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CRITICAL REVIEW

Recent advances in ionic liquid catalysis

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Due to their unique properties, ionic liquids have offered great potential for developing clean catalytic technologies. After a short introduction of their advantages in green catalysis, recent advances in ionic liquid catalysis are reviewed with emphasis on four hot fields, *viz.* biomass conversion in ionic liquids, catalytic production of fine chemicals in ionic liquids, supported ionic liquid phase catalysis, as well as Friedel–Crafts reactions in ionic liquids. In particular, through selected samples, we show here the advantages and potential of ionic liquids in exploring cleaner catalytic technologies, as compared to traditional catalytic processes. Finally, further development of ILs in catalysis is briefly prospected.

1. Introduction

Over the past decade, catalysis in ionic liquids (ILs) has experienced a tremendous growth, and there are numerous examples of a variety of catalytic reactions that have been successfully carried out in such neoteric media.[1–5] The great enthusiasm for catalysis in ILs is not only driven by the curiosity of chemists, but also due to the growing awareness of developing greener reactions or process media in catalytic science. Indeed, there are many advantages to applying ILs as alternative solvents in a range of catalytic processes as compared to traditional volatile organic solvents (VOCs). One of the most promising advantages is their extremely low vapor pressure, which can match the human requirements of developing those greener catalytic technologies.[6] It is the reason that ILs are often called 'green solvents' in many earlier articles, and indeed the link between ILs and green chemistry is mainly related to the characteristic of low volatility.[7,8] According to incomplete statistics, more than 400 papers containing the expression "ionic liquid" or "ionic liquids" have been published in Green Chemistry as of the year 2010, and this number is growing very fast.

In addition to their 'greenness' feature, ILs are often referred to as 'designable solvents', mainly because their physical properties, such as melting point, viscosity, density, solubility, and acidity/coordination properties, can be tuned according to

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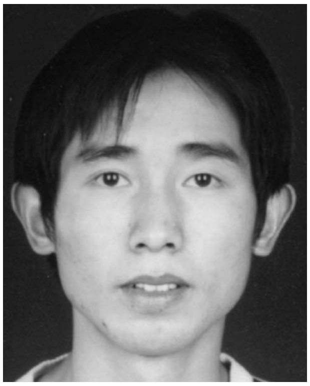
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different reactions or processes by altering the combination of their cations and anions. It is estimated that 10^{18} different ILs are theoretically possible,[9] which presents more opportunities to design or optimize the most suitable system for specific catalytic processes, although the number of commercially available ILs may be not more than 250 up to now. From the view of developing new catalytic technologies with less energy consumption, the use of ILs cannot only enhance the reaction rate to a great extent in many catalytic reactions, in particular those microwave- or ultrasound-assisted processes, but also improve the selectivity of the products greatly. Moreover, it has been generally thought that the ionic character of the ILs, which the molecular solvents lack, can provide the catalysts with a unique ionic environment that plays a positive role in stabilizing the reactive catalytic species or the reaction intermediates.[10] Therefore, catalysts in ILs often show improved catalytic activities over those conducted in traditional solvents, and, in many cases, they can catalyze those catalytic reactions that are not possible to carry out in common organic solvents. What's more, a lot of new knowledge can be obtained by conducting the different catalytic reactions in an ionic environment, which could not be achieved in common molecular solvents.[11]

Another advantage of ILs in catalysis is the immobilization of the catalyst. Besides the tunable solubility to most organic chemicals, ILs are also able to dissolve a wide range of inorganic and organometallic compounds, and therefore large numbers of catalysts having polar or ionic character can be immobilized in ILs, which can greatly facilitate the separation and subsequent reuse of the catalyst. In addition, the technological integration of ILs with other advanced technologies, including supercritical fluids, electrochemistry, biocatalysis, and nanotechnology, *etc.*, with great potential for growth, has received more and more attention in green catalysis, and for a long period to come, the importance of the ILs as excellent process solvents in these integrated technologies will be gradually recognized.

Due to the above mentioned advantages of ILs in catalysis, and with great potential for growth, the applications of ILs as excellent reaction or process media have been widely studied in the past decade, and a great deal of research papers and patents have been published.[12,13] In recent years, there have been a number of excellent reviews concerning catalysis in ILs, including biocatalysts in ILs,[14–17] two-phase catalysis in ILs,[18] asymmetric catalysis in ILs,[19,20] transition metal catalysis in ILs,[21,22] organometallic catalysis in ILs,[23] nanoparticle catalysis in ILs,[24] supported IL catalysis,[25] *etc.* In this paper, recent advances on ionic liquid catalysis are reviewed, and the emphasis will focus on several hot fields, *i.e.* the catalytic conversion of biomass, catalytic production of fine chemicals, supported IL phase catalysis, as well as IL-catalyzed Friedel–Crafts reactions. The review will mainly cover literature published up to January 2011, of which the majority has been reported in the past three years.

2. Biomass conversion in ILs

The catalytic conversion of biomass to biofuels and bio-based chemicals is of great importance in industry, because these biofuels and related platform chemicals can not only reduce global dependence on fossil fuel resources, but also weaken the growing environmental concern induced by the use of fossil fuels.[26–28] As the major component in biomass, cellulose $(C_6H_{10}O_5)_n$ is the most abundant and renewable carbon source on earth (35–50% in lignocellulosic materials, *ca.* 90×10^9 metric tons produced annually).[29,30] Thus, the effective utilization of cellulose to produce biofuels has received considerable attention, both in academic circles and in industry. In this process, an important focus is the depolymerization of cellulose to simple reducing sugars, such as glucose, fructose, xylose, and some partially depolymerized dimers, trimers, and other oligomers. These reducing sugars can be converted to a range of important fine chemicals (Scheme 1). However, due to the robust crystalline structure and the extensive network of intra- and intermolecular hydrogen bonds between its fibrils,[31] cellulose is insoluble in most of the solvents commonly used in the chemical industry, which always leads to the low catalytic efficiency of the depolymerization step.

In 2002, R. D. Rogers and his co-workers reported that some ILs were excellent solvents for cellulose dissolution, which opened a new door for cellulose chemistry.[32] Subsequently, a variety of ILs with good cellulose solubility have been developed, and many articles and reviews concerning the cellulose dissolution in ILs have been available.[33–39] Since the dissolution of cellulose in ILs can break down some physical barriers of cellulose, such as crystallinity index, morphology, surface area, and degree of polymerization, the subsequent depolymerization of cellulose in ILs becomes much easier than in water. Up to now, several catalytic processes involving biomass conversion have been explored in ILs.[40,41] In this section, we will mainly focus on the impressive scope of recent advances in biomass conversion in ILs, including degradation of cellulose in ILs (*i.e.* hydrolysis, alcoholysis, and hydrolysis/hydrogenation), conversion of sugars to 5-hydroxymethylfurfural (HMF) in ILs, as well as enzymatic hydrolysis of IL-pretreated cellulose.

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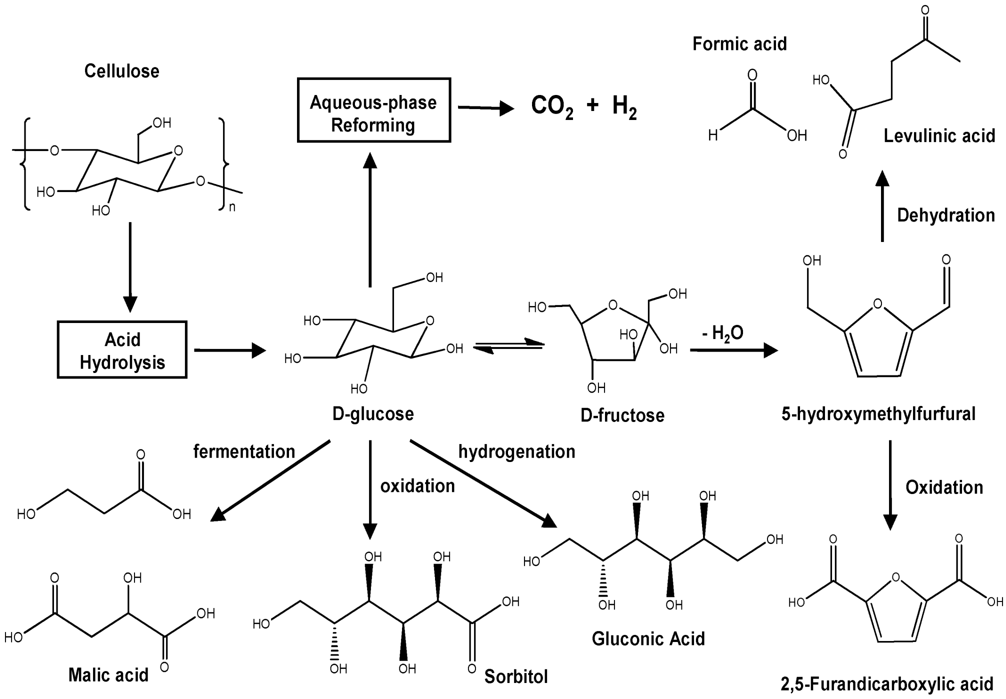


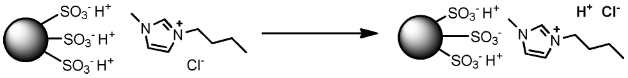
Scheme 1 A schematic diagram for the production of biofuels and bio-based chemicals from biomass resources.

2.1 Depolymerization of cellulose in ILs

In the process of biofuels or chemicals production from biomass, the crucial step is the direct depolymerization of cellulose to fermentable sugars or sugar alcohols through a catalytic process, such as acid-calalyzed hydrolysis, hydrolysis/hydrogenation, or alcoholysis, *etc.*[42,43] Among them, the direct hydrolysis of cellulose to glucose is regarded as the most promising process because of its excellent potential for development in industry. The hydrolysis reaction is a typical acid- or base-catalyzed reaction, in which acid-catalyzed hydrolysis is more commonly practised because the latter always leads to more side reactions. Both homogenous dilute acids (H_2SO_4 or HCl)[44] and heterogeneous solid acids (*e.g.* carbon materials bearing strongly acidic groups or $HNbMo_6$)[45,46] have been proven active catalysts for the hydrolysis of cellulose in water, however, only low glucose yields can be obtained. To date the efficient transformation of cellulose to glucose under mild conditions still remains a significant challenge.

In 2007, Zhao *et al.* reported for the first time that the hydrolysis of cellulose could be efficiently catalyzed by mineral acids in the IL [BMIm]Cl.[47] Under optimized reaction conditions, the H_2SO_4/[BMIm]Cl system can afford 43% glucose yield and 77% TRS yield (Total Reductive Sugar). The amount of H_2SO_4 had a significant effect on the glucose yield and low concentration H_2SO_4 favored the depolymerization of cellulose to reductive sugars. In the hydrolysis of different celluloses with degrees of polymerization (DPs) ranging from 100–450, similarly good results (20–39% glucose yield and 62–73% TRS yield) can be obtained. A later study[48] showed that, in ILs, the hydrolysis of lignocellulosic materials could also be efficiently catalyzed by 7 wt% hydrogen chloride. TRS yields were up to 66%, 74%, 81% and 68% for corn stalk, rice straw, pine wood and bagasse, respectively. Subsequently, Seddon and his co-workers studied the kinetics of the acid-catalyzed hydrolysis of cellobiose as a model for cellulose hydrolysis in 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl). Judging from the results, two competing reactions, polysaccharide hydrolysis and sugar decomposition, varied with the acid strength, and an acid of $pK_a \sim 0.5$ favored the formation of reducing sugars in comparison to their degradation.[49] Moreover, the hydrolysis of cellulose could also be catalyzed by a catalytic amount of $FeCl_2$ in an acidic IL 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate.[50] In the solvent of [BMIm]Cl, the hydrolysis of cellulose can also be catalyzed by acidic ILs.[51] The hydrolysis activity and the product distribution are directly associated with the acidity of the ILs. *In situ* ^{13}C NMR spectroscopy can clearly monitor the evolution of products during different reaction stages.

