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Ionic Liquids-Based Catalysis with Solids: State of the Art

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Abstract: Topics related to ionic liquid (IL)-based catalysis with solids not only open new ways for studies of heterogeneous catalysts, but also minimize many of the negative effects that current ILs have encountered. This review evaluates the various examples in solid-based heterogeneous catalytic systems that have been developed with the aid of ILs. Catalysis over ready-made solid catalysts in the presence of ILs, immobilizations of homogeneous organic and organometallic catalysts with the concepts of supported ionic liquid phase catalysis, metal nanoparticles catalysts in ILs, catalysis over supported ILs as well as metal complexes and the preparation of solid catalysts by using ILs as solvents have been described. In several cases, detailed information on the performance concerning catalytic activity and recyclability is available.

Keywords: heterogeneous catalysis; immobilization of homogeneous catalyst; ionic liquids; metal nanoparticles; supported ionic liquid phase catalyst

1 Introduction

Environmental concern associated with chemical synthesis has posed stringent and compelling demands for greener processes, and the development of cost-effective and environmentally benign catalytic systems has become one of the main themes of contemporary synthetic chemistry. In this context, developments of highly active and selective catalysts are of prime importance. In general considerations, heterogeneous catalysis is preferred in industrial processes to homogeneous catalysis as the extraction of the product and recovery of the catalyst are relatively easier.[1] However, in various examples of heterogeneous catalysis, mass or heat transfer limitations in the solid catalyst may lead to decreased activity. Furthermore, compared with homogeneous catalysis, lower chemo- and stereoselectivities are often obtained.[2] Obviously, a catalytic system, which makes it possible to secure the advantages of both homogeneous and heterogeneous catalysis (i.e., good activity, high selectivity, easy extraction of the product and recovery of the catalyst) would greatly enhance the interest of industry in catalysis.

Yanlong Gu was born in 1978 in Inner Mongolia, P. R.China, He obtained his PhD degree in June 2005 from Lanzhou Institute of Chemical Physicals, Chinese Academy of Science, Lanzhou, China, where he had been working on the synthesis and applications of ionic liquids (with Prof. Y. Deng). He then accepted a post-doctoral position in the University of Tokyo, Japan (with Prof. Shū Kobayashi), where he developed the concept of solid catalysts with ionic liquids for organic reactions in water. After one year, he joined the group of Joël Barrault in the Université de Poitiers, France, where he took part in the development of sustainable synthetic methodologies by using water or glycerol as solvent. Since September 2008, he is a professor in the Department of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, P. R. China. His research interests include the rational design of heterogeneous catalysts for conversions of biomass and synthetic methodologies in green solvent systems.

Guangxing Li was born in 1951 in Wuhan, P. R.China. He studied catalysis chemistry in 1975 in Xiamen University, Xiamen, China, where he had been working on the synthesis of ammonia (with Prof. H. L.Wan). He then studied catalysis chemistry as a visiting research fellow in 1988 in the University of Tasmania, Hobart, Australia (with Prof. F. P. Larkins), where he carried out the research on F-T synthesis over Fe-Co catalyst. After several years working as a research associate at the Hubei Research Institute of Chemistry, Wuhan, P. R-China, he moved to Huazhong University of Science and Technology (HUST), Wuhan, P. R. China in 1993. Since January 2000, he is a Professor in the Department of Chemistry, HUST, and Director of Physical Chemistry and Industrial Catalysis, HUST. His research interests included homogeneous, heterogeneous catalysis and catalytic engineering, especially in the fields of carbonylation, hydrogenation and oxidation.

On the other hand, ILs have gained great attention in the past 15 years, as evidenced by their increasing popularity as innovative and environmentally benign reaction media as well as their use as new vehicles for the immobilization of transition metal-based catalysts. From a chemical point of view, some characteristics of ILs, such as thermal stability and very low vapor pressure, address the problem of emission of volatile organic solvents (VOCs) in the atmosphere, thus making these liquids environmentally attractive alternatives to classical organic solvents. Moreover, the physical properties of ILs can be finely tuned by changing either the anion, the cation or the attached substituents. Thus ILs exhibit an excellent ability to dissolve polar and non-polar organic, inorganic and polymeric compounds, allowing substantial applications of ILs in various types of catalytic and synthetic reactions. There are many reviews in the literature which give comprehensive overviews about the topics related to ILs such as synthesis in ILs,[3] catalysis with ILs,[4] and non-solvent utilizations of ILs.[5]

However, in homogeneous catalysis, there are many problems when ILs are used as reaction media: (i) it requires a large amount of IL, which makes them unattractive based on economic considerations since ILs are still expensive, even though being commercially available today; (ii) in order to separate organic products from the ionic phase, extraction with solvents which are immiscible with the ILs has to be used in the most cases; this procedure causes a drawback concerning the extraction of small amounts of the ILs and of the catalyst; (iii) using ILs as solvents will generate inevitably a large amount of waste at the end of their valid life, however, their potential toxicity[6] and the lack of data about their biodegradability will render the disposal of waste ILs very difficult especially under the pressure of environmental protection;[7] (iv) in some reactions, bulk IL systems may suffer from slow substrate diffusion due to the relatively high viscosities of the ILs, causing the main part of the reaction to proceed in the inter-phase or in the diffusion layer of the catalyst, rather than in the bulk solvent as would be strongly preferred. Thereby, the productivity of the process is limited since a large part of the catalytically active species is not participating in the reaction; (v) in order to minimize the effects of impurities in ILs on the catalysis, it requires generally the use of a very pure IL, which is, however, at this moment, very difficult to obtain.[8] These aspects may be sufficient to explain why, although ILs have shown great potential on the homogeneous catalysis in laboratory scale, there has not yet been any known large-scale industrial application in catalysis.

In order to advance catalysis with ILs, a new strategy which utilizes the advantageous properties of ILs and, at the same time, minimizes the negative effects, would be highly desirable. In this context, solid catalysis with ILs appears to be an ideal choice because of the fact that ILs here are used in small amounts, while their efficiencies are as good as for the utilizations of bulk solvents.[9] The concept of *supported ionic liquid phase catalysis* (SILPC) has gained much attention in this area.[10] Recently, ready-made solid catalysts with ILs, in which the surface of the solid catalyst was coated by IL, offered a new method for re-investigations of many ready-made solid catalysts. Covalently grafting imidazolium cations onto the surface of solid materials not only heterogenizes the expensive IL, but also offers a lot of opportunities to investigate immobilizations of homogeneous metal complexes or metal nanoparticles. Recycling functionalized IL by this method is also possible. The aim of this review is to provide a state of art overview on applying ILs in catalysis with solids. Works related to the use of solid catalysts in ILs are also included. Because some early reviews have summarized parts of the reported results in different ways up to the end of 2005,[9–11] we intend to particularly focus on the results that emerged afterwards.

