Immobilization of Ionic Liquids, Types of Materials, and Applications

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Synonyms

IL, Ionic liquid; SIL, Supported ionic liquid;
SILP, Supported ionic liquid phase; SILLP,
Supported ionic liquid-like phase

Definition

SILs – Supported ionic liquids are obtained by the
immobilization of ionic liquids in a solid support,
either by physical confinement or covalent
grafting.

Introduction

Supported liquid phase materials obtained by
coating a solid support material with a thin liquid
film have been investigated for catalytic applica-
tions for a long time. However, a common prob-
lem in these systems arises from the evaporation

of the loaded liquid, particularly exacerbated
when the liquid phase is water – supported aque-
ous phase systems. A way to overcome this short-
coming is by using liquids that do not evaporate at
atmospheric conditions, as is the case of
supported ionic liquids (SILs) that are obtained
by immobilizing ionic liquids (ILs) in a suitable
support material [1, 2]. Figure 1 depicts a sche-
matic representation of SIL-based biocatalysis.

The concept of SILs involving covalent
anchoring or physisorption of ILs to solid sup-
ports was first described by Mehnert et al. [3] and
Riisager et al. [4], respectively. Both groups of
researchers proposed the use of silica-supported
ILs in the hydroformylation of 1-hexene to form
n,i-heptanal and in the continuous gas- and liquid-
phase hydroformylation of propene and 1-octene,
respectively; since then, distinct applications have
been reported, being expected that this number
continues to grow (Fig. 2).

Immobilized ILs allow to overcome specific
problems often observed with the application of
bulk ILs in the liquid state, namely, high viscosity,
low diffusion coefficients, difficulties in product
purification and solvent recycling, and high cost
derived from the large quantities of ILs required.
From an engineering point of view, SIL materials
present many advantages over classical gas-liquid
or liquid-liquid systems, namely, a high surface
area supplied by the support, a thin film of liquid
that circumvents mass transport problems, adjust-
able solvent properties, application of fixed-bed or
fluidized-bed reactor technologies, and efficient
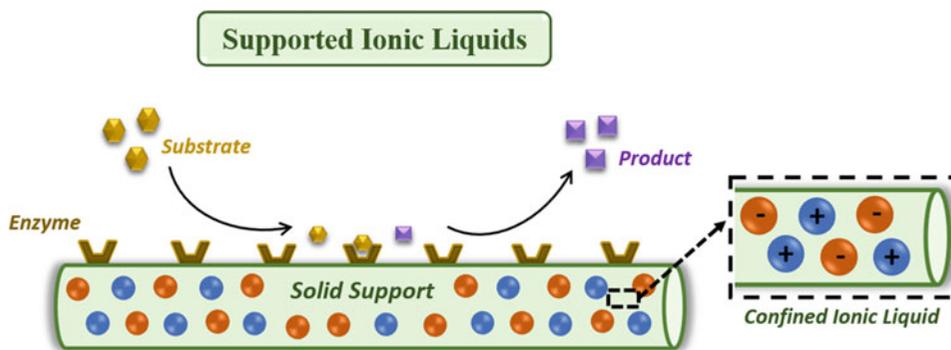
Immobilization of Ionic Liquids, Types of Materials, and Applications, Fig. 1 Representation of a SIL-based biocatalytic application with the detail of the confined IL in the solid support (green)
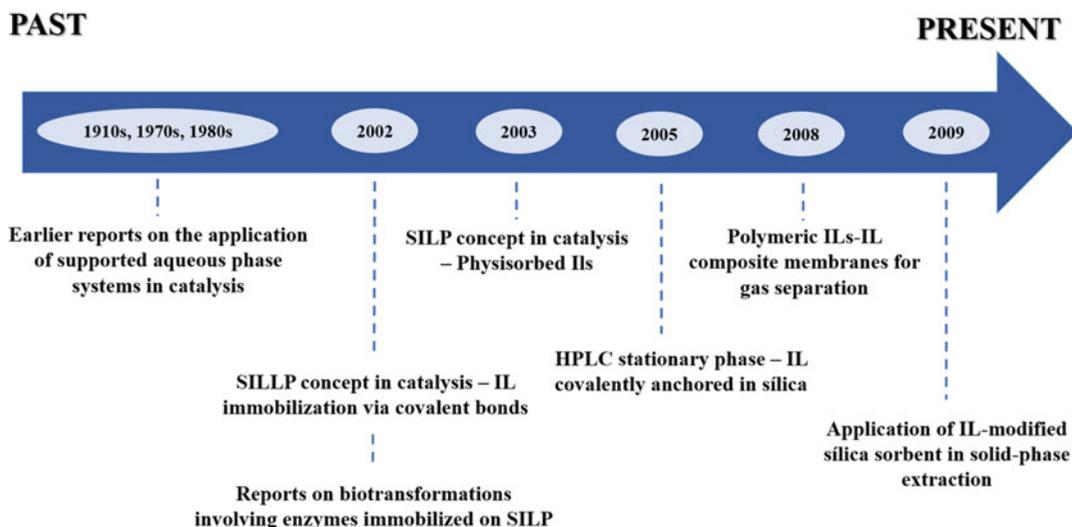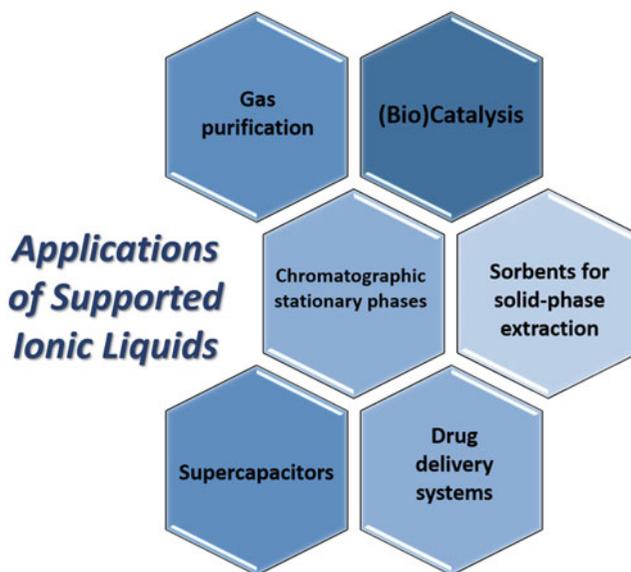