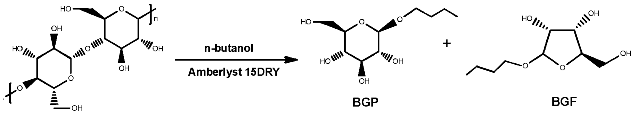
Although high catalytic activity could be achieved in the homogenous hydrolysis of cellulose, the separation of reaction products from the ILs remains a challenge due to the strong affinity of ILs for the reducing sugars. Recently, the hydrolysis of cellulose over solid catalysts is becoming the focus of study.[29,43,52,53] For the solid catalysts, however, a principal problem is that efficient access of the very large cellulose molecule to the catalyst surface is not easy. In 2008, Rinaldi and his co-workers reported that the decomposition of cellulose could be efficiently catalyzed by the acidic resins in [BMIm]Cl.[54] What is striking in this work is that the depolymerization progress can stop at the cello-oligomers stage. In the presence of Amberlyst 15 in [BMIm]Cl, microcrystalline cellulose can be selectively depolymerized, where about 90% yield of cello-oligomers with a degree of polymerization around 30 and only negligible amounts of reducing sugar could be obtained at 100 °C for 1.5 h. In a later study, the factors responsible for the controlled depolymerization were studied, and an ion-exchange catalytic mechanism was presented to explain the depolymerization of cellulose (Scheme 2).[55]



Scheme 2 The ion-exchange process involving $[BMIm]^+$ and $[H]^+$ species (Adapted from Ref. 17).

Microwave irradiation is a powerful tool to accelerate organic reactions. Compared to conventional oil bath heating, microwave irradiation can not only reduce the reaction time, but also greatly improve the catalytic activity of the hydrolysis reaction. Under microwave heating at 240 W using HY zeolite as a catalyst and for Avicel cellulose with a DP value of 220, the glucose yield and TRS yield reached 36.9% and 47.5% in 8 min, respectively. Although microwave irradiation played an important role in promoting the hydrolysis of cellulose, the complete dissolution of cellulose in ILs, which can make the β-glucosidic bonds more H^+-accessible, was the principal contributor to the high activity.[56]

Cellulose can also be directly converted to alkyl glycoside by a one-pot hydrolysis/alkylation process in the presence of alcohol and water.[57] When the reaction was performed in octanol/IL/H_2O, 82 wt% yield of octyl-α,β-glucoside plus octyl-α,β-xyloside could be achieved over Amberlyst 15 in the IL [BMIm]Cl. The amount of water present in the reaction medium and its evolution during the reaction was regarded as the key to success of this process. The solid acid catalyst can also catalyze the alcoholysis reaction between cellulose and *n*-butanol (Scheme 3).[58] Under the optimized reaction conditions and in the solvent of [BMIm]Cl, the cellulose could be completely converted over Amberlyst 15, and the butylglucopyranoside (BGP) yield was up to 86%. Moreover, the IL promoted glycosylation of various alcohols with unprotected and non-activated monosaccharides were investigated under scandium triflate catalysis.[59] However, the separation of the reaction products from the ILs also remains an unsolved problem in these processes.



Scheme 3 The splitting of cellulose with formation of BGP and BGF. (Adapted from Ref. 58).

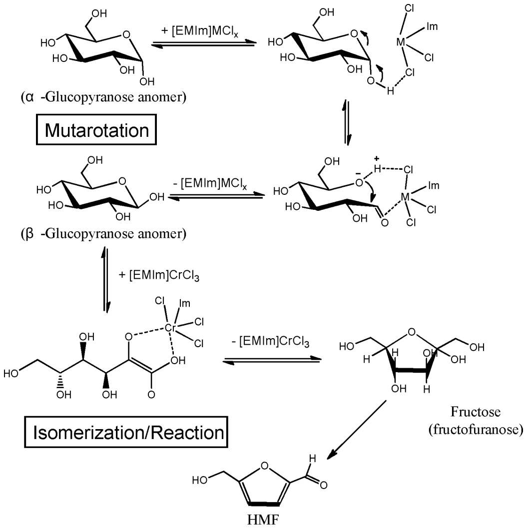
Very recently, a new hydrolysis/hydrogenation process has been exploited for the one-pot catalytic conversion of cellulose into sugar alcohols.[60] In this process, the cellulose could be directly converted to hexitols over a boronic acid binding agent combined with an IL-stabilized ruthenium nanoparticle catalyst. In the presence of sodium formate as the hydrogen donor, the sorbitol yield was up to 94%. During the reaction, the binding agent mainly promotes the rate of cellulose conversion and the Ru nanoparticle plays the role of the hydrogenation catalyst. Moreover, the heterogeneous Pt/C or Rh/C catalysts combined with a homogeneous Ru complex were applied to catalyze cellulose conversion to sugar alcohols in [BMIm]Cl in the presence of hydrogen gas. The sorbitol yield can be achieved as high as 74%.[61] Although good results can be obtained by the hydrolysis/hydrogenation process, noble metal catalysts have to be used, and meanwhile the limited hydrogen supply also restricts its large-scale application in industry to some extent.

2.2 Conversion of biomass to 5-HMF in ILs

As previously mentioned, the acid-catalyzed hydrolysis of cellulose and hemicellulose to glucose can be greatly enhanced in ILs, however, the separation of the polar monosaccharides from ILs remains a big challenge. One alternative approach is further conversion of glucose to a more easily separable compound. 5-Hydroxymethylfurfural (5-HMF), a versatile and key intermediate in biofuels chemistry and the petrochemical industry, can be easily separated from ILs by extraction. Thus, the catalytic conversion of different biomass feedstock, including cellulose, glucose, and fructose, to HMF in ILs has also received great interest. In fact, the dehydration of cellulose or monosaccharides (*e.g.* glucose and fructose) to 5-HMF in ILs is not a new process. As early as 1983, it has been reported that the fructose can be efficiently converted to 5-HMF in a molten salt, pyridinium chloride.[62] However, almost no other research about this process has been reported in ILs in the following twenty years.

In 2003, Lansalot-Matras *et al.* re-visited the acid-catalyzed dehydration of fructose in the presence of IL.[63] When the reaction was carried out over the Amberlyst-15 catalyst in 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIm][BF_4]$), a HMF yield up to 50% could be obtained within 3 h. In this reaction, DMSO was used as a co-solvent in order to solubilize fructose in ILs. In 2007, an impressive progress on the conversion of biomass to 5-HMF in ILs was reported by Zhao and his co-workers.[64] In the solvent of [EMIm]Cl, the chromium(II) chloride could efficiently catalyze the conversion of glucose to 5-HMF with a yield near 70%. The catalytic activity of many other metal chlorides were also tested under the same conditions, and strangely, only $CrCl_2$ exhibited good catalytic performance. The authors proposed that the $[CrCl_3]^-$ intermediate formed by the interactions between [EMIm]Cl and $CrCl_2$ played a role in proton transfer, which could facilitate isomerization to fructose, followed by a rapid dehydration to 5-HMF (Scheme 4).

Recently, a NHC-Cr/IL system has been developed for the selective conversion of sugars into 5-HMF. The HMF yields were as high as 96% and 81% for fructose and glucose, respectively.[65] Moreover, under microwave irradiation, *ca.* 90% isolated yield from glucose could be obtained in the presence of $CrCl_3$ and IL.[66] Although chromium chlorides exhibited good catalytic activity towards the conversion of glucose into HMF, an exact catalytic mechanism for the exceptional effectiveness of $CrCl_3$ in this process remains elusive. A possible mechanism was proposed by Pidko *et al.*, which combined kinetic experiments, *in situ* X-ray absorption spectroscopy (XAS), and density functional theory (DFT) calculations to unravel the molecular-level details of the unique reactivity of chromium(II) chloride towards selective glucose dehydration in [EMIm]Cl.[67] The authors proposed that transient Cr^{2+} dimers formed during the reaction should be responsible for the glucose activation. The Lewis acid $SnCl_4$ was also found to convert glucose into 5-HMF in 1-ethyl-3-methylimidazolium tetrafluoroborate ($[EMim][BF_4]$). The



Scheme 4 The proposed metal halide interaction with glucose in [EMIM]Cl. $CuCl_2$ and $CrCl_2$ catalyze the mutarotation leading to interconversion of α- and β-glucopyranose anomers. $CrCl_2$ leads to the isomerization of glucopyranose to fructofuranose, followed by dehydration to HMF. (Adapted from Ref. 64).

formation of the five-membered ring chelate complex of the Sn atom and glucose might play a key role for the formation of HMF in this process.[68] Moreover, the heteropoly acids[69] were also found to be highly active and selective catalysts for the dehydration of glucose. In the presence of acetonitrile as a cosolvent and using 12-MPA as the catalyst, a glucose conversion of 98% with a HMF selectivity of 99% could be obtained after 3 h at 393 K in [EMIm]Cl. The author also studied the subsequent hydrogenation of HMF dissolved in [EMIm]Cl and acetonitrile to 2,5-dimethylfuran (DMF) over the Pd/C catalyst.

Besides the conversion of glucose, the dehydration of fructose in ILs was also widely studied over a variety of catalysts, such as lanthanide catalysts,[70] sulfonic ion-exchange resin,[71] sulphuric acid,[72] hydrochloric acid,[73] tungsten salts,[74] germanium(IV) chloride,[75] and so on, and excellent HMF yields can be obtained under mild conditions. For example, fructose could be converted to HMF in quantitative yields at room temperature in a binary systems involving ILs.[72] The addition of cosolvents, such as acetone, DMSO, ethanol, methanol, and ethyl acetate, to the IL can not only promote the conversion of fructose into HMF, but also greatly decrease the reaction temperature. Moreover, the dehydration of fructose into 5-HMF can be catalyzed by using Amberlyst 15 as catalyst in the solvent of [BMIM]Cl. A fructose conversion of 98.6% with a 5-HMF yield of 83.3% was achieved in 10 min at 80 °C.[71]

In comparison with the high efficiency of monosaccharide dehydration (fructose and glucose), the direct catalytic conversion of cellulose or lignocellulosic biomass to HMF is much harder, even in the presence of ILs. Recently, a single-step catalytic process was developed, wherein the cellulose as the feed was rapidly depolymerized and the resulting glucose was further converted to HMF under mild conditions.[76] In the presence of [EMIM]Cl, a small amount of $CuCl_2$ paired with an even smaller amount of $CrCl_2$ ($n = 0.005$ in total) was an effective catalyst system for the hydrolysis of cellulose at 80–120 °C (at 55.4 ± 4.0% HMF yield). After extractive separation, the recovered [EMIM]Cl and the catalyst can be reused three times without obvious catalyst deactivation occurring. Moreover, with an [EMIm]Cl/H_2O mixture as the solvent and under relatively mild conditions (120 °C, 6 h), cellulose can be converted directly into HMF in high yield (up to 89%) in the presence of $CrCl_2$.[77] Zhao *et al.* also reported an efficient strategy for $CrCl_3$-mediated production of 5-HMF in a 61% isolated yield from cellulose (Avicel) in IL under microwave irradiation.[66] The coordination chemistry involving $CrCl_3$ was thought to play a key role in this process. The combined study of experimental results and *ab initio* calculations demonstrated that the significantly increased K_w by ILs in the IL–water mixture is responsible for the high activity.

Moreover, the conversion of cellulose and lignocellulosic biomass (*e.g.* corn stover and pine sawdust) to HMF was also reported in the solvent of DMA/LiCl by using [EMIm]Cl as an additive.[78] If the reaction was performed at 140 °C and 2 h in the presence of the chromium(II) chloride and hydrochloric acid, a 54% HMF yield could be obtained from cellulose. If only [EMIm]Cl as the solvent and $CrCl_3$/HCl as the catalyst were employed, a 42% yield of HMF could be obtained from Corn stover. It should be noted that even without any pretreatment, by using this catalyst system, the lignocellulosic biomass could also be readily converted into HMF. And in addition to glucose, fructose, cellulose and lignocellulosic biomass, the macroalgae-derived carbohydrates can also be considered as feedstock for the HMF production. Table 1 lists the partial results of IL-mediated 5-HMF production from biomass.

