChCl-urea eutectic mixture when impregnated into molecular sieves gives an easily prepared supported catalyst for epoxide/CO_2 cycloaddition reactions.[94]

Given our previous experience using cobalt complexes in combination with Bu_4NBr for cycloaddition reactions (TON >2000),[95] and high TOF catalyst systems (TOF >2100 h^{-1}) based on $CoCl_2$ with a range of onium salts,[96] we began our investigations using a cobalt-containing

DES. The metal-containing mixtures were prepared *via* literature procedures[89] to afford liquids or solids with melting points far lower than either of the individual components. A DES based on a 2:1 mole ratio of $CoCl_2{\cdot}6H_2O$:ChCl was studied. Experimental details for our reactions are available in supporting information. After initial reactions using 10 bar CO_2 at 90 °C for 24 h, conditions were optimized (graphs in supporting information) and further reactions were performed using 10 bar CO_2 at 160 °C for 4 h. Increasing CO_2 pressures to 40 bar did not increase conversions. As we were disappointed by our results (Table 2) compared with related studies by Repo and co-workers, Table 3,[96] we noted that their reactions using $CoCl_2/Bu_4NCl$ had been performed in CH_2Cl_2. Our DES was insoluble in CH_2Cl_2 but soluble in CH_3CN. Unfortunately, addition of CH_3CN did not change the yields obtained and all further reactions were performed neat. We then prepared DES containing the other 3*d* transition metal chlorides and screened them for activity in styrene oxide-CO_2 cycloadditions, Table 2. The most active contained Cr(III) and when the SO:Cr ratio was increased to 200:1, conversions of >99% were maintained. The TOF for this system is comparable with the previously reported $ZnBr_2$/ChCl system (data in Table 3). As iron is a favourable metal to use in catalysis because of its low cost and toxicity, we were pleased to see that the Fe(III) system was as active as the Co(III) DES. We repeated reactions using the Fe(III) DES at 120 °C but conversions dropped to 60% indicating that high temperatures are needed to maintain higher TOF for these systems. The one exception in terms of activity was the Cu(II) system. A recent paper has described the use of monometallic and trimetallic copper(II) Schiff base complexes in the production of cyclic carbonates.[97] For ethylene oxide, the trimetallic complex could achieve TON >30 000, whilst for SO TON >3000 were obtained. Therefore, there appears to be no inherent reason why the Cu(II) DES should afford such low yields. Trends for activity in cycloaddition reactions across a series of catalysts with different metal ions have previously been described (supported on silica and for acac complexes).[98, 99] In both cases Ni(II) salts gave the best results, which is related to the Lewis acidity of the metal ions. However, in our hands Cr(III) exhibited superior reactivity which we assign to the less viscous nature of this particular DES. The reactions catalyzed by the metal DES described herein are heterogeneous in nature (the DES is insoluble in SO) and the Cr(III) DES can form a thinner, higher surface area film within the reactor compared with the other DES. Further studies are needed to confirm this conclusion and to understand the lower reactivity of the Cu(II) DES.

Table 2 Cycloaddition of styrene oxide with carbon dioxide using ChCl-metal chloride mixutres.

Catalyst	Yield (Conv.)	TON (moles SC per mole metal ion)
ChCl[a]	- (4%)	-
$CoCl_2 \cdot 6H_2O$[a]	- (4%)	-
ChCl + 2 $CoCl_2 \cdot 6H_2O$[a]	92% (93%)	120
ChCl + 2 $CoCl_2 \cdot 6H_2O$[b]	96% (97%)	134
ChCl + 2 $CrCl_3 \cdot 6H_2O$[b]	99% (>99%)	139
ChCl + 2 $MnCl_2 \cdot 4H_2O$[b]	85% (87%)	119
ChCl + 2 $FeCl_3$[b]	94% (95%)	132
ChCl + 2 $NiCl_2 \cdot 6H_2O$[b]	91% (94%)	127
ChCl + 2 $CuCl_2 \cdot 2H_2O$[b]	35% (38%)	49

[a] Reaction conditions: CO_2 10 bar, 90 °C, 24 h, SO:Catalyst 130:1

[b] Reaction conditions: CO_2 10 bar, 160 °C, 4 h, SO:Metal 140:1

Table 3 Selected catalysts and reaction data for cycloaddition reactions for comparison with choline chloride catalyst systems described herein

Catalyst	Reaction Conditions	Yield (Conv.)	TON	Ref
Quaternized glycine, $(HO_2CCH_2NMeH)I$	SO:Cat 46.5:1 18.6 mmol SO, 120 °C, 12 bar, 2 h	79% (80%)	36.7	[39]

