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Supported Ionic Liquids



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Introduction

Supported ionic liquids (SILs) consist of two components: the support material and the ionic liquid (IL), and there are various types of each. SIL preparation can be divided into two strategies according to the interactions between the IL and support. The first method is a noncovalent preparation strategy, where ILs adsorb onto either the surface or pores of a support with a high specific surface area. In this case, there are only weak interactions, such as van der Waals forces, hydrogen bonding, and π - π interactions, between the support and the IL. Such materials are greatly affected by the surrounding environment, and their reusability is not ideal. The second method is referred to as a covalent preparation strategy, where the support and IL are connected by

covalent bonds. The SILs prepared by this strategy have higher stability and better reusability than those prepared by the first method, but this second preparation process is more complicated. SIL preparation methods vary widely depending on the support being used, especially in covalent preparation methods. This entry focuses on SIL preparation strategies, and their corresponding characterization methods, based on commonly used supports: silica, polymers, carbon nano-materials, metal-organic frameworks (MOFs), and clays.

Synthesis of Supported ILs

Silica-Supported ILs (SSILs)

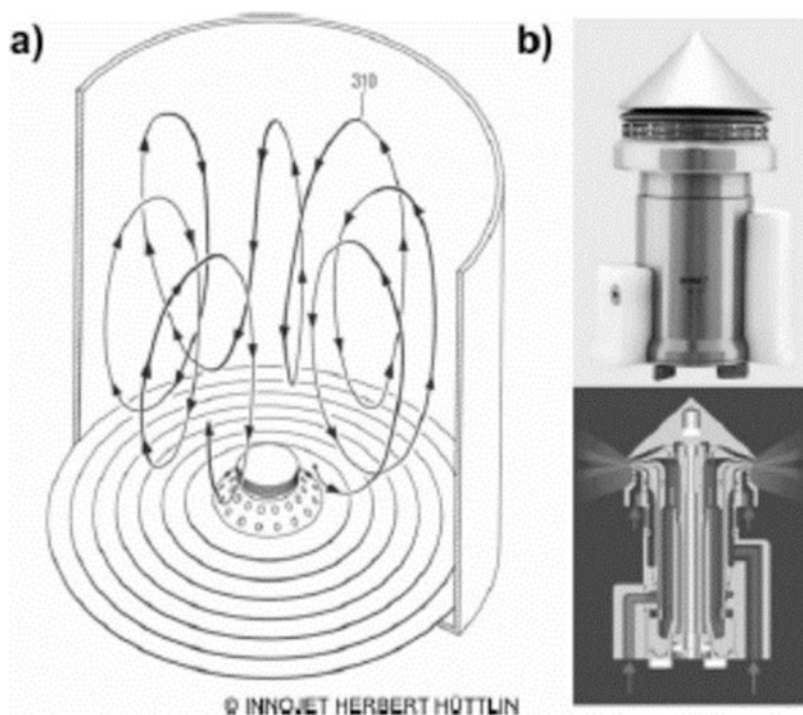
Most supports used in SILs are porous silica gels and silica-based materials because they have large specific surface areas that allow them to carry more ILs. Various methods have been developed for preparing these silica-supported ILs. The simplest of these is a noncovalent method where the SSILs are fabricated by adsorption of the ILs to the silica surface. Alternatively, they can be prepared by a covalent method, where the ILs are anchored to the surface through bonding or grafting.

Noncovalent Preparation of SSILs

Generally, a specific ratio of the IL and silica support is mixed in a suitable solvent, and then the solvent is removed by evaporation or

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Scheme 1 (a) Schematic drawing of the toroidal movement of particles in the Aircoater IAC5; (b) photograph of the spraying nozzle (top) and cross-section of the nozzle, indicating the two flows (bottom) [1]



freeze-drying to obtain the SSIL. However, this method has some shortcomings, the most prominent being that the ILs on the prepared surface are easily lost when the SSILs are used. Unfortunately, this is a problem that most noncovalently prepared SSILs encounter. Additional issues arise when the solvent used in this process forms azeotropes or eutectic solutions with the ILs, which results in the solvent not being completely removed that subsequently impedes any research. However, large quantities of SSILs can be achieved using fluidized bed spray-coating technology, where the silica supports are fluidized by a temperature-controlled gas flow (such as air, nitrogen, or argon), and then the IL solution is added, where it passes through the nozzle and is sprayed onto the material (Scheme 1) [1]. Simultaneously, the gas flow ensures that the solvents are rapidly evaporated. Silica-based materials with three-dimensional mesoporous structures can also be fabricated by a strategy known as the “ship-in-bottle” method. This method mixes alkyl imidazoles (or similar compounds), haloalkanes, and three-dimensional mesoporous materials (such as SBA-16 and MCM-48), where they are

heated and react to generate the ILs. The molecular size of the produced ILs is made to be larger than the pore size, which traps them in the holes. Furthermore, this method successfully solved the problem of IL leaching in noncovalently prepared SSILs.

Nitrogen adsorption is commonly measured when characterizing these SSILs because it can indicate any decrease in the surface area and pore size of the prepared SSILs compared to those of the original porous silica material, which only occurs when the ILs are covering the silica surface. In addition, the compositions of ILs and silica are quite different; therefore, their characteristic peaks can be identified by infrared (IR) and solid nuclear magnetic resonance (NMR) spectroscopy methods to determine if the SSILs were successfully prepared. Scanning electron microscopy (SEM) can also be used to directly observe SSILs, and due to the conductivity of ILs, no electric local charge is formed, which is helpful when using this type of instrumentation. Thermogravimetric analysis (TGA) is also a powerful characterization method, because silicon dioxide is stable at high temperatures

while ILs decompose. This reduces the weight of the SSILs, and the amount of ILs that had been loaded on the surface can be estimated by this mass reduction. Elemental analysis can also be used to quantitatively analyze the IL loading amount by analyzing the amount of nitrogen in the SSILs. Since silica contains no nitrogen and most of the ILs do, the amount of ILs can be calculated.