2 Catalysis over Solid Catalysts with ILs

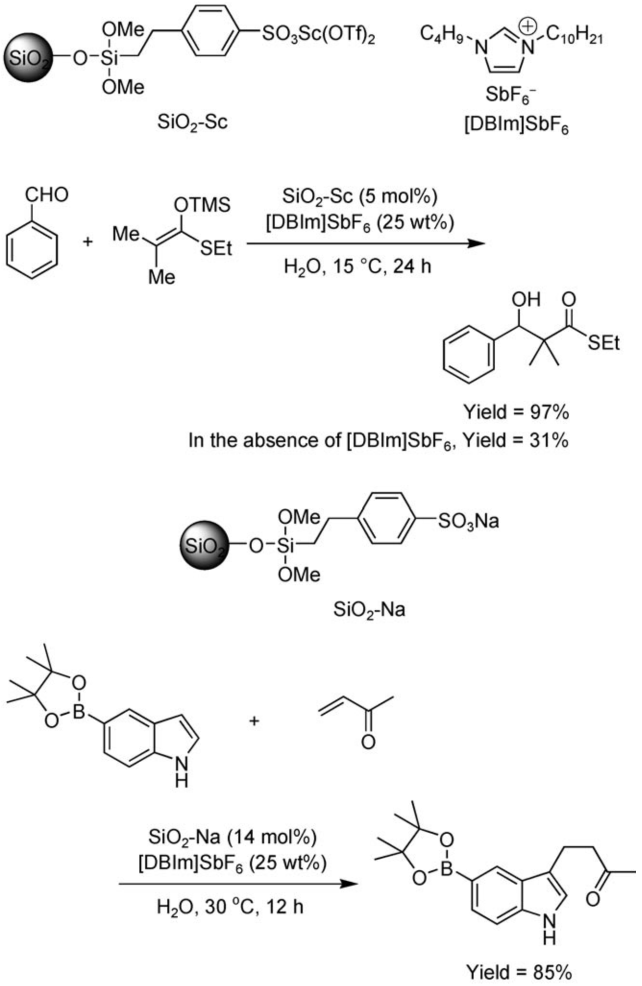
2.1 Solid Catalysts in ILs

Direct use of solid catalysts in ILs has been rarely explored before.[12] In essence, this strategy has combined the advantages of using the IL as solvent with the intrinsic properties of a solid catalyst together in the target reaction system. Researchers may expect, of course, that some synergistic effects could be obtained by this combination. Indeed, some promising results have been achieved, for example, IL solvents gave higher rates and sulfoxide selectivities for titanium/silica-based mesoporous catalysts-promoted selective sulfoxidation of aromatic or aliphatic thioethers than a conventional solvent, dioxane.[13] In these systems, the catalyst is truly heterogeneous and the role of the leached species is insignificant. The excellent performance of ILs in these reactions should be ascribed to many of their intrinsic properties, such as hydrogen bond resulting from the acidic proton in the imidazolium cation, water miscibility which directly links to the mass transfer of substrates, and viscosity.[14] A recent study reported by Schüth's group has clearly demonstrated again the advantages of IL for solid catalyst-based processes.[15] 1-Butyl-3-methylimidazolium chloride ([BMIm]Cl) was used as solvent in this work for an acidic resin, Amberlyst-15 (dry), catalyzed depolymerization of cellulose. Three factors are essential: (i) [BMIm]Cl is able to dissolve cellulose, this great ability of [BMIm]Cl makes the substrate, cellulose, disperse well in the solution; (ii) the Amberlyst-15/[BMIm]Cl system is highly effective for the depolymerization of cellulose including microcrystalline cellulose, which cannot be hydrolyzed by conventional dilute acid processes;[16] (iii) cellulose initially depolymerizes in a very controlled fashion with a size-specific preference for the cleavage of large chains. This preference is so high that only negligible amounts of reducing sugars are released in the beginning of the reaction. Therefore, this can be an ideal method to prepare cellooligomers if the reaction could be stopped at a right time. An analogous Amberlyst-15/IL system has also been utilized for the preparation of quinoline derivatives.[17] Moreover, Amberlite IR-120 acidic resin, which contains an age-old polymer matrix, has been used as catalyst in conjunction with IL as a solvent for the oxidation of aromatic alcohols with urea-hydrogen peroxide at 70 °C.[18] Under similar conditions, tertiary aromatic alcohols have been converted disproportionately into monohydroxyphenol and acetone. Not only acid catalysts, but also basic salts, such as K_2CO_3, can be combined with the IL solvent to form an effective and recyclable catalyst system for organic reactions, such as the synthesis of γ-nitro ketones and γ-nitro esters by means of a condensation reaction between nitroalkanes and α,β-unsaturated carbonyl compounds.[19] On the other hand, ILs have also been used as solvents for selective oxidations of hydrocarbons promoted by solid metal-containing catalysts, and either improved activity or enhanced selectivity was obtained.[20]

2.2 Solid Catalysts with ILs

Solid catalysts with ionic liquids (SCILs) is a new concept proposed independently by us[21] and Jess[22] which uses a free flowing IL to coat the surface of a ready-made solid catalyst. A sharp difference with the SILPC strategy is that now the solid is a ready-made heterogeneous catalyst but not an inert support which is used to immobilize the homogeneous catalyst by the IL. Thus, a homogeneous catalyst is not involved in the SCIL concept though a combination with the SILP technology could be a future option to integrate homogeneous and heterogeneous catalysis. With SCIL, the activity and selectivity of the original solid catalyst may be changed significantly by the coating of the internal surfaces with the IL. The reasons are two fold: (i) the IL may have a positive influence on the "chemical" properties of the catalyst (namely co-catalytic effect); (ii) the IL may change the effective concentrations of substrates or intermediates on the surface of solid catalyst because of the ionic properties of the IL phase (namely a physical solvent effect).[22] One of limitations of SCILs is that the organic phase and the IL have to form a biphasic system without any IL leaching as otherwise the IL film would be washed out of the catalyst. On the basis of this consideration, SCILs should better be applied to some processes which either involve gaseous substrates and products or apply a solvent which is insoluble in the IL phase. Taking advantage of the high surface areas between the well dispersed IL thin layer and the reactant phase into consideration, the SCIL approach can be specially favorable for reactions that contain reactants with less desired solubility in ILs.[22]

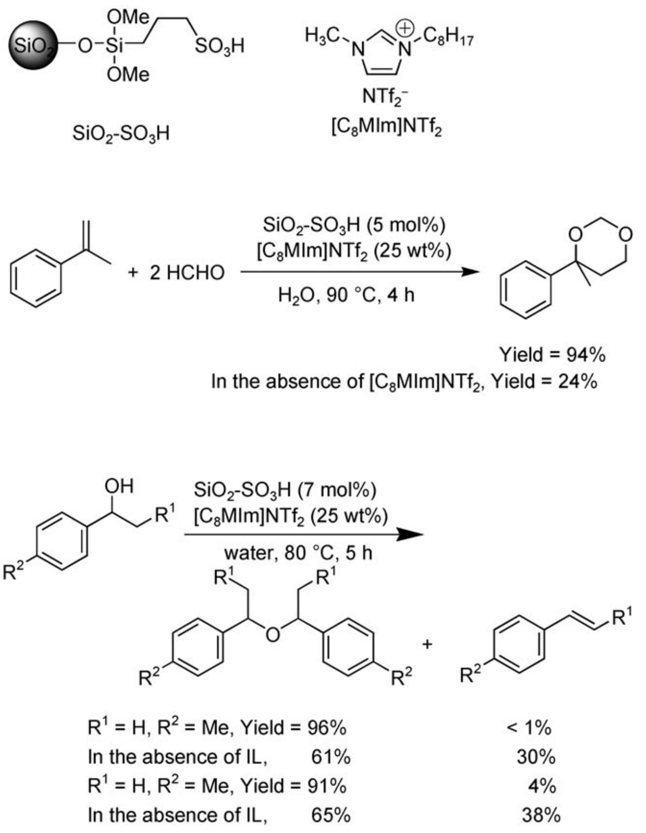
Up to now, two kinds of effects have been observed with SCILs. The first is improvement of catalytic activity. This has been clearly verified by us for organic reactions in water using a silica-supported scandium (SiO_2-Sc) as Lewis acid catalyst.[21] While the Mukaiyama-aldol reaction between an aldehyde and a silyl enol ether proceeded very well in water using SiO_2-Sc coated by a hydrophobic IL, [DBIm]SbF_6, the same reaction proceeded sluggishly using SiO_2-Sc alone under otherwise identical conditions (Scheme 1). Here, the increased concentrations of organic substrates, which are highly hydrophobic, in the hydrophilic surface of SiO_2-Sc might be partially responsible for the improvement of the catalytic activity. SiO_2-Sc with ILs (SiO_2-Sc-IL) can also be applied as catalysts for many organic transformations in water including the Michael addition of indole to α,β-unsaturated ketones, Mannich-type reactions and the allylation of ketone with tetraallyltin, thus proving to be versatile Lewis acid catalysts for organic reactions in water. A significant effect of the coating IL on the catalytic activity has been further demonstrated by a combination silica-supported sodium and a post-coated [DBIm]SbF_6 (SiO_2-Na-IL), which showed an unexpectedly high activity for the Michael addition of indoles to α,β-unsaturated ketones in water (Scheme 1).[23] It should be noted that SiO_2-Na is unable to catalyze the same reaction under identical conditions, highlighting the importance of the IL here. The high activity of SiO_2-Na-IL also makes it possible to perform the reactions under neutral conditions. This is particularly attractive for the synthesis of acid-labile indole derivatives, which are valuable for pharmaceutical synthesis.



Scheme 1. Organic reactions in water catalyzed by SiO_2-Sc and SiO_2-Na with [DBIm]SbF_6.

The second kind of effect rising from the coating of IL in the concept of SCILs is enhancement of catalytic selectivity. Paradigms about this effect can be found in some organic reactions in water catalyzed by a silica-supported sulfonic acid (SiO_2-SO_3H) with a hydrophobic IL, [C_8MIm]NTf_2 (Scheme 2).[24] For example, the Prins cyclization of α-methylstyrene in aqueous solution of formaldehdye proceeded selectively in the presence of IL-coated SiO_2-SO_3H (SiO_2-SO_3H-IL), and produced the corresponding adduct in 94% yield. On the contrary, due to a lack of selectivity, only a 24% of yield was obtained without the coating of IL although α-methylstyrene could be completely consumed (Scheme 2). The selectivity enhancement can be ascribed not only to the improvement of solubility or diffusion of substrates, which occurred in the surface of the solid catalyst, but also, more or less, to the stabilization of intermediates associated with the ionic microenvironment created by means of the coating of IL onto the surface. Furthermore, the coating of SiO_2-SO_3H with IL can also restrict the dehydration of benzylic alcohols to styrenes in water, thus favoring the formation of dialkyl ethers.[24]

The selectivity enhancement has also been illustrated by a sequential hydrogenation of 1,5-cyclooctadiene (COD) to cyclooctene (COE) and cyclooctane on a commercial solid Ni catalyst coated by an IL [BMIm][n-$C_8H_{17}OSO_3$] [Figure 1 and Scheme 3, (**b**)]. In this reaction, COE should be removed as soon as possible from the surface of the solid catalyst in order to maximize the selectivity to COE. The concept of SILC has a great potential in this aspect because the solubility of COE in the ionic phase is relatively lower compared with that of COD in a biphasic system composed of *n*-dodecane and [BMIm][*n*-$C_8H_{17}OSO_3$], therefore, a change of the catalytic performance upon coating with the IL is to be expected (Figure 1). Indeed, the coating of the internal surface with the IL enhances the maximum COE yield from 40% to 70% in *n*-dodecane.[22]



Scheme 2. Examined organic reactions in water catalyzed by SiO_2-SO_3H with IL.