Choline chloride (ChCl) with $ZnBr_2$	140 mmol epoxide, 110 °C, 15 bar; Epoxide:ChCl:Zn 100:1:0.2 SO 12 h	98%	490	93
	PO 1 h	99%	494	
	CHO 24 h	95%	475	
ChCl	10 mmol PO, 80 bar; PO:ChCl 40:1 140 °C, 8 h	83%	33	38
ChCl/Urea/molecular sieves (6.7 nm)	41 mmol epoxide, 110 °C; Epoxide:ChCl 100:1, CO_2:PO 1.67:1 SO 5 h	95%	95	94
	PO 4 h	99%	99	
	CHO 22 h	80%	80	
$CoCl_2/Bu_4NCl$	SO:Co:Bu_4NCl 2000:1:4 40 mmol SO, 0.5 mL CH_2Cl_2, 120 °C, 10 bar, 1 h	n.r.	1031	96
	PO:Co:Bu_4NCl 2000:1:4 40 mmol SO, 0.5 mL CH_2Cl_2, 120 °C, 15 bar, 1 h	n.r.	2223	96
	CHO:Co:Bu_4NCl 4000:1:4 40 mmol SO, 0.5 mL CH_2Cl_2, 120 °C, 15 bar, 1 h	n.r.	42	96
$Ni(acac)_2$	SO:Ni:Et_4NBr 100:1:1 10 mmol SO, 50 °C, 50 bar, 4.5 h	97%	97	99
$Co(acac)_2$	SO:Co:Et_4NBr 100:1:1 10 mmol SO, 50 °C, 50 bar, 4.5 h	60%	60	99

n.r. = not reported

Oxidative carboxylation of alkenes to yield cyclic carbonates using ionic catalysts

A more efficient way to produce cyclic carbonates might be to employ alkenes as starting materials and form the required epoxide *in situ* for the subsequent cycloaddition reaction with CO_2. Progress in this area using ionic catalysts or co-catalysts is summarized in

Table 4.

Table 4 Summary of reaction conditions and yields for alkene conversion to cyclic carbonates using ionic catalysts/co-catalysts

Reference	Ionic Component	Alkene	Reaction Conditions	Yield (Conv.)	TON
Sun *et al.* 2004 [100, 101]	Bu_4NBr	Styrene	Bu_4NBr:Styrene 1:9 [O] = TBHP[a] 80 °C, 150 bar, 6 h	33% (74%)	3
Sun *et al.* 2005[102]	$Bu_4NBr/ZnBr_2$	Styrene	$Bu_4NBr:ZnBr_2$:Styrene 2:1:39 5 wt% Au/SiO_2 (0.1 g per 17.3 mmol styrene) [O] = CHP[b] 80 °C, 10 bar, 6 h	43% (75%)	8.5 per NBu_4
Eghbali and Li 2007 [103]	Bu_4NBr	Styrene	Bu_4NBr:alkene:DBU 1:10:1.3 [O] = H_2O_2(aq) 45-55 °C, 17-20 bar, 15 h	70% (89%)	7
		4-$NaSO_3$-styrene		89% (98%)	9
Ono *et al.* 2007 [104]	$Zn[EMIm]_2Br_4$ in $[BMIm]BF_4$	Styrene	(i) MTO[c]:Styrene 1:50 Styrene 2 mmol, UHP 2.2 mmol [O] = UHP[d] 30 °C, 2 h (ii) Zn:Styrene 1:50	83% (>99%)	41.5

			110 °C, 30 bar, 2 h		
Wang *et al.* 2008 [105]	Bu_4NBr	Styrene	Bu_4NBr:alkene:$Na_2H_5P(W_2O_7)_6$ 35:100:1 [O] = H_2O_2(aq) 4 equiv. 50 °C, 24 bar, 12 h	57% (79%)	57[e]
		4-CH_3O-styrene		83% (100%)	83[e]
		1*H*-Indene		82% (98%)	82[e]
Wang *et al.* 2009[106]	$Bu_4NBr/ZnBr_2$	Styrene	Bu_4NBr:Zn:Styrene 2:1:39 0.024 mmol Au/Fe$(OH)_3$ per 17.3 mmol styrene [O] = TBHP[a] 80 °C, 40 bar, 4 h	43% (90%)	310 per Au; 9 per NBu_4
Bai et al. [107]	Bu_4NI	Styrene	Ru:Bu_4NI:alkene 1:2:25 in CH_2Cl_2 [O] = O_2 30 °C, 5 bar O_2, 11 bar CO_2, 40 h	76% (76%)	19 per Ru; 9 per NBu_4
Chen *et al.* [108]	Bu_4NBr	Styrene	Bu_4NBr:Alkene:Mo 50:1000:1 [O] = TBHP[a] 100 °C for 1 h for epoxidation; 140 °C for 1 h and 30 bar CO_2 for cycloaddition	68%	680 per Mo; 14 per NBu_4
		1-octene		83%	830 per Mo; 17 per NBu_4
		Allyl chloride		45%[f]	450 per Mo; 9 per NBu_4
		Cyclohexene		33%[f]	330 per Mo; 7 per NBu_4

