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Development of ionic liquids as green reaction media and catalysts

Feng Shi, Yanlong Gu, Qinghua Zhang, and Youquan Deng*

Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

A brief review of the work carried out at Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences for development of ionic liquid as green reaction media and catalysts is presented. This includes the processes of ionic liquid to be used as catalyst, reaction media, development of functional ionic liquid and methods for synthesis of immobilized ionic liquid. In the end, some prospects for development of ionic liquid are also addressed.

KEY WORDS: catalysis; green chemistry; ionic liquid; reaction media; review.

1. Introduction

Ionic liquids are in general defined as liquid electrolytes composed entirely of ions. More recently, the melting point criterion has been proposed to distinguish between molten salt (high melting, highly viscous, and very corrosive medium) and ionic liquids (liquid below 100 °C and relatively low viscosity) [1]. Generally, ionic liquids include liquid compounds which involves organic compounds (tetrabutylphosphonium chloride, mp 80 °C) and organominerals (triethylammonium chloride/copper chloride, 1/1, mp 25 °C) [2,3]. Those ionic liquids based on quaternary ammonium or phosphonium salts were usually named room temperature ionic liquids (figure 1), exhibit a relatively wide electrochemically stable window, good electrical conductivity, high ionic mobility, a broad range of room temperature liquid compositions, negligible vapor pressure, selective dissolvability to many organic and inorganic materials, and excellent chemical and thermal stabilities [4–10]. Therefore, the room temperature ionic liquids were extensively used in electronic absorption spectroscopy, liquid–liquid extraction processes [11–12], organic and organometallic syntheses [13], catalytic cracking of polyethylene [14], radical polymerization [15], analytical and physical chemistry [16], lubricant [17], etc. Recently, great advantages were also shown when they were used as solvent for biocatalysis in comparison with those processes using organic solvents [18].

In this paper, an attempt has been made to highlight the developmental approach adopted by us for catalytic reactions.

2. Process of using ionic liquids as catalysts

2.1. *Selective cyclolization of 1-dodecene to cyclo-dodecane [19]*

Cyclo-dodecane is an important intermediate used as starting material for manufacturing Nylon and industriously produced in a long and complicated process by Ni catalyzed hydrogenation of the cyclo-dodectriene produced from the trimerization of 1,3-butyldiene. When we tried the isomerization reaction of 1-dodecene in ethanol buffered chloroaluminate ionic liquids consisting of $AlCl_3$ with 1-alkyl pyridium or 1-methyl-3-alkyl imidazolium quaternary ammonium salts, it was observed that 1-dodecene could be cyclolized to cyclo-dodecane with high selectivity (figure 1).

Ethanol played an important role in the reaction. Before reaction or without addition of ethanol, a bi-phasic reaction system consisted of 1-dodecene and chloroaluminate ionic liquid was observed because the 1-dodecene was immiscible with chloroaluminate ionic liquids. In this case, the conversion of 1-dodecene (4.2%) and selectivity (73.1%) was considerably low perhaps due to the bad-contacting of 1-dodecene with ionic liquids. With the addition of ethanol, the bi-phasic reaction system was converted to a homogeneous one, which greatly facilitated the reaction and the conversion of 1-dodecene raised from 4.2 to 12.4%. Ethanol could be removed easily after reaction and a bi-phasic reaction system will reform with the upper layer as products and unreacted substrate, which greatly simplified the recovery of product and substrate.

When the cyclolization reaction of 1-dodecene was further carried out under moderate N_2 pressure ranged from 3.0 to 6.0 MPa, the conversion of 1-dodecene and selectivity to cyclo-dodecane increased remarkably. For example, the conversion of 1-dodecene and selectivity to cyclo-dodecane reached to 23.4 and 93.4%, respectively when the pressure of nitrogen was 3.0 MPa while the reason was still not clear.

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*To whom correspondence shoud be addressed.
E-mail: ydeng@ns.lzb.ac

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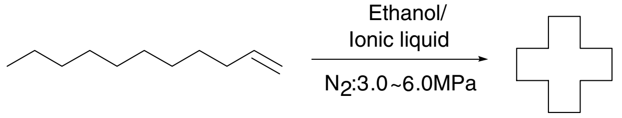


Figure 1. Cyclolization of 1-dodecene to cyclo-dodecane in ionic liquid.