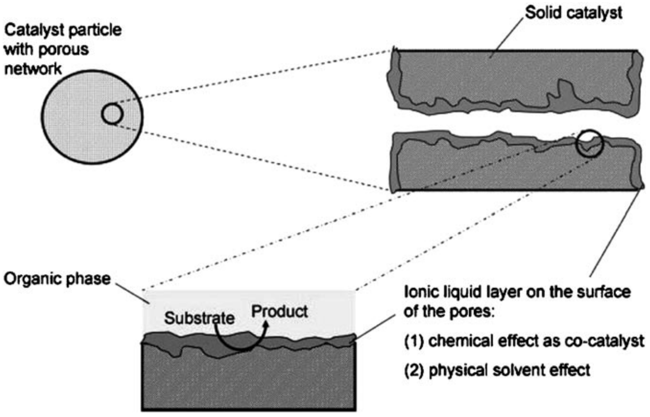
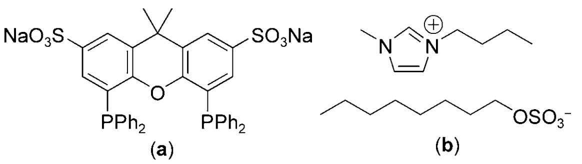


Figure 1. COD hydrogenation to COE over a solid Ni catalyst with IL (from U. Kernchen, A. Jess, *Chem. Eng. Technol.* **2007**, *30*, 985–994;[22a] DOI: 10.1002/ceat.200700050. Reproduced by permission of Wiley-VCH).



Scheme 3. Phosphane ligand and IL used in Riisager's works.

3 Supported Ionic Liquid Phase Catalyst (SILPC)

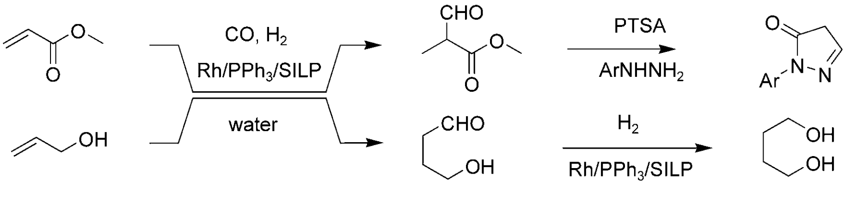
The *supported ionic liquid phase catalyst* (SILPC) is a new generation of the *supported liquid phase catalyst* (SLPC). The later concept, SLPC, is one of effectively heterogenized homogeneous catalysts using organometallic complexes, which are dissolved in a small quantity of a liquid phase dispersed in the form of an islet or film on the surface of a support, as active components.[25] In the SLPC system, although the final material is a solid, the active species in the liquid phase acting as a homogeneous catalyst preserves its high selectivity. The most important component in SLPC is theliquid phase which requires not only a good ability to dissolve organometallic complexes but also a low volatility in order to prevent leaching during the reaction procedure. Many liquid materials have been used such as water, polyalcohols and carbonates. Unfortunately, in many cases, researchers have to face deactivation caused by mass loss of liquid phase due to the high volatility of those molecular materials. Some properties of ILs such as low volatility and good solubilities for many organic and inorganic complexes perfectly fit the requirements of the liquid component in the SLPC system. Mehnert's and Wasserscheid's groups first demonstrated the feasibility for the application of ILs in studies of SLPC and contributed more than 10 papers in the new concept of SILPC.[26,27] In these systems, a thin film of IL is confined to the surface of a highly porous solid by various methods such as physisorption, tethering, or covalent anchoring of the IL fragments. Metal complexes with or without ionic tails can be both used as catalysts. In many cases, the ionic character of the ILs confers to these metal complexes a peculiar spatial environment over the solid surface (e.g., the formation of IL cages around the complexes), thus inducing specific reactivity,[28] which also can be linked to confinement effects of the solid supports. The fluorescence of pyrene has been used to measure the static dielectric constant of a series of SILPCs based on polystyrene networks.[29] Judging from the results, it has been suggested that the change of surface polarity rising from the loading of ILs might be partially responsible for the advanced properties of SILPCs. Because of these attractive features, applications of this concept have attracted much attention in recent years. Some excellent reviews have summarized the published results up to the beginning of 2006.[30] Therefore, here we will mainly focus on the results that emerged afterwards.

3.1 Immobilizations of Organometallic Catalysts with SILPC

One of the particular advantages of SILPC systems is that the mass transport limitation from the gas to a liquid phase can be circumvented because of the high interfacial area in these SILP catalysts. This has been clearly elucidated by means of simulated calculations in the hydrogenation of citral using Pd nanoparticles, which are dispersed in an IL thin layer on active carbon cloth (ACC), as catalyst.[31] It was found that the internal mass transfer of all substrates and products in the IL layer is not pronounced and, regardless of the IL involved, the simulated kinetic values are in the same order of magnitude. This advantage allows the SILPC system to be applicable in a fixed-bed reactor for simple continuous processes. Especially, SILPC was utilized in conjunction with gaseous substrates, whereby product separation and catalyst recycling could be avoided. This has been clearly demonstrated by Riisager et al. who developed an SILPC system for the hydroformylation of propene with the combination of 2,7-bis-(SO_3Na)-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (sulfoxantphos) [(**a**), Scheme 3] modified rhodium complexes and [BMIm] [n-$C_8H_{17}OSO_3$] [(**b**), Scheme 3] dispersed on silica. In a fixed-bed reactor, the resultant SILPC showed very high activty and good selectivity. Particularly, the lifetime of the SILPC system reached up to 200 h time-on-stream although a slight decrease in activity was observed at the end. Interestingly, treatment of the catalyst under vacuum can extend the lifetime to 700 h.[32] Recently, the same authors also investigated the hydroformylation of 1-butene under otherwise identical conditions.[33] These SILPCs were proved again to be highly active, selective and have long-term stability. Compared to former studies using propene, the SILPC system showed a more than 2 times higher activity with 1-butene as feedstock. As mentioned above, no mass transport limitation from the gas to the liquid was observed judging from a linear dependency of the reaction rate on the catalyst loading under the experimental conditions. The effect of the support was also investigated and the best choice is silica gel, which has the smallest pore size and, thus, capillary condensation might occur for 1-butene.

When a hydrophobic IL was used, water can also be used as solvent for the SILPC. For example, methyl acrylates were hydroformylated with high regioselectivity and excellent yield to the corresponding branched aldehydes using the combination of Rh/PPh_3 and silica-supported 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF_6) in water. The generated branched aldehydes can be further converted without purification to 4-methyl-substituted pyrazolin-5-ones in the presence of an acid catalyst (Scheme 4). Using the same system, the regioselective hydroformylation of allyl alcohol could also be performed successfully in water. Subsequent hydrogenation of the hydroformylation products using a Ru-based SILPC system gives 1,4-butanediol in a good yield (Scheme 4).[34] In addition, the hydroformylation of n-hexene has also been investigated using the Rh-P(m-$C_6H_4SO_3Na$)$_3$(TPPTs)-based SILPC system with the aid of 1,1,3,3-tetramethylguanidinium lactate (TMGL) and MCM-41.[35] Under optimized conditions, the reaction over the MCM-41-TMGL-Rh-TPPTs system proceeded with a space-time yield of 4596 mmol h^{-1} g Rh^{-1}, afforded the C_7-aldehdye in a linear/branched ratio of 74/26 with a total selectivity of 98%.

