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INVITED REVIEW PAPER

Catalytic applications of immobilized ionic liquids for synthesis of cyclic carbonates from carbon dioxide and epoxides

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Abstract−The catalytic applicability of ionic liquids immobilized on various support materials such as silica, polystyrene and biopolymers in the cycloaddition of carbon dioxide with epoxides is reviewed in this work. Comparisons of the catalytic efficiency of these various catalysts have been done from the aspect of turnover number and reusability. The studies revealed that ionic liquids or support materials possessing hydrogen bonding capable groups exhibited enhanced catalytic activity towards cyclic carbonate synthesis. Moreover, the increased quest towards environmentally benign materials has renewed the search for biocompatible materials as support for ionic liquids.

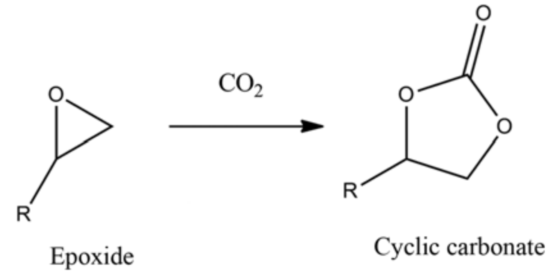
Key words: Ionic Liquids, Carbon Dioxide, Epoxides, Cyclic Carbonates, Immobilization, Silica, Polystyrene, Biopolymer

INTRODUCTION

Since the advent of the Industrial Revolution, atmospheric concentrations of various pollutants have increased exponentially as an inevitable result of the emissions due in part by the growth of heavy industries. Increased environmental concern associated with chemical syntheses has fuelled the quest for greener processes. Therefore, rationally designed chemical technologies that can meet growing global energy demands by effectively utilizing the available renewable resources have become one of the regularly expanding areas of contemporary research. Needless to say, CO_2, a nontoxic gas, has become detrimental owing to its unacceptable levels of increase, resulting in global climatic changes—a direct consequence of global warming.

As experts in various fields discuss the potential of carbon capture and storage (CCS) technologies, the utilization of CO_2 as a chemical feedstock is attracting renewed and rapidly growing interest, evoking the possibility of various research scientists working together toward creating solutions that address environmental concerns. The existing approaches whereby huge quantities of CO_2 are collected by the CCS framework could theoretically function as an unlimited supply of this nontoxic gas and provide a carbon feedstock that could be chemically transformed into a wide range of industrially important products. However, the nonreactive nature of CO_2 demands either harsh/uneconomical reaction conditions or a judicious choice of catalyst or both for effective organic transformations. In the late 1960s, Inoue proposed the possibility of synthesizing cyclic/polycarbonates from CO_2 using epoxides as a high-energy substrate (Scheme 1). Since then, a plethora of catalytic systems of wide genre that fulfill various criteria have been successfully deployed for the effective transformation of CO_2 into cyclic/polycarbonates [1-6].

Likewise, ionic liquids (ILs) have garnered tremendous attention in the past two decades as evidenced by their increased popularity as an environment-friendly reaction medium, i.e., as "green" alternatives to volatile organic solvents (VOCs). This claim usually rests on the fact that ILs are generally nonvolatile under ambient conditions and hence do not contribute to damaging atmospheric photochemistry. Another fascinating feature of ILs is their tunability with respect to polarity by choosing appropriate pendant alkyl chains and counteranion employed, whereby an array of substrates can be dissolved. More than 6000 studies have been published in the past decade relating to IL applications, of which one of the most promising is its catalytic applicability in various organic transformations [7-10]. Even though the above figure provides obvious evidence of the potential of ILs, its application toward catalytic CO_2 fixation has been fraught with limitations: i) requirement of large amounts of this expensive material; ii) tedious separation of/from the organic products; iii) the viscous nature and air/moisture sensitivity of most room-temperature ILs (RTILs), making its handling difficult; and iv) lack of biodegradability data, rendering the disposal of waste ILs difficult.



Scheme 1. General scheme of cyclic carbonate synthesis.

To develop new materials along with the need to overcome the aforementioned challenges has pushed the contemporary IL-based research to the heterogenization of the active species onto stable and durable supports. The immobilization of these highly active ILs in the porous framework of a support material mitigates the known limitations by improving mass transfer (owing to the high viscosity of ILs) and renders them reusable (from a practical point of view), where the immobilized species would offer the same degree of flexi-

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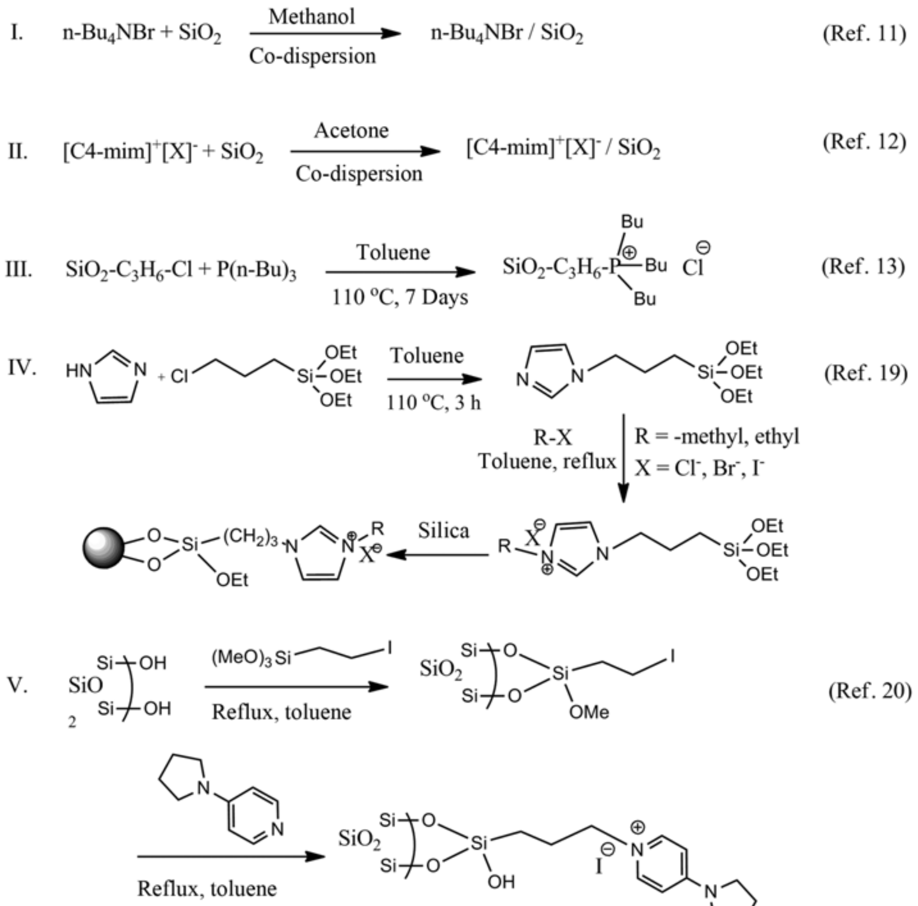
bility as their homogeneous counterparts by varying their alkyl chain length and nucleophilic anions. The ILs (mono/multilayer) have been immobilized over either specifically designed supports (MCM-41, SBA-15, polystyrene (PS), etc.) or naturally available biopolymers (chitosan, cellulose, etc.). Regardless of the focus of the individual researcher, heterogenization of the active species has led to the development of quite a handful of useful techniques. Supported IL-phase catalysis (SILPC) and supported IL catalysts (SILC) are the two broadly developed and employed techniques among them. Suffice it to mention that, SILPC techniques involve an effective heterogenization of homogeneous catalysts using complexes, which are dissolved in a small quantity of liquid-phase IL, dispersed in the form of an islet or a film on the surface of a support. SILCs, as the name suggests, are ILs immobilized on a solid support by either covalent grafting or impregnation. The support materials used for IL catalysis in the cycloaddition of CO_2 with epoxides can be broadly classified as inorganic and organic. The majority of the inorganic support materials are composed of silica in its various forms such as commercial and amorphous (*vide infra*). Our coverage in this review is topical and focuses on the various types of SILCs developed in the last two decades for the cycloaddition of CO_2 and epoxides. Note that the chemical fixation of CO_2 is only a subset of the wide spectrum of applications for which SILCs are employed in the organic transformations. Given the success highlighted in this short review, the SILC-based cyclic carbonate synthesis strives to continue as a dynamic field of research.