Covalent Preparation of the SSILs

For all covalently prepared IL-modified silica gels, the first step requires a strong acidic aqueous solution (usually nitric acid or hydrochloric acid) to activate the silica particles. This increases the silanol group content on the silica surface and eliminates metal oxides and nitrogen-containing impurities. Next, these activated silica particles can be reacted with a silane coupling agent, such as 3-chloropropyltrimethoxysilane or 3-chloropropyltriethoxysilane, in dry toluene to obtain chloropropyl silica, which would be subsequently reacted with an alkyl imidazole or other similar compound to produce the SSILs [2]. The reaction efficiency when using a trimethoxysilane coupling agent is higher than when a triethoxysilane agent is used, which is due to the smaller steric hindrance of the former. The chloride ions of the ILs can then undergo ion-exchange with anions on the silica surface to obtain the desired surface-confined ILs. Alternatively, the silane coupling agent and imidazole (or any imidazole derivative) can be reacted first, and then the generated ILs can react with the activated silica particles. However, the reaction conditions and purity of the synthesized IL silane coupling reagent should be strictly controlled. Another option is to first bond the IL anions to the silica gel surface and then connect the IL cations through ionic interactions. For example, acidic $[Al_2Cl_7]$ anions would react with the free hydroxyl groups on the surface to form an anionic solid surface, which is then connected to the IL cation. The disadvantage of this route is that the material is relatively unstable in ionic solutions. For all three of these methods, the bonding density of the imidazolium silica decreased as the chain length of the alkyl branches of the imidazoles

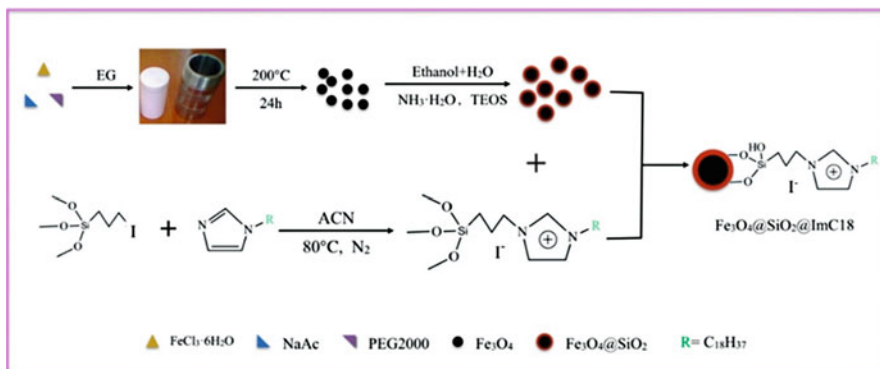
increased, which could be ascribed to the steric hindrance caused by this chain lengthening. Furthermore, these methods can be used to modify the surface of magnetic material covering the silica shell (Scheme 2) [3].

The use of ordered mesoporous silica materials for covalent SSIL preparations has gradually increased in recent years, owing to their adjustable pore size. Similar to IL-modified silica gel, these mesoporous silica materials can also be modified by the three aforementioned covalent methods. However, unlike silica gel, mesoporous silica-based SSILs can be prepared by in situ condensation of an IL silane coupling reagent and tetraethoxysilane by the gel-gel method. However, the addition of the ILs will affect the surfactant template performance for preparing mesoporous silica, and thus the pore size, so the reaction conditions should be regulated.

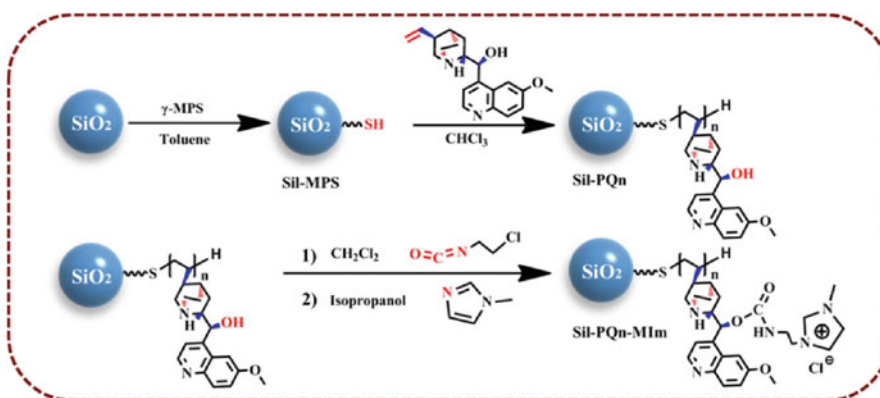
Poly(ionic liquid) (PIL)-modified silica is another important SSIL that overcomes an issue faced by other silica-based materials: the lack of functional groups on the silica surface. For preparing this kind of material, in situ, free radical polymerization is commonly used. This method usually requires the sulfhydryl or unsaturated double bond groups on the silica surface to be modified to achieve covalent connection between the PILs and the silica (Scheme 3) [4]. The characterization methods of covalently prepared SSILs are similar to those used to characterize noncovalently prepared SSILs. Although it is theoretically necessary to verify the covalent bond between the IL and the silica-based materials, most of these bonds are Si-O bonds, which are difficult to be characterized.