SILPC has also been applied to immobilize the Monsanto-type catalyst, $[Rh(CO)_2I]_2$, using 1-butyl-3-methylimidazolium iodide ([BMIm]I) and amorphous SiO_2 as the ionic phase and solid support, respectively. In the course of $[Rh(CO)_2I]_2$ impregnation, the Monsanto catalyst anion, $[Rh(CO)_2I_2]^-$, was formed directly in the supported [BMIm]I. The obtained [BMIm]$[Rh(CO)_2I_2]$-[BMIM]I-SiO_2 system exhibited excellent activity and selectivity towards acetyl products in the continuous, gas-phase methanol carbonylation using a fixed-bed reactor.[36] After a short time for inductive initiation (1 h), complete conversion of methanol was obtained with a TOF of 76.5 h^{-1} and space-time yield (i.e., production rate) of 21.0 mol L^{-1} h^{-1}. The distribution of acetyl products is closely dependent on the gas space velocity in this system. It should also be noted that the obtained pro-

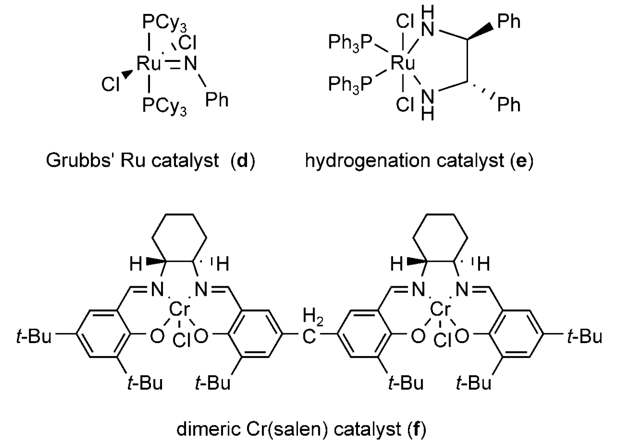


Scheme 4. Hydroformylation of methyl acrylate and allylic alcohol over SILP-Rh catalysts

duction rate is practically the same as that of previous results obtained by using a large amount of IL (100-fold with respect to the volume) in an analogous bubble-column reactor system,[37] indicating thus the efficiency of the highly dispersed IL catalyst layer in the SILPC. Moreover, the process design of the fixed-bed SILPC requires a smaller reactor size than that of existing technology in order to obtain the same productivity, which makes the SILPC carbonylation concept potentially interesting for technical applications.

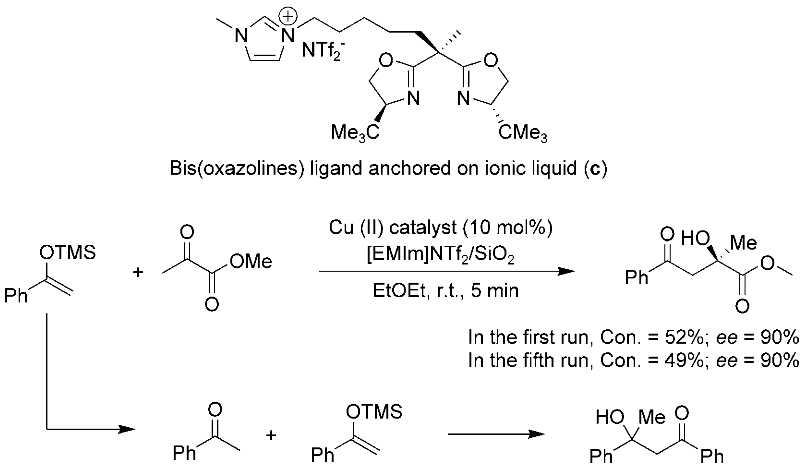
An imidazolium-tagged bis(oxazoline)-Cu(II) complex [Scheme 5, (**c**)] was found to be an effective and enantioselective catalyst for the Mukaiyama-aldol reaction between methyl pyruvate and 1-methoxy-1-trimethylsilyloxypropene in a biphasic system composed of diethyl ether and IL. However, a by-product generated by a reaction between 1-methoxy-1-trimethylsilyloxypropene and acetophenone, which comes from the decomposition of the silyl enol ether, was observed (Scheme 5). Interestingly, supporting the Cu(II) complex on silica or an imidazolium-modified silica with the SILPC strategy completely suppressed the formation of this by-product without reducing the enantioselectivity. Although the SILPC systems were characterized by a drop in catalytic activity, the system could be reused up to five times without a significant loss in conversion or *ee*.[38]

Grubbs' olefin metathesis Ru catalyst (**d**) (Scheme 6) was immobilized by the SILPC strategy in the pores of amorphous alumina with the aid of 1-*n*-hexyl-3-methylimidazolium hexafluorophosphate ([HMIm]PF_6). In benzene, this Ru-SILP catalyst was proved to be effective for various olefin metathesis reactions such as intra- or intermolecular macrocyclization and dimerization, and could be reused up to six times with a simple catalyst recycling.[39] A chiral Ru complex (**e**) (Scheme 6) has also been immobilized by the SILPC method using imidazolium salt-modified silica materials including MCM-41-IL, MCM-48-IL, SBA-15-IL and amorphous SiO_2-IL, as supports.[40] The obtained catalysts were proved to be active and selective for the asymmetric hydrogenation of acetophenone. In the recycling experiments, the SiO_2-IL-supported catalyst could be reused at least four times without a noticeable decrease in catalytic activity.



Scheme 6. Some organometallic complexes examined in SILPC systems.

Another set of chiral rhodium complexes, [Rh(BINAP)L_2]X (L = weakly coordinating ligand; X = non-coordinating anion), have also been immobilized together with a base in a thin film of the phosphonium-based IL, [P(*n*-C_6H_{11})$_3$(*n*-$C_{14}H_{29}$)] [$C_9H_{19}CO_2$], on silica.[41] The obtained systems were highly active for another variation of acetophenone hydrogenation in which 1-cyclohexylethanol was enantioselectively formed as the final product through simultaneous or consecutive reductions of the phenyl ring and the carbonyl group. With this SILPC, the rate of reaction was similar to or higher than the results obtained in homogeneous conditions. It is particularly noteworthy that clear enantioselectivities (30–74%) were ob-



Scheme 5. Mukaiyama-aldol reaction of methyl pyruvate over SILP-Cu(II) system.

served with SILPC/substrate pairs, whereas little chiral selection ($\leq 4\%$) occurred in the corresponding homogeneous catalysis using methanol as solvent. This might be attributed to one of the unique solvent properties of ILs for their objective uses in SILPC, e.g., the formation of IL cages around the complexes, which has been well documented by Müller and his co-workers.[28] For the above-mentioned enantioselective hydrogenation of acetophenone, transition states might be modified within these cages, in an attempt to minimize the potential energy, the sphere of IL molecules around the metal-substrate complex thus assumes a minimum size. Therefore, the substrate is squeezed against the metal, which leads to enhanced metal-substrate interactions.

Combination of a dimeric Cr(salen) catalyst (**f**) (Scheme 6) and a supported IL phase resulted in a novel material which proved to be more reactive and selective for the asymmetric ring-opening reactions of epoxides with $TMSN_3$, than the Cr(salen) complex immobilized by impregnation.[42] In this reaction system, catalyst and IL can be recovered by Soxhlet extraction with acetone. It can also be used in a continuous-flow reactor. An analogous metal complex, Mn(Salen), has also been immobilized onto MCM-48 by using the SILPC strategy with the aid of $[BMIm]PF_6$. The obtained SILP-MCM-48-Mn(Salen) system proved to be an effective catalyst for the asymmetric epoxidation of olefins,[43] and kinetic resolution of alcohols.[44] Particularly, in epoxidation of α-methylstyrene, both the conversion and *ee* value could exceed 99% with this SILPC. Furthermore, the SILP-MCM-48-Mn(Salen) system was quite stable and could be recycled at least three times. In addition, $VO(acac)_2$ was also incorporated with the aid of IL onto mesoporous silica SBA-15 material,[45] and the obtained material was then used as an effective catalyst for the epoxidation of allylic alcohols.

The SILPC strategy has recently been applied to immobilize simultaneously a soft Lewis acid, $[Pd(DPPF)](CF_3CO_2)_2$, and a strong Brønsted acid, trifluoromethanesulfonic acid (TfOH), onto a silica support with the aid of [EMIm]OTf, [BMIm]OTf and [HMIm]OTf, generating a new class of hydroamination catalysts.[46] The obtained SILPCs showed high catalytic activity for the addition of aniline to styrene, providing the Markownikoff product under kinetically controlled conditions and mainly the anti-Markownikoff product in the thermodynamic regime. the ILs here were not only able to dissolve the homogeneous catalysts, and consequently, immobilize them onto the surface of solid, but also play a key role to achieve high activity owing to their high polarities, which are favorable for the stabilization of the ionic intermediates. High activities for the model reaction were also obtained with a combination of the same metal and silica-supported imidazolium salts.[47] The reaction rate was higher compared to those in classic solvents and increased with increasing Pd loading and increasing polarity of the IL. The experimental results obtained in the new SILPC for hydroamination could be perfectly explained by the formation of solvent cages (Figure 2).[28] For example, (i) with increasing temperature, the ILs gain mobility until the solvent cages break down at a specific temperature, which is noticeable as a phase transition; (ii) at temperatures below the phase transition, the catalytic activity was found to be closely dependent on the choice of the IL; (iii) at temperatures above the phase transition, the activity for formation of the Markownikoff adduct was, in contrast, nearly identical with all ILs examined.