Immobilization of Ionic Liquids, Types of Materials, and Applications, Fig. 2 Developments in the applications of SILs

catalyst immobilization in a confined environment. Simultaneously, the immobilization of ILs in the surface of "hard" solids can modify and improve the properties of the solid supports, such as wettability, lubricating features, and separation efficiency [1, 5, 6]. Owing to the remarkable advantages of ILs immobilized in solid supports, a plethora of applications in distinct fields, ranging from chemical to biological sciences, have been developed, as outlined in Fig. 3.

This entry addresses the preparation and application of SILs and is divided into two main sections: the first section describes the immobilization (physisorption vs. covalent anchoring) of ILs in solid supports, the corresponding preparation methodologies, and the support materials usually applied; the second section comprises selected examples of SIL applications.
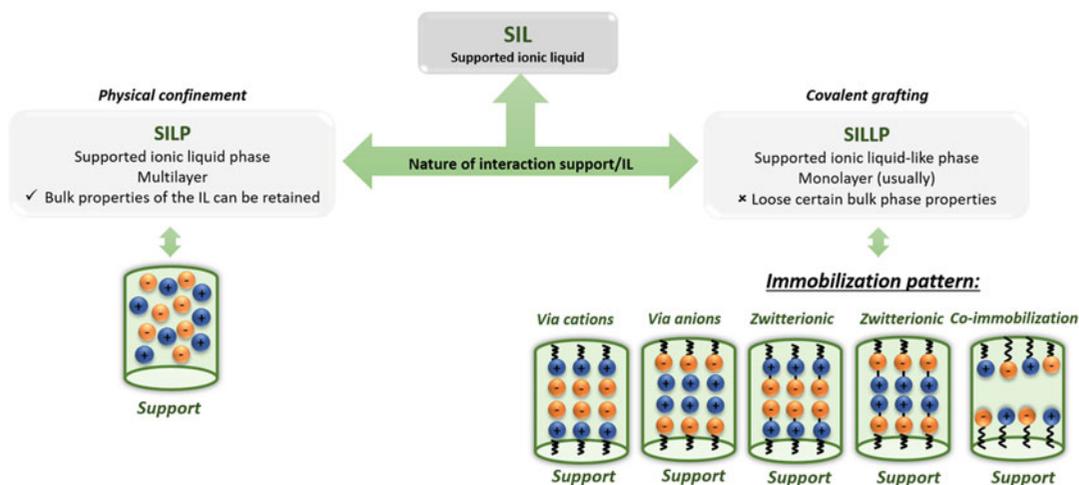
Supported Ionic Liquids

Covalent Grafting (Chemisorption) vs. Physical Confinement (Physisorption)

Up to date, distinct types of supports containing immobilized ILs have been proposed. These types of materials are divided according to the nature of the interactions established between the IL and the support, i.e., non-covalent or covalent, as summarized in Fig. 4: (1) SILLP – supported ionic liquid-like phase – in which the IL is covalently bound to the support material and (2) SILP, supported ionic liquid phase, for physisorbed multilayers of IL, in which the bulk properties of ILs are transferred to the support material. Within these classifications, other definitions have been proposed according to the type of application, such as supported ionic liquid catalysis (SILC), supported ionic liquid catalysts (SILCA), solid catalyst with ionic liquid (SCIL), solid catalysts with ionic liquid layer (SCILL), supported ionic liquid nanoparticles (SILnPs), supported ionic liquid phase catalyst (SILPC), ionic liquid crystalline-SILP (ILC-SILP), structured SILP (SSILP), polymer supported ionic liquid (PSIL), and supported ionic liquid membrane (SILM) [1, 8].