Polymer-Supported Ionic Liquids (PSILs)

Combining ILs with polymers, PSILs can be prepared and used in organic catalytic reactions, membrane and chromatographic separations, and battery electrolytes. There are two kinds of methods to prepare PSILs: noncovalent and covalent. Covalent methods attach ILs on polymers through covalent bonds, whereas noncovalent methods load the polymers by adsorption. Compared with the covalent methods, noncovalent



Supported Ionic Liquids, Scheme 2 Schematic diagrams of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{ImC18}$ synthesis procedure and adsorption process [3]



Supported Ionic Liquids, Scheme 3 Schematic diagram for the preparation of Sil-PQn and Sil-PQn-MIm [4]

methods have some disadvantages, such as poor stability and easy loss of ILs during use [5].

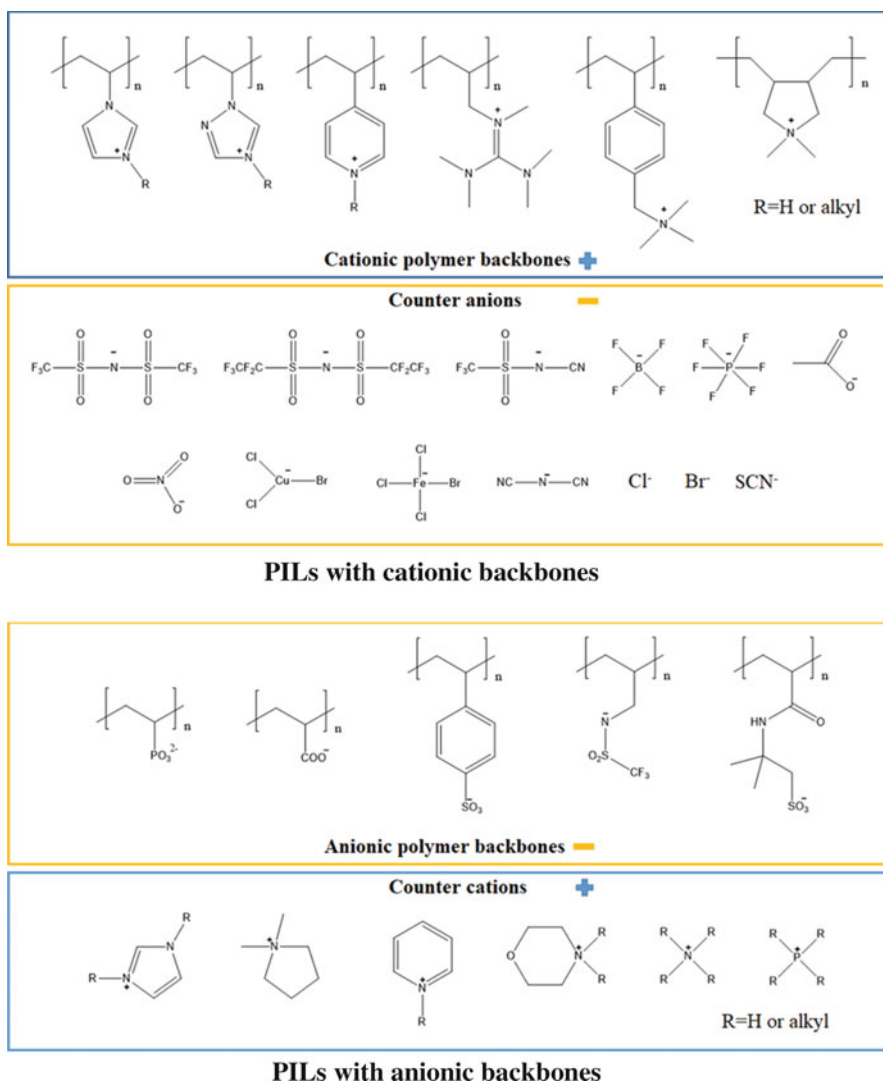
Noncovalent Preparation of PSILs

PSILs prepared by noncovalent methods are usually used for membrane separation. Generally, the preparation process involves placing the porous membrane in a vacuum dryer to remove any water and air from the holes, then adding the ILs into the membrane or loading the ILs on the membrane under pressurized or vacuum conditions, and finally wiping off any excess ILs on the membrane surface with a thin paper. Most of the ILs used are hydrophobic ILs with hexafluorophosphate or bis(trifluoromethylsulfoni) anions, whereas the membranes are mainly hydrophobic ones such as polyfluoroethylene, hydrophobic nylon, and polypropylene fiber membranes. Although IR, NMR,

UV-vis, and SEM can be used for the characterization of these materials, most of the papers have less complete characterization [6].

Covalent Preparation of PSILs

PSILs prepared by covalent methods are also known as poly(ionic liquid)s (PILs). PILs are composed of covalently linked IL species and have the characteristics of macromolecules, thus cleverly combining some of the unique properties and functions of ILs with those of polymers (such as ease of processing and shape durability). There are generally two strategies for synthesizing PILs: synthesis of PILs with cationic moieties in the polymer backbone, and synthesis of PILs with anionic moieties in the polymer backbone (Scheme 4) [7]. For the first strategy, the most commonly used method is to synthesize polymer