2.2. Synthesis of tert-butyl ether from tert-butyl alcohol [20]

Asymmetrical tertiary alkyl ethers, especially methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE) and isopropyl *tert*-butyl ether (IPTBE), are particularly used as octane improvers for gasoline due to the rapidly increasing demand for lead-free octane boosters for gasoline [1,2]. Synthesis of MTBE, ETBE or IPTBE from isobutyl alcohol with corresponding alcohol is an important process and usually manufactured over heteropoly acid, titania supported phosphoric acid, acidic montmorillonite clay and zeolite modified by fluorosulfonic acid or fluorophosphoric acid, etc., while the formation of large amounts of iso-butene with the increasing of conversion of TBA was unavoidable because acids were also effective catalysts for dehydration of TBA to yield iso-butene.

It was found that ionic liquid could be effective dehydration agent for etherization of *tert*-butyl alcohol with high yield if the non-acid ionic liquid whose anion BF_4^- was selected which avoids the dehydration of *tert*-butyl alcohol to iso-butene (Table 1, figure 2). The results showed that the substituted alkyl chain of the imidazolium cations had greater effect on the catalytic activity of the ionic liquids and only 19, 39% of conversions were achieved in $EMImBF_4$ and $BMImBF_4$ ionic liquids while 93% of conversion was obtained over ionic liquid $DMImBF_4$. Further more, some dimethyl ether (about 10% based on the methanol) was also detected if the reaction was conducted at 175 °C, which indicated that the ionic liquid exhibit higher catalytic activity at higher reaction temperature and the dimethyl ether might be effectively synthesized if appropriate reaction conditions were selected. At the same time, the conversion decreased to 45% while no iso-butene was formed if $CMImBF_4$ was used as catalyst. Surprisingly, no reactions occurred when ionic liquids BMImCl, $BMImPF_6$ and $BPyBF_4$ were used as catalysts, which showed that both the anions and cations of the ionic liquid had greater effect on the catalytic activity.

Table 1
Synthesis of *tert*-butyl ether from iso-butene in ionic liquids[a]

Entry	Ionic liquid	Alcohol	Conversions (%)	Selectivities (%)[b]
1	$EMImBF_4$	MeOH	19	~100
2	$BMImBF_4$	MeOH	39	~100
3	$DMImBF_4$	MeOH	93	97
4	$CMImBF_4$	MeOH	45	~100
5	BMImCl	MeOH	~0	–
6	$BMImPF_6$	MeOH	~0	–
7	$BPyBF_4$	MeOH	~0	–

[a] 3 mL of ionic liquid, 3 mL of TBA and 6 mL of methanol were successively introduced into the reactor and reacted at 130°C for 3 h.
[b] The byproduct was only iso-butene.

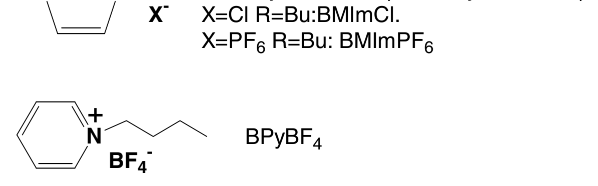


Figure 2. Structural diagram of ionic liquid cations used in etherization reactions.

Chloroaluminate ionic liquids consisted of anhydrous $AlCl_3$ with 1-alkylpyridinium, 1-methyl 3-alkylimidazolium quaternary ammonium salts and trimethylamine hydrochloride could also behave as suitable reaction media and catalysts for etherification of *tert*-bytyl alcohol but the results were not as good as that using the non-acid ionic liquid.

2.3. Cyclo-addition of carbon dioxide to propylene oxide [21]

It is well known that carbon dioxide can dissolve significantly into the ionic liquid phase, but no ionic liquid dissolves in the supercritical carbon dioxide, which therefore may be suitable for reactions carried out in ionic liquids concerning carbon dioxide [22]. Furthermore, the mixture of ionic liquids and supercritical carbon dioxide offers some new opportunities for the development of bi-phasic reactions and it is now collecting interests as new reaction media [23].