Covalent bonding is established for the chemisorption of an IL – usually monolayered – to a support material, as is the case of SILLPs. In these materials, specific properties of the bulk ILs are lost since there is no longer a liquid phase. However, the IL chemical structure and specific functional groups are still present, which may contribute to improve the target material properties and application performance. This chemical coupling method presents however some limitations and drawbacks, such as (1) the low number of ions resulting from the assembly of a monolayer of IL onto a support, which may limit the performance of catalysis, and (2) the material pretreatment requirement, particularly when it is necessary to render them with a large number of linking functional groups in the outer surface before the IL attachment [1, 6, 9].

The second immobilization method in the SIL framework corresponds to the simple physisorption of the IL to the surface of a high surface area support. A disadvantage of this approach is related to the detachment or leaching of the IL from the support since the IL is held by electrostatic interactions, van der Waals forces and/or hydrogen bonding. Nevertheless, this concept presents relevant advantages, such as (1) the extremely low vapor pressure of ILs allows to achieve physical confinement with permanent coating of ILs onto the pore surface through either in situ chemistry or posttreatment of the porous materials; (2) unlike the monolayer of ILs

Immobilization of Ionic Liquids, Types of Materials, and Applications, Fig. 4 Types of SILs according the nature of interactions established between the IL and the support. (Adapted from [1, 7])

resulting from the covalent grafting method, the multilayers of ILs achievable by physisorption allow to retain, in some extent, the specific bulk properties of ILs; (3) the ILs physically entrapped in porous matrices may be removed using adequate solvents, allowing the ILs and material recycling; and (4) there is a larger number of ILs that can be used in the physisorption method, allowing to take advantage of the ILs designer solvents ability to fulfil special requirements of a given application [1, 5, 6].

According to the type of SILs and supports, distinct preparation methods have been described. Physical confined systems can be prepared using relatively simple impregnation techniques of the IL dissolved in a suitable organic solvent or water, the addition of the support, and, finally, solvent evaporation under vacuum. Other methods for introducing ILs into nanoconfined environments are post-impregnation and the "ship-in-a-bottle" method. Contrary to physical confined systems, grafting of functionalized IL fragments can be achieved using traditional sol-gel synthesis and often involves multistep reactions in which pre-functionalized solid supports react with ILs containing specific functional groups. In this case, the chemisorption of the IL to a solid support can be achieved using two synthetic routes, namely, by (1) preparing ILs first, followed by

their direct self-assembly on the support, or by (2) self-assembling of the imidazole moiety on the support surface via covalent bonds, followed by the preparation of ILs directly on substrate surfaces. Covalent grafting of ILs in materials has been achieved by the "thiol-ene" click chemistry, surface radical chain-transfer reaction, nucleophilic substitution reactions, alkylations, and condensations [1, 2, 6, 7, 9, 10]. The main characteristics, advantages, and drawbacks of SILP and SILLP systems are summarized in Table 1.

Support Materials

SILs have been prepared using distinct types of materials, including silica (silica gel [11], mesoporous silica – MCM-41 – [12], or silica nanoparticles [13]); carbon nanotubes (CNTs) [14]; polymers (e.g., polyethersulfone, PES) [15]; crystalline materials such as porous chromium benzenedicarboxylate, $Cr_3O(F/OH)(H_2O)_2[C_6H_4(CO_2)_2]$, MIL-101 (MIL stands for Material of Institute Lavoisier) [16]; and inorganic materials such as γ-alumina [17]. These materials and IL chemical modifications introduced are listed in Table 2. The choice of the support material is important since the structure and properties of confined ILs are significantly influenced by the pore structure and the surface chemistry of the support, which

Immobilization of Ionic Liquids, Types of Materials, and Applications, Table 1 Summary of characteristics, advantages, and drawbacks of SILs, according to the IL-support type of interaction

	IL-support type of interaction	
	Chemisorption	Physisorption
Assembly	Monolayered (usually)	Multilayered
Bulk properties of ILs	Lost	Maintained
Loading amount of IL	Lower	Higher
Preparation methods	Reaction (condensation, alkylation, radical chain transfer, nucleophilic substitution reaction, "thiol-ene" click chemistry) Traditional sol-gel synthesis (sol-gel co-condensation and surfactant-assisted sol-gel co-condensation)	Impregnation Post-impregnation "Ship-in-a-bottle"
Advantages	IL leaching is minimized	Physical confinement easily achieved ILs can be removed, allowing the ILs and material recycling Specific bulk properties of ILs can be retained to some extent Properties of confined ILs can be easily modulated for a given application
Drawbacks	More challenging preparation (reaction required) Specific properties observed in the IL bulk state may no longer be present in the prepared support IL monolayer assembly Pretreatment requirement of inert materials	Weak interactions between the support and the IL can result in the IL leaching

dictates the nature and extent of the IL-pore wall interactions; however, after confinement, changes in the structure and properties of the support materials and ILs are observed, as reviewed by Zhang et al. [6].

