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Imidazolium-Based Ionic Liquids Grafted on Solid Surfaces

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Supported ionic liquids (SILs), which refer to ionic liquids (ILs) immobilized on supports, are a kind of the most important branches of ILs. The immobilization process of ILs can transfer their desired properties to substrates. Combination of the advantages of ILs with those of support materials will derive novel performances while keep properties of both moieties. SILs have been widely applied in almost all of fields involving ILs, and have brought drastic reformation of ionic liquid area. As green media in organic catalytic reactions, based on keeping the ability of ILs to stabilize the catalysts, they have many advantages over free ILs, including avoiding the leaching of ILs, reducing their amount, and improving the recoverability and reusability of both themselves and catalysts. It has critical significance from both environmental and economical points of view. As novel functional materials in surface science and material chemistry, SILs are ideal surface modifying agents. They can modify and improve the properties of solids, such as wettability, lubricating property, separation efficiency and electrochemical response. With the achievements in the field of ILs, using magnetic nanoparticles (MNPs) to SILs has drawn increasing attention in catalytic reaction and separation technologies, and achieved fascinating progress. The perfect combination of MNPs and ILs renders them to be magnetic SILs, which exhibit the unique properties of ILs as well as facile separation by external magnetic field. In this article, we focus that imidazolium-based ILs are covalently grafted to non-porous and porous inorganic materials. The excellent stability and durability of this kind of SILs offer a great predominance compared with free ILs and IL films physically adsorbed on the substrates without covalent bonds. Including examples from our own research, we overview mainly the applications and achievements of covalent-linked SILs in catalytic reactions, surface modification, separation technologies and electrochemistry.

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1. Introduction

Recent decades, room-temperature ionic liquids (RT-ILs), especially imidazolium-based ionic liquids, have been critical issues in chemistry. RT-ILs are a special class of molten salts composed of large asymmetric organic cations and inorganic or organic anions, which melt at or below 100°C, usually close to room-temperature.[1,2] The special structure and interaction of ions determine their unique physicochemical properties, such as negligible vapor pressure, chemical, thermal and photocatalytic stability, nonflammability, relatively high ionic conductivity, and a widely electrochemical potential window. Moreover, RT-ILs can be designed to the desired structures for specific applications through varying cations and anions. Hence, they are often referred to as "designer liquids". As a result, RT-ILs open up new horizons for many areas, such as organometallic catalysis, surface modification, biocatalysis, chemical sensors, analytical techniques as well as electrochemistry, etc. There have been many reviews which presented comprehensive overviews about the topics.[3-6]

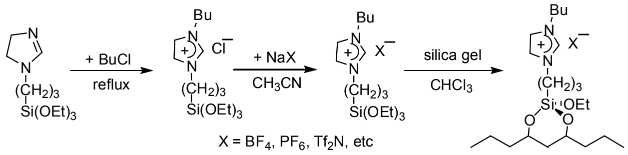
The facile designability and functionalization of ILs derive many innovative trends. Supported ionic liquids (SILs) are one kind of the most important branches in the IL community, and have drawn great attention in both fundamental research and practical applications.[7-10] Supported ionic liquids refer to ILs that are immobilized on solid, polymer, liquid or aerogel supports by either covalent or noncovalent bonds using various methods, including simple physisorption, self-assemble technique or polymerization.[11-13] The unique physicochemical properties of ILs can be transferred to substrates. They not only retain the advantages of ILs and supports but also derive a series of new performances and novel properties due to the synergistic effect of ILs and supports, while have capability to restrict many of the negative effects of the conventional ILs (*e.g.*, leaching and disarrangement, poor recovery and so on). The dramatic advantages of SILs inspire drastic reformation of ionic liquid area. Over the last decade, SILs have been used as green media and functional materials for supports of catalysts, surface modifying agents, stationary phases in separation technologies, and electrodes in electrochemistry.[14-17]

In this critical article, our interest is that imidazolium-based ILs are covalently linked to non-porous and porous inorganic materials. We summarize mainly the achievements of covalent-linked supported ionic liquids in related areas. Section 2 gives the concept of SILs and relatively derivative terms, and describes their synthetic methods and routes. In Section 3, the applications and advances of SILs in organic chemistry are described. We survey two combing types between SILs and catalysts. Section 4 presents the modulation of wetting and lubricating behaviors of substrates through covalently anchoring ILs on their surfaces, and the effect of anions and cations of SILs is discussed. Combining with our group's work, we describe the synthesis of stably dual-stimuli-responsive IL superhydrophobic surfaces. Section 5 summarizes the advances of SILs in the separation technologies. Covalent bonds between ILs and substrates can enhance the stability and avoid the disarrangement of SIL films. In addition, SILs can tailor the electrochemical properties of materials, the approaches appending covalently ILs on electrodes and electrolytes are emphasized in Section 6. Finally, we offer conclusions about this review and an outlook on the future and perspective of the domain of SILs. Considering the rapid developments in this topic, we would like to point out that the achievements of SILs presented here approximately covers the period from 2002 to March 2014.

2. Supported ionic liquids and relatively derivative concepts

In catalytic reactions, aggregation and poor recovery of transition-metal catalysts, and the difficult separation of products from reaction mixtures are the great challenges from both environmental and economical points of view. RT-ILs have ability to overcome these limitations in great degree, and they are suitable reaction media for numerous catalytic reactions.[18] However, the leaching of ionic liquid themselves from reaction system and great amount needed have hindered their widespread practical applications due to their expense and potential toxicity to environment.

Under this background, the concept of "immobilized ionic liquids" on solid surfaces *via* covalent bonds is derived from the term "immobilized liquids".[11] In 2002, Mehnert et al.[19] covalently anchored 1-*n*-butyl-3-[3-(triethoxysilanyl)propyl]-4,5-dihydro-imidazolium onto silica gel surface *via* the reaction between trimethoxysilyl functional group in ILs and the abundant silanol groups on silica gel, forming supported ionic liquids (Scheme 1). In organic catalytic reactions, the reaction phase to dissolve catalyst is necessary, the additional free ILs are absorbed in SIL layer. The community of bonded and mobile phases of ILs forms supported ionic liquid phases (SILPs),[9] as excellent stabilizers for the catalysts and media of reactions. In SILPs, Mehnert et al. dissolved the active Rh catalyst, called as supported ionic liquid catalyst (SILC), which catalyzed successfully hydroformylation reaction with high yields using small amount of ILs.



Scheme 1 Preparation of SILs *via* covalent bonds.[19]

Although it is argued that ILs once bound to a solid support, the cation/anion pair no longer constitutes a true IL, the unique properties of ILs still remain in SILs, even over free ILs. Covalently linked ILs on supports offer a highly attractive strategy to circumvent the leaching of ILs, minimize their amount and improve the stability,[20] while display other fascinating performances applied in other areas. When they are employed in separation technologies, SIL films are often called as supported ionic liquid membranes (SILMs).[8]

Supported-mono-ILs composed of one imidazolium moiety, which refer generally to the self-assembled monolayers of imidazolium ion (SAMIMs) (Scheme 1 and Fig. 1a), often present thin density, and then result in poor performances in modifying solids. Many innovative methods are reported. In organic reactions, supported-multi-ILs (Fig. 1b) which have two or three imidazolium moieties in side chains are grafted on supports with different counteranions, and can offer more catalytic active centres than supported-mono-ILs.[21]

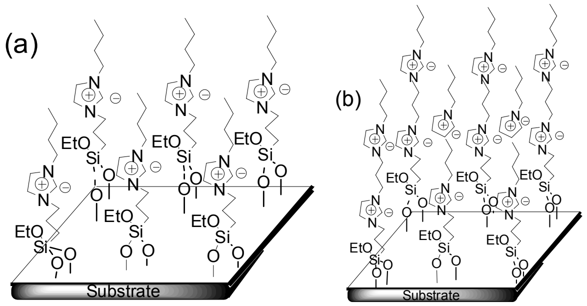
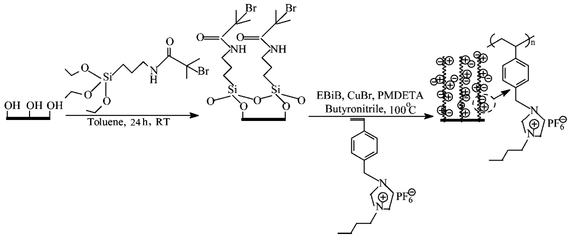


Fig. 1 Supported-mono-ILs (a)[19] and supported-multi-ILs (b)[21] on supports.