2.3 Enzymatic hydrolysis of IL-pretreated cellulose

In comparison with the common molecular or solid catalysts, the biocatalytic reactions are always more environmentally benign because they have many advantages, including mild reaction conditions, high yield, and high selectivity. Thus, in addition to the specific focus on the acid-catalyzed conversion of the biomass, the hydrolysis of cellulose can also be catalyzed by enzymes.[79–81] It is well known that cellulases can selectively hydrolyze cellulose to fermentable sugars under mild conditions.[82,83] However, enzyme catalyzed cellulose hydrolysis in aqueous media always suffers from slow reaction rates due to the robust crystallinity structure and extremely low solubility in water. The pretreatment of microcrystalline cellulose using ILs can change the crystalline structure of cellulose into an amorphous state and increase the accessibility between the enzyme and the β-glucosidic bonds, thereby allowing a more efficient enzymatic hydrolysis. Thus, many attempts were made to disrupt the cellulose structure using the ILs in a cellulose regeneration strategy, which accelerated the subsequent hydrolysis reaction.[84–87] Unfortunately, it has also been reported that significant decreases in cellulase activity can be observed for the hydrolysis reaction of cellulose in the presence of trace amounts of ILs.[85,88] Therefore, the need to develop 'enzyme compatible' or 'enzyme friendly' ILs is very important for the enzymatic hydrolysis of cellulose.

Dordick and his co-workers reported that the IL 1-ethyl-3-methylimidazolium acetate ([EMIm][OAc]) can be used as a pretreatment solvent to extract lignin from wood flour.

Table 1 Partial results of IL-mediated 5-HMF production from cellulose, glucose, and fructose

Substrate/amount	Solvent/amount	Catalyst/amount	$T/°C$	t/min	HMF yield (%)	Ref.
Cellulose (Avicel)/0.1g	[BMIm]Cl/2 g	$CrCl_3 \cdot 6H_2O$/10 mg	~ 100	2 (*MW*)[a]	61	66
a-Cellulose/0.1 g	[BMIm]Cl/2 g	$CrCl_3 \cdot 6H_2O$/10 mg	~ 100	2 (*MW*)[a]	62	66
Cellulose/0.5 g	[EMIm]Cl/2.5 g	$CrCl_2$/0.038 mg	120	180	82	77
Cellulose/0.5 g	[EMIm]Cl/2.5 g	$CrCl_2$/0.038 mg	120	360	89	77
Cellulose/4wt%[b]	DMA-0.203 g/LiCl-10 wt%/[EMIm]Cl-60 wt%	$CrCl_2$/HCl	140	120	54	78
Starch/0.1 g	[EMIm]BF_4/1 g	$SnCl_4 \cdot 5H_2O$/0.0216 g	100	1440	47	68
Fructose/0.072 g	[BMIm]Cl/DMSO 0.5 mL/0.3 mL	Amberlyst 15/143 mg	80	1920	87	63
Fructose/0.05 g	[EMIm]Cl/0.5 g	$CrCl_2$/6 mol%[c]	80	180	65	64
Fructose/0.05 g	[EMIm]Cl/0.5g	$CrCl_2$/6mol%[c]	80	180	69	64
Glucose/100 mg	[BMIm]Cl/1 g	$CrCl_3$/3.6 wt%[c]	~ 100	1 (MW)[a]	91	66
Glucose/100 mg	[EMIm]BF_4/1 g	$SnCl_4 \cdot 5H_2O$/15 mol%[c]	100	180	60	68
Fructose/0.1 g	[BMIm]Cl/1 g	Amberlyst 15/0.05 g	80	10	83	71
Fructose/0.1 g	[BMIm]Cl/DMSO 5.73 mmol/0.862 mmol	Amberlyst 15/0.05 g	25	360	78	72
Glucose/180 mg	[BMIm]Cl/2 g	12-MPA/1 mmol	120	180	89[d]	69
Glucose/180 mg	[BMIm]Cl/2 g	12-MSA/1 mmol	120	180	91[d]	69
Fructose/100 mg	[BMIm]Cl/0.5 g	WCl_6/10 mol%[c]	50	240	63	75
Glucose/100 mg	[BMIm]Cl/1 g	$Yb(OTf)_3$/0.056 mmol	140	240	24	70
Fructose/100 mg	[BMIm]Cl/0.5 g	$(HCl)_6$/8 mol%[c]	23	1440	72	74
Fructose/100 mg	[BMIm]Cl/0.5 g	WCl_6/8 mol%[c]	23	1440	65	74

[a] MW means microwave irradiation; [b] Based on the total mass of the reaction mixture; [c] Based on glucose or fructose; [d] HMF selectivity.

The cellulose in the pretreated wood flour becomes far less crystalline without undergoing solubilization. When 40% of the lignin was removed, the cellulose crystallinity index dropped below 45, resulting in >90% of cellulose in wood flour being hydrolyzed by *Trichoderma viride* cellulase.[86] The stability of hyperthermophilic enzymes in the presence of [EMIm][OAc] was investigated and compared with the industrial benchmark *Trichoderma viride* cellulase.[89] Under the optimum conditions, both hyperthermophilic enzymes are active on [EMIm][OAc] pretreated Avicel cellulose and corn stover. These enzymes can be recovered with little loss in activity after exposure to 15% [EMIm][OAc] for 15 h. As previously mentioned, the microcrystalline cellulose can be selectively depolymerized to the cello-oligomers with a degree of polymerization around 30 by the resin catalyst Amberlyst 15DRY in the presence of [BMIm]Cl, which can make the β-glucosidic bonds more H^+-accessible to the cellulase. Inspired by this work, Rinaldi *et al.* studied the enzymatic hydrolysis of these cello-oligomers by the cellulase.[90] Under mild conditions, the commercial cellulase could hydrolyze these cello-oligomers to a mixture of glucose (40%, 4 h) and cellobiose (54%, 4 h) at 45 °C, reaching very high conversion in only a few hours (94%, 4 h). Although good results have been achieved by an integrated enzymatic approach, there are several significant drawbacks for the degradation of cellulose with enzymes, such as high enzyme cost, long residence times associated with the imposed low reaction temperature, and its rigorous requirement on working environment, which also limit its large scale applications in industry.

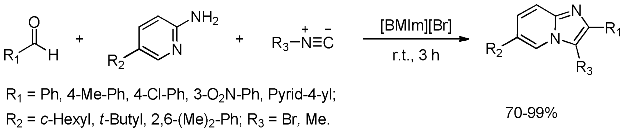
3. Catalytic production of fine chemicals in ILs

Fine chemicals are complex, single, pure chemical substances, which are produced in limited quantities (<1000 metric tons per year) in multipurpose plants by multistep batch chemical or biotech(nological) processes.[91] Inevitably, the large amounts organic solvents were utilized in the processes of fine chemicals production and separations. These solvents are often volatile and sufficiently water-soluble to contaminate air emissions and aqueous discharge streams, thereby adding to the environmental burden and the cost of downstream processing and recovery operations. The syntheses of fine chemicals through the use of ionic liquids has been an active research field in recent years. The ionic nature of ILs determines the lack of a measurable vapor pressure that, associated with a high thermal and chemical stability, makes them intrinsically excellent candidates for industrial applications of fine chemicals in contrast to conventional solvents that consist of covalent molecules. Compared to traditional production methods, the new technologies integrated with the ILs have many advantages, including short reaction time, mild reaction conditions, high selectivity, high yield, simplified operation procedure, and ease of product separation and recyclability of catalyst/ILs.[92]

3.1 Pharmaceutical intermediates

Most pharmaceuticals, pesticides, insecticides, rodenticides, and weed killers are heterocycles, which can be synthesized in ILs, as excellently reviewed by Martins *et al.*[93] Imidazo[1,2-a]pyridine represents an important class of pharmaceutical compounds, which were usually synthesized by the condensation of an aldehyde, an isocyanide and a 2-aminoazine in the presence of a strong protic acid in a multicomponent reaction. In practice, a long reaction time is always required and strongly acidic cation exchange resins are used for the product isolation, which causes a lot of complications when the reactions need to be pushed to completion.

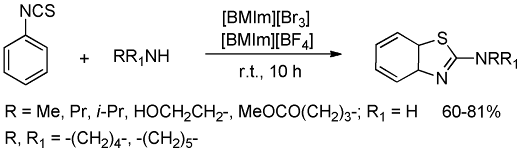
Recently, Shaabani *et al.*[94] developed a new process for 3-aminoimidazo[1,2-*a*]pyridines production *via* a three-component condensation reaction of aldehydes, 2-amino-5-methyl-[Br]pyridines, and isocyanides at room temperature in the presence of [BMIm]Br (Scheme 5), wherein the IL played an important role in the ecocompatibility improvement of the whole process. In the presence of [BMIm]Br, very high conversions could be achieved in 3 h. Typically, the yields are obtained in the



Scheme 5 The synthesis of 3-aminoimidazo[1,2-*a*]pyridines in [BMIm]Br. (Adapted from Ref. 94).

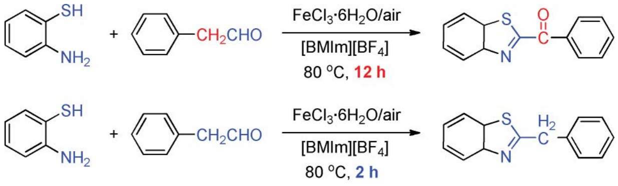
range of 70–99%, and the catalyst can be recycled and reused four times with a gradual decrease in total yield (95%, 92%, 90%, 85%). By contrast, only 25% isolated yield can be obtained in 12 h in the absence of [BMIm]Br, suggesting that [BMIM]Br is an important accelerator for this reaction.

Thiazoles are the active pharmaceutical ingredients in many drugs due to their potential antiinflammatory, antitumor, antihyperlipidemic, and antihypertensive properties. Recently, Le *et al.*[95] reported an efficient method to produce substituted 2-benzothiazoles *via* a one-pot reaction using [BMIM][Br$_3$] as the catalyst. Under mild conditions, the reaction can be successfully carried out starting from phenyl isothiocyanate and amines (Scheme 6). Compared to the traditional methods, the new approach has many advantages, including higher yield and shorter reaction time. Under optimized conditions, 2-(propylamino)benzothiazole and 2-(*N*-piperidino)benzothiazole can be obtained with yields of 80% and 75%, respectively.



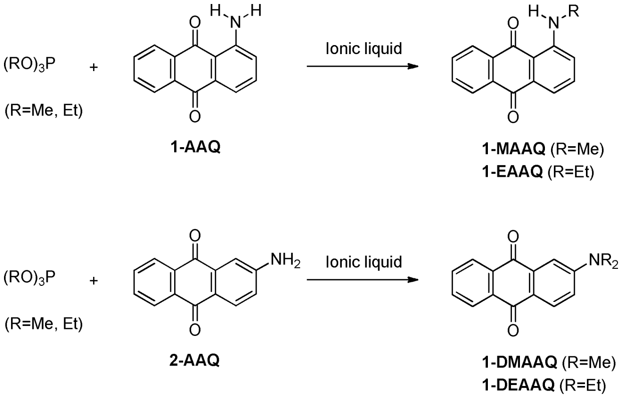
Scheme 6 The catalytic synthesis of thiazoles in ILs. (Adapted from Ref. 95).