Five-membered cyclic carbonates are excellent aprotic polar solvents and can be used largely as intermediates in producing drugs and pesticides. The formation of cyclic carbonates via cyclo-addition of epoxides and carbon dioxide, which is one of the routes for carbon dioxide chemical fixation, has been received much attention in the aspects of utilization of carbon resource and the reduction of CO_2 pollution. Till now, metal halides, onium halides, metal complexes and MgO, Mg–Al mixed oxide, KI/ZnO etc., were extensively investigated while high temperature, high pressure of carbon dioxide, long reaction time and/or high catalyst/substrates ratios are usually needed. Recently, it was found that room temperature ionic liquids based on 1-*n*-butyl-3-methylimidazolium and *n*-butylpyridinium salts could be effective catalytic media for the cyclo-addition of carbon dioxide to propylene oxide (figure 3).

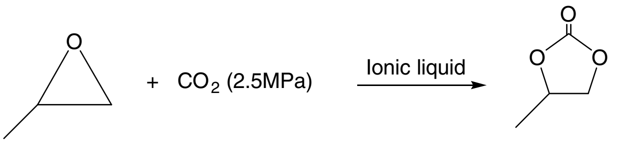


Figure 3. Cyclo-addition of carbon dioxide to propylene oxide in the presence of ionic liquid.

The results of the cyclo-addition of CO_2 to propylene oxide in a series of ionic liquids indicated that both cations and anions had strong impact on the catalytic activities and the best result was obtained over ionic liquid $BMImBF_4$ with conversion and selectivity all nearly 100%. This catalyst system was also reusable. It could be seen that 96.1% of conversion and 86.9% of yield were maintained when ionic liquid $BMImBF_4$ was reused for the fifth time (Table 2).

2.4. Electrocatalytic cyclo-addition of carbon dioxide to propylene oxide [24]

Based on the previous study, electrocatalytic cyclo-addition of carbon dioxide to epoxides using pure ionic liquids, $[BMIm][BF_4]$, $[EMIm][BF_4]$, $[BMIm][PF_6]$ and $[BPy][BF_4]$, as reaction media without any additional supporting electrolyte and catalyst was further investigated (figure 4).

The results of the incorporation of CO_2 into epoxides, i.e., propylene oxide, epichlorohydrin and styrene oxide, in a series of ionic liquids consisting of $BMIm^+$, $EMIm^+$, BPy^+ cations and BF_4^-, PF_6^- anions showed that the conversions being up to 54–92% with 69–100% selectivities were achieved and the best current efficiency was 87%. If $[BMIm][BF_4]$ was replaced with $[EMIm][BF_4]$ or $[BPy][BF_4]$, the conversions were respectively decreased slightly and remarkably, while the selectivities were almost not changed. Poor conversion, however, was obtained when $[BMIm][PF_6]$ was used. This indicates that both cation and anion in the ionic liquid have strong impact on the addition reaction. The best performance was achieved with the ionic liquid consisting of $BMIm^+$ and BF_4^-. This result is also consistent with the work as mentioned above.

Table 2
Reusability of ionic liquid $BMImBF_4$ in synthesis of propylene oxide

No. cycle	1	2	3	4	5
Conversion of propylene oxide, %	100	100	98.2	97.5	96.1
Yield of propylene carbonate, %	90.7	91.8	90.5	89.2	86.9
TON	40	40	39.3	39.0	38.4

Reaction conditions: $T = 110\ ^\circ C$, $t = 6h$, $P_{CO2} = 2.5$ MPa.

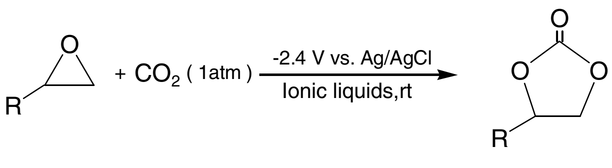


Figure 4. Electrocatalytic cyclo-addition of carbon dioxide to propylene oxide.

2.5. Ionic liquids catalyzed Biginelli reaction [25]

The classical Biginelli synthesis is a one-pot condensation using β-dicarbonyl compounds with aldehydes (aromatic and aliphatic aldehydes) and urea or thiourea in ethanol solution containing catalytic amounts of acid. Recently, it was reported that Lewis acids, such as $BF_3 \cdot OEt_2$, lanthanide triflate, lanthanum chloride, ferric chloride hexahydrate and indium chloride were effective catalysts for this reaction. These methods, however, involve long reaction times, harsh reaction conditions and unsatisfactory yields and improvements in such syntheses have been sought continuously. Recently, the application of ionic liquids was also used as a catalyst in Biginelli synthesis with high efficiency (figure 5).