IMMOBILIZED IONIC LIQUIDS

1. Inorganic Support Materials (Silica-supported Ionic Liquids) (Scheme 2)

Silica is one of the most abundant materials in the earth's crust. From the chemist's point of view, its nontoxicity along with its ready abundance and ease of surface functionalization justifies its choice as an inorganic support for ILs. In 2006, Wang et al. [11] reported the heterogenization of quaternary ammonium moieties onto the silica gel by simple codispersion methods. In the subsequent work [12], they immobilized the imidazolium ILs to silica gel *via* physical interaction and investigated their catalytic efficiencies in the cycloaddition of propylene oxide (PO) with CO_2 to yield propylene carbonate (PC). Under supercritical CO_2 pressures, the reaction proceeded nearly to completion in the temperature range 150-160 °C in 4-5 h of reaction time; the catalytic activities are detailed in Table 1. Concurrently, Takahashi et al. [13] reported that a covalently immobilized phosphonium salt on a silica gel acted as an effective heterogeneous catalyst, which worked even at 100 °C. By carrying out control experiments with PS-supported phosphonium salts, they proposed the possibility of a cooperative catalysis between the acidic silanol groups on the silica support and the basic nucleophile, also known as synergism. The hydrogen bonding between the epoxide

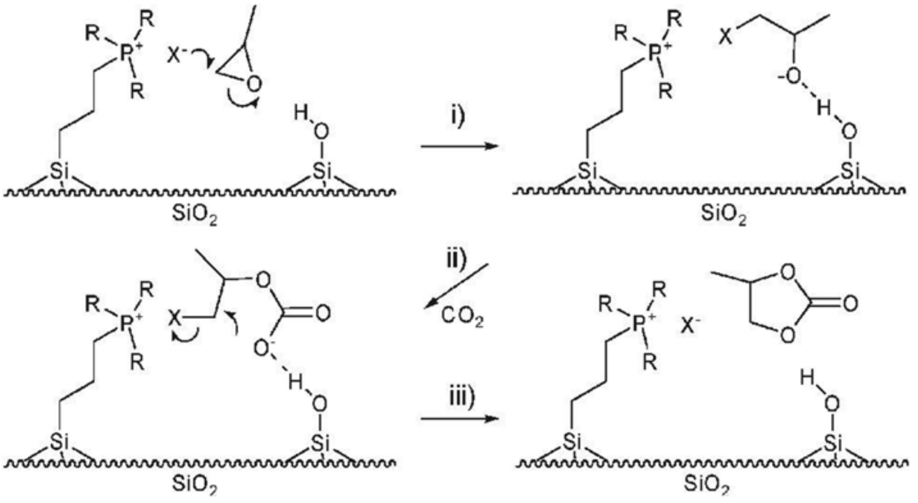


Scheme 2. Representative examples of synthesis of different silica supported ionic liquids.

Table 1. Performance of silica supported ILs in the cyclic carbonate synthesis

Type of support/ Catalyst name	Surface area (m^2/g)		IL^a (mmol/g)	Epoxide	Reaction parameters				Cyclic carbonate		TON	Ref
	Pristine	Immobilized			Catalyst (mol%)	Temp. (°C)	Pressure (MPa)	Time (h)	Yield (%)	Selectivity (%)		
Silica gel/nBu$_4$NBr	550	217	-	PO	1	120	8	10	30	90	30	11
Silica gel/[C4-mIm]$^+$X$^-$	550	239	-	PO	1.8	120	8	4	60	90	37.5	12
Silica gel-C$_3$H$_6$-P(n-Bu3)I	-	-	0.21	PO	1	120	10	-	-	-	-	13
Silica gel/GIL-3	500	131	1.30	PO	1.8	120	2	4	95	100	52.7	22
Silica gel/IMIS-3	500	-	0.36	PO	0.4	110	0.86	3	99	100	212	19
Silica gel/CILBr-Si	500	-	1.30	PO	1.6	110	1.26	3	99	99	60.9	25
Silica gel/Si-IL-Zn	500	-	0.58	PO	0.7	110	1.76	2	98	99	136	24
Clay/TDAC-MMT	28	125	0.88	PO	0.65	120	1.27	3	67.9	81.3	104	26
Sol-gel silica/Im-IL-2	-	0.39	1.86	AGE	2	80	1.76	6	91.6	95.6	41.9	14
MCM-41/THA-MS41	-	-	0.10	AGE	0.25	110	0.75	10	61.5	88.5	63.1	15
MCM-41/nBImBr-MS41	614	-	2.93	AGE	-	110	1.65	6	97.5	98.2	26.6	16
Aerosil 300/SiO$_2$-1(I)	300	-	0.85	SO	0.86	100	0.1	20.5	89	98	103	21

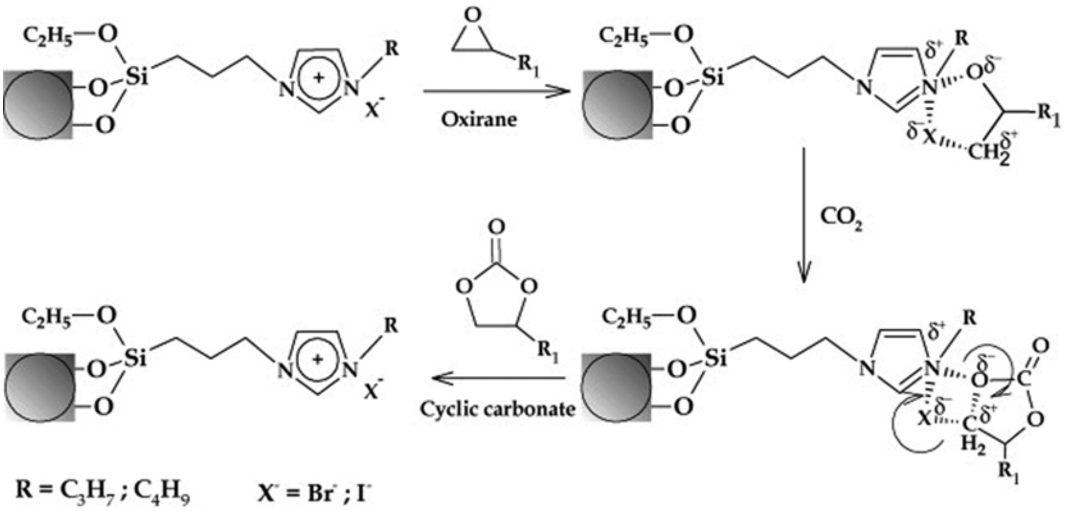
^{a}Amount of immobilized IL onto support



Scheme 3. Mechanistic aspect of co-operative effect of silanol hydroxyl and the ionic liquid in CO$_2$-epoxide cycloaddition [13].

oxygen and the silanol -OH groups played a key role in stabilizing the ring-opened complex (Scheme 3). The kinetic data indicated that the pseudo-first-order rate constant of the catalyst relative to the phosphorous atom was approximately 300 times larger than that of the corresponding homogeneous catalysts. Moreover, a fixed-bed flow reactor experiment using the silica-supported phosphonium halide catalyst reportedly showed a productivity of 580 ton PC per month per ton catalyst.

