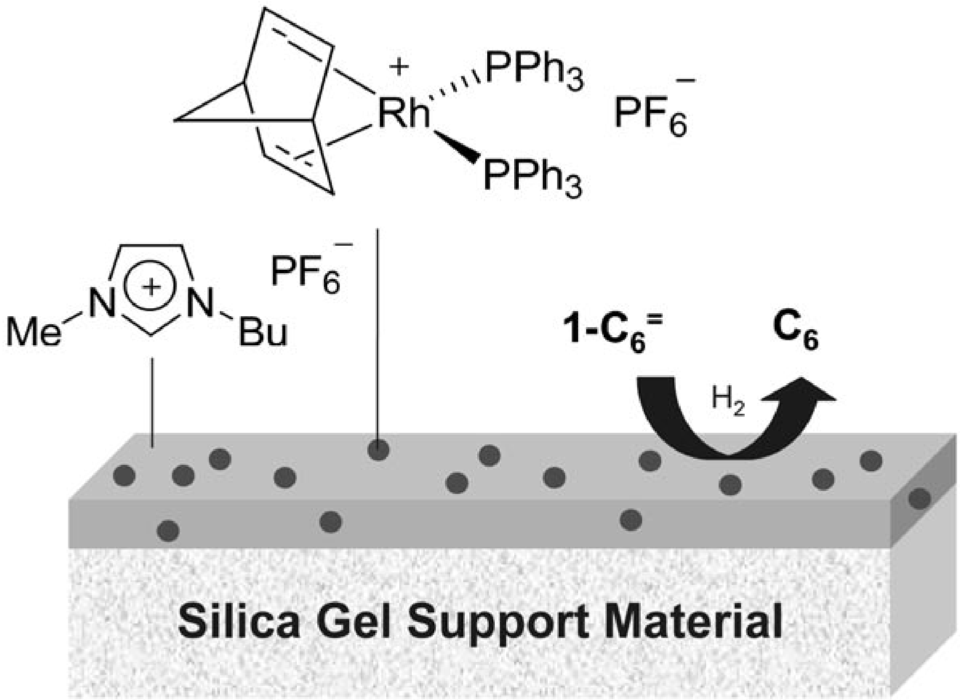
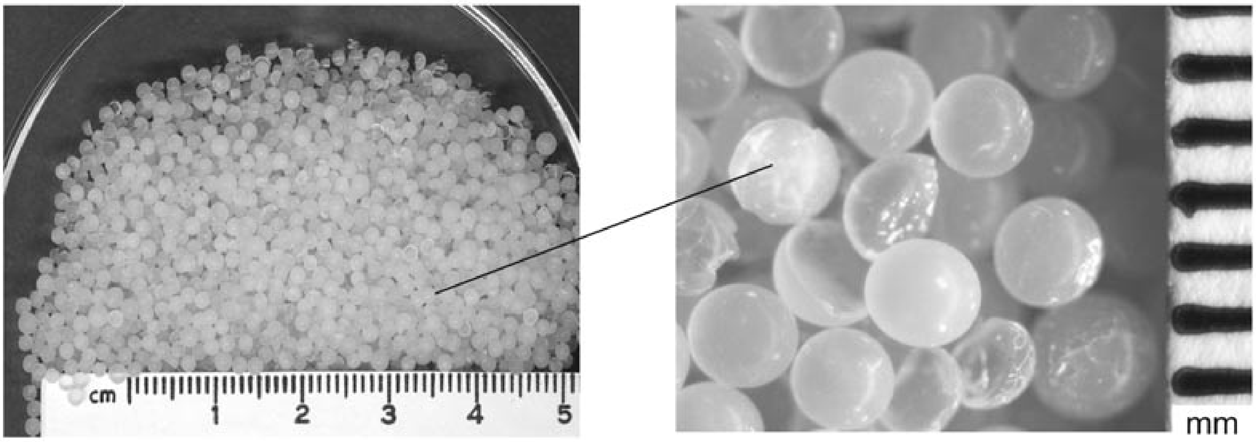
Supported Ionic Liquid Phases