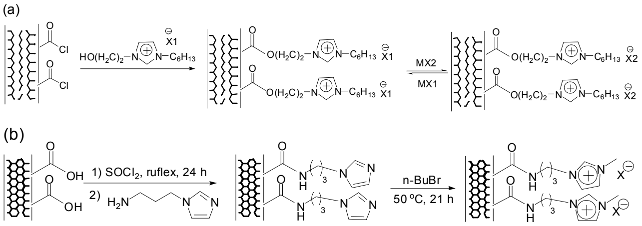
In the parallel fascinating developments of both SILs and poly(ionic liquid)s (PILs) in recent years,[22] supported poly(ionic liquid)s (SPILs) have significantly increased in surface chemistry and material science. For example, [1-(4-vinylbenzyl)-3-butyl imidazolium hexafluorophosphate] ([PVBIm]PF_6) brushes are grafted from the surface of silicon wafer *via* surface-initiated atom transfer radical polymerization (ATRP) technique, as shown in Scheme 2.[23] The diversity of ILs induces a variety of SPILs, and many experiments prove that they can offer higher density and uniformity than SILs, and enhance the performances to a great degree.



Scheme 2 Preparation of supported [PVBIm]PF_6 *via* ATRP technique.[23]

Different supports can form different interactions with ILs.[5,24] The majority of supports which immobilize ILs are often mesoporous silica materials, zeolites and clays (*e.g.*, montmorillonite), carbon nanotubes (CNTs) and metal/metal oxide nanoparticls (NPs) and other materials.[24,25] Among them, silica-based materials, including silica gel, MCM-41 and MCM-48 are the most popular supports due to their large surface areas, high thermal and mechanical stability, on which many studies of immobilizing ILs are reported.[26] In addition, CNTs and graphenes are considered as other kind of promising building blocks for ILs because of inherent advantageous properties, such as good mechanical strength, high chemical stability and large surface area-to-volume ratio.[27] With the achievements of SILs, magnetic iron oxide nanoparticles are becoming one of the most attractive supports. One reason is that they are easily separated from mixtures by applying an external magnetic field due to their magnetic property.[28] The other reason is that they are easy to be prepared and functionalized, and have derived to hydroxyapatite-encapsulated γ-Fe_2O_3, SiO_2@Fe_3O_4 and Fe_3O_4@SiO_2 NPs, *etc.*[29-31]

Though both cations and anions of ILs have chance to react with functional groups of solid surfaces, immobilization of cations is main type in SILs.[11] The covalent strategy is accomplished by the reaction between pre-functionalized solid surfaces and imidazolium-based ILs with the special functional groups, such as trimethoxysilyl-, thiol-, ether-, carboxylic acid-, amino-, and hydroxyl- group.[9] Generally, different substrates need different pre-functionalizing process. Treated with Piranha solvent, the surfaces of silica-based materials and some metal or metal oxides can emerge plentiful hydroxyl groups,[24] and trimethoxysilyl group is realized to be the most stable linking between ILs and them, while thiol- groups are often used to link Au with ILs.[16] To CNTs, common functionalizing process is that oxidize them in aqueous HNO_3 to yield carboxylic acid on the surface,[27] and IL-NH_2 or IL-OH is introduced to the surface *via* –CONH- or –COO- bond, forming IL-CNT systems. Nowadays, grafting ILs onto substrates can be achieved by two synthetic routes according to literatures (Scheme 3),[32-34] (i) ILs are prepared firstly and then self-assembled on the substrate surfaces directly (Scheme 3a).[32,33] However, the purification of ILs is very difficult, and a small quantity of impurities can produce disordering and defective films, and result in the poor reproducibility, (ii) Imidazol moiety is firstly self-assembled on the substrate surfaces *via* covalent bonds, and followed by the preparation of ILs directly on substrate surfaces (Scheme 3b).[34] This route avoids the purification process of ILs, and reproducibility is better than that of the first method. Fortunately, the coating of graphene oxide (GO) with ILs is easier than that of CNTs. GO has plentiful and reactive epoxy groups, a nucleophilic ring-opening reaction can introduce amino-terminated ILs to graphene sheets.[35]



Scheme 3 Schematic depiction of the modification of CNTs with functionalized ILs. (a) preparing ILs firstly, and then self-assembled on the substrate surfaces *via* covalent bonds,[33] (b) anchoring imidazol moiety on surfaces firstly, following by the preparation of ILs directly.[34]

SILs and relatively derivative terms have been studied in catalytic reactions, surface modification, separation technologies and electrochemistry. Here we systematically describe the performance of the cations, counteranions of ILs and their supports in many applications.

3. Applications of SILs in organic reactions

The leaching and great consumption of ILs stimulate the rapid developments of SILs, which are proved to be more excellent green media than free ILs. Firstly, the most advantage of SILs is that they possess higher stability and need lesser dosage than free ILs. Secondly, SILPs can retain the ability of ILs to immobilize transition-metal or metal-free catalysts, having capability to avoid the leaching of catalysts. Thirdly, SILPs combine the advantages of homogeneous with heterogeneous catalysis, which have advantage to catalysis with facile separation. Therefore, they can effectively resolve the difficulties in separation of products, and achieve the recoverability and reusability of catalysts. Further studies find that ILs grafted on supports can mediate to the process of catalytic reactions, affecting the reaction rate, productions, yield and even enantioselective activity of asymmetric reactions.[18] In more than one decade, a large range of SILs have been prepared and have been comprehensively investigated in many catalytic reactions.[7]

De Vos et al.[9] have given a definition about the combining types among catalysts, ILs and solid supports, including covalent and noncovalent linkages. Considering the chemical bonds between ILs and supports in this article, we discuss mainly two combining approaches. One type refers to dissolve catalysts in SILPs, and the other type is that make catalyst be a component of ILs, as either cation moiety or counteranion.

3.1. Dissolving catalysts in SILPs

Following the formation of SILPs, transition-metals are dissolved and efficiently circumvented into SILPs in virtue of the high interfacial area between SILPs and catalysts, forming catalyst/IL/IL-support system.[9] That is, the system acts as not only solvent but also immobilizing agent of catalyst. Both the compositions of supported ILs and supports can affect properties of catalysts and the reaction process, such as stability, recoverability and activity, *etc*.

3.1.1. Effect of compositions of supported ILs on the catalytic properties

(1) Effect of cations of SILs on catalytic properties. The supported-mono-ILs with imidazolium side chains are a kind of concerning topics in the research field of SILs since it was risen in 2002 (Fig. 1a).

Many catalysts, such as Rh, Pd, Zn, Mn, Au complexes and corresponding metal NPs as well as metal-free catalysts have been studied in SILPs.[36-38] Taking Rh catalytic species, for instance, many experiments prove that utilization of SILPs to immobilize Rh complexes can avoid their aggregation and facilitate separation. More importantly, the study on the reaction mechanism reveals that rhodium concentration in SILPs is improved at the large reaction interface. The activity of [Rh]/IL/IL-SiO_2 system (turn over frequency (TOF) of 3360-3600 h^{-1}) in hydroformylation reaction is almost three times higher than those for biphasic [Rh]/[bmim]BF_4 system (TOF of 1320-1380 h^{-1}).[9,19] The other highlight in SILPs is the reaction types. Until now, almost all of catalytic reactions have been evaluated in SILPs, such as Suzuki reaction,[37,39,40] hydrogenation reaction,[41] Baeyer–Villiger reaction,[42] even multi-component reactions[38,43] and continuous fixed-bed reactors.[44] The experimental results demonstrate that SILPs present excellent recoverability and reusability and affect the catalytic activity.