Porous silica gels with a high surface area (ca. 300–500 m^2 g^{-1}) present high thermal and mechanical stabilities, being also low-cost materials, and, as such, correspond to the most widely used supports for ILs. The chemistry of silica surface depends on the content in silanol (Si-OH) and siloxane groups (Si-O-Si); usually, Si-OH dominates the properties of the silica surface and corresponds to the group required to perform (IL) chemical modifications. Foreseeing a reduction in the number of acidic silanol groups and to minimize unwanted reactions of ligands or catalysts with silanol, the thermal treatment of silica gel is usually performed. It was also realized that the trimethoxysilyl group is the most stable linking group between ILs and silica. Other silica-based materials, including SBA-15 and

MCM-41, have been applied in SILs. MCM-41 consists of a regular hexagonal arrangement of nonintersecting cylindrical mesopores. However, MCM-41 is not hydrothermally stable because of the small wall thickness (pore wall thickness of ca. 1 nm) and low degree of cross-linking of the silicate units. On the other hand, SBA-15 is a hexagonally arranged channel-type mesostructure with a pore wall thickness ranging between 3.1 and 4.8 nm but presents higher thermal and hydrothermal stabilities than MCM-41 [2, 9, 18]. As with silica, active species are commonly grafted onto γ-alumina (γ-Al$_2$O$_3$) through their hydroxylated surface, which can be easily casted as a continuous membrane film [17].

Nanoparticles have a large surface area that is highly advantageous in many applications. Sidhpuria et al. [13] investigated the catalytic activity of silica nanoparticle catalysts (SILnPs) for the dehydration of fructose to 5-hydroxymethylfurfural and found an improved performance over zeolites and strong acid ion-

Immobilization of Ionic Liquids, Types of Materials, and Applications, Table 2 Materials used for the preparation of SILs, type of SIL, IL used, and the corresponding application

Type of SIL	Support material	Immobilized IL	Application	Ref.
SILLP	Silica gel	1-Butyl-3-methylimidazolium hexafluorophosphate	Sorbent for the solid-phase extraction of acrylamide	[11]
SILLP	MCM-41 (chloropropylated, MCM-41-Cl)	N-methylimidazolium $PMo_{10}V_2O_{40}$	Catalysis: Epoxidation of alkenes with tert-BuOOH	[12]
SILnPs	Silica nanoparticles	1-(Triethoxysilylpropyl)-3-methylimidazolium hydrogen sulfate	Catalysis: Dehydration of fructose to 5-hydroxymethylfurfural	[13]
SILP	Single-walled carbon nanotubes (SWNT)	1-Butyl-3-methylimidazolium tetrafluoroborate; 1-Butyl-3-methylimidazolium hexafluorophosphate	Immobilization of proteins/ enzymes for bioelectrocatalytic activities	[14]
SILM	Polyethersulfone (PES)	1-Ethyl-3-methylimidazolium tetrafluoroborate; 1-Butyl-3-methylimidazolium tetrafluoroborate 1-Hexyl-3-methylimidazolium tetrafluoroborate 1-Butyl-3-methylimidazolium hexafluorophosphate 1-Butyl-3-methylimidazolium bis (trifluoromethanesulfonyl)imide	SO_2 gas separation	[15]
SILP	MOF, MIL-101	1-Butyl-3-methylimidazolium chloride	Desulfurization	[16]
SILM	γ-Al_2O_3	1-Methyl-3–(3–(diethylphosphinyl) propyl)-imidazolium bromide (ImPE) 1-Methyl-3–(3–((trimethoxysilyl) phosphinyl)propyl)-imidazolium bromide	Gas separations	[17]

exchange resins catalysts. The authors additionally demonstrated that the material can be recycled over seven times without significant losses in fructose conversion and 5-hydroxymethylfurfural yield. In addition to the large surface area provided by nanoparticles, their magnetization may ensure an easy separation of the target product through the application of an external magnetic field. Bouri et al. [19] applied silica-coated Fe_3O_4 magnetic nanoparticles immobilized with the IL N-methylimidazolium hexafluorophosphate for the extraction and preconcentration of sulfonylurea herbicides from water, taking advantage of the easy recovery of the analytes through the application of an external magnetic field. Although less studied, an alternative approach relies on the use of magnetic ILs supported in chitosan nanoparticles, as exemplified with the preparation of chitosan-supported ethylmethylimidazolium tetrachloroferrate ($EMImFeCl_4$)

nanoparticles and further application in catalysis [20]. Ionic liquid-magnetic graphene composites have been prepared by doping graphene sheets with Fe_3O_4 by the in situ ultrasonic-assisted coprecipitation of iron ions in alkaline solution in the presence of graphene oxide, being the ILs later incorporated to the surface by covalent binding. These composites have application in magnetic dispersive solid-phase extraction (MDSPE). The IL plays a double role, namely, by improving the adsorption capacity and by enhancing the dispersion stability of the materials in aqueous solution [21].

Due to their good mechanical strength, high chemical stability, and large surface-area-to-volume ratio, CNTs are also promising building blocks for SILs. Contrary to porous silica, the interior of porous carbons is difficult to confine, often requiring harsh treatment conditions, such as strong acids or high-temperature oxidation. The

functionalization of CNTs is usually achieved by oxidation in aqueous HNO_3 solutions to yield carboxylic acid groups on the surface, and IL-NH_2 or IL-OH is introduced in the surface via -CONH- or -COO- bonds, forming IL-CNT systems [2, 6].