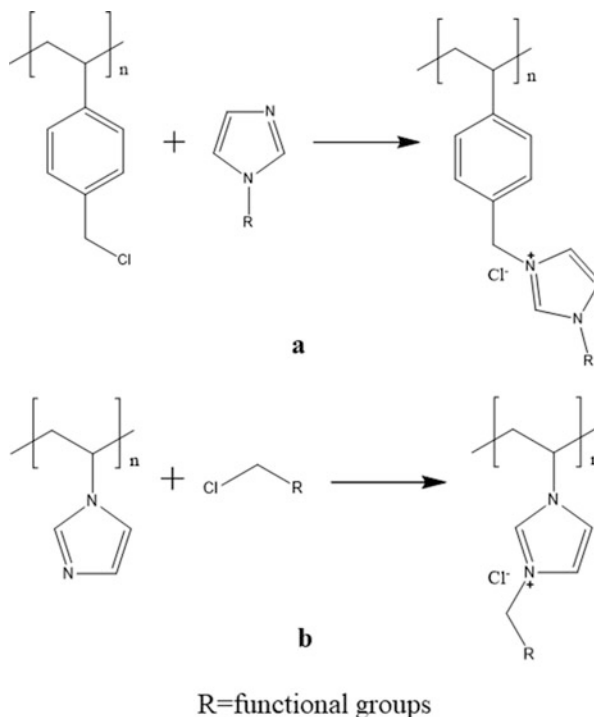
Supported Ionic Liquids, Scheme 4 Typical chemical structures of PILs

backbones with IL cations by a chain-growth polymerization method and then to change the anions of the PILs by ion exchange. A large variety of cations and anions in IL chemistry can be used for the polymers. Cations such as imidazolium, pyridinium, pyrrolidinium, ammonium, and phosphonium have been used, and the utilized anions can be categorized into carboxylates, sulfonates, sulfonamides, and inorganic types. In addition to the traditional free radical polymerization method for the polymerization of IL cations with double bonds, these PILs can be

synthesized by using methods such as atom transfer radical, reversible addition-fragmentation transfer, ring-opening, and ring-opening metathesis polymerizations. Most PILs are polymerized in bulk or in solution. PILs can also be synthesized in emulsions or dispersion media. In addition to linear homopolymers, bi- or trifunctional acrylic or styrene-based IL monomers can be added to synthesize PILs with cross-linked networks by free radical polymerization. PILs with three-dimensional cross-linked networks can also be synthesized by using alkoxy silane-functionalized

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Scheme 5 Postsynthetic methods for preparation of PILs



IL monomers in acid- or base-catalyzed sol-gel polycondensation reactions. Although these methods of synthesizing the IL monomer first and then generating the polymer have many advantages, they involve a number of organic synthesis and purification steps at the monomer level and require the polymerization conditions of each individual monomer to be controlled. Therefore, postsynthetic methods have been used to prepare PILs; that is, polymer backbones containing imidazole or pyridine were first synthesized and then treated with halogenated alkanes to generate the PILs, or polymer backbones with halogenated alkyl functional groups were synthesized and then treated with imidazole or pyridine to form PILs (Scheme 5) [8]. This method reduces the difficulty of monomer preparation, but it still cannot be guaranteed that all imidazole or pyridine moieties in the polymer will be converted into ILs. Far fewer PILs have been synthesized with the second synthesis method than with the first. This may be a result of the difficulty in synthesizing anionic monomers that can be used to form ILs. The PILs have backbones such as poly(vinyl sulfonate), poly

(acrylamido)-2-methylpropane sulfonate, poly(styrene sulfonate), poly(acrylic acid), and poly(phosphonic acid), and the counter cations combined with them to form ILs are mainly of the alkylimidazole, alkylpyridine, or tetra-alkylammonium type. On the basis of these two strategies, ILs can be polymerized with other functional monomers, or IL cationic and anionic monomers can be polymerized to form random and block polymers, thereby improving their performance.

Infrared (IR) spectroscopy is the most commonly used method for characterizing PILs, and the characteristic peaks of the ILs can be observed. X-Ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) are mostly used to observe the morphology of PILs. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) can be used to study the thermal performance of the PILs. If only the ILs in the polymer contain N, S, and O, elemental analysis can also be used to characterize PILs. For the synthesis of PILs by using the first method, the IL monomers used should be characterized by 1H

and ^{13}C NMR spectroscopy to confirm their successful synthesis and purity [9]. Size exclusion chromatography can be used to measure the molecular weight of PILs, but this method cannot be used to measure the molecular weight of cross-linked PILs.

Carbon Nanomaterials Supported ILs (CNMSILs)

