1

Background and Overview

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1.1 Introduction

With the development of science and technology, fossil fuel consumption has increased significantly. The emission of a huge amount of CO_2 and accumulation of spent or discarded synthetic materials pose a huge threat to the current ecosystem and human health. As a result, we are facing the challenges of energy crisis and sustainable development. To tackle these issues, the carbon neutrality goal has been proposed and accepted worldwide. Green chemistry, especially, green carbon science, provides a chemical solution to achieve carbon neutrality, which mainly involves highly efficient utilization of fossil resources, the transformation of renewable carbon resources (e.g. CO_2 and lignocellulose) into chemicals/fuels in a green way, and recycling of spent synthetic carbon-containing materials (e.g. spent plastics) [1–5]. In the past decades, great efforts have been dedicated to the chemical transformation of renewable and recyclable carbon resources into chemicals and fuels, and numerous achievements have been made that afford alternative strategies to access energy and chemicals, which is of great significance to achieve the carbon neutrality goal and sustainable development.

Catalysts are generally needed to achieve the chemical transformation of carbon resources. For example, CO_2 is thermodynamically stable and kinetically inert, and thus its transformation usually needs high energy input and catalysts with high activity. To date, various catalysts have been developed for the transformation of CO_2 into chemicals and fuels through different protocols including thermal catalysis,

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Zhimin Liu and Yanfei Zhao.

electroreduction, and photoreduction. Lignocellulose and its derivatives possess complicated structures, and thus catalysts are highly required to cleave the chemical bonds in lignocellulose and form the target products. Similarly, the recycling of spent plastics cannot be complemented in the absence of catalysts.

Ionic liquids (ILs) are a kind of molten salts composed of organic cations and inorganic/organic anions, remaining in a liquid state below 100 °C. Generally, ILs possess unique properties, such as negligible vapor pressure, good affinity with a wide range of chemicals, high thermal and chemical stability, easy recyclability, high conductivity, and a wide electrochemical window. In particular, they are highly designable and can be designed with specific functions through careful design and choice of task-specific component ions. To date, various kinds of ILs have been synthesized, such as acidic ILs, basic ILs, protic ILs, chiral ILs, and so on. There exist multiple interactions in IL systems, including Coulomb interaction, hydrogen bonding, halogen bonding, Van der Waals force, hydrophilic/hydrophobic interaction, and π–π interaction, which provide the ILs with unique properties and advantages over traditional molecular liquids. Therefore, they have shown wide applications in many fields, such as separation process, chemical reaction process, material synthesis and processing, battery electrolytes, etc.

Due to their designable and unique properties, ILs have emerged as green solvents and/or catalysts to be used in chemical reaction processes. Especially, different kinds of IL catalysts have been designed for the transformation of renewable and recyclable carbon resources into chemicals and fuels, and for green reactions such as oxidation, water-involved reactions (i.e. dehydration, hydration, and hydrolysis), alkylation, and other organic reactions. In particular, the unique properties of ILs endow them with the opportunity to serve as metal-free catalysts, and the combination with metal catalysts makes IL-based catalysts have wider applications.

This book focuses on the IL-catalyzed chemical transformation of renewable carbon resources into chemicals and fuels, together with green protocols relevant to IL catalysis.

1.2 Ionic Liquids

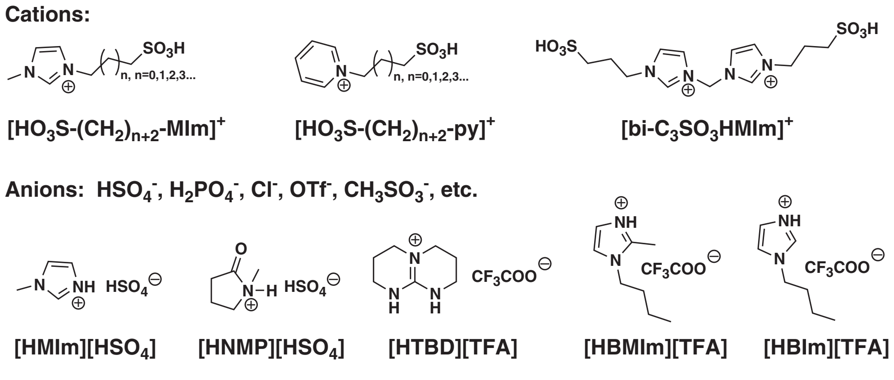
ILs are highly designable; they can be designed with an acidic site, basic site, or hydrogen bond (HB) donor and/or acceptor, and can be complexed with Lewis acids and bases to form Lewis acidic or basic ILs. To date, various ILs including acidic ILs, basic ILs, neutral ILs, and chiral ILs have been applied in different chemical reactions, showing promising application potential. In the following subsections, acidic ILs, basic ILs, neutral ILs, and chiral ILs are described, with their applications in catalyzing reactions.

1.2.1 Acidic ILs

Acidic ILs can be classified into Brønsted acidic ILs, Lewis acidic ILs, Brønsted–Lewis acidic ILs, and heteropolyacid-based ILs, which have their unique properties originating from their structures, and thus have been used as catalysts for different chemical reactions. Compared with acid catalysts (e.g. H_2SO_4), acidic IL catalysts generally display enhanced performance, and can alleviate or inhibit corrosion to the reaction equipment as well. Therefore, acidic ILs may be applied to replace the traditional acid catalysts, and various investigations have been made. Especially, acidic ILs as catalysts display high activity for catalyzing water-involved chemical reactions, including dehydration, hydration, and hydrolysis, and they are also effective for catalyzing the transformation of lignocellulose and its derivatives into chemicals, oxidation reactions, decomposition of polyesters, and so on.

Brønsted acidic ILs are generally a kind of ILs with acidic sites (e.g. $-SO_3H$, $-COOH$, and $-H$) at cations or with acidic anions (e.g. $[HSO_4]^-$), as shown in Scheme 1.1, which can provide protons and exhibit acidity in IL systems. Among the reported acidic ILs, the 1-(1-alkylsulfonic acid)-3-methylimidazolium-based ILs that possess $-SO_3H$ at the alkyl group of cations have been widely investigated, serving as acidic catalysts for various chemical reactions, and they usually display enhanced activity compared with the traditional acid catalysts. For example, 1-(1-butylsulfonic acid)-3-methylimidazolium trifluoromethanesulfonate ($[SO_3H-BMIm][OTf]$) has been reported to exhibit outstanding performance for catalyzing ring-closing metathesis of aliphatic ethers to O-heterocycles [6], and 2-phenyl-2-imidazoline-based SO_3H-functionalized acidic ILs could effectively catalyze the hydrolysis of cellulose to glucose in 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) [7]. Additionally, $[SO_3H-(CH_2)_3-py]_2[TiF_6]$ can effectively catalyze the oxidation of a wide range of sulfides, producing corresponding sulfoxides in high-to-good yields [8]. Compared with $-SO_3H$-functionalized acidic ILs, $-COOH$-functionalized ILs possess weaker acidity, and they usually exhibit lower activity.