Moreover, this strategy shows a favourable availability in asymmetric catalysis reactions.[45-47] Asymmetric reactions have been critical issues in the synthesis of natural products and pharmaceutical compounds for recent decades. Chiral species are very expensive and difficult to be synthesized, and their air-sensitivity can result in the loss of chiral characters. So means to make them be stable and facile recycling is very necessary. Many experiments have demonstrated that SILPs can overcome these limitations in great degree due to promising ability to stabilize chiral catalysts as well as avoid catalysts leaching. Lou[48,49] designed a catalytic system through solubilising chiral Ru complex into IL-modified mesoporous materials, and used it to catalyze hydrogenation of aromatic ketones and acetophenone as heterogeneous catalysts (Fig. 2). Although this catalytic system only exhibited comparable conversions and enantiomeric excess (*ee*) values in the literature report, it gave high stability and could be recycled at least four times without noticeable decrease in catalytic and enantioselective activity, which was superior to other asymmetric catalytic systems. So the advancement of catalyst/IL/IL-support system is very fast in asymmetric reactions.

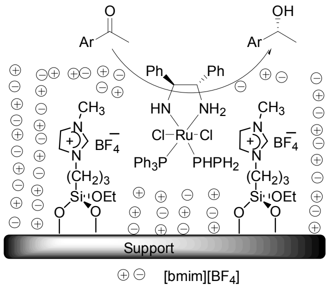
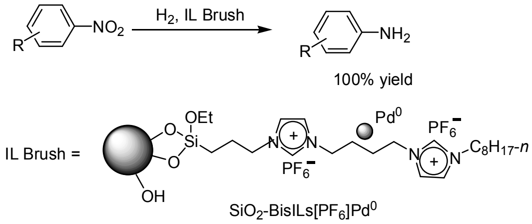


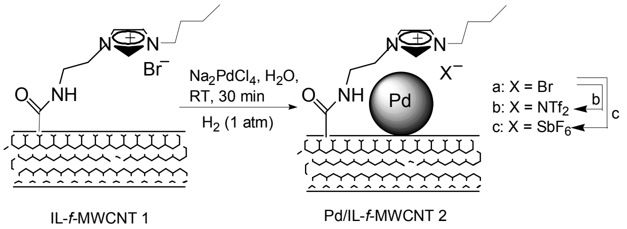
Fig. 2 Chiral [$RuCl_2(PPh_3)_2$(S,S-DPEN)], DPEN = 1,2-diphenylethylenediamine, solubilized in SILPs and used in the asymmetric hydrogenation of acetophenone.[49]

Supported-mono-ILs system can not offer effectively catalytic activity sometimes. Wei group[50] studied the reaction mechanism and found that the amount of catalytic active centres was insufficient in this kind of catalytic system. They synthesized SiO_2-bisILs with bis-imidazolium moieties and SiO_2-triILs with tri-imidazolium moieties in IL fragments (Fig. 1b). The experimental results exhibited that both SiO_2-bisIL$[PF_6^-]_2Pd^0$ and SiO_2-bisILs$[PdEDTA]^{2-}$ achieved nearly 100% yield and selectivity in hydrogenation reactions of nitrobenzene (Scheme 4)[51] and Suzuki cross-coupling reaction,[21] respectively. Moreover, the catalysts of supported-multi-ILs could recycle 10 times in Suzuki reaction,[21] which was much larger than free ILs and the catalytic systems of supported-mono-ILs. Obviously, compared with the traditional supported-mono-ILs, supported-multi-ILs have more prominent three-dimensional environment characteristics, and provide enough active centres for catalysts, reactants and active species.



Scheme 4 SiO_2-bisIL$[PF_6^-]_2$-Pd^0 in hydrogenation reactions of nitrobenzene.[51]

(2) Effect of counteranions of SILs on catalytic properties. Counteranions in SILs retain their facile exchange function, and can tailor the properties of SILs. Lee et al.[52] studied the effect of a series of counteranions on catalytic activities in hydrogenation of *trans*-stilbene based Pd@IL–MWCNTs (multiwalled carbon nanotube) hybrids (Scheme 5). They found that Pd/IL-*f*-MWCNT having SbF_6 anion showed superior catalytic activity compared with hybrids having Br and bearing Tf_2N ($((CF_3SO_2)_2N)$) anions, and led to 50 times recycling with high catalytic activity. Moreover, the counteranion exchange can tailor the solubility of palladium NPs, and then influences their dispersion and aggregation. Therefore, the catalytic activity, separation and recycle of catalysts can be adjusted based on the exchange of counteranions, which provides an ideal approach on the separation and reusability of catalysts. The similar results are found in asymmetric catalytic reactions. The efficiency and enantioselectivity of chiral catalysts can be tuned *via* exchanging counteranions. For example, aldol reaction in a catalytic system composed of SiO_2-immobilized imidazolium-PF_6/proline system affords aldol product only in 15% yield with 52% *ee*. However, simple exchange to BF_4 anion, SiO_2-IL-BF_4/proline, can increase yield to 51% yield with 64% *ee*.[46]

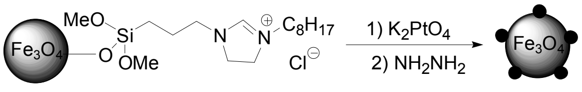


Scheme 5 Synthesis of palladium NPs supported on IL–MWCNTs with different counteranions.[52]

3.1.2. Effect of supports in SILs on catalytic properties

It is well-known that various supports can form diverse interactions with ILs and catalytic species, and their BET surface area and pore morphology can provide different reservoirs for catalyst species, affecting the catalyst loading.[24] SILs possess the combining advantages between ILs and supports, and using different supports to control catalytic properties is an intelligent strategy. The leaching of rhodium from IL/IL-SiO_2 system has bothered researchers. In 2008, Serp et al.[27] used MWCNT instead of SiO_2 as support to prepare [Rh]/IL/IL-MWCNT system. When it was used in the hydrogenation of 1-hexene, Rh/MWCNT–SIL (55% of IL w/w) was reused five times without any loss of catalytic activity, showing more than twice the catalytic activity of Rh/SiO_2–SIL. The results reveal that Rh/CNT–SIL catalytic system can offer higher stability and more catalytic efficiency than IL-SiO_2 system, which simply resolve the Rh leaching. This advantage is probably related to the very open structure of MWCNT aggregates that facilitate mass transport and improves the kinetics.

Using magnetic nanoparticles (MNPs) to support ILs *via* covalent bonds is coming to be an attractive strategy in SIL area, and the formed MNP-ILs systems have been used to support transition metal catalysts (*e.g.*, Pt, Pd and other metal NPs).[29,53,54] Abu-Reziq et al.[55] reduced K_2PtO_4 to Pt NPs by NH_2NH_2, and deposited them on the MNP-ILs surface, preparing a novel MNP-IL-C_8-Pt hybrid catalyst (Scheme 6). It was found to be an excellent selective catalyst for the hydrogenation of alkynes and α,β-unsaturated aldehydes. When diphenylacetylene as substrate, this catalytic system could give 100% conversion, in which *cis*-stilbene was up to 95% and *trans*-stilbene only 5%. As a kind of facile recycling supports, the recycling process of magnetic MNP-IL-C_8-Pt catalyst was very simple. After each recycling run by applying an external magnetic field, the catalyst was washed twice with methanol, and it could be used for the next run after dissolving in the same solvent. Recycle times were up to four cycles without significant loss in activity or selectivity. Magnetic MNP-IL-Pd hybrid catalysts are also a kind of promising catalytic systems, and have catalyzed successfully Suzuki reactions[56,57] and even one-pot dehydration/hydrogenation reactions of benzylic alcohols.[58] More importantly, after the MNP-IL-Pd catalyst is separated magnetically from the reaction mixture, it can be directly applied to catalyze other reactions, carbonylation of iodoarenes, Suzuki and Heck coupling reactions. This strategy can open up a significant method to recycle heavy metals in domain of reusing industrial effluent.



Scheme 6 Supporting Pt NPs onto MNPs using IL as a surface modifier.[55]

As discussed above, the strategy that dissolves transition-metal catalysts in supported imidazolium-based ILs is an effective approach for improving the properties of catalysts. The aggregation and leaching of catalysts and loss of activity still exist in some cases. Hence, immobilizing catalysts to SILs *via* either covalently anchoring on cations or as counteranions are brought forward, and have advantages over the method for dissolving catalysts into SILs systems in improvement of the catalyst' stability.