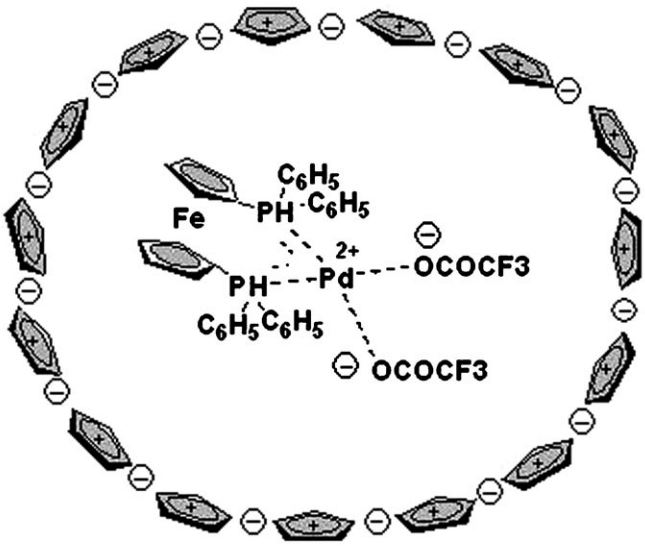
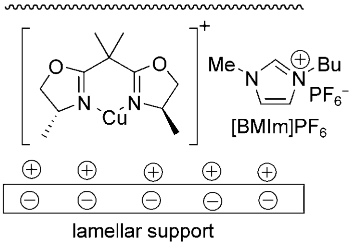


Figure 2. Artist's impression of the solvent cage of ILs around the organometallic Pd complex (reproduced with permission of the authors[47]).

On the other hand, carbon nanotubes (CNTs) have recently emerged as a potential support for the heterogenization of homogeneous catalysts because of their inherent advantageous properties such as good mechanical strength, high chemical stability, and a large surface area-to-volume ratio. Serp et al.[48] recently prepared a series of carbon nanotubes (CNTs) grafted by imidazolium ILs, which can be further utilized as supports of SILPC in conjunction with using $Rh[(cod)(PPh_3)_2]PF_6$ as catalyst. Here, the loading of the free flowing IL, $[BMIm]PF_6$, can be increased to 55 wt% without detectable leaching of the IL, from 20–30 wt% which is generally used in other systems involving the use of an oxide support. In the hydrogenation of olefins, the resulting Rh/CNT-SILP system showed much higher catalytic efficiency compared with other SILPCs composed of oxide supports and the same Rh complex. This might be partially attributed to a sufficient use of Rh catalyst in the hydrogenation because of the good dispersibility of the CNT support in the reaction mixture that minimizes the negative effects of mass transport. Furthermore, the catalysts are quite stable and can be reused many times.

Carbon/metal hybrid fibers composed of sintered metal fibers (SMFs) and carbon nanofibers (CNFs) have also been used as support for an SILPC using the $Rh(H)_2Cl(PPh_3)_3$-catalyzed selective hydrogenation of 1,3-cyclohexadiene as a model reaction.[49] The combination of the IL thin film and CNF/SMF supports not only presents a high interface area, which ensures efficient use of the transition metal catalyst, but also suppresses the formation of hot spots during exothermic hydrogenation reactions because of the high thermoconductivity of the CNF/SMF support. In a fixed-bed reactor, the combined catalyst, $Rh(H)_2Cl(PPh_3)_3$-IL-CNF/SMF, showed a turnover frequency of up to 250 h^{-1} and a selectivity of $>96\%$ with acceptable stability (6 h on stream).

Mayoral and his co-workers[50] reported an SILPC system composed of Laponite (a two-dimensional lamellar support with negative charges in the layers)-supported $[BMIm]PF_6$ and bis(oxazoline)-copper complex, which showed a significant influence of the SILPC on the catalytic selectivity (Scheme 7). As shown in Table 1, although the reaction yield was slightly decreased in the SILPC system compared with the result in homogeneous conditions, both diastereoselectivity and enantioselectitiy were modified with the supported thinner film of $[BMIm]PF_6$. Particularly, the use of the SILPC system altered the enantioselectivity to the *cis* isomer from 45% under homogeneous conditions to −56%, meanwhile the preference for *trans* isomers was reversed from 67% to 33%. Furthermore, only layered solids with negative charges in the layers (clays) give rise to this type of behavior, showing that the formation of ion pairs may be a decisive factor.

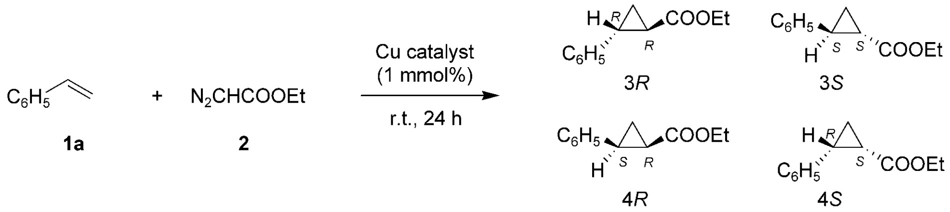


Scheme 7. SILP-Cu(II) with Laponite.

An abundant biopolymer, chitosan, which consists of 2-amino-2-deoxy-(1,4)-β-D-glucopyranose residues (D-glucosamine units) with no or a small amount of *N*-acetyl-D-glucosamine units, has also been used to immobilize Pd(II) catalysts with the aid of $[BMIm]BF_4$ and TPPTs.[51] The obtained SILPC system showed a high activity for Tsuji–Trost allylic substitution reactions and good recyclability (Scheme 8). The recycled Pd catalyst could be reused at least ten times without a significant loss of activity.

It should be noted that, in a liquid reaction system, ILs in SILPC systems can have significant solubility in the liquid substrate, so they are gradually removed along with some of the catalyst. With the aim to improve the long-term stability of SILPC, two strategies have been proposed up to now. The first strategy aims at developing a new variation of SILPC, in which the IL-modified materials can carry out their catalysis in the absence of a non-immobilized IL. A recent study by You,[52] who prepared a novel supported IL *via*

Table 1. Catalytic performance of a Cu catalyst in SILP for cyclopropanation.[a]



Entry	IL/support (mL/g)	Yield [%][b]	*trans*/*cis*	*ee trans* [%][c]	*ee cis* [%][c]
1	homogeneous	42	67/33	54	45
2	0.067	3	41/59	27	-53
3[d]	0.067	16	37/63	28	-50
4[e]	0.067	37	33/67	25	-56

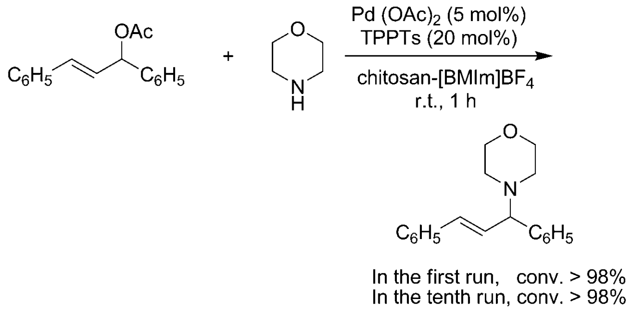
[a] *Reaction conditions:* 1.5 equv. **1a**; 1 mol% catalyst (0.076 Cu mmol mL^{-1} $[BMIm]PF_6$), **2** slowly added within 2 h, room temperature, 24 h, extraction: 5×3×3×3 mL.

[b] Determined by GC.

[c] Determined by GC equipped with a cyclodex-B column.

[d] Extracted with EtOEt.

[e] 3 mol% catalyst.



In the first run, conv. > 98%
In the tenth run, conv. > 98%

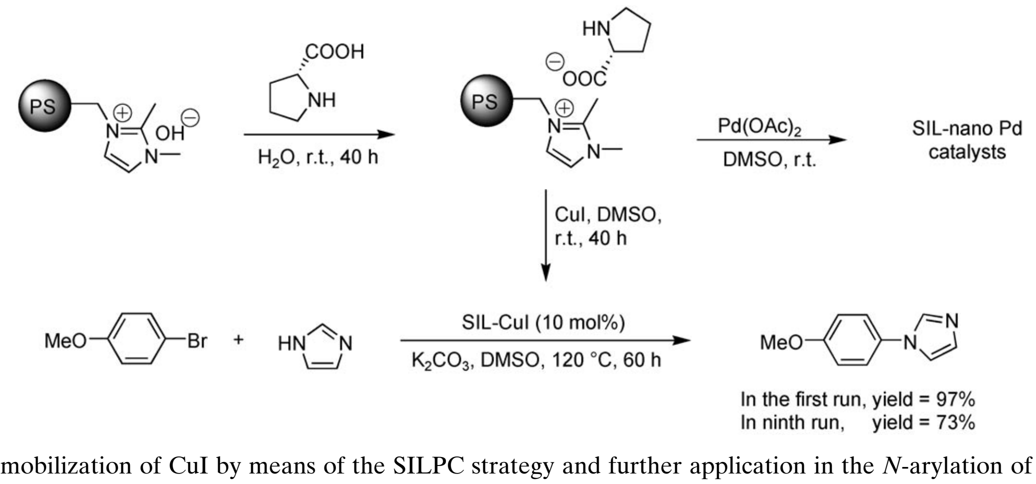
Scheme 8. Tsuji–Trost allylic substitution reactions catalyzed by an SILPC system composed of chitosan and Pd(II).

acid-base ionic pair coupling of polystyrene-supported imidazolium hydroxide with L-proline, can be considered as a representative example in this aspect (Scheme 9). You's supported ILs displayed considerable ability for metal scavenging without the aid of a non-immobilized IL. For example, more than 97% of CuI was soaked on the polymer-supported IL, and the CuI loading level could be controlled by the molar ratios of CuI to the L-proline unit on the support. The resulting CuI-soaked supported ILs can be used as efficient SILPCs for the *N*-arylation of nitrogen-containing heterocycles (Scheme 9). Compared with a system composed of L-proline, CuI and [BMIm]BF_4, much higher catalytic activity and more extensive substrate scope were achieved by using the SILP-CuI system. Particularly, the SILP-CuI catalyst can be recycled for nine runs without any considerable loss of activity. Furthermore, a Pd-soaked material, which was prepared from $Pd(OAc)_2$ and You's IL-polymer, has also shown remarkable activity for the solvent-free hydrogenation of styrene to ethylbenzene. TEM analysis of the SILP-Pd catalyst revealed that some Pd nanoparticles are distributed on the outer PS surfaces with the particles size of *ca.* 2 ± 1 nm. This implies that You's IL-polymer has considerable ability for stabilizing Pd nanoparticles in view of the fact that metallic particles are kinetically unstable with respect to agglomeration to the bulk metal. All these results clearly demonstrated that the homogeneous catalysts could be heterogenized with dramatic improvements of the catalytic performance by the SILPC strategy.