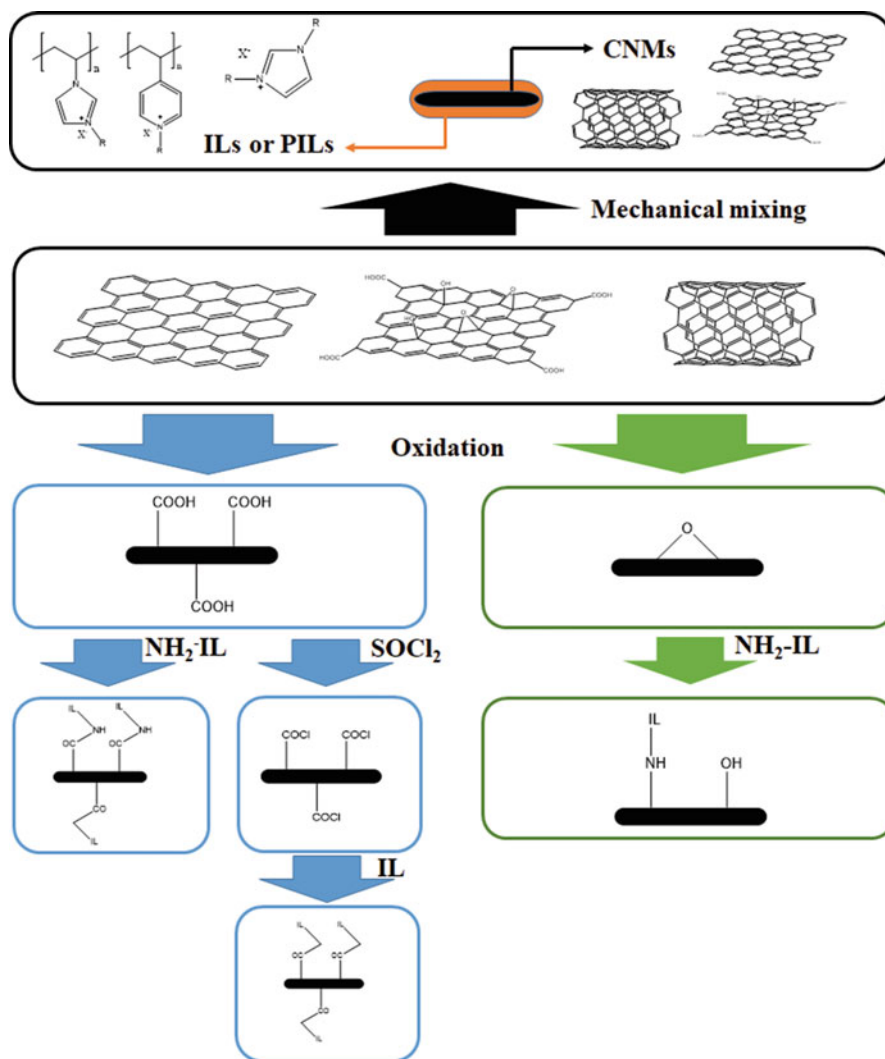
Carbon nanomaterials (CNMs: carbon nanotubes, graphene, and graphene oxide) have unique structures on the nanometer scale, with large specific surface areas and unique thermal, mechanical, or electronic properties. Owing to these structural and performance characteristics, CNMs are widely used in the fields of adsorption, catalysis, and electrochemistry. In addition, there are strong interactions (such as π - π interactions, van der Waals forces, and hydrophobic interactions) within the CNMs and with their target compounds; however, this also makes them difficult to disperse in some solvents, which limits their application. ILs possess the characteristics of miscibility, electrical conductivity, and high thermal stability, and their inherent properties (such as hydrophobicity, hydrophilicity, and polarity) can be changed by selection of the cation and anion components. Therefore, the combination of CNMs with ILs can compensate for the CNM defects, enhance the physical and chemical properties, and increase the scope of application. Generally, according to reports in the literature, the preparation of CNMSILs can be also divided into two types, noncovalent and covalent, according to the interactions between them (Scheme 6) [10].

Noncovalent Preparation of CNMSILs

Noncovalent preparation modifies the surface of CNMs through physical action and is simple and nondestructive. The main mechanism is cation- π , π - π , or dipole- π interactions between the imidazolium cations of the ILs and the π network of the CNMs. The interactions between the CNMs and ILs are weak, and the ILs will gradually be lost when they are used, but this method provides a convenient method for surface modification of CNMs without destruction of the chemical structure. Generally, CNMs and ILs are mixed in an

appropriate ratio, and the mixture is sonicated or vigorously stirred in a mortar until a uniform material is obtained. It was first reported that imidazolium-based ILs and single-walled carbon nanotubes (SWCNTs) were ground to form thermally stable gels (so-called "bucky gels") [11]. In these gels, the bundles of severely entangled nanotubes were stripped into thinner bundles or even individual tubes. The interactions between the ILs and SWCNTs improved the dispersion of the SWCNTs in the ILs. According to the phase transition and rheological properties of the gels, it is speculated that bucky gels are formed by physical cross-linking of the SWCNTs, mediated by the local molecular order of the ILs. Composite materials of graphene (G)/graphene oxide (GO) and ILs can also be formed by grinding their mixtures. ILs can be adsorbed on the surface through noncovalent interactions with G or GO. Moreover, similar to that of CNTs, the dispersibility of G/Go in ILs is enhanced as a result of interactions between G/Go and ILs. Therefore, this method can also be used to exfoliate graphite into graphene sheets or to prepare graphene-based dispersions by using ILs [12]. Although the mechanic method is very simple and the CNMILs prepared are thermally stable, these composite materials are prone to leaching and morphological changes during using.

Functionalization of CNMs with PILs instead of ILs can improve their stability, processability, and durability. PIL and CNM composites can be prepared by in situ polymerization or solution mixing [13]. The first method involves mixing CNMs and IL monomers and using 2,2'-azobisisobutyronitrile as an initiator to perform in situ free radical polymerization of IL monomers on the surface of the CNMs. The second method is to directly and mechanically mix CNMs with presynthesized PILs. This method is similar to the above method for preparing CNM-supported ILs, except that PILs are used instead of ILs. For the combination of noncovalently functionalized multiwalled carbon nanotubes (MWCNTs) with PILs, it was found that in situ polymerization can form a uniform polymer coating on the MWCNT surface, which makes the nanotubes disperse



Supported Ionic Liquids, Scheme 6 Scheme of functionalization of CNMs with ILs

better, whereas the solution mixing method does not achieve uniform functionalization on the MWCNT surface. This is because PILs with larger volumes and molecular weights do not disperse well in solution with the MWCNTs, and the PILs also have larger steric hindrance, which affects the functionalization of the MWCNTs. These preparation methods can also be used to modify SWCNTs and graphene sheets with PILs. In addition, through functional group modification of the PILs and CNMs, new noncovalent forces, such as hydrogen bonding and electrostatic forces, can be generated to improve the modification of the

CNMs with PILs. Tunable changes in hydrophobicity or hydrophilicity of CNM-supported PILs can be realized by anion-exchange reactions with PILs on the surface of CNMs.