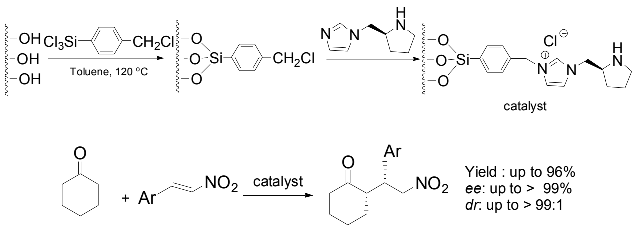
3.2. Catalysts as component moiety of SILs

Catalysts can be neatly designed to be components of cation moieties or counteranions of SILs, obtaining "designer catalysts".

3.2.1. Cations of SILs as catalysts

One case is that cations of supported ionic liquid themselves are catalysts. This kind of typical SILCs mainly involves supported sulfonic acid-, salen and metal-free functionalized ILs. Generally, -SO_3H, -SO_2Cl functionalized ILs are immobilized onto silica materials, ZrO_2, TiO_2, and Al_2O_3. They show good performance in many organic transformations, such as esterification, nitration of benzene, Michael reaction, one-pot multi-component synthesis, *etc*.[59-62] For example, a novel SILC which consists of –SO_3H functionalized benzimidazolium-based IL is immobilized on silica based solid support. As an efficient heterogeneous catalyst for solvent less synthesis of 1-amidoalkyl naphthols from 2-naphthol, amides and aldehydes, 95% yield is obtained. In comparison with other catalyst system employed for this synthesis, supported benzimidazolium-based IL–SO_3H shows a much higher activity in terms of short reaction time and mild conditions. In addition, the catalyst is recovered for five times giving good to excellent yields of the products.[61] Recently, some hybrid magnetic NPs, including Fe_3O_4 anchored onto SiO_2 or silica-coated Fe_3O_4 NPs, are fabricated and used as supports for Brønsted acidic ILs.[30,31] This method offers practical convenience in catalyst separation and recycling as well as avoiding large amount of acidic wastes.

Metal-free chiral organocatalysts, such as L-proline, pyrrolidine, urea (thiourea)-based compounds, are also attached onto the cations of SILs,[63] and are often used to catalyze asymmetric catalysis reactions.[64] Supported pyrrolidine-based chiral ILs are early used to catalyze Michael addition reaction of ketones with nitrostyrenes.[65] Because of providing the ideal recycle times, this catalyst with chiral cation can obtain up to 94% yield with excellent enantioselectivities (up to > 99% *ee*) and high diastereoselectivities (up to > 99:1 *dr*) (Scheme 7). Recently, Huang et al.[66] immobilized covalently lipase on SILs. This strategy greatly promotes the enzymatic properties, including activity, thermal and storage stability and reusability.



Scheme 7 Synthesis of supported pyrrolidine-based chiral IL and application in asymmetric Michael addition to nitrostyrenes.[65]

It is known that chiral salen catalytic system plays an important role in asymmetric catalysis reactions.[67,68] Up to now, chiral metal salen complexes of Cr, Mn and V as substituents have appended to supported imidazolium cation. For example, SIL-(salen) Mn (III) compounds have been applied to catalyze asymmetric epoxidation of unfunctionalized olefins, as shown in Fig. 3. Because of showing comparable or even higher enantioselectivity than homogeneous counterpart, the most prominent of this catalyst is very stable and can be recycled five times without loss of activity, superior to dissolving method.[69]

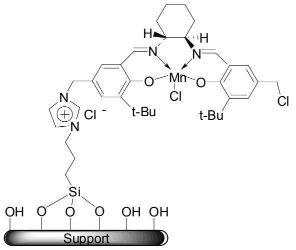


Fig. 3 Structure of SIL-(salen) Mn (III) compounds.[69]

3.2.2. Counteranions of SILs as catalysts

The other effective method to immobilize transition metal catalysts is that transfers them to anionic species to act as counteranions.[70] Friedel–Crafts alkylations of aromatic compounds are heavily polluted reactions due to stoichiometry of acidic chloroaluminates needed in reactions. How to avoid their leaching and overcome their contamination has been a critical topic from a green chemistry standpoint. One of the most effective methods is to immobilize chloroaluminates in different ratios containing $[AlCl_4]^-$, $[Al_2Cl_7]^-$, $[Al_3Cl_{10}]^-$ on ILs-modified solid inorganic materials, which is one of the earliest studied issue.[11] Based on these progress, a series of similar SILCs containing Lewis acid anions, $[PdCl_4]^{2-}$, $[NiCl_4]^{2-}$, $[CuCl_4]^{2-}$, $[SnCl_5]^-$, $[CoCl_4]^{2-}$, $[NiCl_4]^{2-}$, are prepared *via* ion-exchange reaction of SiO_2-ILs.[70] They exhibit efficiently catalytic activity and reusability when evaluated in Friedel–Crafts reactions, Knoevenagel condensations, Kharasch addition reaction and Baeyer–Villiger reaction. This technique is very significant to environment.

Similarly, catalytic species $[W_2O_3(O_2)_4]^{2-}$, $[\alpha\text{-}PW_{12}O_{40}]^{3-}$, $[PMo_{10}V_2O_{40}]^{5-}$, $[RuO_4]^-$, and $[PdEDTA]^{2-}$ are often acted as counteranions of SILCs.[21,71-73] The side chain of imidazolium moiety grafted onto supports can provide the hydrophobic microenvironments, and the anionic metal catalysts and reactants are entrapped in them, forming one kind of similar homogeneous catalytic system while remain the advantages of heterogeneous system. When selective oxidation of sulfide is catalyzed by peroxotungstate immobilized on IL-modified silica with aqueous hydrogen peroxide, the yield can be up to 94.8%, and the catalyst is reused for six times.[71]

4. Applications of SILs in surface modification

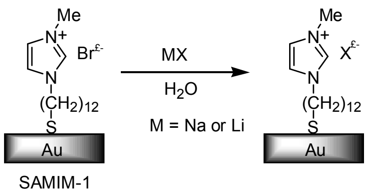
In surface sciences, the wetting and lubricating behaviours are very important in both fundamental research and practical applications. Many cases need to be modulated by modifying agents according to the practical demand. Unique properties of ILs, especially tunable property and facile linking with solids render them to be fascinating hydrophobic agents and lubrications.

4.1. Modulating the surface wettability of substrates

Wettability of a solid surface is an important property, which is governed by surface chemistry and morphology.[74-76] ILs are found to have potential ability to be wettability controlling agents. Firstly, it is well-known that surface tension (γ) of imidazolium-based ILs has the value between organic solvents (*e.g.*, pentane: $\gamma = 16.0\ \mathrm{Nm^{-1}}$, dodecane: $\gamma = 25.6\ \mathrm{Nm^{-1}}$, at 20 °C) and water ($\gamma = 72.7\ \mathrm{Nm^{-1}}$ at 20 °C),[77,78] and it decreases as the prolongation of the length of the side chain in imidazolium moiety. Secondly, supported ILs can offer their tunable property to substrates through exchange of cations or counteranions, and act as on-off to obtain reversibly switchable wettability. Thirdly, their unique stability to acid, base and high temperature is superior to other hydrophobic materials, and can induce long-term durability in environment. Therefore, ILs as one kind of novel hydrophobizing agents are highlighted.[79] Until now, many hydrophobic ILs films have been fabricated using self-assembly technique,[16,80,81] layer-by-layer method,[82] electrospinning,[83] and so on. Among them, the strategy which grafting ILs on the substrates by covalent bonds can provide superior stable and durable films to be engineering materials.

4.1.1. Effect of counteranions of SILs on the wettability

As smart modifying agents, ILs can tailor the wetting behaviour of substrates through the exchange of counteranions. In 2004, Choi's group[16] modified SAMIMs on Au surfaces by submersing Au sheet into thiol-terminated ILs solution for indicated time. To reveal the effect of anions on surface wettability, they exchanged a series of counteranions through directly immersing the SAMIM-1 with Br^- to aqueous solution containing the indicated anion, including BF_4^-, PF_6^-, Tf_2N^-, $CF_3SO_2O^-$ (OTf^-), ClO_4^-, and NO_3^-. As shown in Scheme 8, the SAMIM-1 with Br^- has a relatively hydrophilic property (water contact angle (CA) about 23 ± 1°), whereas the SAMIM-7 with Tf_2N^- exhibits the highest CA with 65 ± 1°. Other SAMIMs bearing different anions display the middle CA values. The effect of counteranions on hydrophobicity of SAMIMs is in the following order: $Tf_2N^- > PF_6^- > OTf^- > ClO_4^- > NO_3^- > BF_4^- > Br^-$. Almost simultaneously, Itoh et al.[84] used this strategy to accomplish the phase-transfer of Au NPs, which simplified their separation and extraction. Further, the tuning wetting behaviour can adjust the aggregation state of gold NPs in water, and then control the colour change solutions, offering a smartly optical sensor for anions.