Silica Support Beads with 25 wt% of Ionic Liquid Loading



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Supported Ionic Liquid Catalysis

Christian P. Mehnert*[a]

Abstract: Supported ionic liquid catalysis is a concept which combines the advantages of ionic liquids with those of heterogeneous support materials. The viability of this concept has been confirmed by several studies which have successfully confined various ionic phases to the surface of support materials and explored their potential catalytic applications. Although the majority of the evaluated supports were silica based, several studies focused on polymeric materials including membranes. The preparation of these materials was achieved by using two different immobilization approaches. The first approach involves the covalent attachment of ionic liquids to the support surface whereas the second simply deposits the ionic liquid phases containing catalytically active species on the surface of the support. Herein recent advances made in this area are described.

Keywords: heterogeneous catalysis · ionic liquids · membranes · supported catalysts · supported ionic liquids

Introduction

The popularity of ionic liquids has significantly increased over the last decade. Many of these ionic phases have been investigated in a variety of different areas reaching from material synthesis to separation science to alternative reaction media. In this respect, several review articles have captured a broad scope of catalytic applications and corresponding separation approaches.[1] Although the first catalysis experiment by using an ionic liquid (at the time referred to as molten salts) goes back more than 30 years,[2] the field has experienced a tremendous growth especially over the last 10 years. Some of the physical properties of these ionic liquids, for example significantly reduced vapor pressures and tunable polarities, have distinguished them from other liquid systems such as organic, aqueous, or fluorous phases.[3,4] Due to the polar nature of ionic liquids, biphasic systems tend to form with either unpolar organic solvents or in certain cases also with aqueous media. It is these particular features which make ionic liquids very attractive liquid media for biphasic catalysis.

The ideal case for a liquid–liquid biphasic catalysis system is given when the ionic liquid is able to dissolve the active species while also being partially miscible with the substrate. In addition, the resulting products should have limited solubility in the ionic phase allowing for their removal via simple decantation without affecting the catalyst. Although this general separation procedure has been used for the majority of catalytic investigations, an alternative approach has recently been established which uses solid supports for the immobilization of the ionic liquids. The prepared materials exhibit similar or advanced chemical behaviors and have the advantage of being a solid. This is an important feature as it facilitates the convenient separation of catalysts from reaction mixtures. The preference for heterogeneous catalyst systems is primarily motivated by the advantages of easy separation and the ability to use fixed bed reactors. Another advantage of supported ionic liquid phases over biphasic reaction systems is that biphasic systems always require larger amounts of ionic liquid which is costly and may effect the economic viability of a potential process.

The following concept article describes the latest efforts in which ionic liquid phases have been combined with solid support materials and the ensuing catalysis and separation investigations.

Ionic Liquids Supported on Solid Supports

In a very early example of supported ionic liquid catalysis an eutectic mixture of palladium chloride/copper chloride was supported on a porous silica gel and investigated for the

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[a] Dr. C. P. Mehnert
ExxonMobil Chemical Company
Baytown Technology and Engineering Complex
5200 Bayway Drive
Baytown, TX 75200 (USA)
Fax: (+1) 281-834-2371
E-mail: christian.p.mehnert@exxonmobil.com

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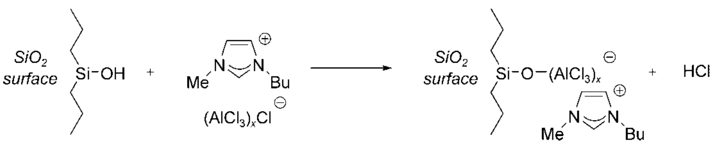
partial oxidation of olefin (Wacker catalysis).[5] Although the melting point of this supported molten salt (423 K) was slightly higher than of room temperature ionic liquids, the potential of such supported ionic systems was recognized thereby contributing to their further exploration. Furthermore the related field of supported aqueous phase catalysis was investigated at the same time and further helped to advance the area of supported catalysis.[6]