The condensation reaction of benzaldehyde, ethyl acetoacetate in stoichiometric ratio and urea in slightly excess amount was tested in the presence of a different amounts of $BMImBF_4$, i.e. 0.2, 0.4 and 0.8 mol% $BMImBF_4$ relative to the amount of benzaldehyde at 100 °C without any additional solvent. Isolated yields of 85, 92 and 95%, respectively could be achieved after the reaction had only proceeded for 30 min. This indicates that the conversion was increased with increasing amounts of ionic liquid. Under the same reaction conditions and substrates, $BMImPF_6$ as catalyst was also examined and even higher yields, i.e. 94, 98, 98 and 92%, respectively, were obtained in comparison with the $BMImBF_4$ as the catalyst. Other substrates as that shown in figure 4 were also investigated in Biginelli synthesis using ionic liquid $BMImBF_4$ as catalysts and good results were also achieved.

3. Process using ionic liquids as reaction media

3.1. Palladium–ionic liquid catalyst system for oxidative carbonylation of aniline [26]

Isocyanates, e.g. toluene diisocyanate and 4,4’-dipheylmethyl diisocyanate, are currently manufactured

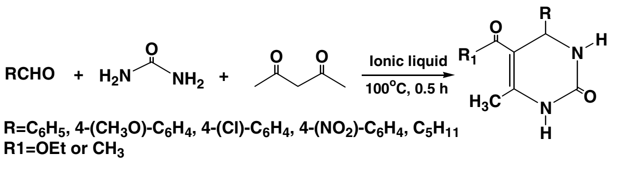


Figure 5. Ionic liquids catalyzed Biginelli reaction under solvent-free conditions.

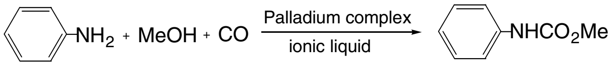


Figure 6. Oxidative carbonylation of aniline in ionic liquid mediated palladium complex.

by phosgenation of the corresponding amines with toxic phosgene in industry, which may cause serious environmental pollution and equipment corrosion. Therefore, produced either by oxidative carbonylation of amines or by reductive carbonylation of nitro compounds in the presence of an alcohol, carbamates as intermediates for the synthesis of isocyanates with non-phosgene routes have been extensively studied for the last two decades. Pd, Ru, Rh, Au and other transitional metal complexes were employed as the catalysts and corresponding catalytic turnover frequency (TOF), however, is still not high enough for industrial application. Furthermore, palladium complexes coordinated with N-containing compounds is usually insoluble in most of conventional organic solvents, and it is well known that reaction media played an important role in the homogeneous catalysis although, so far, such mediation is still not very clear. Moreover, organic solvents, which are available to establish a suitable homogenous catalyst system for the carbonylations of N-containing compounds are very limited. The diversity of ionic liquids may form an optimal homogeneous catalyst system with a specific organometallic complex towards a specific reaction, e.g. carbonylation of amine (figure 6).

With $BMIm^+$ as cation and in the presence of $Pd(phen)Cl_2$, the effect of anions, e.g. BF_4^-, PF_6^-, Cl^- and $FeCl_4^-$ on the aniline carbonylation was examined. Moderate and high conversions with excellent selectivities were achieved in $BMImBF_4$ and $BMImFeCl_4$. The corresponding TOF reached to ca. 4540 $mol\,mol^{-1}\,h^{-1}$, which is much higher than that reported in previous literatures. BF_4^- was slightly better than $FeCl_4^-$ although $FeCl_3$ was one of the most effective cocatalysts in the carbonylation reactions of N-containing compounds. Poor catalytic performances were observed for PF_6^-. This may be related to the instability of $BMImPF_6$ ionic liquids under the reaction conditions employed in this work, because remarkable degradation of this ionic liquid was observed after reaction. Such degradation, however, was not observed with $BMImBF_4$. On the other hand, poor catalytic activity was observed if reaction proceeded in the absence of ionic liquid.