	CA (°)
SAMIM-1: X = Br	23
SAMIM-2: X = BF_4	34
SAMIM-3: X = PF_6	52
SAMIM-4: X = NO_3	35
SAMIM-5: X = ClO_4	46
SAMIM-6: X = OTf	49
SAMIM-7: X = NTf_2	65

Scheme 8 The process of the exchange of anions and the CA values of SAMIMs with different anions.[16]

Exchanging counteranions on SAMIM surfaces are one kind of potential approaches for manipulating surface wetting behavior, and has been applied to tune the behaviour of CNTs, GO, silica-based materials and magnetic iron oxide NPs in many domains,[32,54,80] just like Au sheet and NPs.

CNTs are ideal materials in sensors. However, the poor solubility in a wide range of solvents hinders their widespread applications. In order to improve their compatibility and create more opportunity for applications, chemical modification of CNTs has been studied with various materials. As excellent modifying agents, ILs not only highlight the unique physical properties of CNTs but also tune their wetting behaviour *via* exchanging the counteranions.[32] Compared with other materials, ILs offer a simple and convenient approach in CNT purification and processibility. The interest in modification of CNTs is driving a rapid increase to graphene-based materials. Anchoring ILs on GOs achieves their transfer into the organic phase by changing their properties from hydrophilic to hydrophobic, and improves their stabilization in water, DMF, and DMSO due to tunable solubility and protecting function by the IL units.[35,85] ILs-modified CNTs and GOs extend their applications in materials science and electroanalytical chemistry.

Silica-based materials are widely used in many areas, as mentioned-above in Section 2, and their modulation has been a hot Issue in surface science for many years. As expected, ILs are perfect modifiers to them.[80,86] Following manipulating the wettability of Au, Choi et al.[80] adopted the similar method to control the wetting behaviour of Si/SiO_2 surface, and the results are rapidly extended to flat silicon substrates and glasses, which are widely applied in microfluidics technique, separation techniques and self-cleaning surfaces for solar energy equipment, cars and buildings.

Although the exchange of counteranions of ILs can tailor the values of CA, many studies find that the effect of anions on the wetting behaviour of ILs is determined by the size of countercations in some cases,[80] and the imidazolium-based cations have superior ability to counteranion on tailoring surface wettability because they can alter their length and composition of chain in more scope than anions.

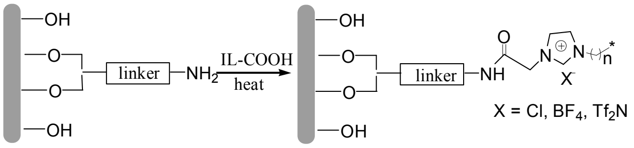
4.1.2. Effect of cations of SILs on the wettability

One believes that long-chain ILs is the favourable hydrophobic materials,[77] and inherently hydrophobic and oleophobic nature of F element can make ILs having perfluoroalkyl chains possess high hydrophobicity.[87,88] To synthesize superhydrophobic IL monolayer, it is necessary to prolong the chain of imidazolium-based ILs or using fluorinated ILs to decrease further the surface tension, combining with hierarchical architectures of substrates.[74-76] In 2012, our group[89] prepared SAMs of long-chained substituent containing fluorinated alkyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium ions (abb. $[C_n\text{Ftespim}]X$[80]) on rough Al surfaces. It was found that the CAs of SAMs of $[C_n\text{Ftespim}]X$ increased with the increase of the chain length of substituents, and could be tuned by the exchange of counteranions. Superhydrophobic SAMs of $[C_n\text{Ftespim}]X$ (X = PF_6^- and Tf_2N^-) with CAs above 160° were obtained at $n \geq 6$. Recently, we[90] prepared novel superhydrophobic ZnO/$[C_8\text{Ftespim}]X$ hybrid materials. ZnO particles were firstly deposited to glass surface, and then $[C_n\text{Ftespim}]X$ was grafted *via* -Si-O- covalent bonds, in which ZnO provided surface roughness while ILs acted as lower surface tension material. Wettability measurements revealed that CAs of ZnO/$[C_8\text{Ftespim}]I$ films were 140.7 ± 2.0°. Exchange of counteranions from I^- to PF_6^- could improve CAs up to 153.7 ± 2.0°. The superhydrophobic ZnO/$[C_8\text{Ftespim}]X$ hybrid materials have two important properties. On the one hand, ZnO micro/nanostructures can impart their photoresponsive property to ZnO/IL films,[91] and can induce them to possess the UV-induced reversible wettability. On the other hand, the photo-induced stability of ILs renders them to be promising coatings of photocatalytic ZnO films,[92] which can make up the degradation of common coatings (*e.g.*, (fluoroalkyl)-silane (FAS), $(CH_3O)_3SiC1_8\text{-}H_{37}$ (ODS)). From the standpoint of stability and benign environment, ILs as coatings of ZnO or TiO_2 films have important predominance. Therefore, the synergistic action of ILs and ZnO NPs results in light-anion dual-stimuli-responsive superhydrophobic surfaces with perfect stability, and could be very significant in intelligent on-off and self-cleaning area.

The reproducibility to obtain superhydrophobic SAMIMs is poor due to their thin density on surfaces. In the recent years, supported poly(ionic liquid)s have drawn attention to achieve high hydrophobicity, and are becoming an innovative trend.[23,93-96] A class of vinyl-, vinylbenzyl- and allyl-substituted imidazolium-based ILs are grafted onto the solid surfaces through radical reactions. Generally, mercapto group is often used to modify silica as linker to tether PILs through surface radical chain-transfer addition. Elemental analysis determines that the amount of imidazolium groups bonded to silica materials is very high, and the wettability of Si-vinyl-based IL bearing PF_6 anion arrives up to 131°,[93] which is higher than the CAs of SAMIM mentioned above. More importantly, the reproducibility of SPILs in wettability is better than that of SILs.

4.2. Modulating the lubricating property of substrates

The potential advantages of IL thin films, such as the stability to environment and high endurance, make them be used as lubrication oils, additives and thin films. Liu's group[97,98] has investigated the tribological property of IL films. However, the ultrathin IL films formed on silicon surfaces by the way of weak physisorption freely migrate on the substrate surface, driving rupture and poor durability. To reduce this limitation, it is necessary to link ILs with chemical bonds to the surface. Wang et al.[99] and Zhou et al.[100] adopted a two-step process to construct SIL films on engineering material surfaces. Firstly, amino-terminated compounds, including (3-aminopropyl)-triethoxylsilane (APS), N-[3-(trimethoxylsilyl) propyl]ethylene-diamine (DA) and dopamine, were employed as linkers to graft on hydroxylated silicon surface, respectively. Then, imidazolium-based IL-COOH was chemically anchored onto amino-terminated SAMs by heat treatment, forming the ultrathin IL films, as shown schematically in Scheme 9. Additionally, mobile ILs were absorbed into supported-IL layer, and the synergistic action between the bonded and mobile phases of ILs has ability to further improve their tribological properties, anti-rupture performance and durability.



Scheme 9 SIL films in lubrication, in which APS, DA[99] and dopamine[100] as linkers.

SPILs are also used as lubrication. Takahara[101] anchored poly (1-(2-methacryloyloxy)ethyl-3-butylimidazolium bis(trifluoro-methanesulfonyl)imide) (PMIS) and poly(*n*-hexyl methacrylate) (PHMA) brushes onto silicon wafers, and investigated their friction coefficient in dry nitrogen atmosphere, water, or 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI), *etc*. It was found that PMIS was superior to PHMA in the friction coefficient and friction cycles, in which the –COOH group in PMIS played an important role.