[a] TBHP = *tert*-butyl hydroperoxide; [b] CHP = cumene hydroperoxide; [c] MTO = methyltrioxorhenium (oxidation catalyst); [d] UHP = urea hydrogen peroxide; [e] TON calculated per mole oxidation catalyst, per mole Bu_4NBr value would be 2 or less; [f] unoptimised conditions.

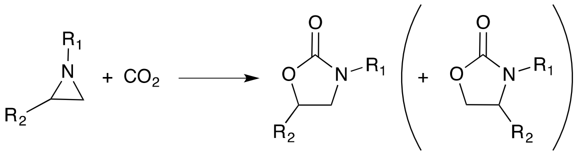
As can be seen in

Table 4, non-metal catalyzed processes have only obtained low TON to date using Bu_4NBr as the ionic component and therefore bromide ions in the redox side of the process. [100, 101, 103] A one-pot multistep process for styrene carbonate has been described using methyltrioxorhenium (MTO) as the catalyst for oxidizing styrene to styrene oxide and a zinc-containing ionic liquid catalyst for the carboxylation reaction.[104] Good yields and moderate TON were achieved for this metal catalyzed process. In an earlier study, gold nanoparticles on silica (Au/SiO_2) had been used as the oxidation catalyst with cumene hydroperoxide as the oxidant,[102] but yields were significantly lower. One of the keys to high yields of styrene carbonate in the work of Ono *et al.* was performing the two steps at different temperatures, as the typically used peroxide oxidants are not stable at high temperatures whilst the cycloaddition reactions require high temperatures. Therefore, the use of flow chemistry in this area might provide opportunities for further improvement as sections of tubular reactors could contain different supported catalysts at different temperatures.

One of the most exciting results to date in this area used dioxo(tetraphenylporphyrinato)ruthenium(VI) as an aerobic oxidation catalyst. As far as we are aware, this is the only example of a system that does not use peroxide oxidants in this two step transformation. Unfortunately, although good yields are obtained, long reaction times are required.[107] In this study, six different alkenes were converted to carbonates (yields 28-78%) thus indicating much promise for the application of aerobic catalysis in this process. Another recent example used $MoO_2(acac)_2$ with TBHP in the oxidation reactions and excellent TONs were obtained.[108] A range of alkenes could be converted and reaction times for each step were generally short. As in earlier work,[104] it was key to optimize each of the individual steps to achieve a satisfactory outcome for the overall process.

CO_2 –aziridine coupling using ionic catalysts

Products of this reaction (Scheme 2), oxazolidinones, are heterocyclic compounds and therefore, this CO_2-utilization reaction will afford high value starting materials for organic synthesis especially if the selectivity towards one regio-isomer is preferred. Reaction data are summarized in Table 5.



Scheme 2. Aziridine and CO_2 coupling reaction. (Minor regio-isomer shown in parentheses).

As with epoxide-CO_2 cycloaddition reactions, some readily available catalysts have been used. For example, α-amino acids yield oxazolidinones in good yields with excellent regioselectivities.[109] 1-butyl-4-aza-1-azaniabicyclo[2.2.2]octane bromide, [C_4DABCO]Br, was prepared and used as an efficient, recyclable catalyst for aziridine-CO_2 coupling reactions.[110] In the same paper, data for [BMIm]Br and some other ionic liquids are also reported. Excellent yields were obtained for ten of the thirteen oxazolidinones prepared. The reaction was found to be strongly pressure and temperature dependent. For example, yields of around 85% at 60 bar CO_2 pressure were found to decrease to 10-15% when the pressure was reduced to 10-20 bar. The same group later studied protic onium salts as catalysts in these reactions.[111] Pyridinium iodide, [HPy]Im, was identified as the superior catalyst and used in the conversion of eleven aziridines. Excellent regioselectivity was achieved in all cases and yields >90% were obtained for eight oxazolidinones. Notably, the reaction times required using this catalyst were significantly shorter than those needed for [C_4DABCO]Br but this might be due to the higher catalyst loading used. Also, [HPy]Im could be re-used four times and activity was maintained.