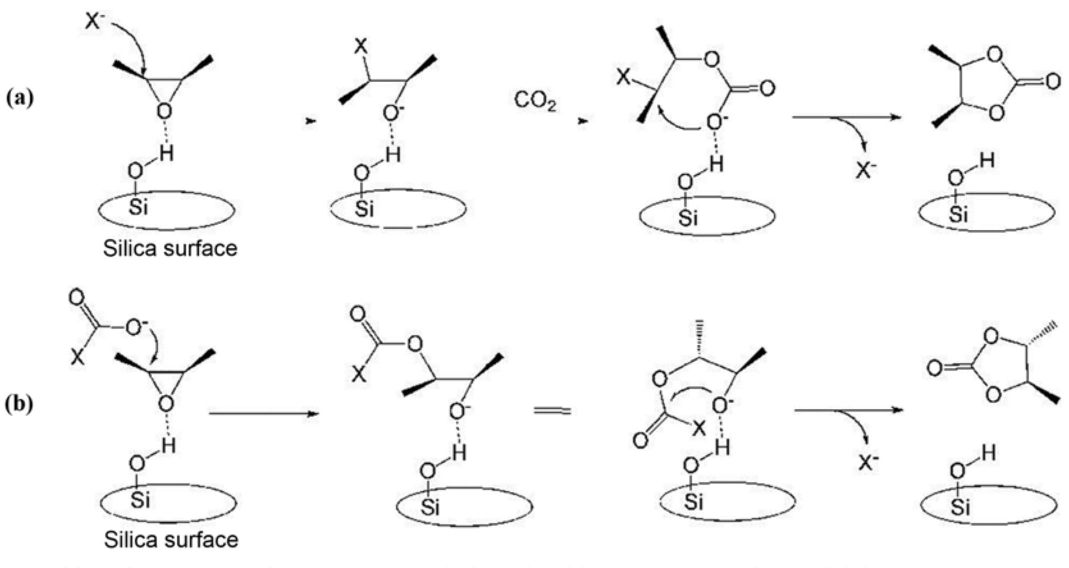
The following years saw the successful deployment of numerous ILs immobilized/grafted onto commercial and amorphous silica through various synthetic strategies in a number of reports by our group [14-19]. A silica-supported imidazolium IL synthesized by a sol-gel method [14] was reported to effectively catalyze the cycloaddition of allyl glycidyl ether (AGE) with CO$_2$ at pressures as low as 0.86 MPa. Utilizing the self-assembling capability of tetraethyl orthosilicate (TEOS) with 3-chloropropyltriethoxysilane (CPTES), ordered mesoporous hybrid structures of silica such as MCM-41 were synthesized and successfully immobilized by the quaternary ammonium (R$_4$Cl-MS41) [15] and imidazolium ILs (RImX-MS41) [16] by Udayakumar et al. The MCM-41-supported ILs displayed uniform pores and higher surface areas with long-range order and better distributed functionality than the materials produced using the postgrafting techniques and were reusable without affecting the long-range order. Further reports by the same group [17,18] described methods without the need of expensive pore-directing agents required during the synthesis of the MCM-41 support; instead, IL-functionalized mesoporous silica (IFMS) was synthesized under template-free conditions. The IFMS not only precluded the use of expensive templates and large amounts of organic solvents for the preparation of mesoporous organic-inorganic hybrid catalysts, but also exhibited a TOF nearly three times higher than those reported for R$_4$Cl-MS41 and RImX-MS41. The catalyst structure-catalytic



Scheme 4. Mechanism of cycloaddition with MCM-41 supported ionic liquid catalyst [18].

activity dependence was proposed through a plausible mechanism where epoxide ring-opening by the cation and anion of the supported IL was considered to be the (reversible) rate-determining step (Scheme 4).

Although these pioneering studies demonstrated an attractive protocol for the synthesis of silica supports for IL immobilization, highly acidic or basic conditions were still unavoidable. To reduce the tediousness and cost of synthetic procedures, Han et al. [19] grafted silyl ether-containing imidazolium ILs to the commercial silica (IMIS) by co-condensation. The methodology was straightforward, and various ILs with different alkyl chain lengths and anions were uniformly distributed over the silica surface. Similar to the previously discussed silica-supported ILs, IMIS also exhibited a progressive relationship to the applied CO$_2$ pressure. The dependence of the anion nucleophilicity to the catalytic activity was evident from the observed trend, I$^-$>Br$^-$>Cl$^-$, for I$^-$ being the strongest and best leaving nucleophile. Additionally, a regular increase in the activity with increased bulkiness was observed and explained; the bulky alkyl groups tend to dislodge the nucleophilic anion toward the epoxide, thereby activating the ring opening. An investigation into the cocatalytic effects of zinc salts in the IMIS showed interesting results: while the catalytic activity of IMIS-Zn with Cl$^-$ increased in comparison to the nonzinc-grafted IMIS, an apparent decrease in the activity was found with other anions, Br$^-$ and I$^-$. This was explained on the basis of the lower charge-to-volume ratio of the supposedly formed [ZnBr$_4$]$^{2-}$ and [ZnI$_4$]$^{2-}$ than that of [ZnCl$_4$]$^{2-}$ in the IMIS-Zn material. The competing effects of the silica material surface area and its pore size in deciding the amount of the grafted IL, and eventually the catalytic activity, were clearly explained. When silica with smaller pore sizes was used, the diffusion effects of the substance played a key role in IL grafting. Even though the IMIS series of catalysts were found easily furnishable and displayed a regular trend in activity with respect to the composition (alkyl chain length and anion type), the amount of the supported ILs reached a maxi-

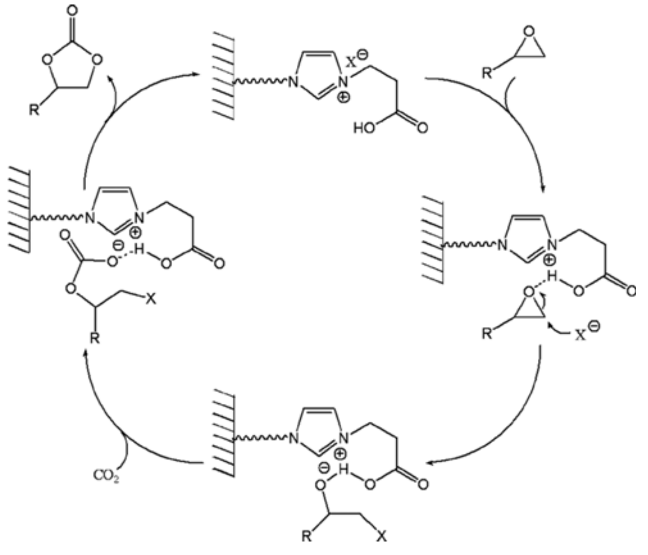


Scheme 5. Cycloaddition of propylene oxide with carbon dioxide with silica supported amino pyridinium salts catalysts. Path (a) Halide mediated ring opening of epoxides. Path (b) CO$_2$ initiated ring opening of epoxides [20].