Li *et al.* demonstrated the synthesis of 1,4-dihydropyridinones (Hantzsch products) and 3,4-dihydropyrimidinones (Biginelli products) in a one-pot reaction of aldehydes, β-dicarbonyl compounds and urea in the presence of the non-toxic IL 1-*n*-butyl-3-methylimidazolium saccharinate ([BMIm][Sac]).[96] Fan *et al.* also reported the synthesis of 2-benzoylbenzothiazole and 2-benzylbenzothiazole by air oxidized tandem process from commercially available 2-aminothiophenols and phenylacetaldehydes by using $FeCl_3·6H_2O$ as a catalyst in the IL [BMIm][BF$_4$] (Scheme 7).[97] In the presence of $FeCl_3·6H_2O$ (0.1 equiv) and in the solvent of [BMIm][BF$_4$], the reaction between 2-aminothiophenol and phenyl acetaldehyde began to yield 2-benzylbenzothiazole in the first several hours. If the treatment time is prolonged further, the desired product 2-benzoylbenzothiazole will be gradually detected. The tandem process from 2-aminothiophenol and phenylacetaldehyde to 2-benzoylbenzothiazole was completed in 16 h at 60 °C. When it was run at 80 °C, the period for a complete transformation was shortened to 12 h. However, when molecular solvents, such as THF, CH_3CN or toluene, were employed, the reaction afforded a mixture of 2-benzoylbenzothiazole and 2-benzylbenzothiazole under similar conditions, and 2-benzoylbenzothiazole was obtained only in a very low yield (≤15%).



Scheme 7 The synthesis of 2-benzoylbenzothiazoles and 2-benzylbenzothiazoles in ILs. (Adapted from Ref. 97).

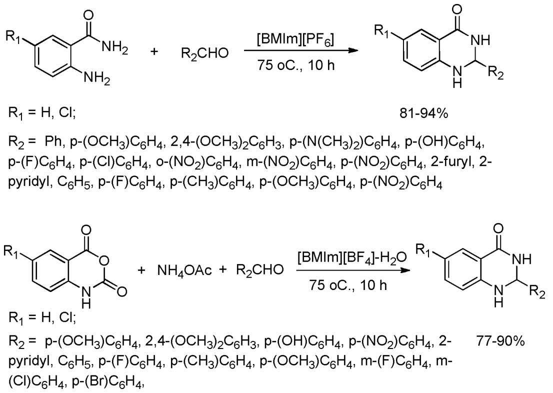
Amino-substituted 9,10-anthraquinones are very important intermediates in the fields of the dye industry, biology, and pharmaceutical chemistry. The 1,3-dialkylimidazolium bromides were found to be excellent catalysts for *N*-alkylations of amino-9,10-anthraquinones by trialkyl phosphites (Scheme 8), in which the IL [BPIm]Br gave the best catalytic activity. The effects of reaction temperature and the type of IL used on the activity and selectivity were investigated The use of ILs can significantly enhance the rate of *N*-alkylation of AAQs, and meanwhile avoid the use of bases and highly polar organic solvents.[98]



Scheme 8 The reactions of 1-AAQ or 2-AAQ with trialkyl phosphites in ILs. (Adapted from Ref. 98).

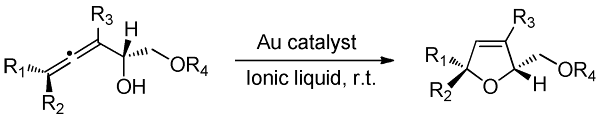
Quinazolinone derivatives, an important class of fused heterocycles, have also attracted much attention due to their potential biological and pharmaceutical activities. Among them, 2,3-dihydroquinazolin-4(1H)-ones have been synthesized in excellent yields *via* a direct cyclocondensation of anthranilamides and aldehydes in ILs or one-pot three-component cyclocondensation of isatoic anhydrides, ammonium acetate and aldehydes in the solvent of IL and water without any additional catalyst (Scheme 9).[99] [BMIm][PF$_6$] in various reaction media, including molecular solvents, was determined to be the most effective reaction medium for this process, and a yield of 92% for the desired product could be obtained through the condensation reaction between anthranilamide and benzaldehyde at 75 °C after 35 min. By contrast, the yield in molecular solvents is less than 36%. The reaction was compatible with a variety of electron-donating and electron-withdrawing substituents in the aryl aldehydes, yields ranging from 81 to 94% were obtained. For the three-component cyclocondensation, [Bmim][BF$_4$]-H_2O gave the best results. Moreover, a series of aldehydes bearing either electron-donating or electron-withdrawing groups on the aromatic ring were also examined, and the desired products could be obtained in excellent yields (77–90%).

2,5-Dihydrofurans and their derivatives have found wide applications as pharmaceuticals, flavor and fragrance compounds. Their structural subunits have been found in a wide



Scheme 9 The direct cyclocondensation of anthranilamides and aldehydes in ILs or one-pot three-component cyclocondensation of isatoic anhydrides, ammonium acetate and aldehydes in [Bmim][BF_4]-H_2O. (Adapted from Ref. 99).

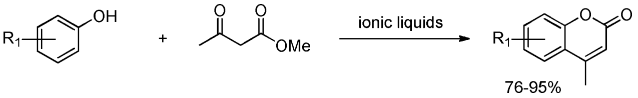
variety of natural products. Recently, Aksin *et al.* reported that nine α-hydroxyallenes were cyclized to the corresponding 2,5-dihydrofurans with complete axis-to-center chirality transfer in the presence of 1 mol% of $AuBr_3$ in the IL [BMIM][PF_6] (Scheme 10).[100] The $AuBr_3$/IL system is air-stable and gives good recyclable performance. The leaching of the gold catalyst during the product separations is extremely low (0.03 wt% after five runs). Among the tested Au(I) and Au(III) catalysts, the AuCl/[EMIM][$MeSO_3$] system gave a complete conversion in 10 min.



Scheme 10 The Gold-catalyzed cycloisomerization of functionalized α-hydroxyallenes to 2,5-dihydrofurans in ILs. (Adapted from Ref. 100).

3.2 Food additives

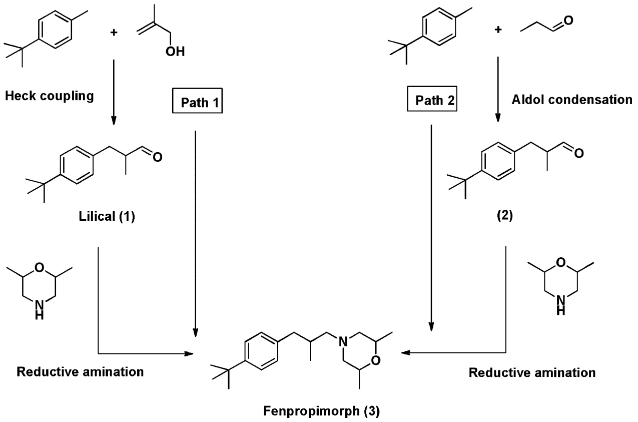
Coumarin and its derivatives are widely used in synthetic organic chemistry. Many products that contain the subunit of coumarin exhibit useful and diverse biological activity. These compounds find application in pharmaceuticals, fragrances, agrochemicals, and insecticides. A very valuable method for the synthesis of coumarins is the Pechmann reaction, which starts from phenols. In the conventional production of coumarins by the Pechmann reaction, concentrated sulfuric acid is used as the catalyst. This process always causes the formation of by-products, needs a long reaction time, and introduces corrosion problems. In 2005, a new catalyst system for the Pechmann condensation was developed by our group, which avoids the use of moisture sensitive reagents or high temperature reaction conditions to promote the reaction.[101] In this process, the non-chloroaluminate acidic ILs were found to be excellent catalysts for the Pechmann condensation. Even when the IL ([MBsIm][CF_3SO_3]) loads were as low as 5 mol%, good to high yields (76–95%) with activated phenols could be obtained at an oil bath temperature of 80 °C (Scheme 11). The acidity determinations of four non-chloroaluminate acidic ILs revealed that the Brønsted acidities of the ILs play a determining role in the rate acceleration of the Pechmann condensation, where the IL [MBsIm][CF_3SO_3] with strong acidity gave an excellent catalytic performance.



Scheme 11 The synthesis of coumarin derivatives in ILs. (Adapted from Ref. 101).

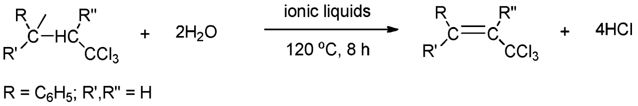
3.3 Pesticides

Fenpropimorph, 4-[3-(4-*tert*-butylphenyl)-2-methylpropyl]-2,6-dimethylmorpholine, is a pesticide, specifically categorised as a morpholine fungicide. The one-pot synthesis of the fungicide fenpropimorph has been reported by Forsyth *et al.* using two different synthetic strategies in an IL (Scheme 12).[102] The first pathway consists of a Heck coupling followed by reductive amination, the yield without solvent is only 14%, and 51% using organic solvent, however, the yield is as high as 81% when using the IL [BMPyrr][NTf_2] as the solvent and $PdCl_2$ as the catalyst; the second pathway consists of an aldol condensation followed by hydrogenation/reductive amination, giving a yield of 75%. Although both Heck and aldol processes proceed efficiently in ILs, only the second pathway can be recycled.



Scheme 12 One-pot sequential pathways to produce fenpropimorph. (Adapted from Ref. 102).

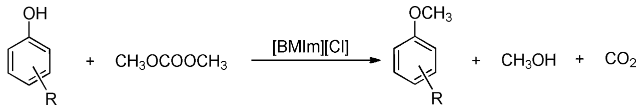
Cinnamic acid is a highly valuable class of fine chemicals with applications in polymer formulations, medication, pesticide, sensitive resin and plastics, as well as general organic synthesis. It is a key intermediate in the synthesis of segontin, cinnarizine, and chlorobenzene ammonic butyric acid. Weng *et al.* demonstrated the catalytic hydrolyzation of 1,1,1,3-tetrachloro-3-phenylpropane to produce cinnamic acid in different ILs (Scheme 13).[103] The hydrolyzation process can be carried out without additional catalyst in the presence of ILs, and the ILs can be easily separated and reused after the reaction. By contrast, both the conversion and the product yield in ILs were much better than that with acetic acid as solvent and sulfuric



Scheme 13 The hydrolytic reaction in ILs. (Adapted from Ref. 103).

acid as catalyst. Among all the tested quaternary ammonium ILs, [Et_3NH][HSO_4] gave the best catalytic performance for the hydrolyzation of 1,1,1,3-tetrachloro-3-phenylpropane, affording a nearly quantitative conversion with a product yield of 88%.

Aryl methyl ethers, a class of valuable intermediates for the preparation of dyes, agrochemicals, fragrances and pesticides, are always produced by *O*-methylation of the corresponding phenols with dimethyl sulfate or methyl halides. However, these methods require not only corrosive and toxic reagents but also a stoichiometric amount of strong base to neutralize acidic by-products, which results in large quantities of inorganic salts that require disposal. Recently, Shen and co-workers reported an efficient and environmentally friendly process for highly selective *O*-methylation of phenols with dimethyl carbonate (DMC) in the presence of an IL, 1-*n*-butyl-3-methylimidazolium chloride ([BMIm]Cl), at 120 °C (Scheme 14).[104] ILs with different anions showed quite different catalytic activities, in which [BMIm]Cl gave the highest yield of anisole (99.8%). In this process, 100% phenol conversion and nearly 100% selectivity of *O*-methylation have been achieved. What's more, the IL [BMIm]Cl can be easily reused without significant loss of activity. Therefore, this is a very ideal green catalytic process.

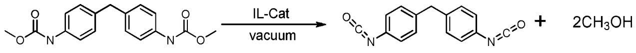


Scheme 14 The hydrolytic reaction in ILs. (Adapted from Ref. 104).