As mentioned above, ILs supported in the substrates can modulate the surface properties, including the wetting and lubricating behaviours, even anti-bacterial properties to protect surfaces.[102] Indeed, SILs have been widely used in separation technologies as stationary phases.[10,17]

5. Applications of SILs in separation technologies

As novel functional materials, ILs have been applied in analytical chemistry for more than two decades.[17,103] The main advantages of employing ILs stem from their unique properties. Firstly, the special interactions in ILs, including the intermolecular interactions among ILs molecules and the electrostatic interactions between the cation moieties and counteranions within ILs, induce analytes in mixtures to present different distribution coefficient and solubility in ILs. Therefore, ILs have remarkable advantages to separate a wide variety of mixtures, such as metal NPs and ions, nonpolar and polar organic molecules, even enantiomer from the racemic mixtures. Secondly, the diverse and designable structures of ILs make the stationary phases to be smart materials, and alter counterions to tune selective capability according to the analytes' properties. Thirdly, the thermal stability and low volatility of ILs make them ideal candidates for separation technologies.

Initially, most imidazolium-based ILs stationary phases are prepared *via* coating IL layers on the support surfaces without chemical bonds.[10,104] However, the driving of mobile phase can disarrange IL films when they flow through physically adsorbed ionic liquid membranes, and then render them unstable. The concept of SILs linked covalently on stationary phase has propelled the advances of separation technologies.[105] Until now, this kind of SILs has been used in solid-phase extraction (SPE), liquid chromatography (LC), gas chromatography (GC) and capillary electrochromatography (CEC), gases capture and mass spectrometry.[106,107]

5.1. Application of SILs in solid-phase extraction

Solid-phase extraction is a technique used solid sorbents to extract sample analytes from liquid mixtures. Since ILs was introduced to the commercial silica *via* the chemical modification as extraction agents in SPE at the beginning of the 21st century,[108] a number of SILs, each possessing different functionalities, have been widely applied in SPE for the pre-concentration of organic compounds and trace heavy metals from waste water on the basis of economic criteria and possible toxicological concerns. It is reported that Pb (II), Sc (III), sudan dyes, acids, amines, aldehydes, phenols have been extracted from aqueous matrixes.[17,108] Meantime, utilization of SILs has carries out the isolation of biological matrixes, such as the extraction of cryptotanshinone, tanshinone I and tanshinone IIA from *Salvia Miltiorrhiza* Bunge, the separation of oxymatrine from *Sophora flavescens* Ait as well as the competitive adsorption of matrine from oxymatrine.[109] Aside from the higher extraction efficiencies obtained compared to conventional sorbents, the higher recovery is shown than that in traditional silica cartridge.[110]

In extraction technique, one concerns the extraction efficiencies, which is mainly determined by the compositions of SILMs. It can be observed that the stationary phase surface coverage with ILs is so sparse and short and the selectivity and sensitivity of SILs is not sufficiently high.[111] SPILs are introduced and have been given a systematic investigation in SPE and solid-phase microextraction (SPME). Anderson group[112-114] coated a series of polymeric ionic liquids on silica supports as selective SPME sorbent coatings, and successfully achieved the analysis of alcohols, aldehydes, esters, alkyl halides and aromatics as well as the separation of genotoxic impurities from aqueous solutions, even the selective extraction of CO_2. Similarly, Feng et al.[115-117] and Pang et al.[118] used SPILs as sorbent materials to coat stainless steel fiber for the separation of organic compounds. Compared with supported-ILs containing the same anions, SPIL-based sorbents exhibit high extraction efficiency due to the high coating density and uniformity of films. In addition, the effect of counteranions was studied. Feng group[116] fabricated a PIL-based SPME sorbent composed of PF_6 anion and an anolgous PIL containing naphthalene sulfonate anion. They applied them for the extraction of PAHs in hair spray and nail polish. The sensitivity of the novel aromatic functionalized PIL was superior to PIL-PF_6. In addition, PIL containing both polymerizable cation and anion, namely, [VC_8IM] *p*-styrenesulfonate is also tethered through covalent linkage to a stainless steel substrate for the analysis of anilines, phenols, and phthalate esters in water samples.[117] This kind of double-confined PIL sorbent coating offers better resistance to high ionic strength aqueous samples compared to a PIL containing no polymerizable anions.

The other focus in SPE is the collection of the sorbents after adsorbing analytes. Following IL-modified silica, carbon nanotubes and steel substrates, IL-modified MNPs become favorable extraction sorbents, which facile separation and efficient extraction capability attract great attention. Fe_3O_4 NPs and $SiO_2@Fe_3O_4$ microsphere coated with ILs by covalent immobilization have been used in SPE, and successfully achieved the extraction of organic compounds and metal NPs (*e.g.*, extracting polycyclic aromatic hydrocarbons (PAHs) and chlorophenols from water samples).[119,120] Under the optimal conditions, the recoveries (70.3–88.8%) are achieved with satisfactory relative standard deviations of less than 6.0%.

With the rapid developments of biphasic IL-supercritical fluids continuous flow system, the combination of SILPs with supercritical CO_2 has been a highly attractive fixed-bed flow system.[4,44,121] This technique achieves not only the continuous catalytic reactions but also extraction, in which supported ILs act as reactors and the stationary phase (fixed-bed) while supercritical fluids as the mobile phase. This technique can avoid ILs dispersing, accelerate the mass transfer in ILs, while provide good catalyst performance and the facile separation of products.

5.2. Applications of SILs in chromatographic separation technique

For several decades, chromatographic techniques, such as LC, GC and CEC, have become the most popular methods for the separation and identification of analytes in complex samples according to their different migration rate.[122]

Since 2004 Liu and co-workers[123] covalently anchored ILs onto LC chromatographic columns as stationary phases, and separated successfully ephedrine mixture with methanol/water mobile phases, utilization of IL-modified LC stationary phases has been a hot research topic and contributed to the rapid evolution of LC. Until now, various IL-modified columns have been prepared *via* covalently tethering different imidazolium-based ILs onto the pre-activated stationary phase, and have achieved the effective separation of anions, hydrophobic compounds, and small polar molecules in multi-mode chromatographies, including ion-exchange, reversed-phase, and hydrophilic interaction liquid chromatographies.[124-126]

The drastic achievements of SILs in chromatography have been highlighted in a number of recent review articles.[122,127,128] In 2012, Afonso et al.[129] summarized the IL-modified silica stationary phase in high performance liquid chromatography (HPLC), including their preparation and physicochemical characterization, chromatographic behavior, and analytical performance.

Similar to in SPE, SPILs are engaged in LC stationary phases in recent years. SPILs present multiple interactions including hydrophobic, π–π, and ion–dipole interactions with different components, in which one can obtain a special selectivity and sensitivity superior to commercially available monomeric octadecylated silica column in multi-mode stationary phase (Fig. 4).[130] For example, Qiu et al.[126] used 1-allyl-3-butylimidazolium bromide to modify mercaptopropyl-functionalized silica through surface radical chain-transfer addition. The obtained IL-modified silica could be used as stationary phase in reversed-phase LC, and separated a mixture of PAHs containing positional isomers using methanol (60%, v/v) as mobile phase.

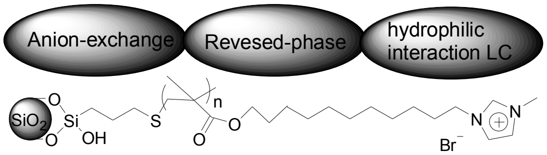


Fig. 4 Poly(ionic liquid)-grafted silica in multi-mode stationary phase.[130]

As a continuation of work, Qiu group[131-133] studied the effect of counteranions on the separation ability of SILs. 1-Vinyl-3-octadecylimidazolium bromide was polymerized on porous silica particles, forming Sil-PImC$_{18}$-Br, and exchanged counteranions by using methyl orange (MO), Sil-PImC$_{18}$-MO can be obtained. It was found that Sil-PImC$_{18}$-MO as the stationary phase offered higher shape selectivity for constrained isomers of PAHs than Sil-PImC$_{18}$-Br both in reversed- and normal-phase HPLC. Obviously, methyl orange dye with big size and π–π interaction as counteranion plays an important role in high selectivity. The reason is that the interposition of MO molecules results in the highly oriented arrangement between the octadecyl imidazolium chain and a rigid segment of MO, as shown in Fig. 5. The π–π interactions among aromatic ring of MO, PAHs and imidazolium moieties can modulate the different distribution coefficient to different components, but Br^- hasn't this capability.