Following this approach the first supported Lewis acidic ionic liquid systems were prepared and explored for catalysis applications.[7,8] Here a solid support material was impregnated with a pre-formed ionic liquid which was also the catalytically active species. Most commonly these ionic liquids consisted of aluminum chloride derivatives and were largely tested for Friedel–Crafts reactions.[9] Although most of the research focused on alkylation reactions, some work was also carried out to evaluate the acylation of arene complexes.[10]

In a typical catalyst preparation a previously dried support was treated with a chloroaluminate ionic liquid until its appearance changed from a dry to a wet powder (Scheme 1).[11] Then the mixture was stirred for an extended period of time before the excess ionic liquid was removed via Soxhlet extraction. The resulting ionic liquids were anchored onto the surface via its chloroaluminate-based anions. The confinement of the ionic liquid to the surface is due to the formation of covalent bonds between the aluminum atoms and the surface OH groups. Detailed surface science analysis and extensive comparison studies with $AlCl_3$ bound on silica gel supported the covalent attachment of the ionic liquids.[12] Depending on the characteristics of the support material different concentrations of ionic liquid could be maintained on the corresponding surfaces (Figure 1). As expected, the low surface area and the reduced amount of OH groups in ZrO_2 and TiO_2 led to reduced loading.[9a] Although most of the supported ionic liquid materials retained respectable surface areas, X-ray diffraction analysis of the crystalline materials showed the partial destruction of the structure. This pore damage was caused by the formation of hydrochloric acid during the bond formation between the chloroaluminum-based ionic liquid and the surface OH groups.



Scheme 1. Immobilization of chloroaluminate-based ionic liquid via impregnation.[11]

In the alkylation reaction of benzene with dodecene these supported Lewis acidic ionic liquid catalysts showed improved activity and selectivity as compared to the free ionic liquid.[9] As catalyst lifetime is an important feature for heterogeneous catalysis, these materials were also tested for their durability. Leaching studies showed only a negligible loss of the active species. Despite this minimal loss, reduced catalyst activity was observed in consecutive runs which was attributed to the presence of moisture and the possible adsorption of reactants.

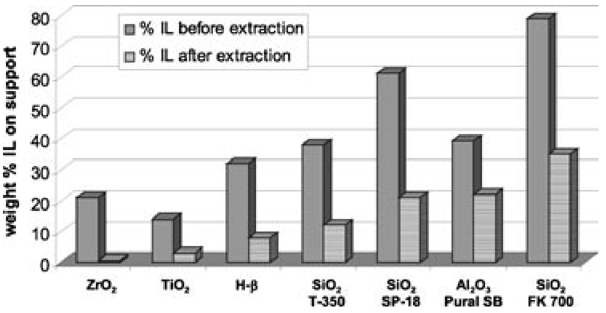
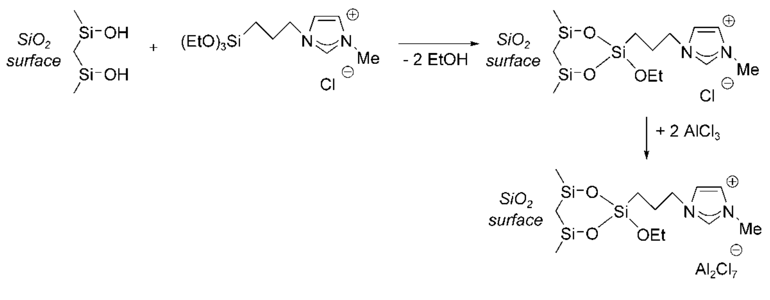


Figure 1. Immobilization of chloroaluminate ionic liquids via impregnation onto different support materials.[9a]

To circumvent the formation of hydrochloric acid in the synthesis of the supported Lewis acidic ionic liquids, an alternative immobilization route was devised which focused on the confinement of the cation.[13] In this approach, instead of adding the preformed ionic liquid to the solid support, an organic anchor group was covalently attached to the surface and was used as the cation in the formation of the ionic liquid. In this preparation the aluminum halide was introduced in the second step which generated a highly acidic ionic complex on the surface of the support (Scheme 2). The resulting catalysts, which were investigated for the alkylation of benzene with different olefins, exhibited excellent activities and selectivities.