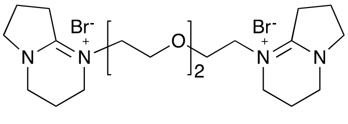


Figure 12 Polymer-supported ionic liquid catalyst, $BrDBNPEG_{150}DBNBr$

A number of polymer supported ionic catalysts have been used in this reaction, which has facilitated catalyst recycling. PEG-supported -NBu_3Br was used in the coupling of CO_2 with fifteen different aziridines and yields of 49-99% were obtained with low catalyst loadings

0.25%.[112] Oxazolidinones were obtained with excellent regioselectivity (86-100%). More recently, a low molecular weight PEG was used to supported -DBNBr catalysts, Figure 12, DBN = 1,5-diazabicyclo[4.3.0]non-5-ene.[113] Good yields could be obtained for a range of oxazolidinones and the catalyst was readily recycled whilst maintaining its activity. Merrifield resin was used as a scaffold to prepare polymer supported diol functionalized ionic liquids for use in these reactions.[114] Eleven different aziridines were converted with the reactions proceeding well at room temperature under solvent free conditions and the products were obtained with excellent regioselectivity (92-99%). Polystyrene supported imidazolium ionic liquids with an $[FeCl_4]^-$ were prepared and used in both epoxide- and aziridine-CO_2 coupling reactions.[63] Good yields were obtained for both types of reaction albeit relatively high temperatures, pressures and long reaction times were required compared with other catalyst systems.

Table 5 Selected samples of reaction data for ionic catalyzed aziridine-CO_2 coupling reactions

Reference	Ionic catalyst	Aziridine	Reaction Conditions	Yield (Conv.)	TON[b]
Sudo *et al.* 2003[115]	Bu_4NBr	R_1 = H, R_2 = Ph	Aziridine:Bu_4NBr 20:1 THF, 25 °C, 1 atm, 24 h	95%	19
Yang *et al.* 2010[110]	$[C_4DABCO]Br$	R_1 = Et, R_2 = Ph	Aziridine:IL 100:1 90 °C, 60 bar 3 h	85% (99%)	85
Yang *et al.* 2011[111]	[HPy]I	R_1 = Et, R_2 = Ph	Aziridine:IL 33.3:1 100 °C, 50 bar 15 min	97% (99%)	32
Du *et al.* 2008 [112]	$PEG_{6000}(NBu_3Br)_2$	R_1 = Et, R_2 = Ph	Aziridine:IL 400:1 100 °C, 80 bar 10 min	89%	356
		R_1 = Bn, R_2 = Ph	45 min	99%	396

Zhao *et al.* 2013 [113]	BrDBNPEG$_{150}$DBNBr	R_1 = Et, R_2 = Ph	Aziridine:IL 100:1 120 °C, 30 bar, 2 h	96% (96%)	96
Watile *et al.* 2011[114]	Polymer supported diol functionalized ionic liquids	R_1 = Et, R_2 = Ph	Aziridine:IL 67:1 25 °C, 50 bar, 3 h	(100%)	67
Gao *et al.* 2012 [63]	PS-MIm FeCl$_4$	R_1 = Et, R_2 = Ph	Aziridine:IL 100:1 100 °C, 80 bar, 26 h	84% (99%)	84

Conclusions

Ionic liquids have been widely studied for the cycloaddition of CO_2 with epoxides since the first report of their applicability in such reactions during 2001. During the past eight years, since the last review of this field, tremendous advances have been made in both the fundamental aspects of such catalyst systems where insight has been obtained from combined experimental and computational approaches, and in applied aspects such as the development of flow methods, which have the potential to significantly improve space-time-yields for such processes. Relatively simple combinations of metal salts and onium salts, including choline chloride, often afford highly active catalyst systems where the individual components possess zero or very little activity. In the design of ionic catalyst systems for this reaction, there are a number of synergistic effects that lead to enhanced activity including the combination of Lewis basic anions (e.g. Br^-) with hydrogen-bonding functional groups (e.g. -OH, -COOH). The use of supported-ionic liquids for these reactions has grown but trends in the reactivity of such materials are less well understood than their homogeneous analogues. For example, it is not clear whether one type of support material (silica, PEG, PS or biopolymer) affords more active, longer lived and more readily re-used catalysts. However, in most cases TON and TOF are very similar to their homogeneous versions and therefore, one can conclude that supports generally do not have an adverse effect on the reactivity of such catalysts in these reactions. The use of ionic catalysts in the related processes of oxidative carboxylation of alkenes and carbon dioxide-aziridine coupling reactions remains much less widely explored. Therefore, significant opportunities remain for the development of new catalytic systems based on ionic liquids for carbon dioxide activation.

Acknowledgements

We thank NSERC, the Canada Foundation for Innovation, the Provincial Government of Newfoundland and Labrador, and Memorial University for financial support. K.A.K. and L.E.T. thank WISE Summer Student Employment Program.

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