3.4 Isocyanates

Isocyanates are major raw materials for the manufacture of polyurethane, which have widely been used in producing elastomers, elastic fiber, coatings, and so on. Currently, isocyanates are produced by direct reaction of phosgene with amines in industry. This method poses great concerns for both environmental and safety problems. Not only is phosgene itself an extremely toxic reagent, but also HCl released as a by-product causes serious corrosion. Thus, there has been increasing interest in developing green alternative catalytic technologies and processes for isocyanate production. One of the most attractive non-phosgene processes is the thermal cleavage of *N*-substituted carbamates to obtain corresponding isocyanates. Up to now, however, the efficient thermal decomposition of carbamates to isocyanates still remains a challenge because this process needs to be conducted under high vacuum and high temperature. Therefore, traditional molecular solvents cannot meet the requirements of this process, such as high thermal stability, high thermal capacity, and low volatility. Fortunately, ILs are very suitable for this process because of their low volatility, high thermal stability, and high thermal capacity.

Very recently, a successful process for isocyanate production from carbamates has been developed over supported metal catalysts and in the presence of ILs (Scheme 15).[105] In this process, the separation of isocyanate can proceed in parallel with the thermal cleavage of *N*-substituted carbamates, and the by-product alcohols can be removed rapidly from the reaction system under reduced pressure. Moreover, compared to traditional process, the reaction temperature can be greatly decreased from 260 °C to <190 °C. Under optimized conditions, the conversion of methylene diphenyl dimethylcarbamate (MDC) and the yield of methylene diphenyl diisocyanate (MDI) can be achieved as 94% and 87%, respectively. The usage of ILs makes this process more environmentally benign and energy saving because the back formation of carbamates by isocyanate and alcohols can be efficiently avoided and less side reactions occur at the relatively mild temperature and in the presence of chemically- and thermally-stable ILs. What is important, some ILs exhibited the ability of polymerization inhibition in this reaction, which thus made the catalyst system very stable for a long period and recycled at least 50 times in a continuous-flow reactor. The results of quasi *in situ* FT-IR showed that there existed some interaction between the carbamate, catalyst, and ILs, which may be responsible for the ILs' properties of inhibiting polymerization.



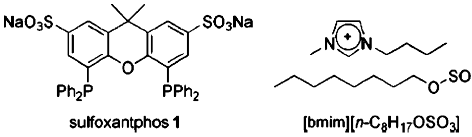
Scheme 15 The thermal decomposition of the MMDC to afford MDI in ILs.

4. Supported IL Phase Catalysis (SILPC)

The homogeneous catalysts in ILs usually present the advantages of high catalytic activity and good selectivity, however, their widespread use in catalytic processes is still hampered by several practical drawbacks, such as product isolation and catalyst recovery. Moreover, the large amounts of expensive ILs are needed in homogeneous catalytic processes, which may cause possible toxicological concerns. SILPC concept has been established to overcome these drawbacks. The SILPC combines the benefits of ILs and heterogeneous catalysis, such as the designability, good "solubility" of the catalytically active species, ease of handling, separation and recycling. In SILPC materials, a small amount of ILs is dispersed on the surface of a porous material. Due to the formation of a mean film thickness in the range of 10–50 Å on the support surface, the catalysts dissolved in the IL layer are very close to the reaction interface, and diffusion pathways are reduced as compared to the bulk biphasic systems, thereby often leading to high reaction rates. Generally, the SILPC materials are composed of three different parts, *i.e.* the porous support (alumina, silica or active carbon), the ILs (always a thin layer on the support surface), and the catalyst (nanoparticles or metal complexes). Up to now, three different synthetic pathways have been developed for the preparation of the SILPC materials: (i) the immersion method; generally, the porous solid support material is directly impregnated with an IL phase containing the catalytically active species or an IL, which itself is the catalytically active species, and a thin film of ILs can form on the surface of the support; (ii) the covalent anchoring method; by using this method, the IL fragment, such as the dialkylimidazolium cation, is usually covalently anchored to the support surface, and then the anions of ILs can coordinate the catalytically active species; (iii) the physical confinement/or encapsulation method; the ILs, either with or without the catalysts, can be physically confined or encapsulated into the pores of solid supports. Because of their attractive feactures, the concept of SILPC has received much attention in recent IL catalysis, and some excellent reviews have been available.[106,107] In this section, therefore, we will mainly focus on recent advances in the SILPC.

4.1 The immersion method

The immersion method is the most widely used approach for the preparation of SILP materials, in particular for the immobilisation of homogeneous metal complexes on the surface of solid supports by using the ILs. Among the reported studies, Wasserscheid's and Mehnert's groups first demonstrated the feasibility for the application of ILs in the concept of SILP catalysis.[108–111] In the SILP material, a thin film of IL is coated on the surface of a highly porous solid by a physical absorption method, and the transition metal complexes are always used as the catalytically active species. In many cases, the ordered three-dimensional structures in solutions of organometallic complexes were formed in a thin film of supported IL. The ordering effect can lead to a drastically reduced mobility of IL and complex molecules and could be used to induce unusual properties in the supported complexes.[112] Riisager and his co-workers demonstrate the applications of the rhodium catalyst containing the bisphosphine ligand sulfoxantphos/[bmim][n-$C_8H_{17}OSO_3$] (Scheme 16) supported on partly dehydroxylated silica in the selective, continuous, gas-phase hydroformylation of propene.[113] In a fixed-bed reactor, the resultant SILPC materials showed very high activity and good selectivity. Particularly, the lifetime of the SILPC reached up to 200 h time-on-stream, although a slight decrease in activity was observed at the end. Moreover, Yuan *et al.* reported a SILPC system for the hydroformylation reaction. The TPPTS-Rh complex [TPPTS = trisodium salt of tri-(m-sulfophenyl-)phosphine, P(m-$C_6H_4SO_3Na)_3$], which was dissolved in the ILs, was immobilized on MCM-41 by the immersion method. The resulting SILP materials showed higher catalytic activity for the hydroformylation of higher olefins, independent of IL type, as compared with their IL–organic biphasic counterparts and the one with SiO_2 as carrier. The catalysts can be reused several times without significant loss of activity or selectivity.[114]



Scheme 16 The structure of the bisphosphine ligand and the IL used for preparation of SILPC material. (Adapted from Ref. 113).

Moreover, Haumann and his co-workers developed a SILPC material by dispersing the IL [BMIM][n-$C_8H_{17}OSO_3$] containing rhodium–sulfoxantphos complex on the surface of silica (Fig. 1).[115] Continuous gas-phase experiments in a fixed-bed reactor revealed these SILPC catalysts to be highly active, selective and stable long-term. Compared to former studies using propene, these novel catalysts showed significantly higher activity and selectivity with 1-butene as feedstock. Later on, another similar SILPC material was developed based on a silica support coated with an acidic chloroaluminate IL and proved to be a highly attractive heterogeneous catalysts for the slurry-phase isomerization of diisopropylbenzenes (DIPBs).[116] Compared to the results in the liquid–liquid biphasic reaction, these materials gave a clearly different selectivity in the isopropylation of cumene, which was related to the reduction of the IL's acidity by the untreated silica support. Very similarly, a highly acidic SILPC material has been developed for the continuous gas-phase isopropylation of cumene and toluene.[117] The use of pre-treated supports for SILPC preparation is essential to obtain systems of high Lewis acidity and stability, and a higher acidity of the IL film on the support has a beneficial effect on the selectivity for mono-alkylated products. In particular, the SILPC material has been utilized in conjunction with gaseous substrates, whereby product separation and catalyst recycling can be avoided.

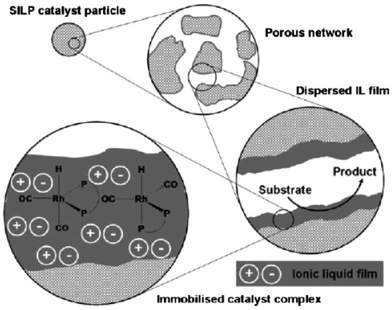


Fig. 1 A schematic representation of SILPC. (Adapted from Ref. 115).

The SILPC concept has also been applied for continuous methanol carbonylation. In this process, a solid, silica-supported IL phase rhodium iodide monsanto-type catalyst system, [BMIm][$Rh(CO)_2I_2$]–[BMIm]I–SiO_2, showed excellent activity and selectivity towards acetyl products in fixed-bed, continuous gas-phase methanol carbonylation.[118] Under optimized conditions, essentially complete conversion of methanol can be achieved with a TOF for acetyl products of 76.5 h^{-1} and space time yield (*i.e.* production rate) of 21.0 mol L^{-1} h^{-1}, with a high selectivity towards the ester relative to the acid (ester/acid ratio of about 3.5) and the DME by-product. Moreover, the SILPC concept for a fast and reliable screening of a series of known and novel homogeneous catalyst complexes (Ru, Ir, Os, Fe, Cu, Mo, Pd, Re, Rh) was applied in the water–gas shift reaction under mild conditions (Fig. 2).[119] Among the tested catalysts, ruthenium-based SILPC system exhibited by far the highest activity and showed reasonable stability over 24 h time-on-stream in a continuous, homogeneous WGS reaction. Similarly, Müller *et al.* used the SILPC strategy to immobilise the organometallic complexes in a thin film of supported ILs for the development of bi-functional catalysts combining soft Lewis acidic and strong Brønsted acidic functions. The resulting materials showed exceptional catalytic activity for the addition

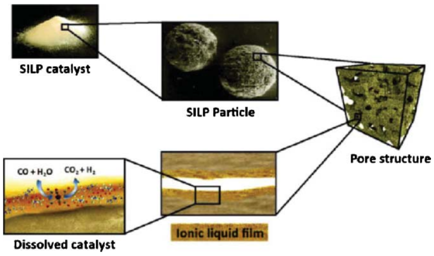


Fig. 2 Schematic principle of SILPC for the WGS reaction. (Adapted from Ref. 119).

of aniline to styrene, providing the Markownikoff product under kinetically controlled conditions and mainly the *anti*-Markownikoff product in the thermodynamic regime. The ILs here played a key role to achieve high activity by stabilizing the ionic intermediates in this reaction.[120]

Gu and his co-workers also developed a SILPC system by combining silica-supported benzenesulfonic acid sodium salt with a hydrophobic IL in water and successfully applied it as the active catalyst in the Michael reactions of indole (Fig. 3).[121] An efficient hydrophobic environment can be created on the surface of the silica–sodium material. Various indole derivatives and α,β-unstaturated carbonyl compounds were successfully applied to this system with water as the sole solvent to afford the desired Michael adducts in high yields. The system could be readily recycled without appreciable loss of reactivity. Simplicity of operation as well as the neutral, mild, and environmentally benign nature of the reaction could enable expansion to a wide variety of acid-labile substrates, even to a larger scale reaction.

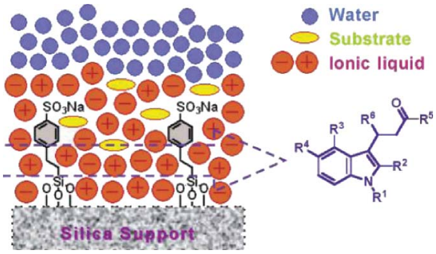


Fig. 3 Silica-supported benzenesulfonic acid sodium salt with hydrophobic IL in water. (Adapted from Ref. 121).

In 2007, Dez and his co-workers reported several new SILPC materials based on chitosan-supported ILs for the allylic substitution reactions (Fig. 4).[122] There were many advantages to use chitosan as catalytic support, such as high sorption capacities, high stability of metal anions (Pt and Pd) on chitosan and physical and chemical versatility of the biopolymer and chirality. When this catalyst was used in the amination reaction, a high level of activity combined with recyclability and reusability (>10 cycles) could be obtained. Recently, the combination of SILP concept with supercritical CO_2 flow systems was reported for the continuous enantioselective hydrogenation.[123] In the asymmetric hydrogenation of dimethyl itaconate, a turnover frequencies (TOFs) as high as 10500 h^{-1} at selectivities of >99% ee (S) can be achieved if the SILPC material with a chiral transition-metal complex and $scCO_2$ as the mobile phase were employed. The use of $ScCO_2$ as mobile phase over SILPC catalysts allows mild reaction conditions for nonvolatile and even solid substrates, making the use of organic solvents or additional purification steps unnecessary.