mum of 1.32 mmol of IL/g silica only, while the MCM-41-immobilized ILs (RImX-MS41) reported by Udayakumar et al. [16] consistently achieved an immobilized amount of 2.3-2.93 mmol IL/g support. In the same period, Motokura et al. [20] reported a surprising result while examining the synthesis of cyclic carbonates at atmospheric CO_2 conditions using a novel SiO_2-supported aminopyridinium halide. The choice of aminopyridinium halides was justified by its ease of synthesis and stability under air compared to imidazolium species. Most of the terminal epoxides examined were found to undergo cycloaddition with CO_2 in approximately 90% yields at 100 °C and 1 atm CO_2 over an extended reaction time of 8-24 h. The retention of configuration by both *cis*- and *trans*-2,3-epoxybutane in the cycloaddition through the acid-base cooperative mechanism as proposed by Paddock and coworkers [21] was examined with the SiO_2-n(X) catalyst (Scheme 5). It was found that the *cis*/*trans* ratio of the carbonate products were 91:9 for *cis*-2,3-epoxybutane and 3:97 for *trans*-2,3-epoxybutane, showing the retention of configuration with SiO_2-n(X); the probable sequence of events based on the stereochemical outcome suggests a double inversion at the carbon center, whereas the ring opening by the activated CO_2 (path B) seems to be a minor pathway (Scheme 5).

The catalytic activity in the SiO_2-n(X)-mediated catalysis also followed the order of stronger nucleophilicity: $I^- > Br^- > Cl^-$. Zhang et al. [22] reported the synthesis of commercial silica-grafted silyl imidazolium ILs strikingly similar to Han et al. [19]. The IL concentrations immobilized on the commercial silica in the two reports were nearly identical (1.3 mmol IL/g). Interestingly, Dharman et al. [23] summarized the physicochemical properties of the immobilized ILs (imidazolium) on different silica supports such as commercial and amorphous silica (MCM-41 and SBA-15), concluding that MCM-41 exhibits the highest loading capacity of ILs, reaching as high as 2.93 mmol IL/g support. The study demonstrated the effect of the silica support structure on the cycloaddition of phenyl glycidyl ether (PGE) in a microwave reactor. The results show that supports with a higher pore diameter, D_p (>4 nm, calculated from N_2 adsorption using the BJH method) yielded high conversions and selectivities irrespective of the surface area. In another study by Han et al. [24], transition metals such as Ni, Co, Cu and Mn in their divalent chloride salt forms were found to enhance the catalytic activity of IMIS in the AGE-CO_2 cycloaddition, the order of activity being Ni>Co~Cu>Mn. This reaction mode uses a different approach in which the metal coordination to the epoxide oxygen, considered crucial, was used to explain the efficacy of the IMIS-metal salt catalyst.

Even though the positive influence of the hydrogen bonding groups in the CO_2-epoxide catalysis was proposed as early as 2005 by Takahashi et al. [13], the incorporation of the carboxyl functional moieties to effectuate a more pronounced hydrogen bonding interaction was only recently realized by Han et al. [25] in 2011. The carboxyl-possessing imidazolium ILs (CILs) were successfully grafted onto the commercial silica; the resulting CILs (TON 170) were found to have better catalytic efficiency than that of IMIS catalysts lacking -COOH groups (TON 40). It is worth noting that even the sterically crowded cyclohexene oxide was efficiently converted to cyclohexene carbonate in 82% yield in 24 h at 1.6 MPa and 115 °C. The reported mechanistic aspect of carboxyl mediated ring opening of AGE is shown in Scheme 6.



Scheme 6. Mechanism of carboxylic acid group assisted cycloaddition demonstrated by CILBr-Si [25].

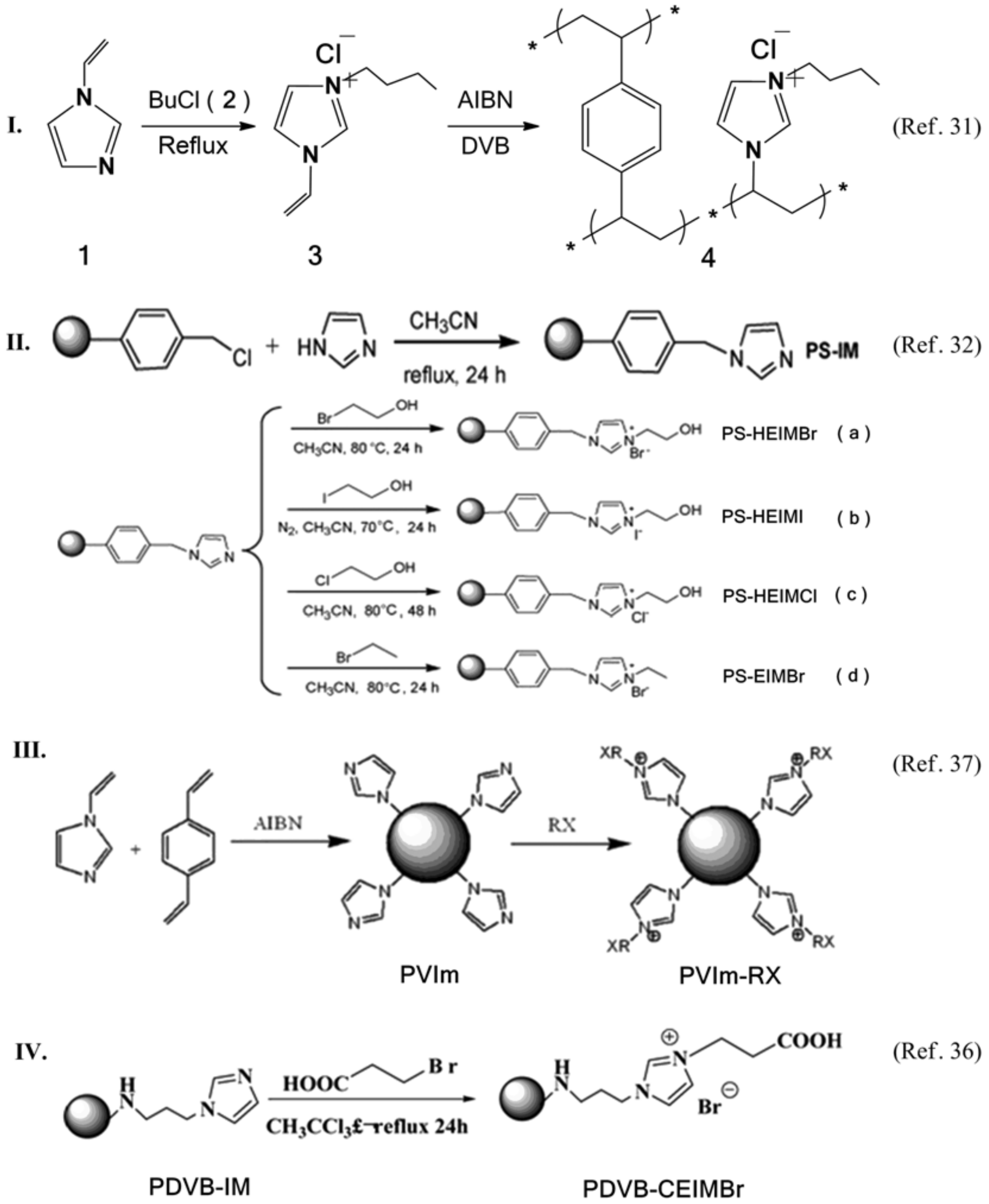
More recently, quaternary-ammonium-based ILs were successfully immobilized onto montmorillonite (MMT) clay through the simple ion exchange of alkylamine with the cation of MMT (0.65 mol%, 120 °C, 1.27 MPa, 3 h, TON 104) [26]. With respect to the development of more environment-friendly technologies, it is remarkable to note that all silica-supported ILs described so far, irrespective of the silica type and IL cation, catalyzed the organic reactions under solvent-free conditions and exhibited easy catalyst separability and excellent reusability. Other than the first three reports cited in this section [11-13], the silica-supported ILs were found to be functional at lower CO_2 pressures 1-3 MPa and temperatures 100-130 °C, with the positive exception of silica-supported aminopyridinium species showing superior activities even at atmospheric CO_2 pressures. Table 1 summarizes the catalytic activities exhibited by the abovementioned catalysts in the cycloaddition of propylene oxide in the temperature range 110-120 °C.