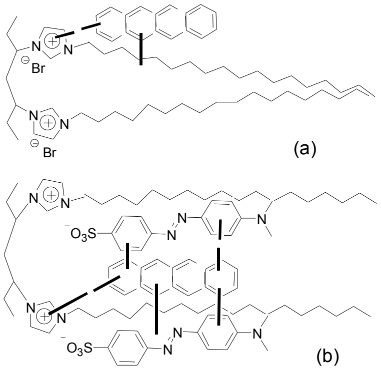


Fig. 5 The effect of MO on the oriented arrangement of octadecylimidazolium chain and the interaction among them, (a) Sil-PImC$_{18}$-Br, (b) Sil-PImC$_{18}$-MO.[132]

Based on these studies, Qiu group[134,135] introduced polymerizable ionic liquid pairs to LC. Both polycation and polyanion are copolymerized on silica to prepare multifunctional hybrid materials in hydrophobic and hydrophilic interaction chromatographies. This strategy enhances further the selectivity and stability of HPLC.

Anion exchangeable technique is another important chromatographic mode. As expected, the immobilization of ILs on stationary phase can transfer their facile exchange of anions to SILs, and form promising anion exchangeable layered materials to provide anion exchangeable sites. The experimental results demonstrate that imidazolium salts (1-butyl (or 1-octyl)-3-(3-triethoxysilylpropyl)-4,5 dihydroimidazolium chloride grafted onto layered octosilicate exhibit a high capacity for sorption of sulfasalazine, and the release behavior of the accommodated sulfasalazine is largely dependent on the pH values, which is potentially applicable to drug delivery systems.[136] More interestingly, Gushikem et al.[137] successfully used this technique to obtain gold NPs. They firstly grafted imidazolium-based IL with Cl^- anion on the surface of SBA-15 mesoporous silica, and then exchanged to $AuCl_4^-$ used anion exchangeable technique. Subsequently, solids containing $AuCl_4^-$ ions were submitted to a chemical reduction process with $NaBH_4$, converting the anionic gold species into supported gold NPs. Obviously, ion-exchange property of SILs creates a new pathway for various practical applications.

GC is one of the most popular techniques to separate volatile and semivolatile analytes in complex samples. ILs possess thermally stable at high temperatures, provide high-efficiency separations, and form multiple interactions with molecules. Therefore, imidazolium-based ILs membranes are ideal GC stationary phase.[138] Generally, ILs are often coated physically on GC columns. The non-uniform film thickness on the wall of the capillary at high temperatures has limited their use. As early as 2005, Anderson et al.[139] cross-linked a class of ionic liquid monomers by free radical reactions to provide a more durable and robust stationary phase which were able to endure high temperatures. Subsequently, the potential of ILs covalently bound in capillary inner wall of GC is further demonstrated, and some covalent-linked SILs and SPILs are used as stationary phases.[140] However, the inner diameter of capillary columns of GC is so small that the development of the surface-bonded IL stationary phases in GC is slower than that in LC.

As an inevitable development results, IL-bonded silica hybrid monolithic columns can be employed as stationary phase in CEC, which uses the electric field to separate mixtures. The first attempt was done by Qin group, they covalently bonded propyl methyl imidazolium chloride to a silica capillary in 2002.[141] They found that the high conductivity and tunable miscibility of ILs reduced interaction between analytes and many mixtures as well as the capillary wall. Subsequently, positively charged pharmaceutical molecules, DNA fragments, alkyl phosphonic acids, esters and metallic cations are successfully separated.[142-145] Compared with an analogous column without IL modification, the electro-osmotic flow (EOF) reversal, better separation efficiency and improved peak shapes are observed for the IL-bonded column.[146]

5.3. Applications of SILs in gases separation and capture

Gases (*e.g.*, CO_2, SO_2, and other gases) capture and removal from power plant are critical issue in both industry and academia from the viewpoint of economic development and environmental protection. Among them, CO_2 is a green house gas, and its separation, capture and storage are very important concerning the sustainable development of human beings. Recent years, SILMs have been found to be ideal capturing agents of gases due to their high selectivity, negligible vapour pressures, high thermal stabilities and tunable properties.[104,147,148] A number of investigations have shown that supported "task-specific" ionic liquids, including amino acid-based ILs, phenol-based ILs have been popular adsorbents and absorbents for CO_2, and the selectivity for CO_2/N_2 and CO_2/CH_4 separations is higher than that of other absorbents. Until now, the achievements in CO_2 capture by SILMs have summarized in many reviews.[149,150] Similar to other separation technologies, SILMs through physisorption have some inherent limitations, facile disarrangment, non-uniformity, poor reusability and so on. Therefore, using covalent bonds to link ILs and adsorbents has an important prospect. In this study field, how to enhance CO_2 absorption capacity, reduce CO_2 absorption enthalpy, and improve CO_2 absorption kinetics are crucial issues. Romanos et al.[151] proposed an advanced strategy to combine the separation with creation of CO_2 from CO_2/CO mixture with high efficiency. They firstly anchored 1-(silylpropyl)-3-methylimidazolium hexafluorophosphate onto siliceous supports and then dispersed ultra small (2-3 nm) and well-stabilized Au NPs onto the SILP acting as heterogeneous catalyst. CO_2/CO separation values above 50 were obtained in cases where liquid crystalline ordering of the IL layers and extended pore blocking had occurred. The SILPs-Au NPs hybrids captured CO_2 while oxidized CO to CO_2 *in situ*.

It has been found that the bonded ILs on solid-phase supports have propelled to the development of separation technologies. However, the choice of suitable SILs with high selectivity to indicated mixtures has been a big challenge because different mixtures present different selectivity in SILs.

6. Applications of SILs in electrochemistry

ILs have been used in electroanalytic chemistry at the end of 20th century.[152] Owing to their high ionic property and wide electrochemical potential window, ILs have ability to provide remarkablely increase in electron transfer rate at interfaces, cause significantly decrease in the over-potential, and thus enhance the electrochemical responses in detection. Up to now, ILs have been participated in both electrodes and electrolyte gel.[6,153]

Using ILs to modify electrodes is a promising strategy. Because their widespread solubility in solutions can drive IL components to easily diffuse into electrolyte in the case of physically mixing to electrodes, the ideal approach is to append ILs on electrodes *via* covalent bonds. As shown in Fig. 6, some forms of IL-modified electrodes are described.[153] Imidazolium-based ILs has modified a series of electrodes, such as Au, different forms of carbon, and boron-doped diamond electrodes.[153,154] Both cations and counteranions have the influence on the properties of electrodes. Several examples should be mentioned in our present review.

The main performance of binding ILs is to improve the conductivity of electrodes. Au-based electrodes are widely used in electroanalytic chemistry. In 2010, Chi and co-workers[155] attached ILs on Au electrode *via* Au–S bonds. The introduction of ILs enhanced the hydrophobicity and conductive properties of Au. At the Au–IL electrode|water interface the electrochemiluminescence (ECL) intensity of luminol-O_2 system was much larger and more stable than that at Au|water interface, resulting in the sensitive and stable ECL response. This could be a promising strategy to construct ideal O_2-related biosensors.