A related immobilization approach was employed for the preparation of an acidic tin catalyst.[14] Here, the new catalyst was synthesized by anchoring $SnCl_4$ on silica that was previously functionalized with an organic quaternary ammonium chloride species. Similar to the formation of the chloroaluminate-based ionic liquids, the addition of tetraalkylammonium halides to $SnCl_4$ resulted in the formation of the pentacoordinated anionic tin species. Such complexes of the general formula $[NR_4][SnCl_5]$ have similar physical properties of ionic liquids and can be used as effective Friedel–



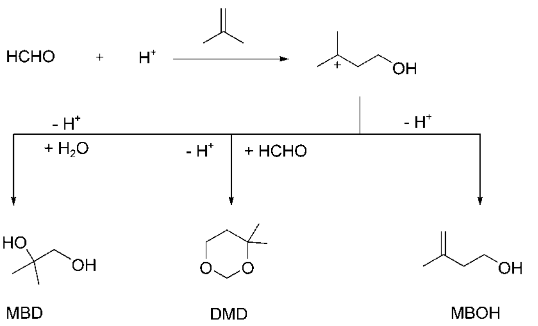
Scheme 2. Immobilization of chloroaluminate-based ionic liquid by grafting of imidazolium chloride followed by the addition of $AlCl_3$.[13]

Table 1. Condensation of isobutene and formaldehyde to give 3-methyl-3-buten-1-ol (MBOH) over silica-based catalysts and with catalyst recycling.[16],[a]

Entry	Catalyst	$SnCl_4$ loading [mmol g^{-1} support]	Conversion of formaldehyde [%]	MBOH selectivity [%]	MBOH yield [%]
1	SIL-$TPA^+SnCl_5^-$[b]	0.32	64.1	88.1	56.4
2	SIL-$TPA^+SnCl_5^-$[c]	0.32	57.0	79.8	45.5
3	silica/$SnCl_4$	0.95	77.9	63.2	49.2
4	recycle 1[d]	0.78	63.3	91.1	57.6
5	recycle 2	–	61.9	91.0	56.3
6	SIL-$NR_4^+SnCl_5^-$[e]	0.78	100	76.1	76.1
7	SIL-$Py^+SnCl_5^-$[f]	0.48	66.3	91.9	60.9
8	SIL-$Py^+SnCl_5^-$[e]	0.48	97.8	82.6	80.7

[a] 56 g isobutene, 3 g paraformaldehyde, catalyst containing 4 mmol $SnCl_4$, and 40 g chloroform were introduced into the reactor and stirred for 2 h at 60 °C. [b] Tetrapropylammonium chloride functionalized silica complex. [c] Direct immobilization of complex on silica. [d] Recycling of SIL-$NR_4^+SnCl_5^-$ after exhaustive washing with dichloromethane. [e] Reaction continued for 3.5 h. [f] Pyridinium chloride functionalized silica complex.

Crafts reagents. Also, these materials were proved to be viable catalysts for the condensation of alkenes with formaldehyde for the production of unsaturated alcohol (Scheme 3). In this application, various silica-based catalysts were tested for the selective synthesis of 3-methyl-3-butene-1-ol (MBOH) (Table 1). The catalysts which were immobilized via the organic quaternary ammonium species exhibited the highest selectivity for MBOH (88–93 %). Leaching studies confirmed full retention of the catalyst on the support and subsequent reactions with the same catalyst did not show any significant drop in activity.



Scheme 3. Prins condensation of isobutene with formaldehyde. MBD = 3-methylbutane-1,3-diol, DMD = 4,4-dimethyl-1,3-dioxane, MBOH = 3-methyl-3-buten-1-ol.[14]

An interesting approach was reported for the preparation of a support material containing a cationic group such as an imidazolium chloride derivative which was prepared via sol–gel synthesis.[15] Here, the complex 1-(triethoxysilylpropyl)-3-methylimidazolium chloride was added to a mixture of a tetraethylorthosilicate and dodecylamine. After the hydrothermal synthesis and the removal of the amine template, the metal halide was introduced leading to the formation of an ionic complex. Catalysts prepared by using this method have been investigated for Friedel–Crafts reactions. The catalytic performance of these solids in the alkylation of benzene was reduced in comparison to materials prepared by the grafting of an organic anchor group followed by the introduction of the metal halide.