3.2 Catalytic Beckmann Rearrangement of Cyclo-hexanone Oxime in Ionic Liquids [27]

It is well known that the most common media for the Beckmann rearrangement to manufacture ε-caprolactam in chemical industry are excess or stoichiometric amounts of those strong Brønsted acids or Lewis acids, i.e., concentrated sulfuric acid, hydrogen chloride in a mixture of acetic acid and acetic anhydride. The application of inorganic acids usually causes large amount of by-products and serious corrosion resulting in environment problems. Development of clean and highly efficient catalytic process for Beckmann rearrangement was still necessary. In a recent work, it was reported that ionic liquid could be a fitful catalytic reaction media for Beckmann rearrangement with high conversion and selectivity (figure 7).

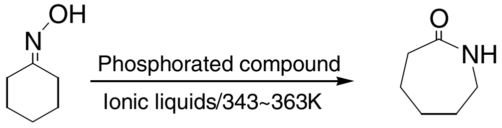


Figure 7. Catalytic Beckmann rearrangement of cyclo-hexanone oxime in ionic liquids.

There was no detectable transformation if pure ionic liquid as catalytic medium was used. The transformation could, however, proceed smoothly when both ionic liquid and acidic phosphorous containing compound, e.g., phosphorous pentachloride, was used and the best result was achieved in ionic liquid $BPyBF_4$ which conversion and selectivity were 100%. The main side reaction was deoximation, and therefore cyclo-hexanone was formed. Some other byproducts (ca. 1% in concentration), including α-chloro cyclo-hexanone and cyclo-hexane were also detected during the reaction.

3.3. Hydroestification oftert-butyl alcohol [28]

Organic carboxylic acids, especially the tertiary carboxylic acids, were a kind of important chemical products widely used in the fields such as paint, micro-gel, surfactant and polymerization initiator. The tertiary carboxylic acids were commonly manufactured by carbonylation alkene or alcohol with CO using Koch reaction, aiming to produce organic caboxylic acids or ester with high degree of branching in the presence of concentric H_2SO_4, HF, BF_3 and solid acids, etc. Although good results were obtained in these process, disadvantages such as corrosion of equipment, difficult in production separation, environment pollution for liquid acids and easily deactivation of solid catalysts still could not be solved successfully.

Relative high ethyl *tert*-valerate selectivity could be obtained if hydroesterification of *tert*-butyl alcohol with CO catalyzed by Pd complexes in the presence of *p*-toluenesulfonic acid (*p*-Ts) in ionic liquids while only iso-valerate formed in traditional organic solvents (figure 8). Since ethyl *tert*-valerate was immiscible with ionic liquids, it was easy to recover ethyl *tert*-valerate from the ionic liquid reaction system, and pivalic acid

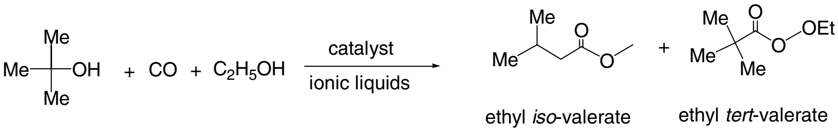


Figure 8. Hydroesterification of *tert*-butyl alcohol in ionic liquids to yield iso-valerate.

could be easily produced by hydrolysis of ethyl *tert*-valerate.

In this process, $Pd(PPh_3)_2Cl_2$ was found to be the most effective catalyst for hydroesterification of *tert*-butyl alcohol using ionic liquid $BMImBF_4$ as solvent and 90.5% of *tert*-butyl alcohol conversion and 78.7% of total selectivity to ethyl iso-valerate and ethyl *tert*-valerate were obtained. Other metal complexes, such as $Au(PPh_3)Cl$, $Co(PPh_3)_2Cl_2$, $Cu(PPh_3)_2Cl_2$ and $Pt(PPh_3)_2Cl_2$ were also used in hydroesterification of *tert*-butyl alcohol but no ethyl *tert*-valerate was detected.

3.4. Selective hydroxylation of benzene to phenol [29]

Direct hydroxylation of benzene with hydrogen peroxide to form phenol has been attracted much attention and been extensively investigated. The oxidation of benzene and its derivatives by Fenton's reagent (Fe^{2+}–H_2O_2) has been known for a long time. However, its selectivity is rather poor since phenol is more reactive towards oxidation than benzene itself, and classical Fenton chemistry requires large quantities of iron(II) salts, which are consumed stoichiometrically during reaction. Although much effort has been devoted to new processes that produce phenol directly with high yield and selectivity, nevertheless, relatively few catalytic processes have successfully been developed.