2. Organic Polymeric Supports

Organic support materials are attractive because of their basic tunability of physicothermal properties such as thermal stability, hydrophilic and hydrophobic nature, easy and versatile functionalization of pendant linkers, swelling capability, uniform morphologies, and reproducibility. Of the myriad organic functional supports developed worldwide, PS resins stand out, owing to their use in a number of industrial applications as well as the versatility of the appended reactive functional groups. The following section deals with PS-supported ILs applicable in CO_2 cycloaddition reactions.

2-1. Synthetic Polymer Supports (Polystyrene Supported Ionic Liquids) (Scheme 7)

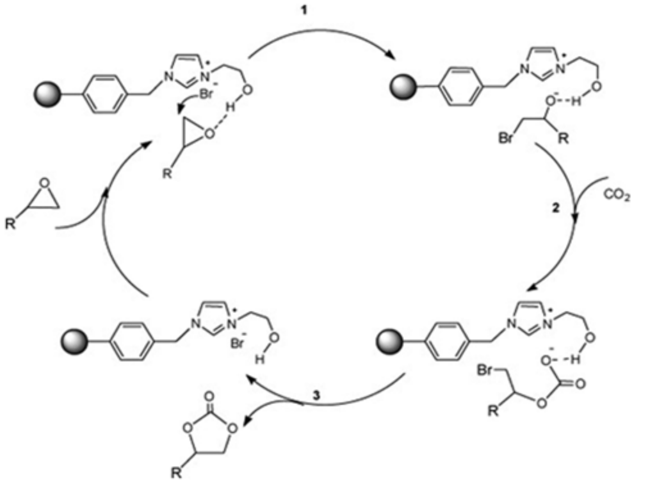
Insoluble PS beads of varying cross-linking structures and pendant reactive functional groups such as halogen, cyano, amino, and carboxyl entities have found immense potential in peptide synthesis (e.g., Merrifield resins), drug delivery, and covalent tethering of homogeneous catalytic species [27,28]. Insoluble PS beads bearing quaternary ammonium or phosphonium salts have also been widely applied as phase-transfer catalysts in a number of organic transformations since their discovery. However, the first report of utilizing



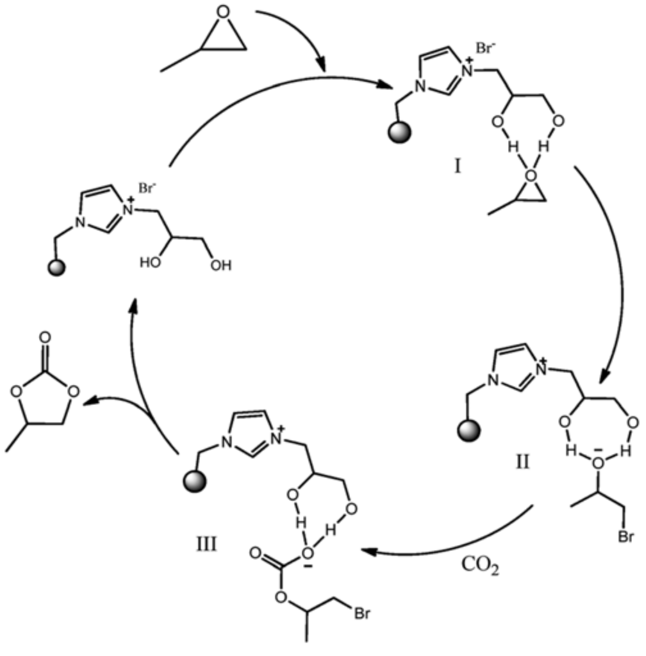
Scheme 7. Scheme of polystyrene grafted ionic liquids using representative examples.

quaternary ammonium-tethered PS (PS-QAm) catalysts for cyclic carbonate synthesis using oxiranes and CO_2 dates back to 1993 by Nishikubo et al. [29]. The cycloaddition of terminal epoxides with CO_2 proceeded quite smoothly in organic solvents (toluene, DMF (*N,N*-dimethylformamide), DMA (*N,N*-dimethylacetamide)) with a 1-2 mol% PS-QAm salt catalyst loading, yielding the corresponding cyclic carbonates in high yields at 80-90 ºC and atmospheric CO_2 pressure. It was also reported that the PS-QAm salts with a low degree of ring substitution (DRS) of the onium salt polymer residues and degree of cross-linking (DC) of the PS beads with long alkylene spacer chains were found to have higher catalytic activity than low-molecular-weight quaternary ammonium salts [30]. Among the different solvents studied, the cycloaddition in toluene gave the highest conversion rate. In 2001, our group revived the utilization of PS-QAm salts for cycloaddition chemistry in a broader context. PS supports prepared by the copolymerization of styrene (ST), divinyl benzene (DVB), and vinylbenzyl chloride (VBC) were found to be efficient platforms for the immobilization of quaternary ammonium salts. The amount of IL generated *in situ* by the covalent grafting of trialkylamines to PS was found to level at 0.3-0.6 mmol IL/g support. The performance of these catalysts in the cycloaddition of phenyl glycidyl ether (PGE) was affected by the amount of cross-linking agent (DVB), with 2% DVB established as the optimum amount. Too low a concentration of DVB made the resin soft and flexible, leading to mechanical deterioration of the catalyst at higher temperatures. Too high a concentration of the cross-linker reduced the mobility of polymer chains bearing the catalytic moieties, thereby retarding the reactant diffusion into the active sites, leading to a less active catalyst. Nonetheless, a DVB-PS-QAm catalyst resulted in appreciable conversions at 100 °C and atmospheric CO_2 pressures in aprotic solvents such as DMF and DMSO. The catalyst was reusable, and kinetic studies revealed that the addition of CO_2 to PGE can be considered as a pseudo-first-order reaction with respect to the concentration of PGE, with activation energy estimated to be 20 kJ/mol in DMF. Han and coworkers synthesized a unique PS-supported IL by the copolymerization of [BVIm]Cl and DVB, where an imidazolium moiety worked as the catalytically active species for CO_2-epoxide cycloadditions [31]. Under solvent-free conditions, this system exhibited equivalent or even better activities than its homogeneous counterparts do ([BMIm]Cl or [VBIm]Cl) and a relatively higher TOF of 70 compared to the supported ILs previously reported [11-13]. Unlike silica, because PS does not possess free hydroxyl groups, postfunctionalization of the PS-supported imidazolium moieties with hydroxyl groups (PS-HEIMX) were carried by Sun et al., which evoked the hydrogen-bond-mediated catalysis in PS-supported catalysts [32]. The PS-HEIMX catalysts were found to be superior, with a conversion rate of 99% PO and 99% PC selectivity over its nonhydroxyl analog PS-EIMX (64% PO conversion) at 120 °C and 2.5 MPa CO_2 in 4 h in the absence of a solvent. The TOF obtained with the best catalyst (PS-HEIMI) reached 156, which, to our knowledge, is the highest number achieved with any supported IL systems so far. A plausible mechanism in which the ring-opened epoxide is stabilized by the hydroxyl group of the IL was proposed in Scheme 8. PS-HEIMX exhibited an appreciable thermal stability up to 300 °C, which is the first thermal degradation temperature that is well above the cycloaddition reaction temperature.