The Brønsted acidic ILs with $[HSO_4]^-$ anion and various cations, such as $[BMIm][HSO_4]$, $[SO_3H-BMIm][HSO_4]$, $[SO_3H-(CH_2)_4-py][HSO_4]$, $[HOOC-CH_2-py][HSO_4]$, and $[HOOC-CH_2-MIm][HSO_4]$, have been widely applied as acidic catalysts for different reactions. For example, $[BMIm][HSO_4]$ as both a reaction medium and a catalyst can efficiently realize dehydration of xylose to furfural at 120 °C [9]. The $[HSO_4]^-$ anion-based ILs are found to be effective for oxidative desulfurization using H_2O_2 as the oxidant because the $[HSO_4]^-$ anion as an acidic counterion can provide an acidic medium to enhance the oxidation ability of H_2O_2 [10].



Scheme 1.1 Chemical structures of typical Brønsted acidic ILs.

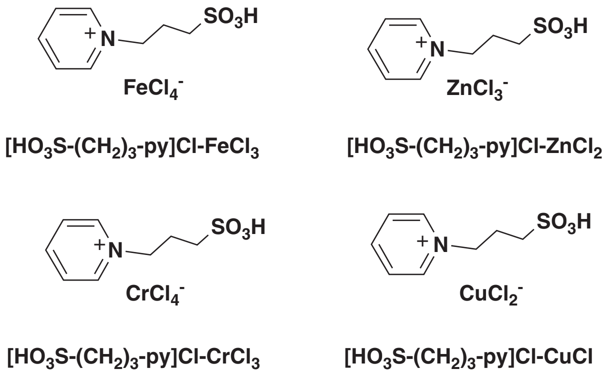
Protic Brønsted acidic ILs refer to those derived from the neutralization of a Brønsted acid (e.g. H_2SO_4, HBF_4, CF_3COOH, HNO_3, HCl, etc.) with an organic base (e.g. pyridine, imidazole, *N*,*N*-dimethylformamide, etc.) that is a proton acceptor, which show high acidity and related activity for catalyzing some reactions. For example, protic ILs with $[HCPL]^+$ cation obtained from caprolactam (CPL) and Brønsted acids (e.g. CF_3COOH, HNO_3, and H_2SO_4) exhibit high catalytic activity for oxidative desulfurization of S-containing compounds using H_2O_2 [11]. $[Hpy][HSO_4]$ originated from pyridine and H_2SO_4 can achieve the direct conversion of hemicellulose to furfural [12]. The protic Brønsted acidic ILs with $[TFA]^-$ anion, such as [HBMIm][TFA] and [HTBD][TFA] (Scheme 1.1), are demonstrated to work well for various organic amine dehydration formylation reactions with formic acid under mild conditions, yielding a series of N-formylation products with high yields [13,14].

Lewis acidic ILs are generally derived from Lewis acids (e.g. metal halides) and ILs that have the same anion with the Lewis acids. For example, as $AlCl_3$ is dissolved in [BMIm]Cl, the metal ion, Al^{3+}, can coordinate with more Cl^- ions to form metal-containing anions such as $[AlCl_4]^-$, $[Al_2Cl_7]^-$, and so on, thus forming a series of Lewis acidic ILs based on the molar ratios of $AlCl_3$ to [BMIm]Cl. To date, various Lewis acidic ILs have been developed by choosing Lewis acids and ILs. Among the Lewis acids, metal halides, such as $AlCl_3$, $CrCl_2$, $FeCl_3$, $CuBr_2$, $SnCl_2$, have been widely applied to construct Lewis acidic ILs in combination with different ILs, especially 1-alkyl-3-methylimidazolium-based ILs. This kind of IL generally displays the liquid state at temperatures lower than melting points of metal halides and ILs. They usually display enhanced Lewis acidity compared with their corresponding Lewis acids, which have found a lot of applications and are successfully used as catalysts, cocatalysts, or reaction media in various fields of chemistry, especially in catalysis.

There are many kinds of Lewis acidic ILs, and they have wide applications in catalysis. For example, Lewis acidic ILs derived from metal halides and 1-alkyl-3-methylimidazolium chloride could catalyze the conversion of glucose to 5-hydroxymethylfurfural (HMF). Especially, $CrCl_2$ in combination with 1-ethyl-2-methyl imidazolium chloride ([EMIm]Cl) afforded HMF in a yield near 70% under mild conditions (e.g. 100 °C), displaying better activity than H_2SO_4 and Lewis acids [15]. As a promising example, $[BMIm][FeCl_4]$ could convert herbaceous lignin into methyl *p*-hydroxycinnamate in methanol at 420 K [16], and it is also very active for oxidation of alkali lignin to vanillin in aqueous media at room temperature [17]. Dual-core sulfonic acidic IL, $[bi{-}C_3SO_3HMIm][CH_3SO_3]$, in combination with $MnCl_2$ also demonstrates good performance for direct dehydration of cellulose in [BMIm]Cl, attaining the highest yield of HMF at 66.5% [18]. Lewis acidic ILs are also shown to exhibit good performance in both H_2O_2- and O_2-involved oxidative desulfurization processes [19]. For example, $[Et_3NH][FeCl_4]$, $[Et_3NH][SnCl_3]$, $[Et_3NH]_2[CuCl_4]$, and $[Et_3NH]_2[ZnCl_4]$ have been reported to be capable of catalyzing their oxidation to corresponding sulfones with O_2 [20]. Lewis acidic chloroaluminate-based ILs, for instance, *N*-butylpyridinium chloride with anhydrous $AlCl_3$ in a 1 : 2 molar ratio (denoted as $[C_4Py]Cl{-}2AlCl_3$), have been reported to be capable of achieving selective upcycling of polyolefins (including polyethylene and polypropylene) with iC_5 into liquid isoalkanes (C_6—C_{10}) at temperatures below 100 °C [21].

The acidic ILs derived from Brønsted acidic ILs and Lewis acids are generally named Brønsted–Lewis acidic ILs, which show both Brønsted and Lewis acidity. The acidity of Brønsted–Lewis acidic ILs can be regulated by altering the molar ratio of Brønsted acidic ILs to Lewis acid, which, in turn, determines the anion structure. As illustrated in Scheme 1.2, the Brønsted–Lewis acidic ILs synthesized from *N*-propylsulfonic acid pyridinium chloride ($[HO_3S—(CH_2)_3—py]Cl$) and Lewis acids, such as $FeCl_3$, $ZnCl_2$, $CrCl_3$, and CuCl, can promote the dissolution of cellulose by forming HBs and further catalyze the hydrolysis of cellulose to glucose and further to HMF under the joint catalysis of Brønsted and Lewis acids [22]. The protic Brønsted–Lewis acidic IL, $[HDBN]Cl/ZnCl_2$ (where DBN = 1,8-diazabicyclo [5.4.0]undec-7-ene), performs well for the deep oxidative desulfurization of fuels with H_2O_2, which can achieve almost complete removal of dibenzothiophene [23]. The acidic ILs 1-hexyl-3-methylimidazolium chloroaluminate (III) ([HMIm] $[Al_xCl_y]$) as both reaction medium and catalysts are demonstrated to be effective for the oxidation of cyclic cyclobutanones to γ-butyrolactones with various bis(silyl) peroxides at room temperature [24]. $[SO_3H—BMIm]Cl—FeCl_3$ can achieve glycolysis of poly(ethylene terephthalate) (PET) with high performance [25].