Herein, an aqueous/ionic liquid bi-phasic catalytic reaction system, for direct oxidation of benzene to phenol with hydrogen peroxide as oxidant and ferric dodecanesulfonate ($Fe(DS)_3$) as catalysts, was established (figure 9). In this aqueous/ionic liquid bi-phasic process, both catalyst and benzene were dissolved into ionic liquid, while the oxidant, i.e., H_2O_2 was mainly dissolved in the aqueous phase but much less dissolved in the ionic liquid since the water solubility, for example, in the 1-octyl-3-methylimidazolium hexafluorophosphates could be as low as 0.2 g/100 mL and H_2O_2 could be well dissolved in the water. Phenol produced could be extracted into the aqueous phase, thus possible over-oxidation of the resulted phenol could be minimized.

In this process, the product detected after reaction was phenol only over the catalysts used in this work, so the selectivities of phenol based on benzene were almost 100%. Beside moderate high (54%) conversion of benzene, high selectivity of H_2O_2 (90%) for benzene conversion was achieved, indicating that such aqueous/ionic liquid bi-phasic reaction system for benzene hydroxylation was successfully established.

3.5 Synthesis of symmetric ureas with carbon dioxide [30]

Until today, the studies of carbonylation reactions of nitrogen containing compounds using CO_2 were relatively fewer in comparison with those using CO most probably due to its chemical inert. In previous studies, although good yields (ca. 60–90%) for desired products were achieved, large amounts of dehydrating agents such as PCl_5, $POCl_3$, dicyclohexylcarbodiimide etc., or relative expensive R'Cl were needed, and even worse things are that large amounts of byproducts such as Et_3NHCl, $Et_3NHPOCl$, HCl etc. were inevitably formed. These made that using CO_2 as a carbonyl source to substitute phosgene in the synthesis of isocyanate and its derivatives were not only economically less favorable but also environmentally less friendly. Study of ionic liquid affords new opportunity to solve this problem because of the special dissolvability of carbon dioxide in ionic liquids.

A series of aliphatic amines and even aromatic amines could react with CO_2 to afford corresponding ureas with moderate to high yields in the presence of CsOH/ionic liquid catalyst system (figure 10). Both cations and anions of the ionic liquids had strong impact on the formation of ureas when cyclo-hexane amine was used as substrate. When the conversion was high enough, the desired product would "precipitate" when ca. 10 mL water was added into the resulted liquid mixture after reaction because urea is insoluble in water, while CsOH/ionic liquid was still "dissolved" into the ionic liquid. Therefore, desired solid product and

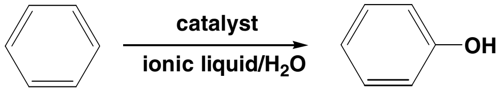


Figure 9. Selective oxidation of benzene to phenol in ionic liquid–water biphasic system.

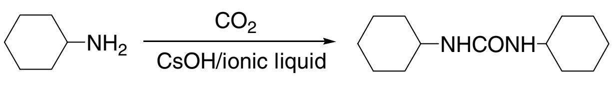


Figure 10. Synthesis of symmetric ureas with carbon dioxide in CsOH/ionic liquid catalyst system.

corresponding yield could be recovered and obtained after filtration and dryness, and an isolated yield of 98% was achieved when BMImCl ionic liquid containing CsOH was employed.

3.6. Synthesis of α-methylene cyclic carbonates [31]

With our continuous research in fixation of CO_2 using ionic liquid catalyst system, it was also found that ionic liquid could be efficient and environmentally benign solvent in the presence of transition metal salts, e.g., CuCl, for synthesis of α-methylene cyclic carbonates from CO_2 and propargylic alcohols (figure 11).

In this process, the use of large amounts of toxic tertiary amines and nitrogen-containing organic solvent were avoided, and furthermore, the ionic liquid catalyst systems were reusable. Various reactions of propargylic alcohols with CO_2 in [BMIm][$PhSO_3$]/CuCl catalytic system were conducted to produce the corresponding α-methylene cyclic carbonates with high to quantitative yields (>95%).