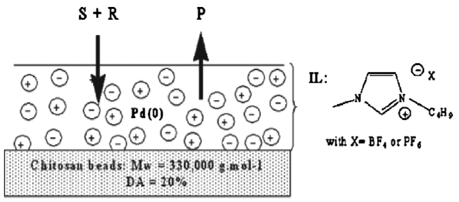
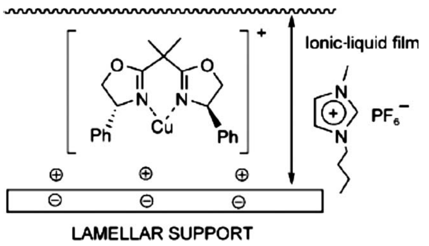


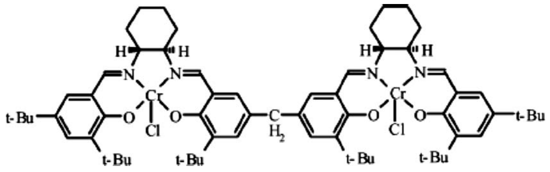
Fig. 4 Chitosan–SILPC system. (Adapted from Ref. [122].).

Mayoral and his co-workers developed an SILPC system composed of Laponite-supported [BMIm][PF_6] and bis(oxazoline)-copper complex (Scheme 17).[124] This material displayed good catalytic activity in enantioselective cyclopropanation reactions. When the IL was supported as a thin film on the surface of clay, the system behaves as a nearly two-dimensional nanoreactor in which the restrictions on rotational mobility and the close proximity to the surface support enantioselectivities, leading to a complete reversal of the overall selectivity of the reaction. The use of the SILPC system can alter the enantioselectivity to the *cis* isomer from 45% under homogeneous conditions to −56%, meanwhile the preference for *trans* isomers was reversed from 67% to 33%.



Scheme 17 The structure of the supported IL/copper complex film. (Adapted from Ref. 124).

The chiral Cr(salen) complex is an effective and highly selective catalyst for the asymmetric ring-opening (ARO) reactions of epoxides. Because this transition metal complex is expensive, catalyst recycling is mandatory. Jacobs and his coworkers attempted to apply the SILPC concept to immobilise the dimeric Cr(salen) catalyst (Scheme 18) in a silica-supported IL.[125] The resulting material offers very high selectivity and good reactivity for asymmetric ring-opening reactions of epoxides. In this reaction system, catalyst and IL can be recovered by Soxhlet extraction with acetone. It can also be used in a continuous-flow reactor.



Scheme 18 The structure of the dimeric Cr(salen) catalyst. (Adapted from Ref. 125).

Sintered metal fibers (SMF) were also proven to be good supports for the preparation of SILPC materials.[126] An SILPC Rh-based catalyst was shown to be active in the gas-phase hydrogenation of 1,3-cyclohexadiene (Fig. 5). SMF plates with high porosity were coated with a layer of carbon nanofibers (CNFs), and the IL thin film immobilized on CNF/SMF support with high thermal conductivity and large interface area ensures efficient use of the transition metal catalyst without mass-transfer limitations and isothermal conditions during the exothermic reaction. Excess phosphine ligand and acid in the IL phase are required to maintain catalyst activity and selectivity. The SILP catalyst, [$Rh(H)_2Cl(PPh_3)_3$/IL/CNF/SMF], showed high selectivity (>96%) and turnover frequency (TOF) up to 250 h^{-1} with acceptable stability during 6 h on stream.

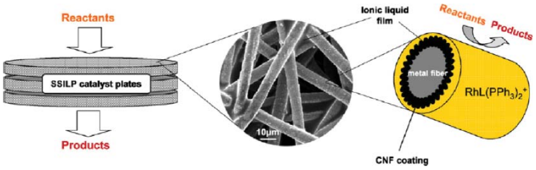


Fig. 5 A schematic presentation of the structured SMF support applied for SILP catalysis during gas-phase hydrogenation. (Adapted from Ref. 126).

Transition metal nanoparitcles are also immobilized as the catalytically active species in the ILs for the preparation of SILP catalysts. Han *et al.*[127] demonstrated the SILP concept by immobilizing Pd nanoparticles with a lactate-based IL on molecular sieves and used the resulting material for the liquid-phase hydrogenation of cyclohexene and 1-hexene (Fig. 6). The *in situ* generation of Pd nanoparticles has been observed in immobilized Pd(II) salt-catalyzed Suzuki reactions by using diethylaminopropylated alumina as support. Like the cases in the above-mentioned reports, owing to the presence of IL fragments on the surface of the support, the Pd nanoparticles formed were dispersed very well in the pores or channels of the support materials, and consequently, high activity and good recyclability were obtained for Suzuki reactions between aryl halides with arylboronic acids.[128]

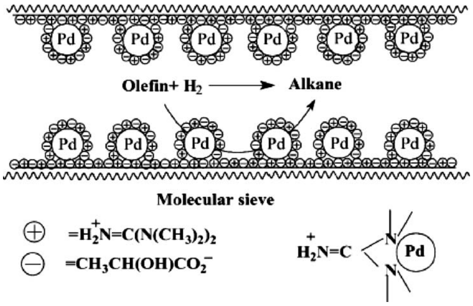


Fig. 6 An illustration of the immobilization of Pd nanoparticles on the surface of a molecular sieve with an IL layer. (Adapted from Ref. 127).

4.2 The covalent anchoring method

As mentioned above, a variety of SILPC materials have been developed by dipping the porous support in the ILs containing the metal complex. For these materials, however, the leaching of the ILs and metal-complex catalyst seems unavoidable, in particular under rigorous reaction conditions. To overcome this drawback, the covalent anchoring method has been established for the preparation of the SILPC materials through the treatment of a monolayer of covalently attached IL on the surface of a support material. Several SILPC materials prepared by the covalent anchoring method were developed by Gruttadauria *et al.*[129] In these materials, the L-proline was supported on the surface of modified silica gels with a monolayer of covalently attached IL with or without additional adsorbed IL. These materials can be applied to the aldol reaction between acetone and several aldehydes. Good yields and ee values, comparable with those obtained under homogeneous conditions, can be achieved. After reaction, these catalysts can be easily recovered by simple filtration, and can be reused at least up to seven times. Liu and his co-workers demonstrated that Mn(III) salen complexes could be easily immobilized by an imidazolium-based IL modified MCM-48 (Fig. 7). These heterogeneous catalysts were stable, recyclable and exhibited comparable activity for the asymmetric epoxidation of unfunctionalized olefins, Compared to those obtained by the homogeneous counterparts, remarkably higher enantioselectivities (*e.g.*, >99% and 92% ee for α-methylstyrene and 1-phenylcyclohexene, respectively) were achieved.[130]

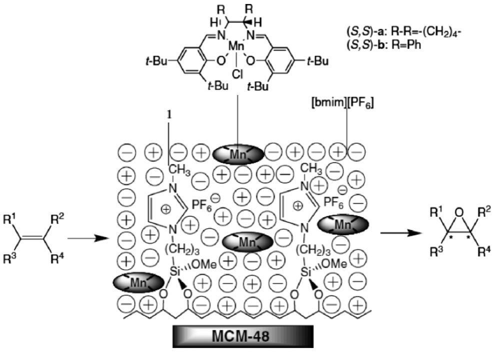
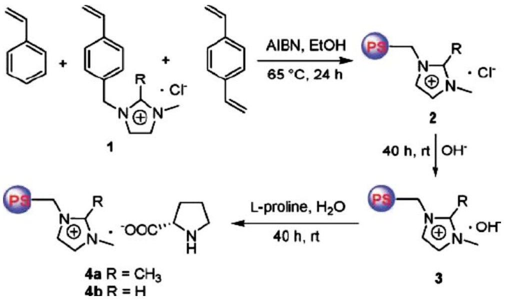


Fig. 7 The asymmetric epoxidation of olefins over the chiral Mn(III) salen complexes immobilized on IL modified MCM-48. (Adapted from Ref. 130).

Polymers have also been used as good covalent anchoring supports for the preparation of SILPC materials. You *et al.* developed a series of polymer-supported task-specific ILs *via* the ionic-pair coupling of imidazolium cation of the modified polystyrene support with L-proline (Scheme 19). These materials exhibited an efficient metal scavenging ability (*e.g.*, CuI, $Pd(OAc)_2$, Pd^0, and $IrCl_3$) without the aid of a nonimmobilized IL.[131] These SILPC materials were successfully applied in the CuI-catalyzed *N*-arylation of nitrogen-containing heterocycles and exhibited much higher catalytic activity than those by free L-proline in combination with CuI in a homogeneous reaction. These catalysts allow for a simple filtration step for liquid and solid recovery and can be recycled for nine runs at least without any considerable loss of activity. Very recently, several new polymeric materials containing functional sites analogous to ILs were also reported.[132] Those materials are a supported reservoir for active Pd species. Their catalytic activity has been evaluated for the Heck reaction, proving an excellent performance in terms of both activity and recyclability. Although soluble Pd species seem to participate in the catalytic cycle, as for many other supported Pd systems, the new SILPC materials present the ability to efficiently release and recapture those soluble species.



Scheme 19 The preparation of the polymer-supported task-specific ILs PS[DMVBIM][Pro] and PS[MVBIM][Pro]. (Adapted from Ref. 131).

This allows the amount of Pd leached into the final solution to be dramatically reduced or eliminated, in particular at higher temperatures, and opens the way, based on a release and catch strategy, for the development of active-supported Pd catalytic systems, easily recoverable and reusable for a large number of catalytic cycles.

Multi-walled carbon nanotubes (MWCNTs) were also used as a potential support for the preparation of SILPC materials because of their inherent advantageous properties, such as good mechanical strength, high chemical stability, and a large surface area-to-volume ratio.[133] The synthetic route involves two steps: (i) external surface functionalization of MWCNTs to improve their compatibility with and dispersion in ILs, and (ii) rhodium complex immobilization in the IL film (Fig. 8). Here, the maximum loading of the IL [BMIm]PF_6 can be increased to 55 wt% without detectable leaching of the IL. Among the studied SILP catalysts, the Rh/CNT2a-SIL (55%) catalyst presents a significantly higher activity than SILPCs supported on oxide supports, including silica or activated carbon, with full retention of the Rh/IL active phase upon recycling.

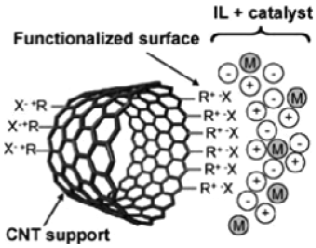
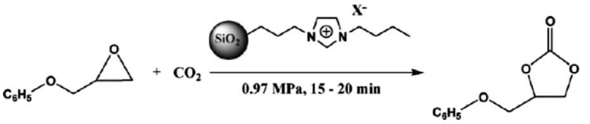


Fig. 8 The surface functionalization of CNTs with imidazolium-based ionic groups. (Adapted from Ref. 133).

Recently, SILPC materials based on different silica supports, such as commercial and amorphous silica, SBA-15, and MCM- 41 were developed and used in a microwave-assisted cycloaddition of CO_2 to phenyl glycidyl ether under solvent-free conditions (Scheme 20).[134] The catalytic activity of the SILPC materials was found to depend strongly on the morphology of the support. Compared to the conventional heating reactions, microwave-induced reactions were greatly superior and ILs catalysts immobilized on silica supports with relatively large pore diameters (greater than 4 nm) showed very high PGE conversion and excellent selectivity of cyclic carbonate within 15 min. Luo *et al.* developed a silica gel supported acidic IL catalyst *via* anchoring 3-sulfobutyl-1-(3-propyltriethoxysilane)-imidazolium hydrogen sulfate onto silica gel with covalent bonds.[135] These SILP materials can effectively catalyze the one-pot synthesis of amidoalkyl naphthols by the multicomponet condensation of aldehydes with 2-naphthol and amides under solvent-free conditions Moreover, several silica or polymer supported acidic IL catalysts have been developed for the Baeyer–Villiger reaction,[136] esterification and nitration reactions,[137] acetal formation,[138] and hydrolysis of cellulose.[139]



Scheme 20 The cycloaddition of PGE and CO_2 using silica supported ILs. (Adapted from Ref. 134).