The acidic ILs possessing heteropolyacid anions, e.g. $[PMo_{11}VO_{40}]^{4-}$, $[HPMo_{11}VO_{40}]^{3-}$, $[PW_{12}O_{40}]^{3-}$, and $[SiW_{12}O_{40}]^{3-}$, with commonly used organic cations (as shown in Scheme 1.3), are called heteropolyacid-based ILs, which combine the properties of heteropolyacids and ILs, showing unique properties. They are



Scheme 1.2 Chemical structures of typical Brønsted–Lewis acidic ILs.

Scheme 1.3 Chemical structures of cations in typical heteropolyacid-based ILs.

usually applied as catalysts for oxidation, and their activities depend on the combination of their cations and anions [26, 27]. For example, $[SO_3H—C_3NMeC_{12}]_3[PW_{12}O_{40}]$ and $[SO_3H—C_3NMeC_{12}]_4[SiW_{12}O_{40}]$ display strong Brønsted acidity and good redox activity, as well as excellent surface activity and good solubility in water [27]. These unique properties render them to work well for selective oxidation of alcohols with aqueous H_2O_2 at 70 °C, with slightly different performances depending on their heteropolyanion structures. Compared with its monocationic counterpart of $[BMIm]_3[PW_{12}O_{40}]$, the IL having PEG-functionalized di-imidazolium IL cations with Keggin PW-anion (i.e. $[PIPA]_3[PW_{12}O_{40}]_2$) exhibits enhanced catalytic efficiency for the oxidation of benzyl alcohol to benzaldehyde with aqueous H_2O_2 [28].

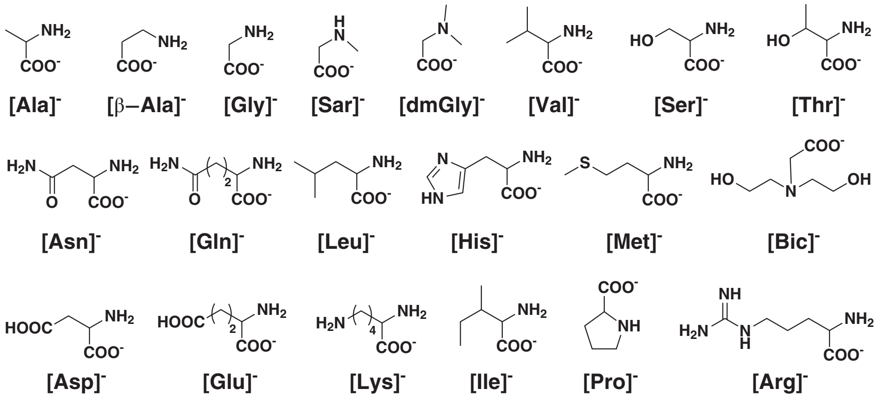
1.2.2 Basic ILs

Basic ILs can be grouped into hydroxide ILs, carboxylate ILs, amino-containing ILs, CO_2-reactive ILs, and so on. The ILs with hydroxide anion are typical basic ones, which are generally derived from the ion exchange of an IL with a basic resin possessing hydroxide anion. This kind of IL usually shows strong basicity and has been widely used in many base-catalyzed chemical reactions. As basic ILs, [BMIm][OH], choline hydroxide ([Ch][OH]), and tetrabutylammonium hydroxide triakonta hydrate ($[TBA][OH]\cdot 30\,H_2O$) have been reported to be effective for PET glycolysis [29, 30]. [BMIm][OH] can efficiently catalyze the Michael addition reaction of active methylene compounds to conjugated ketones, carboxylic esters, and nitriles, the addition of thiols to α,β-acetylenic ketones, and the alkylation of 1,3-dicarbonyl and -dicyano compounds without requiring any other catalyst and solvent [31]. It is also effective for Markovnikov addition of five-numbered *N*-heterocycles (such as imidazoles, pyrrole, pyrazole, and triazole) to vinyl esters [32]. Additionally, [BMIm][OH] can efficiently catalyze Knoevenagel condensation without the requirement of any organic solvent at room temperature [33].