Another immobilization approach involved treatment of a solid with a substantial amount of ionic phase (5–50 wt %). In contrast to the earlier studies, the ionic liquids used here were non-acidic and did not undergo reactions with the support. This approach resulted in the formation of multiple layers of free ionic liquid on the carrier which then acted as an inert reaction phase to dissolve various homogeneous catalysts.[16] Although the resulting material was a solid, the active species dissolved in the ionic liquid phase and acted like a homogeneous catalyst (Figure 2).

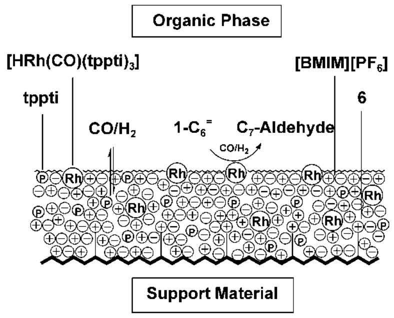


Figure 2. The concept of supported ionic liquid catalysis used in the hydroformylation reaction of hexene-1 to form *n*,*i*-heptanal.[16a]

This concept of supported ionic liquid catalysis combined the advantages of ionic liquid phases with those of heterogeneous support materials and is related in nature to supported aqueous-phase catalysis.[6a] More importantly, this novel methodology overcomes the main limitation of supported aqueous-phase catalysis, namely the depletion of the aqueous layer. This improvement is due to the favourable miscibility characteristics and the low volatility of the ionic liquids.

Although several studies have focused on the evaluation of biphasic hydroformylation reactions in ionic liquids,[17] this was the first time that a homogeneous catalyst in an ionic liquid was actually immobilized onto a heterogeneous support material. In this catalyst preparation a solution of the precursor $[Rh(CO)_2(acac)]$ (acac = acetylacetonate) was either treated with the ligand tri(*m*-sulfonyl)triphenyl phosphine trisodium salt (tppts) or tri(*m*-sulfonyl)triphenyl phosphine tris(1-butyl-3-methyl-imidazolium) salt (tppti) (Rh/P ratio 1:10). The ligand tppti dissolved in both ionic media, $[BMIM][BF_4]$ and $[BMIM][PF_6]$, while the ligand tppts only exhibited solubility in $[BMIM][BF_4]$. The resulting solutions were combined with the ionic liquid phases and added to the corresponding support materials. After the solvent was removed the catalysts were obtained as free-flowing powders. To further enhance the interaction between the free ionic liquid and the surface, a modified support material with a monolayer of covalently attached ionic liquid fragments can be used.

The prepared catalysts were investigated for the hydroformylation reaction of hexene-1 to produce *n,i*-heptanal (Table 2). A comparison between the supported ionic liquid catalyst and the biphasic ionic liquid reaction showed that the supported system exhibited a slightly enhanced activity with comparable selectivity (*n*/*i* ratio). The supported system containing the ionic liquid [BMIM][BF_4] produced *n,i*-heptanal with a TOF of 65 min^{-1}, while the biphasic ionic liquid system showed a value of 23 min^{-1}. This improved activity was attributed to a higher concentration of the active rhodium species at the interface and to the generally larger interface area of the solid support as compared to the biphasic system. For further comparison, the aqueous biphasic reaction and the conventional homogeneous catalyst in toluene were investigated under similar reaction conditions. As expected the aqueous system was significantly less active due to the low solubility of hexene-1 in the aqueous phase. With respect to the homogeneous catalyst system, a TOF of 400 min^{-1} was recorded. Although the homogeneous system is clearly favored due to its higher activity, the supported ionic liquid system is very attractive based on its convenient product separation.