MOFs are a new generation of porous crystalline materials known for their high surface area, large pore volume, and high tunability of their pore size and shape. MOFs have recently shown high potential as appropriate microporous matrices for the immobilization of ILs [6, 16]. ILs are introduced into the pores of MOFs by ionothermal synthesis or a post-impregnation method, and in general the bulky imidazolium cations of ILs are found in the open cage of MOFs near the organic linkers, while the IL anions are near the metal sites of MOFs [6]. Among the numerous MOFs reported so far, one of the most important is MIL-101, which derives from the association of a chromium(III) trimeric building unit and 1,3,5-benzenetricarboxylate, exhibiting a cubic cell with a volume close to 380,000 Å [6]. The mesoporous structure and high porosity displayed by MIL-101 contribute to their enhanced performance in adsorption processes [16].

In addition to silica-based materials, CNTs, and MOFs, polymers have been also modified with ILs. Envisaging the stabilization of a high amount of palladium nanoparticles, multilayered materials were prepared by the polymerization of bis(vinylimidazolium) bromide on silica and SBA-15 [5]. The advantage of these polymeric materials is that the polymer, or the polymer anchored to a solid support, is highly stable, easy to handle, and can be easily separated from the reaction mixture [9]. In addition to these, the polymers themselves can be directly used as porous hosts for ILs, often resulting in the formation of flexible membranes [6]. For example, hydrophilic polyethersulfone (PES) has been used as a support material of different imidazolium-based ILs, creating supported ionic liquid membranes (SILM) for gas separation [15]. Generally, polymer-confined ILs are obtained by in situ polymerization of monomers in ILs or by a solvent casting method [6].

Applications of Supported Ionic Liquids

The relevant properties displayed by ILs supported in a wide range of materials attracted the interest of researchers to develop novel applications in fields ranging from chemistry and biotechnology to environmental related fields. Selected applications of SILs are provided in Table 3.

SILs have been mainly used in catalysis, namely, in Friedel-Crafts reactions, such as alkylations and acylations, and oligomerizations, esterifications, conjugate additions, Diels-Alder reactions, Knoevenagel condensation, hydroformylations, epoxidations, and hydrogenation [3, 4, 10, 12, 18], among others. By choosing a suitable cation/anion pair, the properties of ILs can be properly tailored, thus resulting in ILs endowed of catalytic properties and that can ultimately behave both as catalysts and solvents [10]. SIL-based catalysis relies on two main approaches, consisting either in the dissolution of the transition metal catalyst in the IL or being the IL the catalyst itself [2]. Furthermore, ILs and solid supports can be combined in various ways: (1) the support can be impregnated with the IL containing the dissolved catalyst (usually a metal); (2) the IL may be covalently anchored to the support and the catalyst impregnated on the modified support; (3) the covalently attached or physisorbed IL contains specific functional groups and acts as the catalyst; and (4) the IL is firstly covalently anchored to the support via the cation, and the anion is exchanged by an anionic catalyst species [18]. Taking into account economic features and toxicity/biodegradability concerns, it is highly desirable to minimize the amount of ILs used [3]. Due to an increase in the number of accessible active sites of the catalyst and decrease of mass transfer restrictions, SILPs allow a more efficient use of the catalyst and a significant reduction of the amount of IL required [10].

Due to their advantages, SILPs are particularly relevant in biocatalytic applications. Enzyme-SIL biocatalytic systems have been successfully applied with distinct enzymes, which may be immobilized by simple physisorption (SILP) or through chemical bonding (SILLP) in a wide

Immobilization of Ionic Liquids, Types of Materials, and Applications, Table 3 Selected examples of applications of SILs in distinct fields

Domain	Type of SIL	Support material	IL	SIL synthesis	Application	Ref.
Catalysis	SILLP (SILC)	Silica gel	1-Butyl-3-methylimidazolium tetrafluoroborate; 1-butyl-3-methylimidazolium hexafluorophosphate	Refluxing in chloroform of pretreated silica gel with complexes bearing the imidazolium moiety and the corresponding IL anions	Hydroformylation reaction of 1-hexene to form n,i-heptanal	[3]
Biocatalysis	SILP	Polymeric hybrid monolith	1-octyl-3-methylimidazolium tetrafluoroborate	Polymeric hybrid monolith is prepared; *Candida Antarctica* lipase B is dissolved in the IL and used to impregnate the support	Synthesis of biodiesel (methyl oleate) by the methanolysis of triolein	[22]
Solid-phase extraction	SILLP	Graphene (doped with magnetic Fe_3O_4)	1-(3-aminopropyl)-3-methylimidazolium chloride hydrochloride (ApMeImCl)	Magnetic graphene is obtained by consecutively adding the following reagents to graphite oxide: ApMeImCl, $FeCl_2,4H_2O$ and $FeCl_3,6H_2O$, and KOH	Isolation of triazine herbicides from surface water	[21]
Chromatographic stationary phase	SILP	Fused silica	1,6-Di(3-vinylimidazolium)hexane bis[(trifluromethyl)sulfonyl]imidate 1,9-Di(3-vinylimidazolium)nonane bis[(trifluoromethyl)sulfonyl]imidate; others	Capillaries are coated using the static coating method and coating solutions of monomers or cross-linker ILs are prepared in dichloromethane (the radical initiator is added before dichloromethane); after coating, the ends of the capillary are flame sealed	Gas chromatography stationary phase for the separation of fatty acid methyl esters (FAMEs) and polycyclic aromatic hydrocarbons (PAHs)	[23]
Gas separation	SILM	γ-alumina	1-Ethyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate	The IL is impregnated in the top of two γ-alumina layers of a tubular porous asymmetric membrane support	Gas purification: assessment of permeabilities of pure CO_2, CH_4, C_2H_6, and C_3H_8 and mixed gas permselectivity	[24]