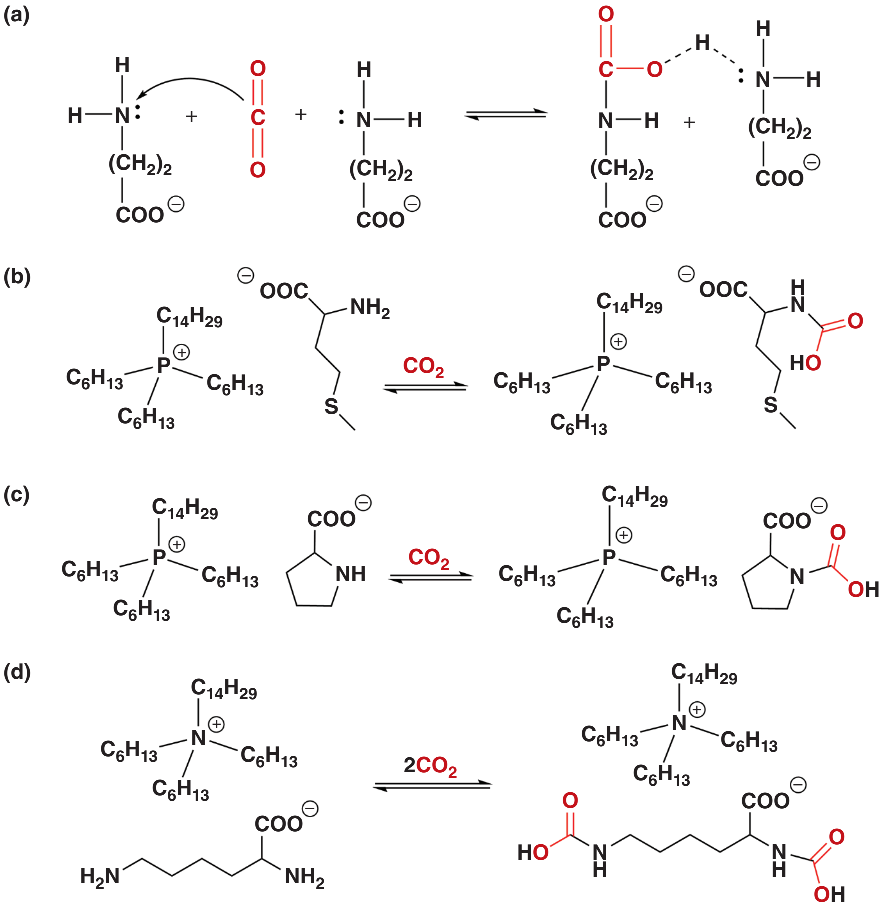
Carboxylate ILs are a kind of basic ILs derived from the neutralization of carboxylic acids and organic bases (e.g. imidazole, pyridine, choline, etc.), which generally display weak basicity compared with hydroxide ILs. However, the carboxylate anion can serve as an HB acceptor, which renders this kind of IL to show unique performance for some chemical reactions. For example, 1-ethyl-3-methylimidazolium acetate ([EMIm][OAc]) is reported to be effective for catalyzing the esterification of cellulose under relatively mild conditions [34], and it is highly effective for oxidative esterification of aliphatic and aromatic alcohols with O_2 in the temperature range of 80°C–110°C under metal-free conditions [35]. Remarkably, this IL enables the synthesis of various esters in high selectivity, from oxidative self-esterification and cross-esterification of alcohols. The acetate ILs, such as [Ch][OAc] and [EMIm][OAc], are also effective for the methanolysis of polyesters, and [Ch][OAc] exhibits higher activity than [EMIm][OAc] because the $[Ch]^+$ cation forms the stronger hydrogen bonding interaction with carbonyl O of polyester than the $[EMIm]^+$ cation [36]. Lactate-based ILs such as [EMIm][Lac], $[N_{1111}]$[Lac], $[N_{2222}]$[Lac], and $[N_{4444}]$[Lac] ([Lac] = lactate, $[N_{1111}]$ = tetramethylammonium, $[N_{2222}]$ = tetraethylammonium, and [N_{4444}] = tetrabutylammonium) could effectively catalyze aminolysis of polylactic acid (PLA) with anilines under mild conditions, generating a series of N-aryl lactamides in 100% selectivity and good-to-excellent yields [37]. In this protocol, the lactate anion serves as both an HB donor and acceptor, which can simultaneously activate the ester group of PLA and amines through hydrogen bonding interactions, thus achieving the aminolysis of PLA. The hydroxyl-containing carboxylate ILs are found to be capable of reacting with biodegradable polyesters, thus achieving the degradation and transformation of this kind of polyester [38]. [HDBU][OAc] (where DBU = 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium) is an excellent basic IL catalyst for aza-conjugate addition of aliphatic or aromatic amines to various electro-deficient alkenes under solvent-free conditions and at room temperature [39]. Basic ILs with carboxylate anions, like lactate and acetate, are reported to be effective for different types of aldol condensation [40].

Amino acids (AAs) are readily available, which can be applied in the construction of the cation and anion of ILs, and therefore various AA-based ILs have been developed and applied in chemical reactions. The AA anion-based ILs (as illustrated in Scheme 1.4) can be synthesized through the neutralization of AAs with organic bases. Regarding this class of ILs, the AA anion serves as both an HB donor and a receptor, which are capable of forming multiple HBs, thus showing high performances originating from hydrogen bonding catalysis. The imidazolium-, choline (Ch)-based ILs with AA anions such as glycinate ([Gly]$^-$), lysinate ([Lys]$^-$), alaninate ([Ala]$^-$), prolinate ([Pro]$^-$), histidinate ([His]$^-$), leucinate ([Leu]$^-$), and argininate ([Arg]$^-$) have been reported to be effective for glycolysis of PET, and their activity mainly depends on the structures of their AA anions [30, 41, 42].

The AA anion-based ILs (AAILs) with cations of [P_{4444}]$^+$, [N_{2222}]$^+$, and [BMIm]$^+$, and anions of [β-Ala]$^-$, [Gly]$^-$, [Ala]$^-$, [Ser]$^-$, [Lys]$^-$, [Met]$^-$, [Leu]$^-$, [Val]$^-$, and [Pro]$^-$ can chemically capture CO_2 through the 1:2 interaction mechanism that two amino groups from two AA anions attract one CO_2, as illustrated in Scheme 1.5a, thus achieving the CO_2 activation [43–47]. Equimolar CO_2 absorption capacities can be achieved by judicious selection of the cation and anion of AAILs. The AAILs



Scheme 1.4 Chemical structures of AA anions.



Scheme 1.5 Proposed absorption mechanism of CO_2 by AAILs. (a) $[P_{4444}]$[β-Ala], (b) $[P_{66614}]$[Met], (c) $[P_{66614}]$[Pro], and (d) $[N_{66614}]$[Lys]. Adapted from [44], [48] and [52].

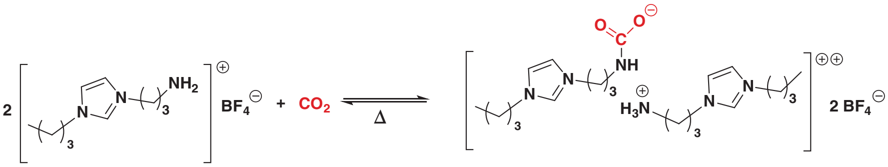
with trihexyl-(tetradecyl)phosphonium cations, such as $[P_{66614}]$[Met], $[P_{66614}]$[Pro], $[P_{66614}]$[Gly], $[P_{66614}]$[Sar], and $[P_{66614}]$[Ile], can absorb CO_2 with a capacity around 1.0 mol per mol IL under ambient conditions, following a 1:1 reaction stoichiometry mechanism by forming carbamic acid as illustrated in Scheme 1.5b,c [48–51]. The AAILs with the anion tethered to two primary amino groups have been reported to show higher CO_2 absorption capacity than the single amino-containing AAILs [52]. For example, $[N_{66614}]$[Lys], $[N_{66614}]$[His], $[N_{66614}]$[Asn], and $[N_{66614}]$[Gln] exhibit CO_2 absorption capacity around 2.0 moles of CO_2 per molar IL under ambient conditions by forming carbamic acid as shown in Scheme 1.5d [52]. The differences in the CO_2 sorption capacities of these AAILs are probably ascribed to the discrepancy in the cation–anion interactions and the reactivity of the amino group on the different anions, suggesting that the amino group on different anions shows a different ability to activate CO_2.

The aforementioned AAILs can chemically capture CO_2 by forming AA anion-based complexes, meaning that these ILs can react with CO_2, which are therefore named CO_2-reactive ILs. The other CO_2-reactive ILs mainly include amino-containing ILs, azolate ILs, phenolate ILs, and pyridine-containing ILs, which are capable of chemically capturing CO_2 by forming cation- or anion-based carbonates, carbamates, or carbamic acids. These ILs change the form of CO_2 and lower its activation energy, thus enabling the transformation of CO_2 to chemicals under mild conditions.