Table 2. Evaluation of the hydroformylation reaction of hexene-1 to form *n,i*-heptanal using supported ionic liquid catalysis (silc), biphasic catalysis, and homogeneous catalysis.[16a]

Entry	Condition[a]/ ligand	Solvent	*t*/ min	Yield/ %	*n*/*i*	TOF[b]/ min^{-1}
1	silc/tppti	[BMIM][BF_4]	300	33	2.4	65
2	silc/tppts	[BMIM][BF_4]	240	40	2.4	56
3	silc/tppti	[BMIM][PF_6]	270	46	2.4	60
4	silc/no ligand	[BMIM][PF_6]	180	85	0.4	190
5	biphasic/tppti	[BMIM][BF_4]	230	58	2.2	23
6	biphasic/tppti	[BMIM][PF_6]	180	70	2.5	22
7	biphasic/tppts	H_2O	360	11	23	2.4
8	homog./PPh_3	toluene	120	95	2.6	400

[a] Reaction conditions: All runs were conducted at 100 °C with a Rh/P ratio of 1:10, silc runs were evaluated in a 70 mL autoclave at 1500 psi and biphasic and homogeneous catalyst systems were evaluated in a 300 mL autoclave at 600 psi. [b] TOF defined as mol(aldehyde) per mol(rhodium) per minute (full reaction time).

The concept of supported ionic liquid catalysis has been further extended to hydrogenation reactions.[18] In this study the complex [Rh(nbd)$(PPh_3)_2$]PF_6 (NBD = norbornadiene, PPh_3 = triphenylphosphine) was investigated in ionic liquids and organic media and was then compared to the supported catalyst system. The catalyst evaluation revealed enhanced activity for the supported ionic liquids in comparison to both the homogeneous and the biphasic reaction systems. For example the homogeneous base case with hexene-1 as a substrate showed an initial rate constant k_h of 0.4 min^{-1} at a reaction temperature of 50 °C, while the supported ionic liquid catalyst achieved a k_h of 11.2 min^{-1} for the same reaction at 30 °C. The enhanced activity of the rhodium complex in an ionic liquid phase has been previously observed and may be explained by the absence of any coordinating solvent.[17c] In addition to the higher activity, the supported ionic liquid catalysts also showed excellent long-term stability. The same catalyst was reused for 18 batch runs without any significant loss of activity. The level of the leeched rhodium remained below the detection limit and the isolated organic phases did not exhibit any further reactivity, which additionally verified full retention of the active species.

As a further extension of the concept of supported ionic liquid catalysis rhodium, palladium, and zinc complexes in ionic liquids have been confined on heterogeneous supports and investigated for hydroamination reactions.[19] The catalytic performance of the supported ionic liquid system for the direct addition of 4-isopropylaniline to phenylacetylene was higher than for the corresponding homogeneous catalyst.

In a continuing effort to explore the potential of supported ionic liquids the concept has also been extended to continuous gas-phases reactions.[20] Rhodium catalyst precursor and biphoshine ligands such as sulfoxanthpos were supported in the presence of [BMIM][PF_6] or [BMIM][*n*-octylsulfate] on silica and tested for the hydroformylation of propene. As expected the supported rhodium sulfoxantphos catalyst proved to be more regioselective than the catalysts without any ligand. Furthermore, the performance of the catalyst was strongly influenced by the catalyst composition. Low activities and low selectivities were obtained for catalysts with low ligand to rhodium ratios. It is believed that under such reaction conditions most of the active rhodium species are ligand-free complexes. In contrast, the catalyst with a high ligand to rhodium ratio of 10 and 20 showed a higher selectivity giving an *n*/*i* ratio of up to 23.7. Furthermore, the increased ionic liquid loading led to a decrease in activity, which indicated that the catalysts were operating under mass-transfer limitations.