The amount of ILs or PILs grafted onto the CNMs can be determined by TGA in air and an inert atmosphere. The thermal decomposition of ILs and PILs in air is basically complete below 500 °C, whereas the thermal stability of CNMs is better at this temperature. When ILs or PILs are attached to CNMs, the thermal stability of the CNMs decreases. ILs and CNMs are prepared by noncovalent interactions, so SEM and TEM can

be used to observe directly whether CNMs have been successfully modified with ILs or PILs. Energy-dispersive X-ray spectroscopy (EDX) with a copper grid as a substrate can also provide strong support. The N peaks in the EDX spectrum of the functionalized CNMs are caused by ILs or PILs.

Covalent Preparation of CNMSILs

As mentioned before, owing to the weak interactions, CNMs noncovalently functionalized with ILs often encounter leaching problems when exposed to solvents. To solve this problem, a covalent functionalization method has been developed. Unlike noncovalent functionalization, covalent attachment reduces the loss of ILs during use and leads to high thermal and chemical stability, as well as excellent durability. However, this method requires several functional steps, which destroy the CNM structure, interrupt the π network of the CNMs, and reduce the CNM mechanical and electrical performance. It is controversial whether the ILs are still real liquids once they are chemically combined with the CNMs. However, the unique properties of the ILs and CNMs remain in the CNMSILs. Generally, covalent functionalization oxidizes the surfaces of the CNMs and connects the ILs to the surfaces through chemical reactions. Surface oxidation of CNMs produces a large number of functional groups, such as hydroxy, carboxyl, and epoxy groups, through strongly oxidizing acid treatment. Thereafter, ILs are introduced onto the surface of oxidized CNMs through chemical bonds. Covalent functionalization of CNMs and ILs can usually be achieved through condensation and nucleophilic ring-opening reactions.

Condensation functionalization can be performed in two ways: ILs can be directly grafted onto the surface of CNMs, or they can be generated on the surface of CNMs after imidazole grafting [14]. For the first method, amine- and hydroxy-terminated ILs are first prepared, and then the functional groups on the surface of the CNMs are oxidized to carboxyl functional groups. However, the two cannot react directly. Only when the carboxylic acid group on the surface of the CNM is activated by thionyl chloride or *N*,

N'-dicyclohexylcarbodiimide in *N*, *N*-dimethylformamide, can the condensation reaction occur. In the second method, imidazoles are partially grafted onto the surface of the CNMs with covalent bonds and then treated with alkyl halides or compounds containing halogenated alkyl groups to generate the corresponding CNM-supported ILs. This method avoids the purification of ILs, and the reproducibility is better than that of the first method. Nucleophilic ring-opening reactions can be achieved by attack of the epoxy group of GO with amine-terminated ILs. Compared with the other methods, this reaction occurs easily. Because GO has a large number of reactive epoxy groups, this method is mostly used to introduce ILs into GO. In general, condensation reactions can be applied to the covalent functionalization of most CNMs, whereas nucleophilic ring-opening reactions are mainly used for GO.

XRD analysis can be carried out to characterize the CNMSILs. It is worth noting that no obvious peaks attributed to CNMs could be found for IL-functionalized CNMs. In addition to the characterization methods for noncovalently prepared CNMSILs, IR spectroscopy and X-ray photoelectron spectroscopy (XPS) can also be used to determine whether CNMs modified with ILs generate new IL characteristic peaks [15].

MOF-Supported ILs (MSILs)

To make ILs widely applicable, the concept of impregnating porous supports with ILs has been proposed. As a new host material for ILs, metal-organic frameworks (MOFs) have great potential for tuning the properties of ILs through interactions between the host and guest. The preparation of such materials can be divided into noncovalent and covalent methods.

Noncovalent Preparation of MSILs

Combinations of MOFs and ILs were first obtained from ionothermal syntheses in which ILs were used as solvents. Ionthermally synthesized MOFs usually have a negatively charged framework, and the IL cations remain in the MOF as counter ions to maintain electrical neutrality. Owing to strong host-guest interactions, the cations are embedded in the MOFs in an ordered

structure. However, because the IL cations strongly bind to the MOFs, these cations in synthetic MOFs are not considered to have the same useful properties as the original ILs. In addition, the choice of ILs and MOFs that can be used for ionothermal synthesis is limited, which restricts the widespread use of these MSILs [16].