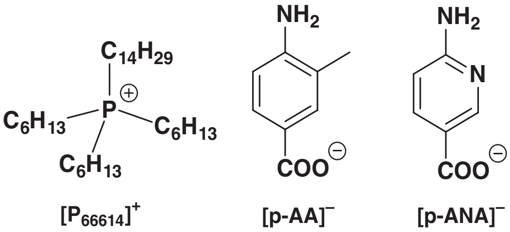
The amino-functionalized ILs involve the ILs with the cation- and/or anion-containing amino group ($—NH_2$), which can capture CO_2 by the reaction of CO_2 with the amino group. 1-Propylamide-3-butylimidazolium tetrafluoroborate ([Apbim][BF_4]) was first reported to chemically capture CO_2 by forming CO_2—[Apbim][BF_4] complex, as shown in Scheme 1.6, with maximum molar ratio CO_2 to [Apbim][BF_4] of 0.5 at ambient pressure [53]. That is, one CO_2 molecule reacts with two amino groups from two IL cations to form a carbamate group, which changes the form of CO_2 and makes it activated. Similarly, the amino-functionalized imidazolium-based (e.g. 1-(3-aminopropyl)-3-methylimidazolium, 1-(2-aminoethyl)-3-methylimidazolium) ILs with different anions can chemically absorb CO_2 by forming the similar complex [54–57].

Additionally, other amino-containing anion ILs are also developed for 1:1 CO_2 capture. For example, amino-functionalized methylbenzolate-based ILs and nicotinate-based ILs with an amino group at the para or ortho position, i.e. [P_{66614}][p-AA] and [P_{66614}][p-ANA]) (Scheme 1.7, can also capture CO_2 with high absorption capacities of 0.94 and 0.78 moles of CO_2 per molar IL, respectively [58].

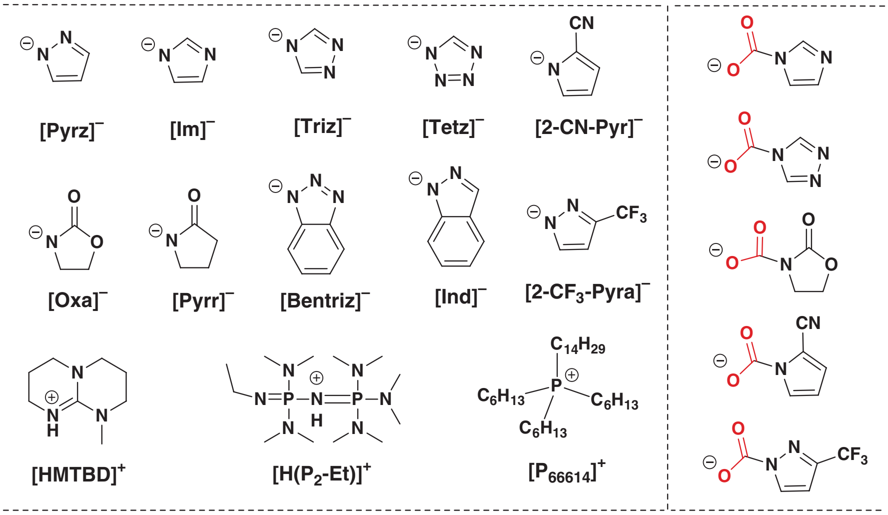
Azolate-based ILs are generally synthesized by the neutralization of superbases, such as 1,3,4,6,7,8-hexahydro-1-methyl-2 H-pyrimido[1,2-a]pyrimidine (MTBD) and trihexyl-(tetradecyl)phosphonium hydroxide ([P_{66614}][OH]), with weak proton donors like imidazole (Im), pyrazole (Pyrz), 1,3,4-trizole (Triz),



Scheme 1.6 Possible reaction between [Apbim][BF_4] and CO_2. Adapted from [53].



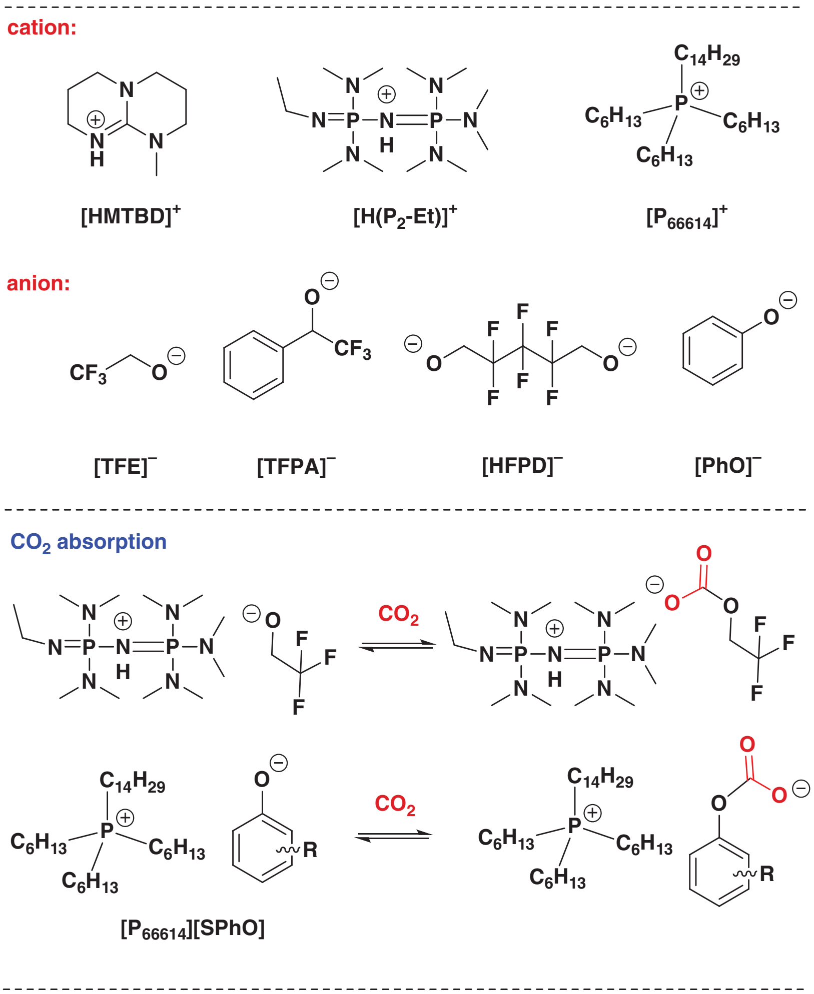
Scheme 1.7 Chemical structures of [P_{66614}][p-AA] and [P_{66614}][p-ANA]. Adapted from [58].