3.7. Epoxidation of olefins [32,33]

The epoxidation or hydroxylation of alkenes catalyzed by metalloporphyrin complexes is a subject of many investigations. Homogeneous sterically hindered metalloporphyrin catalysts, and those containing sophisticated chiral auxiliaries, or strongly electron-withdrawing groups could exhibit high regio-, stereo-, and enantioselectivity, and high chemical processes is potentially catalyst turnovers. However, the difficulty in recovery and the high cost of the catalysts outweigh these appealing features and so far have made their applications to synthesis is impractical.

While using manganese (III) porphyrin, (*meso*-tetrakis(pentafluorophenyl) porphinato) manganese (III) chloride, for the epoxidation of alkenes with PhI(OAc) in a [bmim]PF_6/CH_2Cl_2 mixture at room temperature, the yield of styrene could be reached to 89% while it was only 65% while using CH_2Cl_2 as a solvent and 84% of yield was maintained when the ionic liquid catalyst system was reused for the fifth time.

The epoxidation reactions of electron-deficient olefins such as α, β-unsaturated carbonyl compounds, which are widely applied in the synthesis of intermediates in pharmaceutical and fine chemicals, are usually unsatisfactory because of poor reactivity of those unsaturated compounds. Through optimizing the reaction conditions, such as reaction time, temperature, the amount of oxidant (H_2O_2) and sodium hydroxide, 100% conversion and 98% selectivity could be achieved in the epoxidation of mesityl oxide. The mass transfer model for the epoxidation of α, β-unsaturated carbonyl compounds in 1-butyl-3-methylimidazolium hexafluorophosphate ([C4MIm][PF6])/water bi-phasic system was also proposed.

4. Application of functional ionic liquid [34–36]

It is well known that esters could be obtained through reaction of olefins and aliphatic acids, which is atom economy and avoids removing of coproduced water during reaction. A number of acid catalysts such as ion exchange resins, heteropoly acids, silica-supported sulfuric acid, zeolite, *p*-toluenesulfonic acid and $BF_3 \cdot Et_2O$, etc., have been employed in this process. However, many problems, e.g., catalyst deactivation, recovery and reuse of catalysts, inhibited their industrial application. The SO_3H-functionalized ionic liquids (figure 12), which were acid position uniform, nonvolatile, non-corrosive and immiscible with many organic solvents, have exhibited great potential in substitution of conventional homogenous and heterogeneous acidic catalysts. This SO_3H-functionalized ionic liquid was also found to be efficient catalyst for addition of aliphatic acids with various olefins with high efficiency. In this process, Ethylene, propylene and butene-1 all underwent the addition of acetic acid to give corresponding acetate with nearly 100% selectivity. In the case of long chain alkene, such as pentene-1, (1-methyl) butyl acetate and (1-ethyl) propyl acetate were detected in selectivity of 66% and 34%, respectively. Additionally, all produced esters were insoluble in the SO_3H-functionalized ionic liquids and, therefore, the products could be simply decanted out from the ionic liquid after reaction and the ionic liquid could be reused four times without occurring deactivation.

5. Immobilization of ionic liquid and its application [37,38]

Immobilization of ionic liquid should be an important branch in study of ionic liquid because of the easy separation and small amount of ionic liquid used. A typical process for support or immobilization of ionic

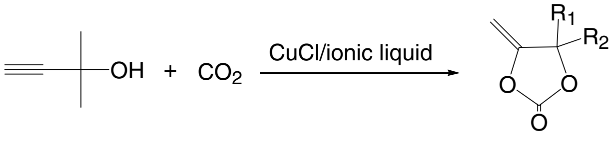


Figure 11. A typical process for synthesis of α-methylene cyclic carbonates.

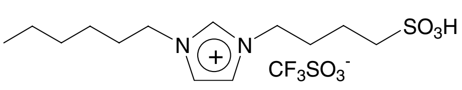


Figure 12. The SO_3H-functionalized ionic liquids used in esterification of aliphatic acid with olefin.