In a series of experiments carried out under continuous reaction conditions a variety of monodentate phoshine ligands were investigated for the hydroformylation of propene and 1-octene.[21] The rhodium precursor together with bis(*m*-phenylguanidinium)phenylphoshine or NORBOS was immobilized in a multiple layer of ionic liquid on the surface of silica gel. The catalysts were tested in the continuous gas- and liquid-phase hydroformylation of propene and 1-octene, exhibiting TOF values of up to 88 h^{-1}. Despite the respectable activities, the selectivity for the *n*-aldehyde was reduced to only 74 % (*n*/*i* ratio 2.8); this emphasizes the advantages of multidentate phosphine ligands for the production of highly linear aldehydes.

In a different approach ionic liquid phases have been immobilized in membrane materials. Although the primary driver of this work was the use of these materials as electrochemical devices, they have also been investigated for catalytic applications.[22] Membrane materials composed of airstable, room temperature ionic liquids and poly(vinylidene fluoride)-hexafluoropropylene copolymers were prepared with the incorporation of an active catalyst species in the form of palladium on activated carbon. Optical imaging revealed that the prepared membranes contained a high dispersion of the palladium catalyst particles. Studies on the materials included evaluating their gas permeability and their catalytic activity for the hydrogenation reaction of propylene.

In a more recent study palladium-based nanoparticles have been stabilized with the help of ionic liquid phases in molecular sieve materials.[23] The resulting catalysts have been investigated for the solvent-free hydrogenation reaction and exhibited enhanced activity, selectivity, and durability.

A further example for a hydrogenation study using supported ionic liquids involved the incorporation of a homogeneous catalyst into the porous framework of the membrane.[24] A series of different imidazolium-based ionic liquids with perfluoroanions were treated with the complex $[Rh(nbd)(PPh_3)_2]PF_6$ and loaded into poly(vinylidene fluoride) filter membranes. During the investigation, the olefin was maintained at atmospheric pressure on the feed side of the membrane, while hydrogen at the same pressure was swept over the permeate side and sent through a sampling loop for product analysis. Hydrogenation of the olefin to the corresponding alkane took place as the olefin diffused through the ionic liquid region of the composite membrane structure. A detailed analysis of reaction rates was carried out and showed that the maximum rates for the propene hydrogenation to propane in different ionic liquids followed the order $[EMIM][NTf_2] > [EMIM][OTf] > [EMIM][BF_4] > [BMIM][PF_6]$. The rates for the propene hydrogenation using the supported ionic liquid membranes compare favourably to the rates determined for the hydrogenation of pentene-1 in the liquid–liquid biphasic catalysis reaction using the identical rhodium catalyst.[17c]

In addition to hydrogenation catalysis, supported ionic liquid membranes were also studied for use as oligomerization catalysts. Membranes were prepared by loading porous polyethersulfone support membranes with chloroaluminate-based ionic liquids with and without a nickel dimerization catalyst.[25] Although both catalyst types converted ethylene with high activity, the nickel containing membrane exhibited the higher selectivity for butene production.

Apart from catalysis, supported ionic liquid membranes have also been investigated for a variety of separation applications.[26] These applications ranged from the separation of isomeric amines[27] to the enzyme-facilitated transport of (*S*)-ibuprofen through a supported liquid membrane.[28] The latter study demonstrated the selective separation of the (*S*)-enantiomer from the racemic mixture (Figure 3). The idea was that by employing certain enzymes, such as lipase, it would be possible to enantioselectively catalyze the hydrolysis or the esterification of ibuprofen. In this investigation lipase from *Candida rugosa* facilitated selective esterification in the feed phase while lipase from *Porcine pancrea* was responsible for hydrolysis of the ester. The formed ibuprofen ester dissolved in the supported ionic liquid membrane and diffused across to the receiving phase where it was hydrolysed.