Scheme 1.8 Chemical structures of azolate ILs and complexes of azolate—CO_2. Adapted from [59, 60].

tetrazole (Tetz), indole (Ind), 2-oxazolidone (Oxa), pyrrolidone (Pyrr), and bentrizole (BenTriz) (Scheme 1.8) [59, 60]. They exhibit equimolar CO_2 absorption capacity by forming azolate-based carbamates. For example, trihexyl-(tetradecyl) phosphonium 2-cyanopyrrolide ([P_{66614}][2-CN-Pyr]) and trihexyl-(tetradecyl) phosphonium 3-(trifluoromethyl) pyrazolide ([P_{66614}][2-CF_3-Pyra]) could reach an absorption capacity of about 0.9 mole per molar IL, ascribing to the chemical interaction between CO_2 and the nitrogen atom with negative charge on the anion [61, 62]. In most cases, the basicity of the anion is the determining factor for CO_2 capture and the capacity can be controlled by tuning the basicity of ILs. The azolate anion–CO_2 interaction studied by density functional theory (DFT) calculations indicates that the linear CO_2 molecule needs to bend more than 40° to overlap its π^* orbital more efficiently with the nitrogen lone pair electrons in the azolate anion to form a σ_{C-N} bond [63], meaning the activation of CO_2 by the azolate ILs. The imidazolide-based ILs (e.g. [BMIm][Im] and [BMMIm][Im], [BMMIm]=1-butyl-2,3-dimethylimidazolium) could achieve aza-Markovnikov addition of imidazole to vinyl esters under solvent-free conditions at room temperature, affording the products in excellent yields [64].

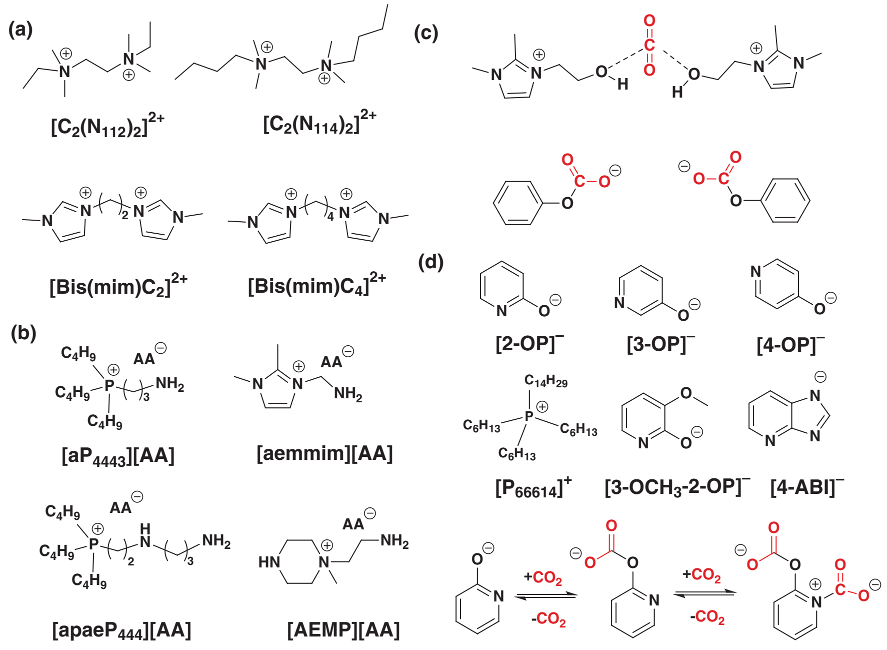
Alcoholate and phenolate ILs are a kind of protic ILs, derived from the neutralization of a superbase (e.g. [P_{66614}][OH] and MTBD) with weak proton donors, such as trifluoroethanol (TFE), 1-phenyl-2,2,2-trifluoroethanol (TFPA), 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (HFPD), and phenol (PhOH), in which the superbase acts as a strong proton acceptor to directly deprotonate the weak proton donor to form the ILs. Most alcoholate ILs show an equimolar CO_2 capture under atmospheric pressure by forming anion-based carbonates (Scheme 1.9), and the absorbed CO_2 can be released at a higher temperature (e.g. 80 °C) with the IL regeneration



Scheme 1.9 Chemical structures of alcoholate and phenolate ILs (top) and CO_2 absorption by [(P_2—Et)H][TFE] and [P_{66614}][SPhO] (bottom). Adapted from [59] and [65].

[59]. In comparison, the phenolate ILs show low CO_2 absorption capacity depending on the basicity of the ILs [65].

Scheme 1.10 shows some typical CO_2-reactive ILs with multiple sites including dicationic amino acid–based ILs (AA-DILs) (Scheme 1.10a [$C_2(N_{112})_2$][Gly]$_2$ or [$C_2(N_{114})_2$][Gly]$_2$, [Bis(mim)C_2][Pro]$_2$, [Bis(mim)C_4][Pro]$_2$, [Bis(mim)C_2][Gly]$_2$, [Bis(mim)C_4][Gly]$_2$, [Bis(mim)C_2][Im]$_2$, and [Bis(mim)C_4][Im]$_2$) [66, 67], ILs with one diolate-based anion and two cations (e.g. [MTBDH]$_2$[HFPD]) [59], dual amino-functionalized ILs at both cation and anion (Scheme 1.10b [aP_{4443}][AA], [aemmim][AA], [apaeP_{444}][AA], and [AEMP][AA]) [68–71], ILs with the HO-functionalized cation and phenolate anion (Scheme 1.10c) [72], and ILs with multiple cooperative sites on the anion (Scheme 1.10d) [73–74], which have been reported for chemical capture of CO_2. These multiple-site ILs generally attract CO_2 by reacting with each



Scheme 1.10 Chemical structures of some typical CO_2-reactive ILs with multiple sites. (a) Cations of dicationic ILs; (b) dual amino-functionalized ILs that consist of an amino-based cation and AA anion; (c) ILs with HO-based cation and phenolate anion and possible mechanism of CO_2 absorption; and (d) pyridine-containing anion-functionalized ILs and plausible mechanism of CO_2 absorption by $[P_{66614}][2—OP]$ through multiple-site cooperative interactions. Adapted from [59], and [66–74].

active site to form complexes or adducts, thus showing high CO_2 absorption capacity; meanwhile, CO_2 is activated by the ILs. For example, hydroxypyridine anion–based ILs (Scheme 1.10d, e.g. $[P_{66614}][2—OP]$) can capture CO_2 by forming both anion-based carbamate and carbonate, thus activating CO_2 cooperatively.

Aforementioned CO_2-reactive ILs with sites can efficiently activate CO_2 by forming anion- or cation-based complex or adduct, which changes the formation of CO_2 and lowers its activation energy. Thus, they can further catalyze the transformation of CO_2 into value-added chemicals.

1.2.3 Neutral ILs with HB Donor/Acceptor

There are various kinds of neutral ILs that are also capable of serving as catalysts. For these IL catalysts, their cations or anions generally possess HB donors or acceptors, which can form opposite HBs with different reactants, thus promoting the reaction under the synergistic catalysis of the IL cation and anion. Herein, some typical neutral ILs are introduced, with their chemical structure and catalytic performance for chemical reactions.