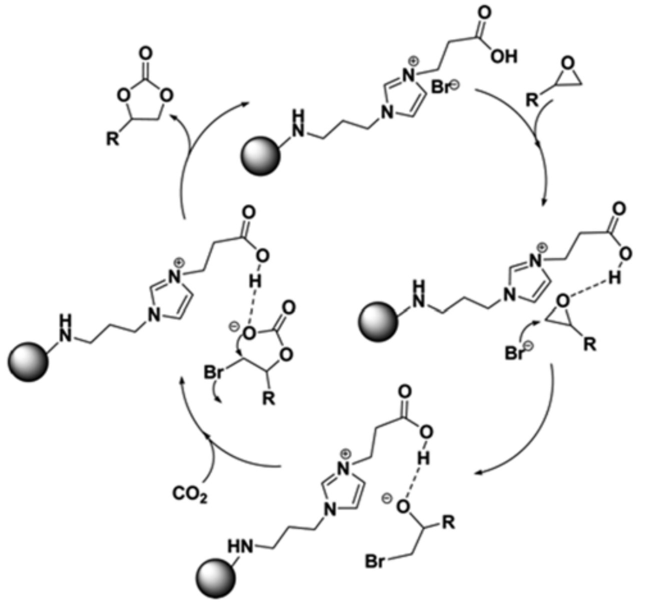
Following this, Dai et al. [33] also synthesized hydroxyl IL catalysts grafted to the cross-linked polymer PDVB and carried out the cycloaddition of PO with CO_2 at 140 °C and 2 MPa using 0.44 mol% of PVDB-HEIMBr. The reaction proceeded to completion in 4 h with a moderate TOF of 60. It was at this juncture that the superior capability of vicinal hydroxyl groups on a support over the monohydroxyl entities in enhancing the CO_2-epoxide cycloaddition was proposed by Liang et al. [34] using a cellulose/KI system. Inspired by this work, Bhange et al. [35] employed diol-functionalized PS-supported ILs, abbreviated as PD-DFILX for the above reaction. Although the above approach yielded quite high conversions in short reaction times of 1-3 h for most of the usually employed epoxides (PO, styrene oxide, epichlorohydrin), with the exception of cyclohexene oxide, the lack of data on the influence of catalyst loading on epoxide conversion hindered us from arriving at a direct comparison with the monohydroxyl IL-grafted PS supports (Scheme 9). Meanwhile, Han et al. [36] synthesized an imidazolium IL grafted on the highly cross-linked porous poly-*N*-vinylimidazole-co-divi-



Scheme 8. Mechanism of CO_2 cycloaddition for hydroxyl group grafted ionic liquid on polystyrene [32].



Scheme 9. Diol group posessing IL grafted polystyrene mechanism of CO_2 cycloaddition [35].



Scheme 10. Mechanism of CO_2 cycloaddition with carboxyl group containing IL grafted onto PS [37].

nylbenzene (PVIm) beads of various pore sizes and surface areas. A higher grafted IL amount of 0.92 mmol IL/g was achieved with one of the PVIm supports examined (PVIm-2) and a TON of 74 was obtained with PVIm2-BuBr, which was markedly higher than that obtained using the same IL grafted on commercial silica (TON=46) and MCM-41 (TON=27). The stronger nucleophiles were found to be better catalyst in effectuating the catalysis, the order being $I^- > Br^- > Cl^-$.

The CO_2 cycloaddition chemists should be considered to have followed the same trend in immobilizing the ILs to silica and PS. With the success of monohydroxyl- and dihydroxyl-functionalized IL grafting to PS, the next step clearly was the introduction of -COOH groups to the PS-supported ILs. Zhang et al. [37] were the first to report on the carboxyl-functionalized imidazolium-based ILs grafted onto a cross-linked DVB polymer (PDVB-CEIMBr) to examine PO-to-PC conversion. As expected, the PDVB-CEIMBr system resulted in excellent conversion rates and a better TON figure (>224) in comparison to a similar carboxyl-containing IL-grafted silica catalyst with TON of 170. The synergistic role played by the -COOH group and the nucleophilic anion in carrying out the catalysis was

Table 2. Performance of various polystyrene supported ionic liquids in the cyclic carbonate synthesis

Catalyst particulars	Amount of IL	Reaction parameters				Cyclic carbonate		TON	Ref
		Catalyst (mol%)	Temp. (°C)	Pressure (MPa)	Time (h)	Yield (%)	Selectivity (%)		
						Propylene carbonate			
PS-Hydroxyl IL; PS-HEIMBr	3.2	1.6	120	2.5	4	99	99	625	32
PVIm2-BuBr	0.92	1.15	110	1.82	6	98	99	87.0	36
PS-Diol IL; PS-DHPIMBr	-	1.2	130	2	3	97	99	81.7	35
PS-COOH IL; PDVB-CEIMBr	-	-	140	2	4	96.1	99.8	224	37

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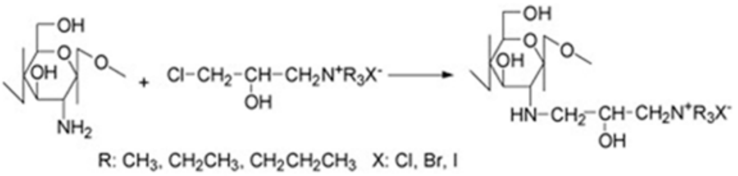
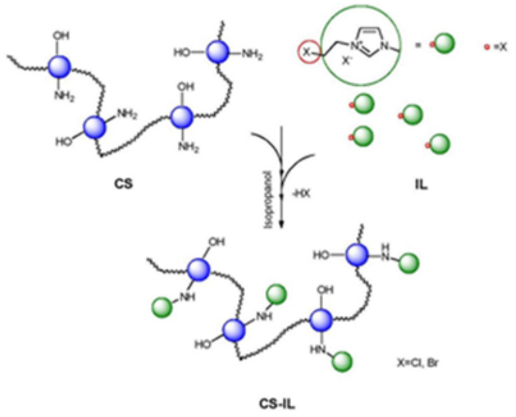


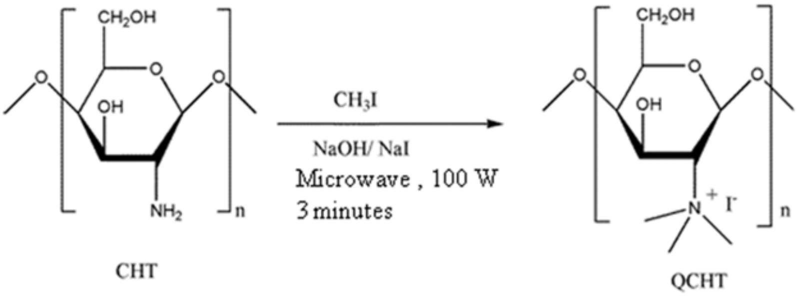
Preparation of chitosan bound covalently grafted quaternary ammonium moeities (Ref. 37)

II.