The second strategy is the combination of SILPC with $scCO_2$. Although $scCO_2$ is soluble in ILs and can dissolve many organic compounds, it does not dissolve ionic compounds.[53] These properties minimize possible leaching of IL and the ionic organometallic complexes in the SILPC system, thus improving the stability and recyclability of the SILPC. Moreover, the use of $scCO_2$ should also improve the mass transfer between the organic phase and the thin layer of IL, thus, accelerating the reaction rate. Indeed, with this strategy, a stable and an efficient catalyst system was obtained for the hydroformylation of 1-octene in a continuous flow reactor using an SILPC composed of $[C_3MIm][Ph_2P(3\text{-}C_6H_4SO_3)]$, $[Rh(acac)(CO)_2]$ and SiO_2-supported $[C_8MIm]NTf_2$. A high reaction rate (up to 800 h^{-1}) was obtained with a good process stability (40 h) as well as limited Rh leaching (0.5 ppm). In addition, the use of $scCO_2$ also offers another advantage concerning extraction of by-products, which are generated from aldol condensations of the products, and prevents the fouling of the catalyst that, sometimes, occurred in catalytic reactions with SILPCs.

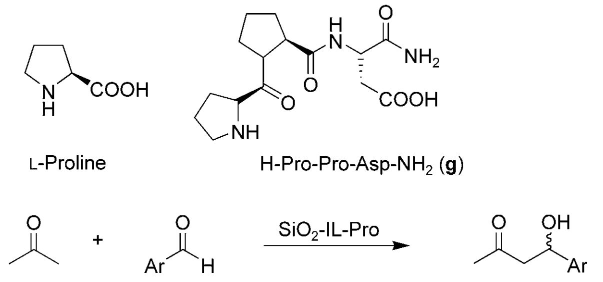
3.2 Immobilizations of Organocatalysts and Enzyme with SILPC

The concept of SILPC has also proven to be applicable for the immobilization of organocatalysts by Noto et al.[54] A commonly used organocatalyst, L-proline, and the tripeptide H-Pro-Pro-Asp-NH_2 (**g**)



In the first run, yield = 97%
In ninth run, yield = 73%

Scheme 9. Immobilization of CuI by means of the SILPC strategy and further application in the *N*-arylation of nitrogen-containing heterocycles.



Scheme 10. Catalytic reaction over SILPC with organocatalysts.

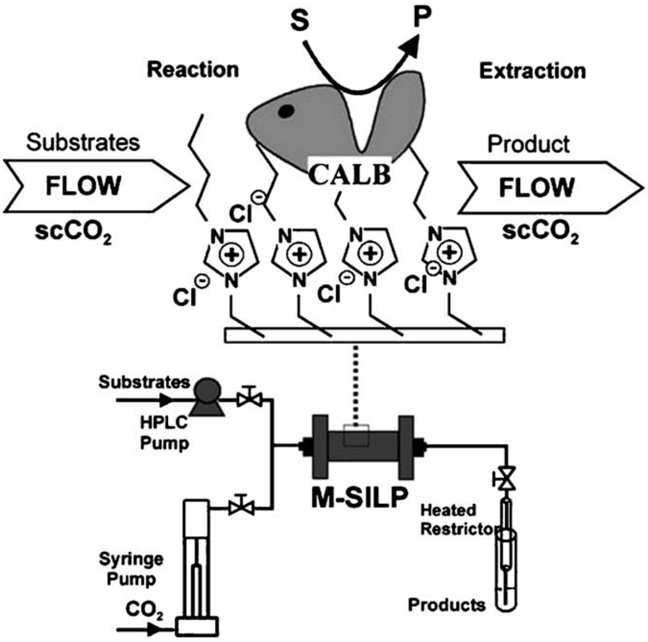


Figure 3. Immobilization of the enzyme with combination of SILPC and scCO$_2$ under flow conditions (from P. Lozano, E. García-Verdugo, R. Piamtongkam, N. Karbass, T. D. Diego, M. I. Burguete, S. V. Luis, J. L. Iborra, *Adv. Synth. Catal.* **2007**, *349*, 1077–1084; DOI: 10.1002/adsc.200600554.[57] Reproduced by permission of Wiley-VCH).

(Scheme 10) have been supported on the surface of modified silica gels with a monolayer of covalently attached IL with or without additional adsorbed IL.[55] The resulting materials were then used as catalysts for the aldol reactions between ketones and several substituted benzaldehydes. Benefited by synergistic effects between ionic heads and organocatalysts, which were found to be particularly significant in the cases using imidazolinium-modified and 4-methylpyridinium-modified silica as support, good yields and *ee* values (comparable with those obtained under homogeneous conditions) were achieved in aldol reactions between aromatic aldehydes and ketones (Scheme 10).[56] Moreover, these materials have been easily recovered by simple filtration, and can be used at least seven times. Notably, the deactivated imidazolinium-modified silica support, which was recovered after many times of reuse, can be regenerated, giving again a recyclable material with high isolated yields and reproducible *ee* values.

Recently, Luis and Iborra[57] found that it is also possible to immobilize biocatalyts with SILPC. They modified the SILPC to serve as a bioreactor in which imidazolium units were covalently anchored to the matrix of polymeric monoliths composed of either styrene-DVB or 2-hydroxyethyl methacrylate-ethylene dimethacrylate. The obtained SILPC retains characteristic properties of IL, thus being able to absorb *Candida antarctica* lipase B (CALB) by means of strong interactions between the protein molecule and the IL phase, leading to highly efficient and robust bio-SILPCs. In a continuous transesterification of vinyl propionate and citronellol using scCO$_2$ as reaction medium, the obtained bio-SILPC showed good activity and acceptable stability (Figure 3). The efficiency of the system was dependent on both the microenvironment provided by the support and the supercritical conditions. Particularly, when a hydrophobic monolith, which was prepared through stepwise procedures involving co-polymerization between 4-chlorostyrene and DVB and following quarternerization with *N*-butylimidazole, was assayed at 80 °C and 10 MPa, a total turnover number (TTON) of 35.8×10^4 mol product/mol enzyme was obtained.

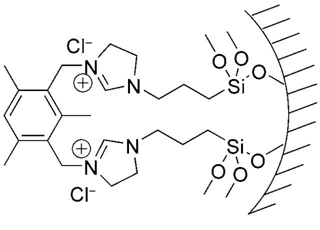
4 Metal Nanocatalysts with ILs

Catalysis with metal nanoparticles has gained considerable attention in the past two decades. Catalytic activities of metal nanoparticles have been shown to depend strongly on the size of nanoparticles, surface properties, and sometimes, the metal oxidation states.[58] One of the problems of metal nanoparticle catalysts is the difficulty of stabilizing particles in a narrow size range while retaining sufficient catalytic activity. In order to obtain an active and stable nanometal catalyst, much effort has been made in searching a suitable stabilizer, or in other words, protector. However, as mentioned by Prof. Y. Kou, Beijing University, 'no matter what a stabilization strategy is considered, the balance between the activity and the stability of the nanoparticles rather than their stability is necessarily the aim of catalysis',[59] the key in this field, thus, is to find an effective way for controlling such a balance. Preparation of metal nanoparticles in ILs has been extensively discussed in many early reviews[60] since the first observation of Dupont's group in 2002.[61] Advantages of ILs in this field are (i) the driving forces for nanoparticle aggregation are much lower in ILs, therefore, the metal nanoparticles could be stabilized, to some extent, with or without the use of additives;[62] and (ii) simultaneous use of metal nanoparticles as well as IL solvent offers a multiphase system, which allows an easy recovery and reuse of the metal nanoparticles catalyst. Despite the appealing features, the argument about the effects of ILs on catalysis with metal nanoparticles still exist because a recent report showed that it is also possible to poison the catalytic activities of Ir nanoparticles for the hydrogenation of acetone with [BMIm]PF_6.[63] Up to now, the most of metal nanoparticles prepared in ILs were used as catalysts either for C–C coupling reactions such as, Heck, Suzuki and Sonogashira reactions, or hydrogenations of aromatic rings, double bonds and carbonyl groups. In spite of good (and sometimes promising) results, from the viewpoint of practical synthesis, the use of solid catalyst is still preferred because of the inherent convenience for work-up procedure. In this respect, a new strategy was developed in this area, that is, the preparation of solid-supported metal nanoparticles using ILs. The IL here not only acts as a stabilizer, but also plays a crucial role for the immobilization. In this section, advances both on synthesis of metal nanoparticles in ILs and on the immobilization of metal nanopartiles onto solid supports are summarized, and the most of them are new results that emerged after 2006.