4.3 The physical confinement or encapsulation method

So far, the majority of the SILPC materials have been prepared by the immersion method and the chemical bonding method. However, both methods have drawbacks: (i) the leaching of the ILs and metal complex catalyst was unavoidable in SILP–liquid contact under rigorous reaction conditions if the SILPC materials was prepared by physical adsorption or by coating the IL as a thin layer on a support material, and (ii) although the leaching of catalytically active species can be avoided, the chemical bonding of the dialkyl imidazolium cation to a solid surface may limit the degrees of freedom of the dialkyl imidazolium cation and even change the physicochemical properties of the ILs.

In 2005, a new concept of designing and synthesizing SILPC material was developed for the first time by our group,[140] *viz*. physical encapsulation of ILs or ILs containing metal complex into the pores of the porous silica gels through a sol–gel process (Fig. 9). Carbonylation of aniline and nitrobenzene for the synthesis of diphenyl urea, carbonylation of aniline for synthesis of carbamates, and oxime transformation between cyclohexanone oxime and acetone were used as test reactions for these novel SILPC materials. Catalytic activities were remarkably enhanced with much lower amounts of ILs needed with respect to bulk ionic-liquid catalysts or silica-supported IL catalysts prepared with simple impregnation. Such unusual enhancement in catalytic activities may be attributed to the formation of nanoscale and high-concentration ILs due to the confinement of the IL in silica gel.

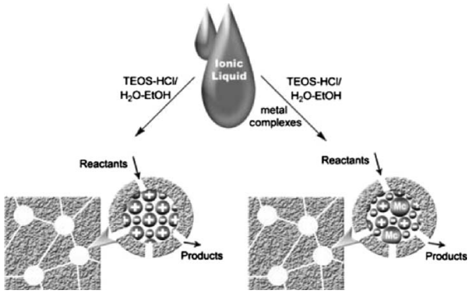


Fig. 9 Illustration of the synthesis of silica-gel-confined ionic liquids with and without the metal complex. (Adapted from Ref. 140).

Similarly, Dupont *et al.* reported that the Rh(0) nanoparticles dispersed in IL ([BMIm][BF_4]) could be easily confined within a silica network through a sol–gel method.[141] The use of ILs for the preparation of both nanoparticles and silica affords encapsulated IL/Rh(0)/silica materials with different morphology, texture, and catalytic activity. This combination exhibits an excellent synergistic effect that can enhance the activity and robustness of the Rh hydrogenation catalysts. All the supported systems were more active than those constituted of isolated Rh(0) nanoparticles for the hydrogenation of alkenes, in which the silica-based systems prepared under acidic conditions were shown to be the most active, exhibiting higher TOF in comparison to that of commercial Rh/C (5 wt%).

Moreover, another new approach for building the SILPC system was developed *via* the integration of the free metal

Table 2 Partial results for isobutene/butane alkylation using ILs as catalyst

Catalyst systems	Butene	$iC_4/C_4^=$	T/K	Conv.% of butane (%)	Selectivity of C_8 (wt%)	TMP/ DMH	Calculated RON	Ref.
$[Et_3NHCl]$-2$AlCl_3$	2-butene	10	303[a]	97	56.2	2.8	89.8	149
$[Et_3NHCl]$-2$AlCl_3$ + CuCl (5% mol)	2-butene	10	303[a]	96	74.8	6.5	94.7	149
$[Et_3NHCl]$-2$AlCl_3$ + CuCl (50% mol)	2-butene	15	283[b]	> 98	98.1	19	99.7	150
$[Et_3NHCl]$-2$AlCl_3$/Benzene (1.0 wt%)	2-butene	10	288[a]	98	80.9	8.0	95.6	151
$[Et_3NHCl]$-2$AlCl_3$/Hexamethylbenzene (0.8 wt%)	2-butene	10	288[a]	99	78.6	9.7	—	151
[OMIm]$[HSO_4]$/H_2SO_4 (84 wt%)	1-butene	10	281[c]	98	51.3	6.6	—	152
[OMIm]$[HSO_4]$/CF_3SO_3H (76.3 wt%)	1-butene	10	281[c]	95.3	76.8	6.8	—	152
[BMIm]$[HSO_4]$/CF_3SO_3H (76.8 wt%)	1-butene	10	281[c]	98.1	72.4	8.1	—	152
[OMIM]Br-1.5$AlCl_3$/$[(HO_3SBu)MIM][HSO_4]$ (50 wt%)	2-butene	13	268[d]	> 98	> 52.7	—	94.8	153
[OMIM]Br-1.5$AlCl_3$/water (225 ppm)/Resin(0.16 wt%)	2-butene	13	268[d]	> 98	> 63.9	—	96.2	153
NLAC II	raffinate II	20	353	> 95	59.7	—		154
PPHF	2-butene	24	309[e]	> 98	79.8	—	93.7	155
PEIHF	2-butene	24	309[e]	> 98	76.2	—	93.3	155
PVPHF	2-butene	24	309[e]	> 98	81.8	—	94	155

[a] continuous unit, pump rate 500 ml h^{-1}, agitation rate 800 rpm, [b] stirred pressure reactor, agitation rate 1700 rpm, [c] stirred autoclave reactor, [d] stirred autoclave reactor, pressure 600 kPa, [e] autoclave, agitation rate 720 rpm.

complex and the IL molecule into a complete catalytically active species inside the super-cage of a NaY zeolite (Fig. 10).[142] An investigation of these SILPC materials for the carbonylation of aniline to methyl phenyl carbamate showed that far higher catalytic activity was achieved using much lower amounts of IL as a solvent and less metal complex as well.

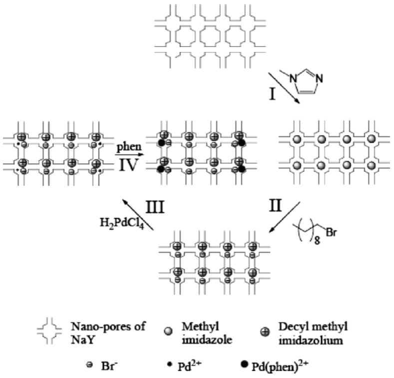


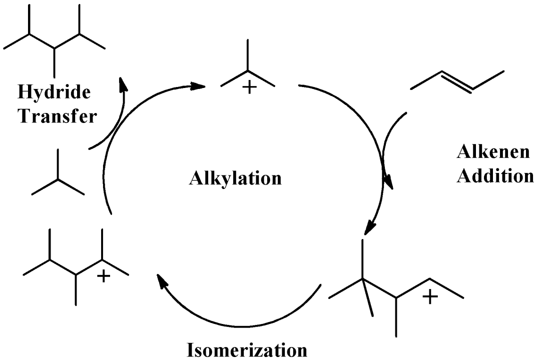
Fig. 10 The self-assembly of IL and Pd complex in the super-cage of NaY. (Adapted from Ref. 142).

5. Friedel–Crafts alkylations

Among so many catalytic processes studied widely in ILs, the alkylation reactions have received more attention due to their great potential in the petroleum industry. Thus, in this review we also expressed more concerns to the recent advances in this process, which mainly include the isobutane/butene alkylation (C_4 alkylation) and the alkylation of benzene with olefins.

5.1 C_4 alkylation

The alkylation of isobutane with butane plays an important role in modern petroleum refining because its target product trimethylpentane is an ideal blending constituent for gasoline with high octane numbers and clean burning characteristics (Scheme 21).[143] In industry, this process is mainly catalyzed either by concentrated sulfuric acid (H_2SO_4) or hydrogen fluoride (HF). However, both commercial processes are exceedingly toxic, corrosive, and very detrimental to the environment, and some other problems, such as cooling and separation, acid sludge treatment, high operating cost, and safety aspects, also handicap their practical industrial application.[144] It is obvious that, in such a climate, there is a high incentive for the development of a new alkylation technology that makes use of the non-toxic, non-corrosive, environmentally friendly catalysts. Due to the strong Lewis acidity of the anions of $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$, acidic chloroaluminate ionic liquids have been regarded as very promising candidates to solve those problems.[145] As early as the 1980s, the mixtures of 1,3-dialkylimidazolium chloride and aluminium chloride have been found to be catalytically active in Friedel–Crafts reactions.[146] The main advantages arising from the use of ILs are the higher alkylate quality than that obtained from conventional liquid acids and simple product separation after reaction. Meanwhile, this reaction is always performed under mild conditions, which is very well suited for the usage of ILs. Up to now, a variety of IL catalysts have been explored for the isobutane/butene alkylation, and even PetroChina have publicly announced that this process had been tested in a 1000 ton sale,[147] which was by far the largest commercial usage of ILs reported to data.[148] Table 2 lists the partial results for isobutene/butane alkylation using ILs as the catalyst.

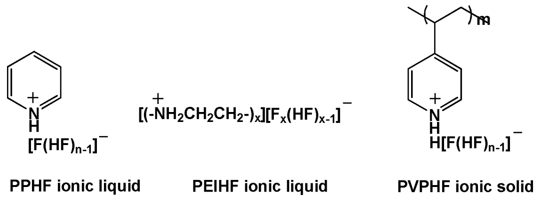


Scheme 21 The simplified mechanism of isobutane/butene alkylation. (Adapted from Ref. 143).

In earlier studies, the chloroaluminate ILs based on the imidazolium cation were widely investigated as high-efficiency catalysts in alkylation reactions due to the strong Lewis acidity of the anions. However, the high cost of these ILs, which results from the inactivation of ILs in the presence of water, weakens their industrial potential over concentrated sulfuric acid. Recently, Liu *et al.* investigated the C_4 alkylation by using a cheap IL triethylamine hydrochloridealuminium(III) chloride ($[Et_3NHCl]$-$AlCl_3$) as the catalyst.[149,150] If only $[Et_3NHCl]$-$AlCl_3$ was used, the catalytic performance of this catalyst system was inferior to conventional liquid acid catalysts. After adding some additives like cuprous chloride (CuCl) into the catalytic system, however, the catalytic efficiency of the composite catalyst was greatly improved. The selectivity of isooctane (C_8) was up to 75% and the ratio of trimethylpentane (TMP) to dimethylhexane (DMH) in isooctane reached 6.5, which could catch up with the catalytic performance of concentrated sulfuric acid. Similarly, Chen *et al.* studied the effect of adding aromatic compounds on the catalytic performance of chloroaluminate ILs in the C_4 alkylation.[151] The addition of benzene can increase the selectivity of isooctane as well as the TMP:DMH ratio in the alkylate, and the used catalyst can be regenerated by replenishment of the aromatic additives.