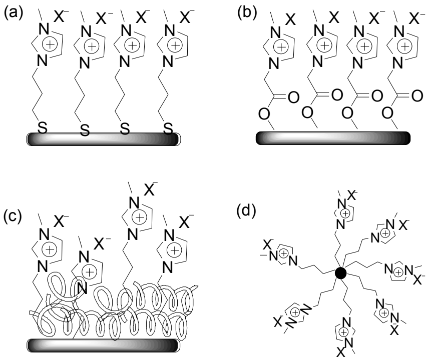
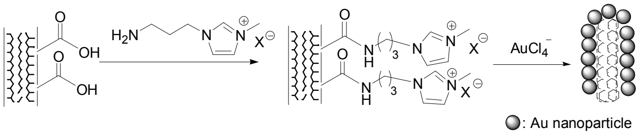


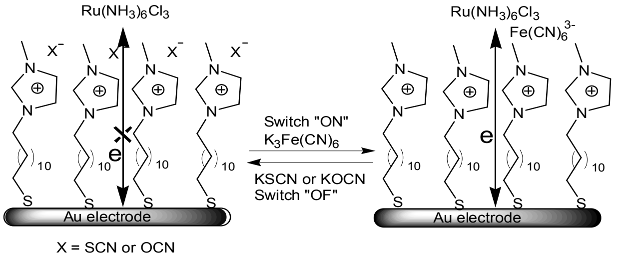
Fig. 6 Schematic depiction of electrodes or electrode materials prepared from appended IL.[153]

Another important performance of SILs on electrodes is to induce the deposition of noble-metal NPs to electrodes. The strategy of coating noble-metal NPs on electrode is a common tool in many applications ranging from advanced sensors to highly efficient fuel cells, which increase the efficiency, specificity and selectivity of electrodes. However, there are usually insufficient binding sites for anchoring the precursors of metal ions or metal NPs on common electrodes, which leads to poor dispersion. Therefore, surface functionalization of electrode is necessary. CNT/Au hybrid NPs are popular electrodes. During the preparing procedure of CNT/Au from CNTs, common methods which deposit Au NPs on CNT surfaces involve tedious assembly processes and multi-step reactions, and often load low density of NPs. It limits many practical applications. Ionic liquids, as stabilizer of metal NPs, can offer more binding sites for the precursors of metal ions. Niu's group[156] grafted IL-NH_2 to MWCNT surfaces to create more opportunity to capture $AuCl_4^-$, and finally obtained MWCNT/IL/gold NP hybrid materials (Scheme 10). This kind of electrode can increase the electrocatalytic activity of MWCNT toward reduction of oxygen. The good property may result from two factors. Firstly, the average diameter of gold NPs is about 3.3 nm in the hybrid of MWCNT/IL/Au, which is much smaller than that in the MWCNT/thionine/Au hybrid, and the distribution is also quite uniform. As known, the electrocatalytic property of gold NPs is size-dependent, and the smaller size will lead to higher activity.[157] Secondly, the presence of ILs also plays a great role in the good electrocatalysis of MWCNT/IL/Au hybrid because the high conductivity of ILs facilitates the electron transfer for oxygen reduction. With the developments of SILs, SPILs are also used to modify electrodes similar to other domains. As an example of vinyl-substituted imidazolium-based ILs, the graft of 1-vinyl-3-ethylimidazolium tetrafluoroborate onto the CNT surface can form the CNT-PIL hybrids.[158] This kind of SPILs can introduce a large number of surface functional groups on the CNTs, and has been used to capture more precursors of metal ions, such as $[PtCl_6]^{2-}$ and $RuCl_3$. Finally, a uniform PtRu or Pt NP layer grows on the CNTs-PIL surface with ethylene glycol as reductants. The PtRu or Pt/CNTs-PIL catalyst offers the higher electrochemical surface area and better performance for methanol electrooxidation than PtRu/CNTs (or Pt/CNTs) catalyst.



Scheme 10 Illustration of the procedure for preparing MWCNT/IL/Au hybrids.[156]

Anchoring ILs onto electrodes *via* covalent bonds can offer another important function. The tunable property of SILs *via* exchanging counteranions can be transferred to electrodes, and presents great advantages over other electrodes in selective electron-transfer toward redox-probe molecules. For instance, electrodes containing IL-SWCNTs (single-walled carbon nanotube) can display unusual tunable wettability and charge-transfer activity, which has opened up a novel kind of electrodes. Lee et al.[14,159] exchanged counteranions between $Fe(CN)_6^{3-}$ and other anions on SILs, and found that the electron-transfer occurred in the presence of $Fe(CN)_6^{3-}$ (anionic redox-probe molecule) but did not occur in the presence of $Ru(NH_3)_6^{3+}$ (cationic redox-probe molecule). The SAMIM having $Fe(CN)_6^{3-}$ as an anion showed electron transfer toward $Ru(NH_3)_6^{3+}$, and the $Ru^{3+/2+}$ redox-switchable SAM was generated by reversible anion exchange between $Fe(CN)_6^{3-}$ and SCN^- (or OCN^-) (Scheme 11).



Scheme 11 Anion-directed $Ru^{3+/2+}$ redox-switchable surfaces.[159]

Besides modifying electrodes, SILs are coming to be important component to electrolytes. To improve both thermal and mechanical properties of electrolytes modified by ILs, it is necessary to alter ILs to gel states through polymerization or grafting onto inorganic nanoparticles.[86,160] They not only maintain most of the attractive features of the untethered ILs but also exhibit substantially improved conductive and mechanical properties of electrolytes. For example, anchoring 1-trimethoxysilyl-C_{11}-3-butylimidazolium-Tf_2N on ZrO_2 nanostructure can act as solventless electrolytes.[160] These hybrid fluids exhibit exceptional redox stability windows, excellent thermal stability, good lithium transference numbers, long-term interfacial stability in the presence of a lithium anode. These materials offer exciting opportunities for applications in electrochemical storage and conversion devices.

7. Conclusions and outlook

In this critical article, we have given an overview of the recent achievements and applications of SILs, and presented a systematic and well-done discrimination of this class of ILs against free ILs and other supported IL systems through physisorption. Immobilizing ILs on solid supports have derived many novel functions, forming a variety of functional materials. Until now, SILs have involved in all fields where ILs can be used. They bring great reformation in catalytic reactions, surface science, separation techniques and electrochemistry.

SILs have significantly increased in recent years, and the designability of ILs and supports offers fascinating opportunity for novel functional materials. Nowadays, MNPs-SILs and SPILs present a drastic development. Magnetic NPs-supported ILs combine the advantages of MNPs with ILs, and simplify the recycling handling as well as improve efficiency. Meanwhile, the high loading density and uniformity of SPILs can optimize the qualities of films, and can be applied in more widespread fields.

Compared with the achievements in catalytic reactions and separation technologies, applications of SILs in surface science are still at an infancy stage. In the wake of new developments in the wettability of solids, smart surfaces that are reversibly switched between superhydrophobicity and superhydrophilicity *via* external stimuli have aroused great interest. Grafting ILs onto M_xO_y (e.g., TiO_2, ZnO, WO_3, V_2O_5, SnO_2, *etc.*) with photoresponsive property through covalent bonds can construct dual-stimuli-responsive superhydrophobic surfaces with reversible switching by both anion exchange of ILs and photo-induction of M_xO_y. Moreover, the photocatalytic stability of imidazolium-based ILs can make up the photocatalytic degradation of common coatings (FAS, ODS, *etc.*) of M_xO_y films with photocatalytic property. We believe that ILs-modified stimuli-responsive superhydrophobic films will have innovative perspectives.

Abbreviations in paper

SIL	supported ionic liquid
IL	ionic liquid
RTIL	room temperature ionic liquid
SILP	supported ionic liquids phase
SILC	supported ionic liquid catalyst
SILM	supported ionic liquid membrane
SAMIM	self-assembled monolayers of imidazolium ion
PIL	poly(ionic liquid)
SPIL	supported poly(ionic liquid)
$[PVBIm]PF_6$	[1-(4-vinylbenzyl)-3-butyl imidazolium hexafluorophosphate]
ATRP	atom transfer radical polymerization
CNT	carbon nanotube
NP	nanoparticl
GO	graphene oxide
TOF	turn over frequency
ee	enantiomeric excess
MWCNT	multiwalled carbon nanotube
DPEN	1,2-diphenyl-ethylenediamine
Tf_2N	$(CF_3SO_2)_2N$
MNP	magnetic nanoparticle
OTf	CF_3SO_2O
CA	water contact angle
FAS	(fluoroalkyl)-silane
ODS	$(CH_3O)_3SiC1_8$-H_{37}
APS	(3-aminopropyl)-triethoxylsilane
DA	N-[3-(trimethoxylsilyl)propyl]ethylenediamine
PMIS	poly(1-(2-methacryloyloxy)ethyl-3-butylimidazolium-bis(trifluoromethanesulfonyl)imide)
PHMA	poly(*n*-hexyl methacrylate)
EMImTFSI	1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
SPE	solid-phase extraction
LC	liquid chromatography
GC	gas chromatography
CEC	capillary electrochromatography
PAH	polycyclic aromatic hydrocarbon
HPLC	high-performance liquid chromatography
SPME	solid-phase microextraction
MO	methyl orange
ECL	electrochemiluminescence
SWCNT	single-walled carbon nanotube

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