range of support materials, including ceramics, macroporous membranes and monoliths, celite, magnetic nanoparticles, polymers, and resins [22]. As shown with *Candida antarctica* lipase B, the biological activity may be enhanced by supporting the enzyme onto a SILLP, although a higher concentration of IL-like fragments decreases the enzyme activity. In the field of bio-catalysis, the amount of IL, its distribution on the solid surface, and the nature of the IL ions are of crucial importance to preserve and improve the enzymes catalytic performance [9].

The remarkable advantages of ILs in liquid-liquid separation processes are also patent in SILs. The high performance of ILs in separation processes is mainly a result of the multitude of interactions that ILs can establish with the target species, allowing to improve recovery efficiency and selectivity by a proper tailoring of the IL ions chemical structure. SILs have been applied as sorbent materials for solid-phase extraction of organic compounds and trace heavy metals. In this regard, magnetic MDSPE emerged as a new mode of solid-phase extraction, which is performed under an external magnetic field without centrifugation or filtration procedures and avoiding the need to pack a column. Furthermore, the application of magnetic adsorbents dispersed into the sample solution increases the contact area with the analytes, thereby improving mass transfer. Foreseeing the determination of triazine herbicides in surface water, an IL-magnetic graphene composite was applied as the adsorbent in MDSPE. In addition to the reduced pretreatment time required, this method leads to a higher recovery, a lower limit of detection (LOD), and a lower relative standard deviation (RSD) in comparison to other methods [21]. An additional breakthrough in this field was achieved by introducing supported poly-ILs (SPILs) in solid-phase extraction and solid-phase microextraction. Compared to supported ILs containing the same anions, SPIL-based sorbents exhibit high recovery efficiencies due to the high coating density and uniformity of the films [2].

Chromatographic stationary phases containing immobilized ILs are one of the most relevant findings of the past decade in the SIL arena. The pioneering work conducted by Anderson and Armstrong (2005) [24] has led to the development of the first high stable gas chromatography stationary phases based on ILs, which are currently commercialized by Supelco/Sigma-Aldrich (St. Louis, USA). More durable and robust gas chromatography stationary phases were developed; in particular, by cross-linking the IL monomers by free radical reactions, specific limitations hitherto observed were exceeded. Separations with high efficiency and selectivity are achieved at low-to-moderate temperatures (30–280 °C) using partially cross-linked IL stationary phase mixtures, while for higher temperatures (300–400 °C), more highly cross-linked stationary phases are well-suited to provide high selectivity and efficient separations with low column bleed [24]. In addition to gas chromatography, immobilized ILs on supports like silica and monoliths have been widely applied as stationary phases in liquid chromatography, allowing to work in a multimode separation approach based on the establishment of several intermolecular interactions, including anion-exchange, electrostatic, π-π, and hydrophobic interactions [7].

Silica gel, hierarchical mesoporous silica and silica nanoparticles, and single-walled CNTs and MOFs are usually applied as solid supports and have been used as sorbents for solid-phase extraction, in catalysis (epoxidations, dehydrations), for immobilization of enzymes, and in desulfurization [6, 11–14, 16].

Significant achievements have been achieved with SILs in the pursuing of alternative cost-effective strategies for gas sweetening and gas capture and purification. Among the strategies used for carbon dioxide capture and recovery, liquid amine solutions are one of the most widely applied, even though they present many disadvantages such as high-energy consumption during absorbent regeneration, equipment corrosion, unavoidable loss, and degradation of the amine. A way to overcome such limitations displayed by liquid amine solutions is by using ILs, which due to their negligible volatility allow to recover a non-contaminated target gas. An additional interesting feature is that the captured CO_2 can undergo catalytic conversion into valuable

compounds, especially in the case of electrochemical reduction [6]. Furthermore, by knowing the solubilities and diffusivities of gases in ILs, it is possible to design absorption processes, namely, in gas sweetening [23]. Nanoconfinement of ILs in solid supports appears as a solution to the slow sorption and diffusion rates often observed with bulk ILs. The IL confinement may also lead to an increase in CO_2 solubility [6]. Selective permeation through SILMs (γ-alumina, polyethersulfone-based, among others) has shown to be particularly promising for the separation of a target compound from a mixture of gases [15].