4.1 Pd Nanoparticles

Among different metal nanocatalysts, Pd nanoparticles have gained a high reputation. This is because Pd is a versatile catalyst in modern organic synthesis. There have been many efforts to immobilize Pd nanoparticles on suitable support surfaces with ILs.[64] For example, a weakly basic IL, TMGL, has been used by Han's group[65] for the immobilization of Pd nanoparticles onto an acidic support, molecular sieve. The obtained Pd nanoparticles are highly active and stable for the hydrogenation of benzene. Recently, an analogous method was again applied to the preparation of SBA-15-supported Pd nanoparticles, which showed an excellent catalytic activity for Heck reactions under solvent-free conditions, by means of TMGL.[66] It is easy to separate the supported catalyst from the reaction mixture and this catalyst can be reused at least 6 times without considerable deactivation. Importantly, the cations of the IL were proved to be necessary for the excellent stability of the catalyst. In addition, control experiments about the mechanism of the catalysis showed that the support acts merely as a reservoir for a more active soluble form of Pd. A natural porous material, sepiolite, was also used, recently, as the support for the immobilization of Pd^{2+} salts with the aid of an IL, 1,1,3,3-tetramethylguanidinium trifluoroacetic acid ([TMG]TFA). The following reduction with hydrogen at 150 °C resulted in the formation of Pd nanoparticles, which existed in a size range of about 5 nm. The obtained sepiolite-IL-Pd showed a very high efficiency for the hydrogenations of some alkenes (e.g., cyclohexene and 1,3-cyclohexadiene) and Heck reactions.[67]

Pd nanoparticles could also be prepared in an *in situ* manner during their catalytic use with the aid of ILs. This strategy is very convenient, especially with the use of an IL-grafted silica-based material as support. For example, Enders and his co-workers[68] prepared silica-supported Pd(II) salts by means of a stepwise procedure involving (i) incorporation of a Pd salt with a 1-*N*-[3-(trimethoxysilyl)]propyl-3-methylimidazolium chloride IL, and (ii) grafting of the generated dialkylimidazolium IL onto silica. The obtained materials are highly active (TTON = 33600) for Heck coupling reaction between bromobenzene and methyl acrylate. Importantly, Pd nanoparticles, which have an irregular shape and a wide-size distribution (10–40 nm), were formed after the reaction in the surface of silica materials. As a typical case of a solid catalyst, the supported Pd nanoparticles could be reused smoothly in the next runs.[68] Recently, Qiao and his co-workers[69] also reported an analogous method to immobilize Pd nanoparticles using an imidazolium salt-modified silica as support. The obtained Pd nanoparticles on SiO_2-IL not only showed excellent activity and selectivity for the hydrogenation of cinnamaldehdye to hydrocinnamaldehdye, but also could be recycled successfully without either leaching of Pd species or loss of catalytic activity. A more complex disilylated dihydroimidazolium salt-functionalized mesoporous material showed relatively higher activity for the Suzuki reaction compared with both Enders's and Qiao's SiO_2-IL-Pd catalysts, because of the fact that it even works for the reaction of less reactive aryl chlorides (Scheme 11).[70] Similar to the previous reports, *in situ* formation of Pd nanoparticles in recycling experiments was also observed. Although the recycling of Pd nanoparticle catalysts is not perfect in view of the moderate yields obtained in the reuse experiments, here, both the inorganic matrix and the organic moiety of the hybrid materials make contributions to the nanoparticle stabilization. The dihydroimidazolium salts should also facilitate a good dispersion of metal nanoparticles in the material. The struc-

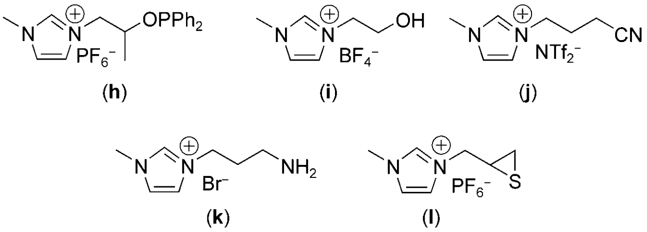


Scheme 11. Disilylated dihydroimidazolium salt-functionalized mesoporous material.

ture and high porosity of the materials should facilitate the diffusion of reactants, and surely the structure of the organic ligand presented in the hybrid material is more important for its catalytic activity and recyclability.

The *in situ* generation of Pd nanoparticles has been observed in immobilized Pd(II) salt-catalyzed Suzuki reactions by using diethylaminopropylated alumina[71] or dialkylimidazolium salt-grafted SBA-15[72] as support. Like the cases in the above-mentioned reports, owing to the presence of IL fragments in the surface of support, the formed Pd nanoparticles were dispersed very well in the pores or channels of the support materials, and consequently, high activity and good recyclability were obtained for Suzuki reactions between aryl halides with arylboronic acids. In addition, the *in situ* formation of Pd nanoparticles could also be extended to carbonylations of aryl halides catalyzed by the activated carbon-supported [BMIm]BF_4/Pd$(OAc)_2$-TPPTs system.[73]

In search of another heterogenization method with IL for Pd nanoparticles, a phosphorylated imidazolium salt [(**h**), Scheme 12], was synthesized and utilized as both a complexing and reducing agent for Pd(II) in a xerogel.[74] In this case, the IL-doped xerogel was deposited on a glass slide by immersion of the glass into the gel for a very short time (15 s). Highly dispersed, uniformly sized Pd nanocatalysts (average size = 70 nm), which are tightly supported on the surface of the silica and not embedded in the bulk of the xerogel, were obtained by contact of the phosphorylated IL-modified xerogel with a solution of palladium acetate. Control experiments revealed that the presence of the imidazolium cation is very important. This is due perhaps to the worm-like self-assemblies of the neighboring imidazolium rings in sol-gel matrices through π-π stacking interactions.[75] The obtained Pd nanoparticles were found to be highly active, recyclable, and stable catalysts for Suzuki and Heck coupling reactions in both organic solvents and water. The high catalytic capacity of the Pd nanoparticles was also demonstrated in a chemiluminescent reaction of lumigen PS-atto and H_2O_2. Note that the Pd nanoparticles catalysts can be used several times without a significant loss of its catalytic activity in both Suzuki and the chemiluminescent reactions.



Scheme 12. Some functionalized ILs applied to the preparation of metal nanoparticles.

Lee and his co-workers[76] reported that multi-walled carbon nanotubes (MWCNTs) covalently functionalized by imidazolium bromide exhibited preferential solubility in ILs as compared to water and/or organic solvents. It should be noted that CNTs have an extremely low solubility in IL, and as a result, it is hard to prepare CNTs-supported metal nanoparticles in IL. Encouraged by this result, Pd nanoparticles have been recently deposited, by Lee's group, onto these IL-modified MWCNTs through hydrogen reduction of Na_2PdCl_4 in water without the aid of surfactants.[77] By changing the counteranion of the IL to the hydrophobic NTf_2^- or SbF_6^- from the hydrophilic Br^-, the dispersion of the MWCNTs-IL support in water could be varied, to some extent, without changing the size or distribution of the Pd nanoparticles (Figure 4). Especially, it was found that the MWCNTs-IL-Pd having the SbF_6 anion preferentially dispersed in [BMIm]SbF_6 over water and *i*-PrOH. Making use of this advantage, a combination of the MWCNTs-IL-Pd with [BMIm]SbF_6 created a new recyclable IL-based catalytic system, which allowed up to 50 times recycling in the hydrogenation of *trans*-stilbene.[77] This elegant method to use IL not only utilizes the beneficial effect of imidazolium salts on the stabilization of metal nanoparticles but also stems from the ease in the manipulation of their physical properties by tuning of the counteranions of ILs, thus this can be one of the best examples to maximize the sufficient use of all the functions of ILs in heterogeneous catalysis.

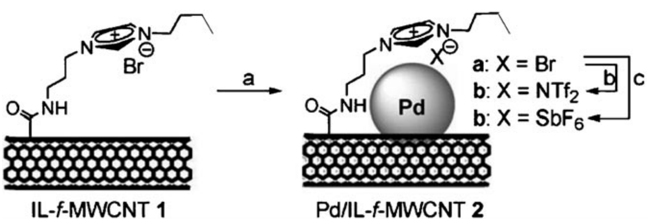


Figure 4. Synthesis of Pd nanoparticles supported on IL-functionalized MWCNs in water (from Y. S. Chun, J. Y. Shin, C. E. Song, S.-G. Lee, *Chem. Commun.* **2008**, 942–944.[77] Reproduced by permission of the The Royal Society of Chemistry. http://dx.doi.org.10.1039/b715463a).