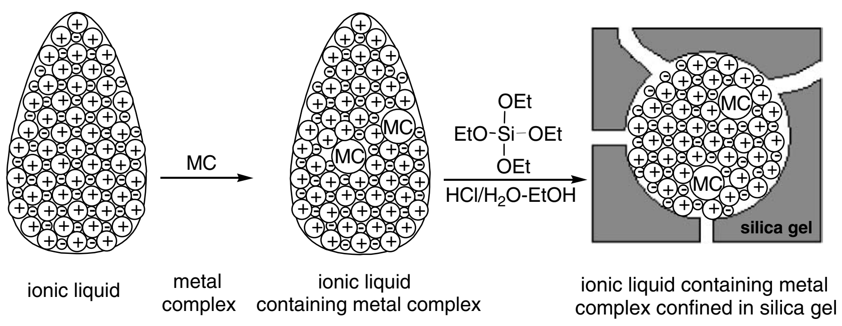


Figure 13. Process of immobilization of ionic liquids containing metal complexes.

Table 3
Results of oxidative carbonylation of aniline for synthesis of carbamate

Entry	Catalysts	Con. (%)	Sel. (%)	TOF[a]
1[b]	Pd(phen)$_2$Cl$_2$	7.2	98	223
2[b]	Pd(phen)$_2$Cl$_2$ + BMImCl	21	99	650
3	0.11%Pd-20.2%BMImCl/SiO$_x$	47	99	2678
4	0.1%Pd-18.4%BMImCl/TiO$_y$–SiO$_x$	96	96	5470
5	0.05%Pd-4.6%BMImCl/TiO$_y$–SiO$_x$	91	95	10,372

[a] Mol substrate/mol palladium/h.

[b] 1 mg of Pd(phen)$_2$Cl$_2$ and 40 mg of BMImCl were used.

liquid catalysts was reported recently [39], in which ionic liquid fragment such as dialkyl imidazolium cation was covalently bonded to the surface of silicon dioxide while the chemical bonding of dialkyl imidazolium cation to a solid surface may limit the free degree of dialkyl imidazolium cation and even change the physicochemical properties of the ionic liquids. Another method for immobilization of ionic liquid was by dipping the porous silicon dioxide in the mixture of ionic liquid containing the catalysts [40] and it was obvious that the leaching of the ionic liquid was unavoidable.

If confining or encapsulating ionic liquids without or with containing metal complex into solid silica gel with "one-pot assembly" of ionic liquid (or ionic liquid + metal complex), and silicate ester through a proper sol–gel process, the establishment of new kind of silica gel confined (immobilized) ionic liquid catalysts should be possible (figure 13).

The results of application of this silica gel confined ionic liquid catalyst system in oxidative carbonylation of aniline for synthesis of carbamate showed that the immobilization of ionic liquid was successful. As it was shown in table 3, the catalytic activity was enhanced greatly, the TOF number reached to 2678, even the amounts of palladium containing was decreased to about 0.1 mg from 1 mg. Further experiment also indicated that titanium was an effective cocatalyst for this reaction.

Another process about immobilized ionic liquid catalyst was used for deoximation reactions (figure 14). Several acid-functional ionic liquids (figure 15) were physically confined into the silica gel through a sol–gel process and used as effective catalysts for deoximation reactions, which proceeded under ambient temperatures without addition of any cocatalysts or oxidizing and reducing agents. The conversion of cyclo-hexanone oxime exceeded 90% with a selectivity nearly 100%.

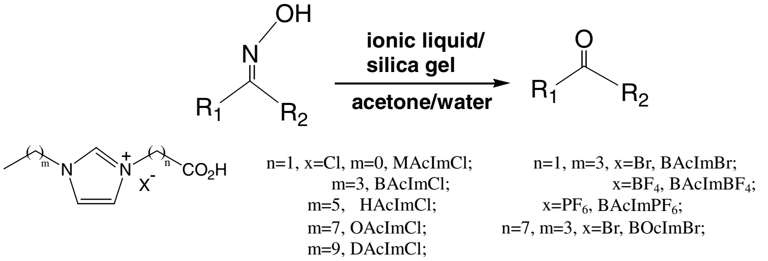
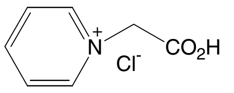


Figure 14. Deoximation of oximes using ionic liquid/silica gel as a catalyst in acetone/water.



PyAcCl

Figure 15. Functional ionic liquids used for synthesis of ionic liquid/silica gel.

6. Conclusion

The development of using ionic liquid as green reaction media or catalytic system in our institute in the last few years was introduced. It has been demonstrated that ionic liquids themselves could be effective catalysts for many reaction processes and this new kind of reaction media offered new opportunities for the development of homogeneous catalysis, organic synthesis and "supported liquid" catalyst system.

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