Synthesis of Imidazolium ionic liquids grafted onto chitosan (Ref. 38)

III.



Synthesis of quaternized chitosan (Ref. 41)

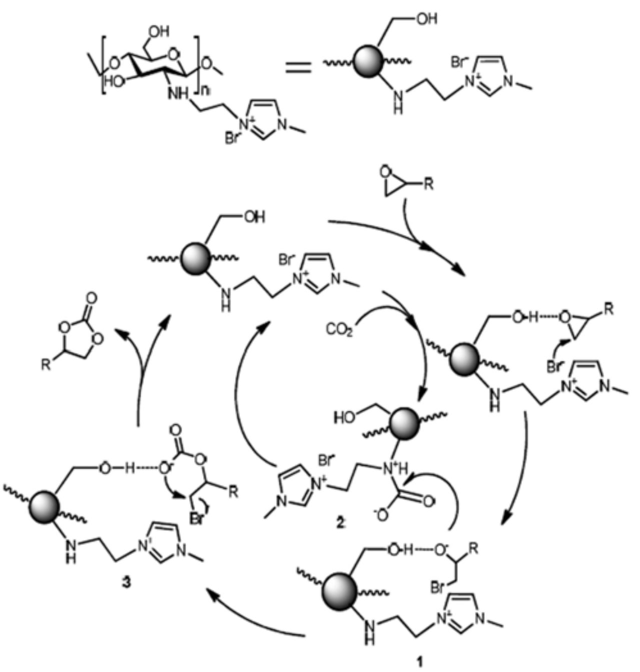
Scheme 11. Biopolymer tethered ionic liquids synthesis.

proposed as having a similar function as that of the silica-supported -COOH IL catalysts (Scheme 10). All PS-supported ILs exhibited good thermal stability (>300 °C) and reusability crucial to the industrialization of cyclic carbonate synthesis from CO_2 and epoxides; the data of a few distinct PS-based ILs for a given temperature range are given in Table 2 for easy comparison.

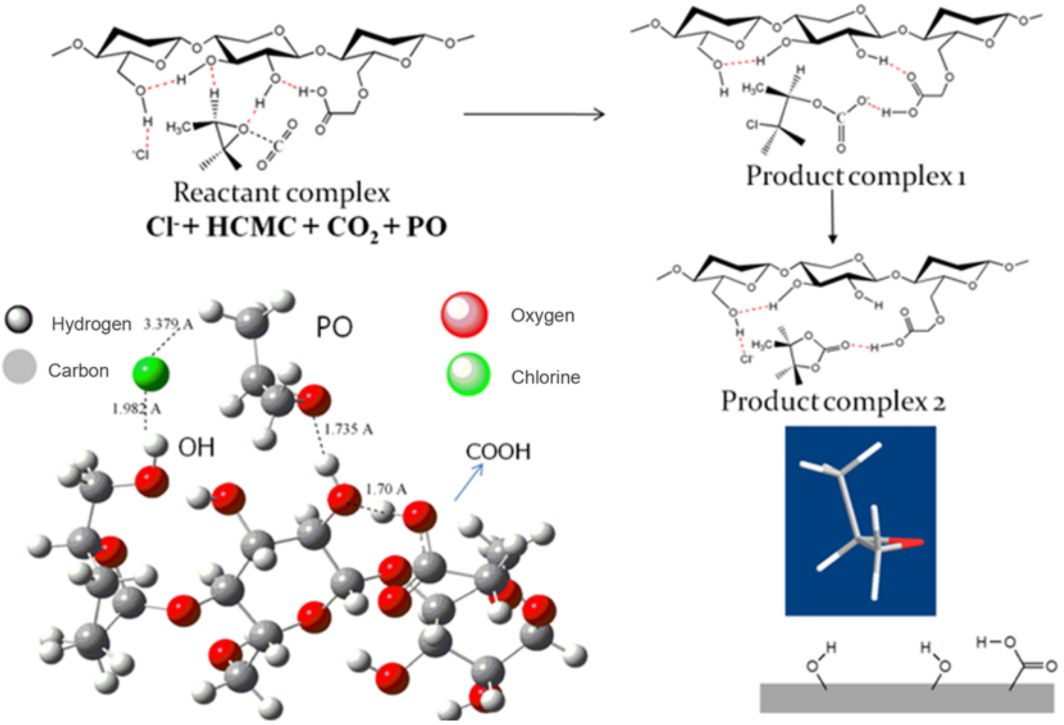
Despite all these advantages, the choice of PS support for IL immobilization still poses the challenges of nonbiodegradability of PS and its high cost of manufacturing. The increased demands toward environment-friendly processes and ecological conservation have thus driven the development/finding of environmentally benign and renewable supports. Nature has a vast wealth of polymers that are evolved for specific functions such as support and protection in the form of cell walls, scaffolds, or tough exoskeletons through optimized chain length, functionalization, and monomer sequence. Hence, the generation of functional materials based on biopolymers would bring the environmentally benign approach a step closer toward sustainability and green processes; transformations of CO_2 using nonvolatile ILs anchored on biopolymer supports would further contribute to an environment-friendly synthesis of cyclic carbonates.

2-2. Organic Polymers of Biological Origin (Biopolymer Supported Ionic Liquids) (Scheme 11)

Biopolymer-based catalysts have recently been introduced as effective catalysts for the synthesis of cyclic carbonates from epoxides and CO_2. Biopolymers such as cellulose (cell) and chitosan (CHT) are the most abundant polysaccharides on the earth. As a natural renewable resource, biopolymers have attracted attention for their physicochemical characteristics and bioactivities. In addition to their biocompatibility, biodegradability, and nontoxicity, biopolymers can be easily modified chemically or physically, making them versatile supporting materials. Another interesting property with respect to employing biopolymer-supported catalysts for CO_2-epoxide cycloaddition reactions is the presence of free hydroxyl groups in the biopolymeric repeating units, which in turn enhances catalytic activities for cyclic carbonate synthesis by epoxide ring activation *via* hydrogen bonding with the epoxide oxygen atom. A survey of the available literature reveals that few studies have investigated biopoly-



Scheme 12. Imidazolium ionic liquid grafted IL on chitosan mediated catalysis mechanism [39].