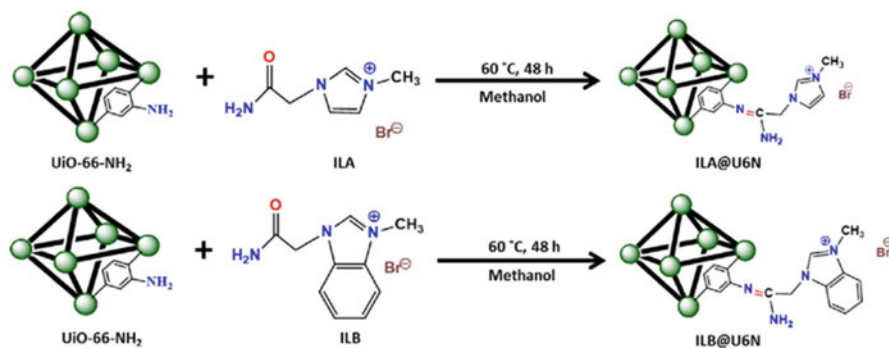
In addition to this *in situ* impregnation method, several strategies for postsynthesis impregnation have been developed. For MOFs with coordinated unsaturated sites, IL-modified MOFs can be prepared by mixing alkaline ILs with them. Taking HKUST-1 as an example, the amino-functionalized IL ([AIL][OH]) and HKUST-1 powder were mixed in [AIL][OH] ethanol solution and stirred at room temperature. HKUST-1 has coordinated unsaturated sites, which cause the [AIL][OH] ions to be pinned by the Lewis acid. Excess [AIL][OH] can be removed by filtration and solvent washing. Another strategy is tandem postsynthesis modification. This ship-in-bottle process can effectively confine ILs to the channels of MOFs. In this way, Brønsted acidic ILs have been confined in the mesopores of Cr-MIL-101. N–Cr coordination occurs between coordinated unsaturated sites of Cr-MIL-101 and N-heterocyclic compounds containing two nitrogen atoms (triethylenediamine or imidazole). Subsequently, 1,4-butane sultone was added to react with the N-heterocyclic compounds to generate the ILs. Finally, after addition of H₂SO₄, the anions of the ILs are exchanged with HSO₄[−]. In a third strategy, ILs are introduced into the pores of MOFs by capillary action. This method only requires the ILs to be mixed with the MOFs; the ILs enter the pores of the MOFs through physical action, and diffusion is enhanced by capillary action. The advantage of this strategy is that it can be widely used with various types of ILs and MOFs, but the obvious disadvantage is that the ILs are easily leached from the MOFs during use [16].

Nitrogen adsorption or IR absorption measurements were performed to confirm the presence of ILs in the pores of MOFs after impregnation by using these strategies. Nitrogen adsorption isotherms and pore-size distributions indicate that the pore volumes of the MOFs decrease after the

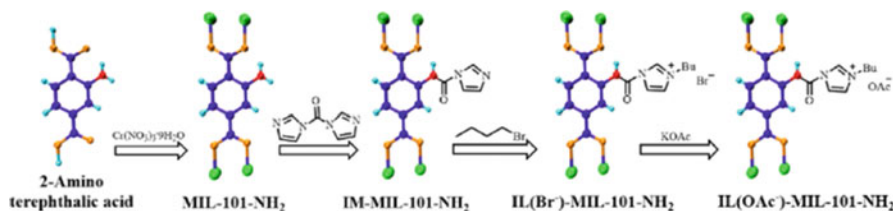
addition of ILs, indicating that IL molecules are present in the pores of the MOFs. In addition, the observed IR spectrum shows C=N, C=C, and C–N stretching bands, which can also indicate the presence of nitrogen heterocycles in ionic liquids. However, this characterization method is not very accurate because these stretching bands may also exist in the MOFs. Beside these characterization techniques, analysis of the observed XRD patterns by the maximum entropy method (MEM) and Rietveld refinement is a useful characterization technique. MEM analysis enables visualization of the electron density of guest molecules included in porous materials from the observed XRD patterns. Before the introduction of the ILs, there is no obvious charge density in the pores of the MOFs, indicating that the MOFs do not contain guest molecules. By contrast, apparent electron density peaks appeared in the pores of the MOFs after the introduction of the ILs, indicating that the ILs have successfully entered the pores of the MOFs.

Covalent Preparation of MSILs

To immobilize ILs on MOFs, it is usually necessary to prepare MOFs (such as UiO-66, and MIL-101) with amino groups (NH₂-MOFs) by a mild hydrothermal process. The ILs can then be directly grafted onto the NH₂-MOFs (Scheme 7), or they can be generated on the NH₂-MOFs after imidazole grafting (Scheme 8) [17]. In the first method, the NH₂-MOFs react directly with ILs containing carbonyl groups through coupling reactions. Fourier-transform IR spectroscopy and XPS analysis were used to monitor the molecular interactions and functionalization of the material. By comparison with those in NH₂-MOFs, the characteristic peaks of imidazole, C=N, and N–H bonds in IL-MOFs after impregnation can confirm the coupling of ILs with the NH₂-MOFs. In addition, the presence or absence of characteristic peaks corresponding to the IL anions can also be observed after synthesis. TGA of IL-MOFs showed an initial weight loss of around 150 °C, which was ascribed to loss of the ILs and confirms the presence of covalently bound ILs on the MOFs. For ¹H NMR spectroscopic analysis, IL-MOFs can be digested in D₂SO₄ with



Supported Ionic Liquids, Scheme 7 Synthesis of MILs based on UiO-66 [18]



Supported Ionic Liquids, Scheme 8 Synthesis of MILs based on MIL-101 [19]

sonication, and the peaks of the ILs in the ^1H NMR spectra indicated that the ILs were successfully anchored on the MOFs [18]. For the second method, imidazole-modified MOFs (IM-MOFs) were prepared by the reaction of *N,N*-carbonyldiimidazole with the amino groups of NH_2 -MOFs. The IL-MOFs were then prepared by alkylation of an alkyl halide with the imidazolyl moiety of the IM-MOFs. Nitrogen adsorption isotherms can also be used to confirm the immobilization of MOFs with ILs. The decreasing total pore volume, pore size, and Brunauer–Emmett–Teller surface area can be attributed to the incorporation of ILs inside the pores of the MOFs. In addition, if the anions of ILs have special UV absorption, UV–visible spectroscopy can be used to determine whether the ILs have been successfully attached to the MOFs [19].