Conclusions

The favorable properties displayed by ILs, such as high thermal, chemical, and electrochemical stabilities, nonvolatility at atmospheric conditions, and the possibility of establishing a multitude of interactions, allowed significant advances in several application domains. However, their exceptional performance may be hindered when ILs are used in the liquid state, due to problems mainly associated with the ILs high viscosity and poor mass transfer and difficulties in IL recycling. The advent of SILs obtained by the immobilization of ILs onto solid supports provides some solutions to these shortcomings, justifying the more recent interest and accomplishments achieved with SILs.

SILs are prepared by the immobilization of the IL in a suitable material by physical confinement or covalent grafting. Physisorption can be easily achieved by simple impregnation, and properties of confined ILs can be easily modulated for a given application. Furthermore, ILs can be removed at the end of a given application, allowing both the ILs and material recycling. However, the weak interactions established between the IL and the support in these systems may result in the IL leaching, a problem that is overcome with the chemisorption of an IL onto a support. However, due to the IL covalent attachment, specific properties observed in the IL bulk state may no longer be present in the prepared support, and the loading amount of monolayered ILs is usually lower. The corresponding preparation methodologies are also more technical challenging since at

least one reaction step is required, whereas inert materials usually require pretreatment before grafting.

Immobilization of ILs can be performed in different support materials, such as silica, CNTs, polymers, crystalline materials, and inorganic materials. CNTs present a large surface area-to-volume ratio, but unlike silica, their interior is often difficult to confine, requiring pretreatment steps. Crystalline materials such as MIL-101 show high porosity and large surface areas, and their properties (e.g., pore size and surface area) can be properly tailored. Polymers and inorganic supports such as γ-alumina have been investigated as support materials to immobilize ILs, allowing to prepare membrane films. Among all materials that can act as the support, silica-based materials tend to be the preferred choice, which is due to their high mechanical stability, low toxicity, low cost, and easiness in functionalization. Most of these materials can be magnetic, e.g., by using a Fe_3O_4 magnetic core, thereby permitting an easier separation of products, while avoiding extensive filtration and centrifugation procedures.

IL-modified supports with well-defined and tunable properties have been obtained, with a high performance in distinct applications. SILs have been mainly used in chemical catalysis and biocatalysis. SIL-based catalysis can be accomplished by dissolution of the catalyst in the IL or being the IL the catalyst itself. Due to an increase in the number of accessible active sites of the catalyst and decrease of mass transfer restrictions, SILPs allow a more efficient use of the catalyst and a significant reduction of the amount of IL required. In addition to catalysis, SILs have been largely investigated in separation processes. This interest is due to the multitude of interactions that ILs can establish with the target species, allowing to improve recovery efficiency and selectivity by a proper tailoring of the IL ions chemical structure. SILs have been investigated as sorbent materials in the solid-phase extraction of organic compounds and trace heavy metals, leading to a higher recovery, a lower LOD, and a lower RSD in comparison to more common methods. In this field, gas chromatography stationary phases containing immobilized ILs are one of the most relevant findings of the past decade, being

currently commercialized. Significant achievements have also been accomplished with SILs in the pursuing of alternative cost-effective strategies for gas sweetening and gas capture and purification. Nanoconfinement of ILs in solid supports is a solution to the slow sorption and diffusion rates often observed with bulk ILs.

It was already demonstrated that SILPs allow to improve the performance of several processes. However, given the plethora of ILs chemical structures, types of materials that can be modified, and applications, the SILPs arena is still in its infancy. Accordingly, more related investigations are expected in the following years, ultimately resulting in materials with commercial potential for catalysis, gas purification, as chromatographic columns, among others.

Cross-References

▶ Effect of Ionic Liquids on Activity and Stability of Enzymes
▶ Ionic Liquid in Cyclization Reaction
▶ Ionic Liquid in Hydrogenation
▶ Ionic Liquid Materials for the Adsorption of Toxic Gases
▶ Ionic Liquid-Based Microextraction and Determination of Components in Food-Related Products
▶ Ionic Liquid-Promoted CO2 Reductive Functionalization
▶ Ionic Liquids in Clean and Sustainable Biocatalytic Organic Reactions
▶ Ionic Liquids in Nucleophilic Substitution
▶ Ionic Liquids in Selective Oxidation
▶ Polyoxometalate-Based Ionic Liquid Catalysis for Carbon Dioxide Conversion