Moreover, liquid acids were also used as the additive to construct new binary IL/acid catalysts. For example, Subramaniam *et al.* reported that the C_4 alkylation could be efficiently catalyzed by the binary mixtures of certain acidic imidazolium ILs and strong acids, such as sulfuric acid or trifluoromethanesulfonic acid, and the selectivity of $C_8 > 70\%$ and the ratio of TMP/DMH > 7 were achieved in the presence of the mixture of $[HMIm][HSO_4]$ and triflic acid.[152] Bui *et al.* investigated the catalytic activity of the C4 alkylation in the presence of pure $[OMIm]Br$-$AlCl_3$ or the mixture with compounds containing SO_3H-groups.[153] The acidity of the catalyst was modified by the addition of acidic cation exchange resins (dry or with a small amount of water), or by the addition of a second IL ($[(HO_3SBu)MIM][HSO_4]$). In this case, the yield of TMPs and the RON was comparable or higher than that with H_2SO_4 as the alkylation catalyst. Due to the drawbacks of pure ILs, such as high cost and easy deactivation, the immobilized ILs were also tried for the alkylation reaction. By using the Lewis-acidic ILs immobilized on solid supports, Kumar *et al.* developed a new kind of catalyst called a "Novel Lewis-Acid Catalyst" (NLACs) for the liquid phase alkylation of raffinate II and isobutene.[154] In this study, the immobilized ILs had shown high activity in the production of isooctane under batch conditions, and the performance of the immobilized ILs grafted on siliceous material or on silica was found to be better than that of other tested solid acid catalysts, such as zeolite H-Beta and SAC 13 *etc.*

Beside the frequently used chloroaluminate ILs, Olah *et al.* put forward a different avenue for the alkylation process involving the IL concept.[155] A series of new environmentally safe, immobilized liquid and solid modified HF equivalent catalysts for C_4 alkylation, including pyridinium poly(hydrogen fluoride) (PPHF), poly(ethylenimine) poly(hydrogen fluoride) (PEIHF), and poly(4-vinylpyridinium) poly(hydrogen fluoride) (PVPHF) have been developed (Scheme 22). Isobutane–isobutylene or 2-butene alkylation gave excellent yields of high octane alkylates (up to RON = 94). Apart from their excellent catalytic performance, the new catalyst systems significantly reduce environmental hazards due to the low volatility of complexed HF.



Scheme 22 The structures of HF equivalent amine-poly-(hydrogen fluoride) complexes. (Adapted from Ref. 155).

5.2 Benzene/olefins alkylation

Similar to the C_4 alkylation, commercial alkylations of benzene with olefins also have many drawbacks, such as poor selectivity, troublesome product recovery and purification, corrosion, and safety problems, *etc.* Therefore, many efforts to develop greener catalytic processes have been made. Now it has been widely recognized that the usage of ILs in these benzene/olefins alkylations can greatly enhance reaction rates, conversion and selectivity under mild conditions. As early as 2001, the alkylation of benzene with dodecene in chloroaluminate ILs modified with HCl as catalysts has been studied by our group.[156] In comparison with anhydrous aluminium chloride catalysts, higher conversion and favorable distributions of products were obtained due to the superacidity of the ILs induced by the presence of HCl. For different chloroaluminate ILs, the variety of the alkyl chains and the halogen anions also had some effect on their catalytic activities in benzene/1-dodecene alkylation.[157] Under the optimum conditions, a 91.8% conversion of 1-dodecene with a 38.0% selectivity to 2-dodecylbenzene could be achieved in the presence of $[BMIm]Br$–$AlCl_3$. Unfortunately, the conversion decreased greatly after the ILs were used twice. The deactivation of the catalysts might be attributed to the decrease of the Lewis acidic strength and density resulting from the loss of the highly Lewis acidic species $Al_2Cl_6Br^-$. Moreover, the cheap acidic ILs $[Et_3NHCl]$–$FeCl_3$ and $[Et_3NHCl]$–$AlCl_3$ can also be used to efficiently catalyze the alkylation of benzene with 1-hexene.[158] In the presence of $[Et_3NHCl]$–$FeCl_3$ modified with HCl, the selectivity of monoalkylated products reached 100%, and the resulting products could be separated from the ILs simply by decantation. Table 3 lists the partial results of the alkylation of benzene with linear olefins using ILs as the catalyst.

Besides acting as the catalysts, ionic liquids were also be used as the solvent for the immobilisation of acidic catalysts. Song *et al.* dissolved scandium(III) trifluoromethanesulfonate $[Sc(OTf)_3]$ in hydrophobic ILs, such as 1-ethyl-3-methylimidazolium hexafluorophosphate ($[EMIm][PF_6]$) and 1-ethyl-3-methylimidazolium hexafluoroantimonate ($[EMIm][SbF_6]$) to catalyze the aromatic alkylation processes.[159] In this catalytic system, the alkylation of aromatic compounds with alkenes proceeded readily under ambient conditions and good olefin conversion and monoalkylation selectivity could be obtained. Interestingly, when the same reaction was carried out in common organic solvents, water or hydrophilic ionic liquids, almost no monoalkylated products could be detected. In

Table 3 Partial results of the alkylation of benzene with linear olefins using ILs as catalyst

Catalyst	Olefins	Temp./K	Time/min	Conv.% (alkene)	Sel.% 2-Phenyl	Sel.% 3-Phenyl	Ref.
[EMIm]Cl-2AlCl$_3$	1-dodecene	293	5	almost 100	34.7	20.1	156
[EMIm]Cl-2AlCl$_3$+HCl	1-dodecene	293	5	almost 100	40.5	18.1	156
[BMIm]Br-2AlCl$_3$	1-dodecene	305	25	91.8	38.0		157
[Et$_3$NH]Cl-2FeCl$_3$ (0.0088 mol)+HCl (0.2 mol)	1-hexene	363	60	100	64.2	35.8	158
[EMIm][SbF$_6$]+ Sc(OTf)$_3$ (0.2 mol)	1-hexene	293	720	99	57.6	38.4	159
[BMIm][PF$_6$]+ Sc(OTf)$_3$ (0.2 mol)	1-hexene	293	720	99	64	32	159

2007, Wasserscheid *et al.* reported that acidic ILs of the type [cation][bis(trifluoromethanesulfonyl)imide anion]–aluminium trichloride {[cation][NTf$_2$]/AlCl$_3$} could be been applied to catalyze a continuous Friedel–Crafts alkylation reaction in liquid–liquid biphasic reaction mode using a loop reactor concept.[160] The immobilisation of Lewis acids in ILs can provide high activity, stable selectivity, and effective product separation. The catalyst system AlCl$_3$/[BMIM][NTf$_2$] = 2.5 was applied in an 18 h continuous run in which more than 18 litres of reaction mixture were processed in the reactor with yields greater than 90% with respect to the stoichiometric limiting component propene. This new catalytic system offered an attractive method for continuous, liquid–liquid biphasic Friedel–Crafts alkylation reactions.

6. Conclusions and outlook

Catalysis in ILs is growing at a surprising speed, and a huge quantity of new findings are springing up in which the IL enables the catalytic reactions to take place more efficiently in comparison with molecular solvents. Indeed, the combination of multiple advantages of using ILs as the catalyst or the solvent or both has opened up promising possibilities for developing those greener catalytic technologies. On the other hand, although a number of catalytic reaction processes in which ILs are used have been established in industry, there were also some unexpected problems, such as unintelligible aberrance or degradation of so-called task specific ILs occurring in developing reaction processes involving ILs on the pilot plant scale. So, much work should be done before a variety of catalytic processes could be effectively established in industry, and several urgent questions regarding the fundamental aspects of ILs need to be clarified or answered.

i). Cost. Obviously, the high cost of ILs is one of the most important issues hampering their large scale application in catalysis, in particular those widely used dialkylimidazolium ILs with a functional group. Thus, the development of less expensive ILs is of great importance, which will stimulate the large-scale application of ILs not only in catalysis but also in the fields of electrochemistry, engineering fluids, and analysis and separation, *etc.* The effective recovery and reuse of ILs can reduce the IL's costs greatly, however, the effective recycling of the ILs has not been well established at this stage, particularly in those reactions where the desired product can be dissolved well in ILs. Anyway, how to reduce the cost of ILs is still one of the most important issues for the industrial applications in the future.

ii). Purity. At the early stage of IL R&D, the purity of ILs is always ignored due to a lack of understanding of the ILs. Now this issue is receiving more and more attention because it has been well known that the impurities, such as water, halides; unreacted organic or inorganic salts, *etc.* can greatly influence the catalytic performance. Under extreme situations, it may be possible that it is just those unknown impurities that make a great contribution to the catalytic activity and selectivity. So, the ILs purity issue in the catalytic reaction application should not be emphasized overmuch and only the catalytic performance should be highly important. However, in order to understand and control the catalysis in ILs, the effect of the IL purity on the catalytic activities needs to be clarified in every catalytic reaction and the depth of study about how the impurities influence the catalysts or catalytic mechanism needs to be further strengthened in future research.

iii) Stability. ILs are generally regarded as highly stable, and it has been reported that most of the dialkylimizolium ILs are even thermally stable up to 300 °C. However, most studies about the thermal stability are always evaluated by thermogravimetric analysis under a nitrogen atmosphere. Under a harsh reaction environment (*e.g.* highly active reagents, higher temperatures, stronger acidities or basicities, *etc.*), the ILs, in particular those functionized ILs, may be not as stable as they are expected to be. So, unexpected evolvement and aberrance of ILs during catalytic reactions occurred and should be carefully investigated and understood before large scale applications in catalysis. From the standpoint of industrial catalysis, only those catalytic reactions or processes performed under mild conditions, *e.g.* lower temperatures, oxygen-free, product-insoluble in ILs, neutral and anhydrous reactions, *etc.* should be more suitable for ILs as media or catalysts. It needs to be noted that those catalytic processes that need to be conducted under vacuum, as shown in ref. 105, are also very suitable for the usage of ILs by utilizing their low volatility, which is also one of the ignored areas in IL catalysis.

iv) Viscosity. Another drawback of ILs hampering their large scale applications in catalysis is their high viscosity. In general, the viscosity of ILs is always much higher as compared to most molecular solvents, which often leads to difficulty in the mass transfer between the catalyst and the substrate. In a catalytic reaction, the mass transfer is very important since it is always the limiting step in kinetics and can determine some thermodynamic constraints. Therefore, from the view of catalysis, to develop ILs with low viscosity will facilitate an increase in the reaction rate. Moreover, the IL films on the surface of SILP catalysts can also minimize the limitation of mass transfer due to very short diffusion distances in the film surface. Indeed, the poor mass-transfer issue caused by the high viscosity of ILs will be one of the biggest problems that have been besetting the application of ILs in catalysis.

v). Green aspects. A major driving force behind the enthusiasm for catalysis in ILs is to develop green chemical processes, in which the catalysis in ILs is regarded as a potentially greener technology. In spite of their great potential in green chemistry, the greenness of the ILs is encountering some doubt due to their unclear toxicity and biodegradability. It has been recently recognized that the ILs are not as green as they used to be expected to be, *e.g.* the ILs are often made from ions that are toxic. And according to data, studies about their ecotoxicity and biodegradability, as well as an understanding as to how the components of an IL determine its toxicity and biodegradability are still scanty. The toxicity and effect on human health should be further evaluated before a wide and large-scale applications of ILs in catalysis. Moreover, the methods concerning the regeneration of the deactivated catalyst in ILs and the reprocessing of disused ILs have not yet been established. Therefore, more efforts need to be made for the development of truly green ILs without toxicity or those ILs with the characteristic of easy biodegradability, *e.g.* by using the choline cation, or amino acid anions, or the renewable resources, *etc.*

v) In-depth exploration. Although tremendous success has been realized in a wide variety of catalytic reactions involving ILs with satisfactory performance, most of them were conducted based on “try and see”. The “true” influence of ILs on the reactant, transition state, reaction pathway, and reaction mechanism is still unclear at the molecular level, and it was generally attributed to the so-called “IL effect”. Undoubtedly, the unique behavior and performance possessed by ILs could be strongly related to its intrinsic nature since ILs are composed solely of ions and reaction in ILs experienced an “IL enviroment” completely different from molecular solvents. However, the intrinsic nature of ILs has been little known to date. For example, althogh ILs are believed to be of strong electrostatic field, its absolute or relative strength (to molecular solvents), and the relationships of structure–elctrostatic field and elctrostatic field–performance have been unclear. Thus, further investigation of intrinsic nature (electrostatic field, ionicity, *etc*), physicochemical properties, and ILs/solute interaction is urgent. The in-depth exploration will be helpful for further explaining and promoting the catalytic reactions.

vi) An integrated technology. Finally, the potential of catalysis in ILs is tremendous if they are integrated appropriately with other advanced technologies, including supercritical fluids, electrochemistry, biocatalysis, nanotechnology, microwave, reaction-rectification, micro-reactor technology, *etc*. When more efforts are devoted to such an integrated approach on a deeper and larger level, the catalysis in ILs will usher in a brighter tomorrow.

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