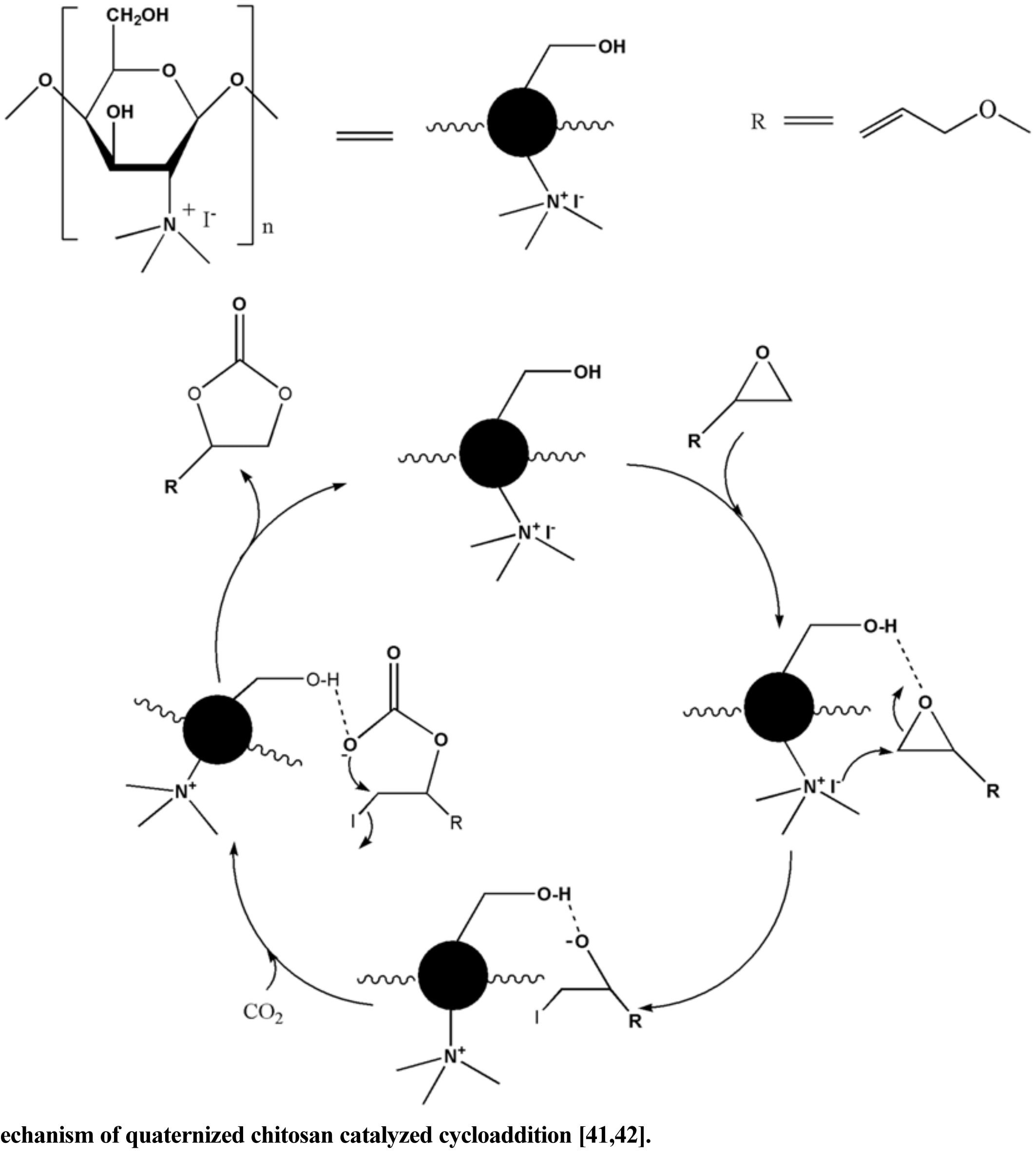


Scheme 13. Carboxymethyl cellulose supported ionic liquid catalysis of propylene carbonate formation from CO_2 and propylene oxide [40].

mer-supported catalysts for use in cycloaddition reactions. Zhao et al. [38] first introduced the CHT-supported quaternary ammonium ILs (1.7 mol% of PO, 140 °C, 4 MPa, 6 h, TON 59), followed by Sun et al. [39], who succeeded in covalently immobilizing the imidazolium-based ILs onto a CHT support (1 mol% of PO, 120 °C, 2 MPa, 4 h, TON 96). In these systems that utilized CHT as a support, not only was catalyst recovery made possible, but more significantly, the presence of a hydrogen-bonding-capable hydroxyl group acting in synergy with the halide anion enhanced catalytic activity (Scheme 12).

Similarly, our group showed the influence of the -COOH group in enhancing the catalytic activity of a carboxymethyl cellulose-IL catalyst system (CMIL) for use in cyclic carbonate synthesis (Scheme) [40]. This work introduced the immobilization of IL onto the cell materials for the preparation of cyclic carbonates in which carboxyl moieties on the carboxymethyl cellulose (H-CMC) support supposedly stabilize the product complex *via* strong hydrogen bonds, thereby promoting the reaction as corroborated by the density functional theory calculations (Scheme 13). Utilization of this environmentally benign biopolymer support for the synthesis of cyclic carbonates from CO_2 and epoxides has great potential for industrial applications because of its advantages in terms of stability, low cost, easy preparation from renewable biopolymers, and simple separation from the product.

In a similar vein, our group has recently reported [41,42] the novel utilization of quaternized chitosan (QCHT) as a catalyst for cyclic carbonate synthesis, in which the quaternization was performed on the primary amine group inherent to the CHT itself. Quaternization allows the formation of a cationic biopolymer rather than covalently tethering an already quaternized species such as quaternary ammonium or imidazolium salts into the CHT backbone. In such catalytic systems, the coexistence of hydrogen bond donors (-OH), positively charged nitrogen of the quaternary ammonium moiety ($-N^{+}Me_3$), and halide anions showed a synergistic effect in promoting the cycloaddition reaction rather than acting merely as a support (Scheme 14). A comparison of the catalytic efficiency of the above-discussed biopolymer supports is shown in Table 3. This illustrates



Scheme 14. Mechanism of quaternized chitosan catalyzed cycloaddition [41,42].

Table 3. Catalytic activities of the reported biopolymer assisted ionic liquid catalysts

Catalyst particulars	Reaction parameters				Cyclic carbonate		TON	Ref
	Catalyst (mol%)	Temp. (°C)	Pressure (MPa)	Time (h)	Yield (%)	Selectivity (%)		
					Propylene carbonate			
Chitosan-quaternary ammonium CS-$N^+Me_3Cl^-$	1.7	120	4	6	30	99	17.6	38
Chitosan-Imidazolium CS-EMImBr	1	120	2	4	95	99	95	39
Carboxymethylcellulose/imidazolium CMIL-4I	1.2	120	2	2	98	98	81.7	40
Quaternized Chitosan-QCHT	1.6	120	1.17	6	89	99	56.8	42

that biopolymer-supported IL catalysts hold great promise as future catalysts for the atom-economical synthesis of cyclic carbonates, with the added advantage of sustainable catalysis. Table 3 displays the catalytic efficiencies of the best biopolymer-based IL catalytic systems in the PO-CO_2 cycloaddition at a chosen temperature of 120 °C.

CONCLUDING REMARKS

The ever-expanding implementation of CO_2 as a renewable C1 feedstock is directly proportional to the design of capable catalysts. The well-known catalytic potential of ILs and heterogenization of the same for ensuring reusability by immobilization over a solid support has been mainly discussed in terms of silica, PS, and biopolymer supports. In a broader context, all the above approaches were intended to design stable and reusable IL-based solid catalysts without compromising the catalytic ability of its homogeneous counterparts. However, with the added interest (and demand!) toward a sustainable society, the search for bio renewable materials, which could serve as economic and ecologically safer alternatives to conventional support materials, has gained increased attention. The generation of high charge-density-possessing ionic materials in conjunction with tunable (hydrophilic) biopolymer supports is likely to develop in the future studies of SILC. A comparative study made with different functional groups revealed the supreme ability of carboxyl entities in the SILC mediated CO_2 cycloaddition with epoxides.

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