Neutral halide–based ILs are generally used as solvents and seldom as catalysts. The commonly used neutral ILs (e.g. [BMIm]Br and [BMIm]Cl) are effective for the glycolysis of PET at a temperature around 180 °C [41]. 1-hexyl-3-methylimidazolium bromide has been reported to be very effective for the synthesis of linear thioethers from activated and inactivated styrene derivatives or secondary benzyl alcohols and thiophenols in good-to-excellent yields with high regioselectivity under metal-, base-, and radical-free conditions at 40 °C [75]. By investigating the interaction between 1-butyl-2,3-dimethylimidazolium chloride ([BMMIm]Cl) and methyl benzoate (MB) through nuclear magnetic resonance (NMR) analysis, it is found that the hydrogen bonding interaction between [BMMIm]Cl and ester group of MB enhances the nucleophilicity of Cl^- anion and activates the C_{alkoxy}—O bond of MB [76]. As a result, the halide-based ILs are found to be effective for catalyzing degradation of polyesters by breaking the C_{alkoxy}—O bonds. For example, the bromide anion–based ILs with different cations, such as [BMMIm]Br, [BMIm]Br, [N_{4444}]Br, and [P_{4444}]Br, can catalyze the depolymerization of polyesters with β–H to unsaturated carboxylic acids or carboxylic acid with alkene under metal-free conditions, among which [P_{4444}]Br exhibits the highest activity. In combination with hydrogenation over Pd/C, halide-based ILs can achieve the degradation of polyesters into carboxylic acids and alkanes, which provides a conventional strategy to recycle polyesters.

The neutral ILs with bis(trifluoromethylsulfonyl)imide anion ([NTf_2]$^-$), e.g. 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BnMIm][NTf_2]) as both the solvent and catalyst, can catalyze the oxidation of 2-phenoxyacetophenone to benzoic acid under 1 MPa O_2 at 413 K in the presence of a little amount of water [77]. As both the solvent and catalyst, the conventional IL [BMIm][BF_4] has been reported to be capable of catalyzing selective oxidation of thioethers to sulfoxides using 35% aqueous H_2O_2 at room temperature, and a variety of thioethers with different functional groups could be converted into corresponding sulfoxides [78].

The hydroxy-functionalized ILs with trifluoromethyl sulfonate anion ([OTf]$^-$), such as 1-hydroxyethyl-3-methylimidazole-trifluoromethyl sulfonate ([HO—EtMIm][OTf]), 1-hydroxyethyl-2,3-dimethylimidazole-trifluoromethyl sulfonate ([HO—EtMMIm][OTf]), and 1-hydroxyethyl-2,3,4-trimethylaminotrifluoromethyl sulfonate ([HO—EtN_{111}][OTf]), are another kind of neutral ILs, whose cation and anion can serve as an HB donor and acceptor, respectively. Therefore, the synergistic effect between the cation and anion to form HB renders these ILs to have catalytic activity for some reactions. For example, they can effectively catalyze the dehydration of alcohols to ethers [79], and are also effective for catalyzing metathesis of alkyloxy alcohols to cyclic ethers [80]. Among these ILs, [HO—EtMIm][OTf] shows the best performance, which can achieve the metathesis of alkyloxy alcohols under mild conditions (e.g. 120 °C), accessing a series of cyclic ethers in high yields (e.g. up to > 99%) [80]. It can efficiently catalyze intramolecular dehydration of various diols, solely yielding cyclic ethers, including tetrahydrofuran, tetrahydropyran, morpholine, dioxane, and 1,4-dioxane, in high yields [79].

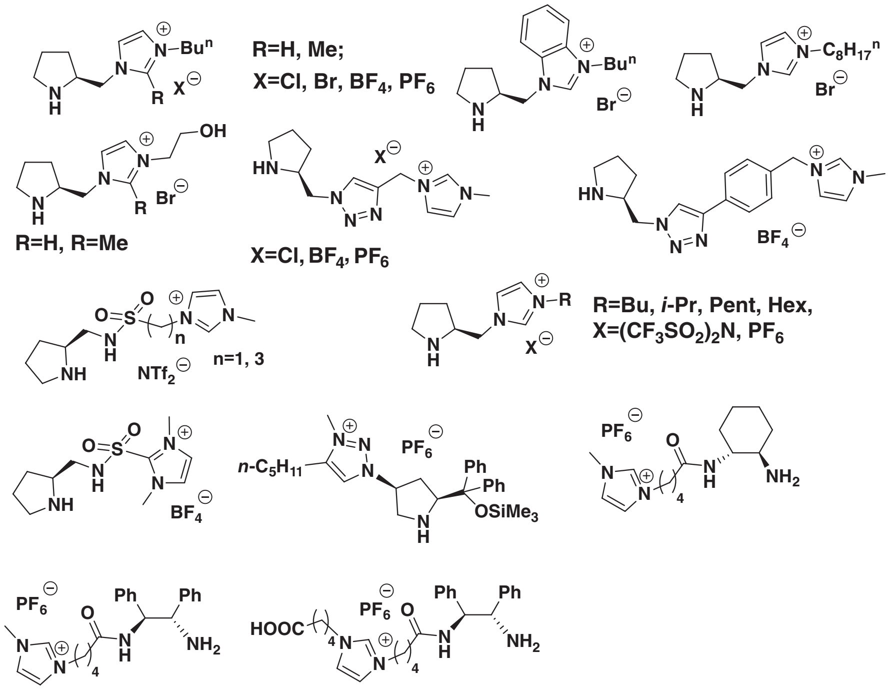
As an HB acceptor, the succinimide anion has a strong ability to form an HB, thereby being capable of catalyzing some chemical reactions through hydrogen bonding interaction. The succinimide anion ([Suc]$^-$)–based ILs, including [P_{4444}][Suc], [N_{4444}][Suc], [Ch][Suc], and [HDBU][Suc], have been presented to be effective for degrading poly(succinates) with butylamine to access *N*-butyl succinimide under mild conditions [81].

1.2.4 Chiral ILs

Chiral ILs refer to those with chiral centers at the cation or anion, which have been intensively investigated in the synthesis of chiral chemicals. Since Seddon's group [82] reported the first example of a chiral IL, 1-butyl-3-methylimidazolium lactate ([BMIm][Lac]) for Michael reaction, various chiral ILs have been reported, most of which consist of chiral cations and achiral anions, as shown in Scheme 1.11.

Proline-derived ILs, including L-prolinate and L-prolinium ILs, have been widely used as chiral agents for asymmetric organic synthesis, e.g. aldol reaction, Baylis–Hillman reaction, and Michael addition, due to the asymmetric feature from L-proline [83, 84].

Besides the IL catalysts described earlier, many other IL catalysts have been designed with task-specific functions and applied as catalysts in various chemical reactions. ILs have been raised as a great appliance to pursue many organic transformations. In the following chapters, the recent advances in IL-catalyzed chemical reactions, including chemical conversion of CO_2, transformation of lignocellulose and its derivatives, water-involved chemical reactions, oxidations, C—C/C—O/C—N coupling reactions, and degradation of polymers, will be introduced, with a focus on the roles of ILs in chemical reactions and insights into catalytic mechanism.