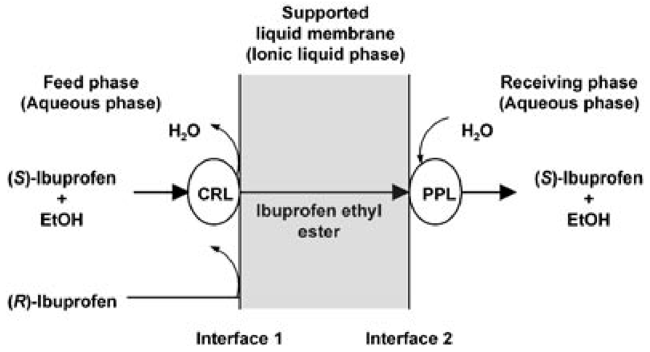


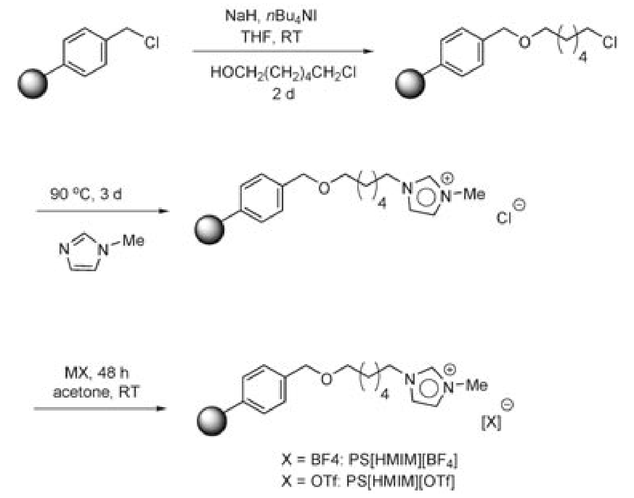
Figure 3. Schematic diagram of enantioselective transport of (*S*)-ibuprofen through a lipase-facilitated supported liquid membrane based on an ionic liquid.[26a]

Other carriers have also been explored as potential supports for ionic liquids in catalytic applications.[29] In one preparation, a transition metal catalyst and the ionic liquid were impregnated into a polymeric material such as poly(diallyldimethylammonium chloride). In the system, the polymeric phase simultaneously heterogenized the catalyst and the ionic liquid. The resulting material displayed activity for a variety of liquid-phase hydrogenation reactions. For example, the substrates 2-cyclohexene-1-one and 1,3-cyclooctadiene were hydrogenated with Wilkinson's catalyst $[RhCl(PPh_3)_3]$ in a polymer supported $[BMIM][PF_6]$ matrix. In all evaluations the polymer supported ionic liquid catalysts showed higher activities than the unsupported ionic liquid system. The improved behaviour of the polymeric system was attributed to improved mass transfer between the ionic liquid phase and the substrates. Furthermore, analysis of the products did not show any metal content and confirmed the full retention of the catalyst on the polymeric support.

In a different approach a polymer-supported ionic liquid was prepared via the covalent anchoring of an imidazolium salt to a polystyrene resin.[30] In this multi-step synthesis a Merrifield peptide resin was modified with 1-*n*-hexyl-3-methylimidazolium cations (Scheme 4) and investigated for nucleophilic substitution reactions including fluorinations. These novel materials together with alkali-metal fluorides proved to be highly efficient catalysts, which converted various haloalkanes and sulfonylalkanes to their corresponding fluorinated products. Furthermore, the polymer-supported systems showed a much higher activity than if the catalysis were to be carried out in free ionic liquids.

Summary and Outlook

The concept of supported ionic liquid catalysis has been successfully demonstrated for a variety of catalysis and separation areas. By supporting ionic liquids, the required amount of the ionic phase can be significantly reduced and it opens the possibility to use fixed-bed reactor systems. Due to the



Scheme 4. Preparation of polymer-supported imidazolium salts PS[HMIM][BF$_4$] and PS[HMIM][OTf] with PS = polymer support.[28]

low volatility of the ionic liquids these supported catalysts are especially attractive for gas-phase reactions. Furthermore by using structured supports like membranes or large pore-size zeolites, novel catalyst systems can be designed and prepared which combine the advantages of homogeneous and heterogeneous catalysis. The recent advances in supported ionic liquid catalysis have showed a tremendous potential and will help to accelerate their introduction into commercial processes. Continuing research in the area of catalysis and separation will inspire novel applications of supported ionic liquid systems and hopefully demonstrate that ionic liquids have the ability to rival or even surpass conventional solvent systems.

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