References

1. Fehrmann R, Riisager A, Haumann M (2014) Introduction. In: Fehrmann R, Riisager A, Haumann M (eds) Supported ionic liquids: fundamentals and applications, 1st edn. Wiley, Weinheim, pp 1–9
2. Xin B, Hao J (2014) Imidazolium-based ionic liquids grafted on solid surfaces. Chem Soc Rev 43:7171–7187
3. Mehnert CP, Cook RA, Dispenziere NC, Afeworki M (2002) Supported ionic liquid catalysis – a new concept for homogeneous hydroformylation catalysis. J Am Chem Soc 124(44):12932–12933
4. Riisager A, Eriksen KM, Wasserscheidb P, Fehrmann R (2003) Propene and 1-octene hydroformylation with silica-supported, ionic liquid-phase (SILP) Rh-phosphine catalysts in continuous fixed-bed mode. Catal Lett 90:149–153
5. Meijboom R, Haumann M, Muller TE, Szesni N (2014) Synthetic methodologies for supported ionic liquid materials. In: Fehrmann R, Riisager A, Haumann M (eds) Supported ionic liquids: fundamentals and applications, 1st edn. Wiley, Weinheim, pp 75–93
6. Zhang S, Zhang J, Zhang Y, Deng Y (2017) Nanoconfined ionic liquids. Chem Rev 117(10):6755–6833
7. Shi X, Qiao L, Xu G (2015) Recent development of ionic liquid stationary phases for liquid chromatography. J Chromatogr A 1420:1–15
8. Campisciano V, Giacalone F, Gruttadauria M (2017) Supported ionic liquids: a versatile and useful class of materials. Chem Rec 17(10):918–938
9. Giacalone F, Gruttadauria M (2016) Covalently supported ionic liquid phases: an advanced class of recyclable catalytic systems. ChemCatChem 8:664–684
10. Skoda-Foldes R (2014) The use of supported acidic ionic liquids in organic synthesis. Molecules 19:8840–8884
11. Zhao H, Dai B, Xu L, Wang X, Qiao X, Xu Z (2014) Preparation and application of immobilised ionic liquid in solid-phase extraction for determination of trace acrylamide in food samples coupled with high-performance liquid chromatography. J Sci Food Agric 94 (9):1787–1793
12. Hajian R, Tangestaninejad S, Moghadam M, Mirkhani V, Mohammadpoor-Baltork I, Khosropour AR (2011) Olefin epoxidation with tert-BuOOH catalyzed by vanadium polyoxometalate immobilized on ionic liquid-modified MCM-41. J Coord Chem 64 (23):4134–4144
13. Sidhpuria KB, Daniel-da-Silva AL, Trindade T, Coutinho JAP (2011) Supported ionic liquid silica nanoparticles (SILnPs) as an efficient and recyclable heterogeneous catalyst for the dehydration of fructose to 5-hydroxymethylfurfural. Green Chem 13:340–349
14. Du P, Liu S, Wu P, Cai C (2007) Preparation and characterization of room temperature ionic liquid/single-walled carbon nanotube nanocomposites and their

application to the direct electrochemistry of heme-containing proteins/enzymes. Electrochim Acta 52:6534–6547

15. Jiang Y-Y, Zhou Z, Jiao Z, Li L, Wu Y-T, Zhang Z-B (2007) SO$_2$ gas separation using supported ionic liquid membranes. J Phys Chem B 111(19):5058–5061

16. Khan NA, Hasan Z, Jhung SH (2014) Ionic liquids supported on metal-organic frameworks: remarkable adsorbents for adsorptive desulfurization. Chem Eur J A 20(2):376–380

17. Pizzoccaro MA, Drobek M, Petit E, Guerrero G, Hesemann P, Julbe A (2016) Design of phosphonated imidazolium-based ionic liquids grafted on γ-alumina: potential model for hybrid membranes. Int J Mol Sci 17(8):E1212

18. Van Doorslaer C, Wahlen J, Mertens P, Binnemans K, De Vos D (2010) Immobilization of molecular catalysts in supported ionic liquid phases. Dalton Trans 39:8377–8390

19. Bouri M, Gurau M, Salghi R, Cretescu I, Zougagh M, Rios Á (2012) Ionic liquids supported on magnetic nanoparticles as a sorbent preconcentration material for sulfonylurea herbicides prior to their determination by capillary liquid chromatography. Anal Bioanal Chem 404(5):1529–1538

20. Khalafi-Nezhad A, Mohammadi S (2013) Highly efficient synthesis of 1 and 5-substituted 1H-tetrazoles using chitosan derived magnetic ionic liquid as a recyclable biopolymer-supported catalyst. RSC Adv 3:4362–4371

21. Zhang H, Yuan Y, Sun Y, Niu C, Qiao F, Yan H (2018) An ionic liquid-magnetic graphene composite for magnetic dispersive solid-phase extraction of triazine herbicides in surface water followed by high performance liquid chromatography. Analyst 143:175–181

22. Lee C, Sandig B, Buchmeiser MR, Haumann M (2018) Supported ionic liquid phase (SILP) facilitated gas-phase enzyme catalysis-CALB catalyzed transesterification of vinyl propionate. Cat Sci Technol 8:2460–2466

23. Althuluth M, Overbeek JP, van Wees HJ, Zubeir LF, Haije WG, Berrouk A, Peters CJ, Kroon MC (2015) Natural gas purification using supported ionic liquid membrane. J Membr Sci 484:80–86

24. Anderson JL, Armstrong DW (2005) Immobilized ionic liquids as high-selectivity/high-temperature/high-stability gas chromatography stationary phases. Anal Chem 77(19):6453–6462