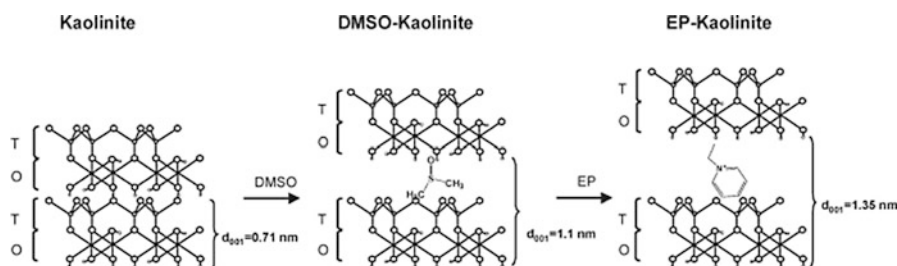
Clay-Supported ILs (CSILs)

The various advantages of ILs have led researchers to investigate their potential use for the modification of clay minerals (sepiolite, palygorskite, smectites, halloysites, kaolinites, etc.), thereby improving the physical and

chemical properties of the latter. The resulting hybrid materials have been successfully applied in various fields, including catalysis, energy production, and depollution. Methods for the preparation of clay-supported ILs (CSILs) can be classified as noncovalent and covalent, similar to those for other IL-modified materials. Although there are many types of clay, their preparation methods are similar; hence, kaolinite is used as the representative material for the description herein [20].

Noncovalent Preparation of CSILs

Kaolinite is a layered clay mineral, and intercalation is a common method for the noncovalent preparation of CSILs. The preparation involves mixing and heating the ILs (imidazolium and pyridinium ILs) and kaolinite under nitrogen protection in DMSO (for preintercalation), followed by washing off the excess ILs thoroughly with the solvent (Scheme 9). In addition to DMSO, urea and other polar compounds can be used for preintercalation [20]. The synthesis of pyrrolidinium ILs is similar to that of ILs based on imidazole and pyridine. However, pyrrolidinium ILs can



Supported Ionic Liquids, Scheme 9 Process of intercalation of IL in the interlamellar spaces of kaolinite [21]

intercalate with kaolinite in the absence of a solvent and preintercalation reagent. The choice of washing solvent is crucial because it should remove only the ILs adsorbed on the surface but should not have sufficient polarity to prevent intercalation. In this regard, isopropanol is the ideal solvent. Moreover, the larger the particle size of the ILs, the smaller is the amount of organic compounds between the clay mineral layers. Besides, unlike montmorillonite intercalation, it shows more than one layer of modifier in the interlayer space. In the case of kaolinite modified by ILs, only one layer is stable. The strong dipole between adjacent layers (along the *c*-axis direction) can explain this phenomenon. The strong electrostatic attraction will inevitably prevent the formation of multilayer films of less stable ILs in the interlayer space. Because of their large size, it is difficult to use PILs for the intercalation of kaolinite; hence, they are mainly used for the exfoliation of kaolinite.

Kaolinite intercalated with ILs can be characterized by XRD in addition to traditional characterization methods. For example, in 1-ethylpyridine chloride intercalated kaolinite, the resulting IL intercalated kaolinite was completely replaced by 1-ethylpyridine chloride in DMSO [21]. The d_{001} value increased from 0.71 nm for the original kaolinite to 1.10 nm for the kaolinite with DMSO, eventually reaching 1.35 nm. The increase in d_{001} (0.64 nm) is consistent with the size of the organic cation inclined by 30° relative to the *a*, *b* planes of kaolinite.

Covalent Preparation of CSILs

Kaolin has a large number of aluminol groups. Hence, ILs with hydroxyl groups (imidazolium

and pyridinium ILs) can be functionalized with aluminol during the synthesis. In contrast, the synthesis of kaolinite functionalized with alkylammonium ILs requires two steps. In the first step, the hydroxyl group in the alkylammonium derived from diethanolamine and triethanolamine can form a covalent bond with the aluminol group. In the second step, haloalkanes are used for quaternization. During the synthesis, haloalkanes of different sizes can be used to adjust the properties of the resulting compounds. XRD also plays an important role in the characterization of CSILs prepared by covalent methods. The XRD results revealed that despite the difference in lengths of the haloalkanes added for the quaternization of amino alcohols, the resulting materials showed short basal spacing distances (between 1.10 and 1.13 nm). This phenomenon could be attributed to the preferred orientation of the grafted organic cations in the interlayer space.

Summary

This chapter summarized the recent developments in supported ionic liquids, especially in the novel preparation strategies and characterization methods. Generally, based on the interaction between the supporting material and ionic liquid, the preparation strategies of supported ionic liquids are divided into two groups, which are non-covalent and covalent preparation methods. We have described the preparation strategies and the corresponding characterization methods of supported ionic liquids with five commonly used supports: silica, polymers, carbon nanomaterials, metal-organic frameworks (MOFs), and clays.

The synthetic strategies and characterization methods discussed in this entry not only provide strategies in the synthesis of custom-designed supported ionic liquids, but also present important information in the understanding of molecular structure of supported ionic liquids.

Cross-References

- ▶ [Bronsted Acid Ionic Liquids: Not Only Simple Acid Catalysts or Solvents](#)
- ▶ [Immobilization of Ionic Liquids](#)
- ▶ [Ionic Liquid-Based Microextraction and Determination of Components in Food Related Products](#)
- ▶ [Ionic Liquids Based Adsorbents for the Removal of Toxic Dyes from Wastewater](#)
- ▶ [Ionic Liquids Materials for the Adsorption of Toxic Gases](#)
- ▶ [Magnetic/Ionic Liquids for the Exclusion of Phenolic Compounds Form Aqueous Medium](#)
- ▶ [Nanopore-Confined Ionic Liquids](#)
- ▶ [Task-Specific Ionic Liquids: Design, Properties and Applications](#)

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