Scheme 1.11 Chiral ILs with imidazolium-bearing chiral functional moieties.

1.3 Structure of This Book

The chemical transformation of CO_2 into value-added chemicals and fuels is an interesting topic for complementing natural carbon recycling and achieving carbon neutrality, which has been intensively investigated in the past decades. However, since CO_2 is thermodynamically stable and kinetically inert, its chemical conversion generally requires high energy input and active catalysts to drive. ILs, especially CO_2-reactive ILs, provide a new opportunity for CO_2 transformation due to their unique properties, which have achieved the transformation of CO_2 under metal-free and mild conditions. The reductive transformation of CO_2 is an important way to convert CO_2, and H_2-promoted CO_2 reductive transformation particularly offers a green strategy to access chemicals, which generally requires catalysts or catalytic systems that are capable of simultaneously activating CO_2 and H_2. Many IL-metal catalytic systems have been developed to meet this requirement, which has achieved the reductive transformation of CO_2 with H_2 to fuels and chemicals. Meanwhile, since ILs can significantly reduce the activation energy of CO_2 by forming the IL–CO_2 complex, the IL-based electrolytes have been applied in the CO_2 electroreduction, greatly increasing the efficiency of CO_2 electroreduction. To date, numerous researches on CO_2 transformation relevant to ILs have emerged, and many interesting results and achievements have been reported. Therefore, the advances in IL-catalyzed or promoted CO_2 transformation are first summarized in Chapters 2–4, which involve the transformation of CO_2 into chemicals under metal-free and mild conditions (Chapter 2), reductive conversion of CO_2 with H_2 (Chapter 3), and electroreduction of CO_2 in IL-based electrolytes (Chapter 4).

As naturally renewable carbon resources, lignocellulose and its derivatives provide alternative and green feedstocks for the production of chemicals, fuels, and materials, and therefore their chemical transformation has attracted much attention in recent years. ILs as a kind of powerful solvents and/or catalysts have shown promising performances for lignocellulose dissolution and chemical transformation, and a large amount of research work has appeared. Based on the chemical structures of cellulose, hemicellulose, and lignin, various IL-based catalytic systems have been constructed and used in their transformation, which significantly promotes the progress of lignocellulose utilization. In Chapter 5, the IL-catalyzed lignocellulose transformation is described, with a focus on the chemical conversion of cellulose and its derivatives to oxygen-containing chemicals (e.g. reduced sugars, HMF, levulinic acid, 5-methylfurfural, formic acid, and so on) and transformation of lignin and its platforms to various aromatic compounds. In these transformations, the IL-based catalytic systems work well for lignocellulose transformation, affording environmentally friendly strategies to access oxygen-containing chemicals and aromatics, which are promising alternatives to these fossil-based routes.

Oxidation reactions are a fundamental chemical process with significant importance in industrial production. Especially, oxidation reactions using oxygen or hydrogen peroxide (H_2O_2) as oxidants are considered green approaches to access valuable chemicals. In recent years, the field has seen the emergence of catalytic-capable ILs that exhibit good performance and unique advantages for oxidation reactions. In Chapter 6, the research findings related to oxidation reactions of various chemicals such as alcohols/aldehydes, organic sulfides, olefins, allylic alcohols, amines, and others over IL catalysts are introduced, with a discussion on the reaction pathway and catalytic mechanism of the IL catalysts. It is demonstrated that the IL-catalyzed oxidation reactions provide novel strategies for the synthesis of oxygen-containing chemicals, which may have promising application potentials.

Water-involved chemical reactions including hydrolysis, hydration, and dehydration are considered green routes to access corresponding chemicals, which are traditionally catalyzed by acid and base catalysts. Since ILs can be designed with acidic and basic features, along with an HB donor and acceptor at the cation and/or anion of the ILs, such ILs can efficiently catalyze the water-involved reactions. Especially, for the ILs with HB donors and acceptors, they can form dual HBs with water molecules. Therefore, the cooperation of the hydrogen bonding interaction resulting from the HB donor and acceptor of the IL can efficiently catalyze this kind of reaction. In comparison to the acid or base catalysis, the IL catalysis generally displays enhanced activity; meanwhile, it avoids the shortcomings of the acid or base catalysis. In Chapter 7, the IL-catalyzed dehydration (e.g. dehydrative esterification, etherification, and amidation), hydration reactions of alkynes, propargylic alcohols, nitriles, and epoxides, along with the hydrolysis of esters/ethers are summarized, with a discussion on the catalytic mechanism of the IL catalysts. The used ILs in these reactions are classified into acidic ILs, basic ILs, and ILs with HB donor and acceptor, which catalyze the reactions through the cooperation of the IL cation and anion. In particular, the cation- and anion-confined hydrogen bonding catalysis can achieve the intermolecular dehydration of diols to corresponding cyclic ethers in 100% selectivity.

Besides the aforementioned chemical reactions, other C—C, C—O, and C—N bond formation reactions, such as alkylation reaction, Michael addition, Diels–Alder reactions, Baylis–Hillman reactions, Markovnikov additions, Aldol condensation, and ring-closing C—O/C—O and C—O/O—H bond metathesis, have been widely applied in the synthesis of chemicals. ILs as a new class of emerging catalysts have been widely applied in catalyzing these organic reactions, and display superior performance compared with traditional catalysts. Especially, chiral ILs have been designed for the synthesis of chiral chemicals, showing high performance and obvious advantages. In Chapter 8, the advances of the aforementioned reactions catalyzed by ILs are briefly summarized, with a focus on the roles of the IL catalysts and the possible reaction mechanism.

The chemical recycling of plastic wastes is of great significance for solving the environmental problems caused by the accumulation of plastic wastes and for sustainable development. As a kind of powerful solvents and/or efficient catalysts, task-specific ILs have been widely used in the recycling of plastics, and much progress has been made. In Chapter 9, advances in the IL-catalyzed decomposition of various plastics, including polyesters, polyamides, polyolefins, and mixtures of some plastics, are summarized, with a focus on degradation strategies and catalytic mechanisms. Since polyesters can be easily decomposed through hydrolysis, alcoholysis, aminolysis, and hydrogenolysis, much research work has been dedicated to the recycling of polyesters over IL catalysts. It has been indicated that IL catalysts show high performance for the chemical recycling of polyesters, which especially can achieve the decomposition of polyesters under mild and metal-free conditions. The cooperation of the cation and anion is responsible for the high activity of IL catalysts. Compared with polyesters, polyolefins, including polyethylene, polypropylene, and polystyrene, are more difficult to degrade due to their special structures. Interestingly, some task-specific ILs are effective for catalyzing the breakage of C—C bond of polyolefins, which provide a novel protocol to recycle this kind of plastics. In addition, most IL catalysts exhibit good recyclability and stability, having promising application potentials.

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