Furthermore, on the structured CNF/SMF composites, monodispersed Pd nanoparticles were synthesized using 1-(2-hydroxyethyl)-3-methylimidazolium *N*-bis(trifluoromethanesulfonyl)imidate [HOC_2MIm] NTf_2) by the simple heating of Pd$(acac)_2$ in the absence of additional reducing agent. The obtained supported Pd nanoparticles with an IL phase showed good selectivity and excellent long-term stability for the hydrogenation of acetylene to ethylene in a continuous-flow tubular reactor.[78] The unique solubility of IL which allows an equilibrium in favor of the substrate acetylene, but not of the product ethylene, might be mainly responsible for this improvement of selectivity. The cation-anion network of IL surrounding the Pd nanoparticles might ensure the isolation of the active site, thus making the catalyst very stable. An analogous selective hydrogenation of conjugated diene has also been investigated by using other supported IL systems in conjunction with Pd nanoparticles as catalyst.[79] Another carbon-based support, mesoporous hydrophilized soot, has also been examined as support material of Pd species, and the formed supported Pd nanoparticles can be used in IL as catalyst for the Heck reaction between aryl bromides and styrene.[80]

Another way to support Pd nanoparticles onto a solid using IL is to use polymeric material, which contains monomers functionalized by an IL fragment, as support. For example, a co-polymer of styrene and 3-butyl-1-vinylimidazolium chloride ([BVIm]Cl), is capable of entrapping Pd salts in ethanol. Simultaneous alcoholic reduction leads to the formation of Pd nanoparticles, that were then immobilized by the polymer matrix. These materials showed good catalytic activity and recyclability for Heck reactions in water in the absence of a phase-transfer co-catalyst.[81] A structurally active carbon cloth (ACC) has also been used as support for the immobilization of Pd nanoparticles in conjunction with the use of ILs as stabilizers.[82] Testing of these materials as catalysts for the hydrogenation of citral showed that they are active and stable for the model reaction with the activity being determined by the structure and loading of ILs.[83] The reaction rate can be enhanced by coating of a very small amount of IL.[84] Furthermore, the selectivity profile could be altered by applying different ILs in which the same Pd species was dissolved (Figure 5).[85]

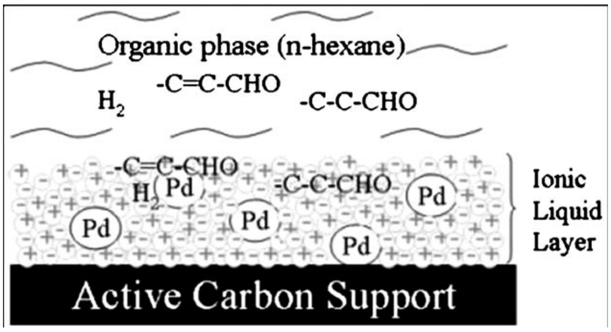


Figure 5. Diagram showing a supported IL catalyst used in the hydrogenation of citral (from P. Virtanen, J.-P. Mikkola, T. Salmi, *Ind. Eng. Chem. Res.* **2007**, *46*, 9022–9031; DOI: 10.1021/ie0707467.[84] Reproduced by permission of the American Chemical Society).

Besides immobilization of Pd nanoparticles on solids, another use of ILs for catalysis with Pd nanoparticles is to act as solvent for the preparation of Pd nanoparticles which were then used in some organic reactions.[86,87] Although it is well established that ILs are able to stabilize metal nanoparticles, functionalized ILs and ionic polymer additives have to be used in most cases in order to maximize the activity and stability. For example, quite recently, highly stable Pd nanoparticles in a hydroxy-functionalized IL, [HO-C_2MIm]BF_4 [(**i**), Scheme 12], were prepared by means of using a charged PAMAM dendrimer as encapsulating template, which could maintain hydrogenation efficiency for up to 12 recycles in the conversion of styrene to ethylbenzene.[88] The IL here not only acts as a convenient medium for the catalyst recycling, but also plays a key role in dissolving the charged PAMAM dendrimer-Pd catalyst. Characteristic studies by TEM and capillary electrophoresis (CE) clearly demonstrated that Pd nanoparticles resided in the dendrimer interior before and after the catalytic runs. One of the underlying forces for such a high stability of Pd nanoparticles is probably the repulsive interaction between the charged PAMAM dendrimers, which could be achieved by means of saponification of the corresponding ester derivatives under weak basic conditions (Figure 6).

Recently, Dyson prepared an imidazolium-based ionic polymer [IP (**m**), Scheme 13] which can be used as co-protector for the synthesis of Pd nanoparticles in IL. Particularly, the combination of Dyson's IP and

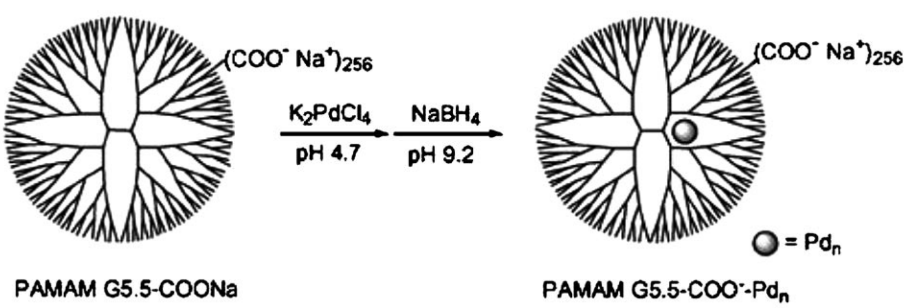
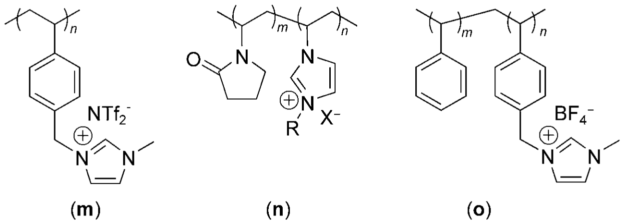


Figure 6. Formation of carboxylate-terminated PAMAM G5.5-COO^- encapsulated Pd nanoparticles (Pd DENs) (from G. Ou, L. Xu, B. He, Y. Yuan, *Chem. Commun.* **2008**, 4210–4212.[88] Reproduced by permission of the The Royal Society of Chemistry. http://dx.doi.org.10.1039/b806163).



Scheme 13. Some co-polymers applied to the synthesis of solid catalysts with ILs.

a CN-functionalized IL (**j**) (Scheme 12) proved to be an effective means for Pd nanoparticles to achieve an optimum balance between stability and reactivity. The obtained Pd nanoparticles have an average size about 5.0±0.2 nm, and were found to be excellent precatalysts for Suzuki, Heck, and Stille coupling reactions and can be stored without undergoing degradation for at least two years.[89] Furthermore, the Pd nanoparticles in the [CN-PMIm]NTf_2-IP (**m**) system could be recycled at least five times without a significant loss of activity in the Stlle reaction between tributylvinylstannane and iodobenzene.

Metal nanoparticles in IL also involve a new trend in which tetraalkylammonium salts were used instead of imidazolium-based ILs as solvents. In fact, the use of TBAB as solvent for catalysis with Pd nanoparticles was widely explored a few years ago.[90] From those pioneering studies, the advantages of using tetraalkylammonium salts as solvents, such as good stability and avoidance of co-protectors, were discovered. Encouraged by these advantageous features, much effort has been made to develop new chemistry about Pd nanoparticles in tetraalkylammonium salts. For instance, an efficient Pd(0) colloid-catalyzed Ullmann-type reductive homocoupling of aryl, vinyl and heteroaryl halides, which generates symmetrical biaryls, can be promoted by an aldehyde in tetraalkylammonium ILs under very mild reaction conditions.[91] The IL is crucial for this process because it behaves simultaneously as a base, ligand and reaction medium. Hydrodehalogenation of aryl chlorides in molten tetrabutylammonium bromide catalyzed by Pd nanoparticles has also been reported using tetrabutylammonium acetate as the base under hydrogen at atmospheric pressure.[92]

4.2 Rh Nanoparticles

Rh nanoparticles are widely used as catalysts for various hydrogenations. In order to achieve a satisfactory balance between stability and activity, co-protectors such as polymers and ligands have to be used during the synthesis of Rh nanoparticles. One of the most commonly used co-protectors is polyvinylpyrrolidone (PVP). Unfortunately, despite the good capacities observed in water or alcohols, the poor solubility of PVP in common ILs, such as [BMIm] PF_6 and [BMIm] BF_4, restricts its applications in these ILs. To address this issue, two strategies have been proposed. First, by developing a functionalized IL which is capable of dissolving PVP. This way has just been successfully realized by Dyson,[93] who prepared highly stable and active Rh nanoparticles for styrene hydrogenation using PVP as stabilizer in a hydroxy-functionalized imidazolium IL, [HOC_2MIm] BF_4 [(**i**), Scheme 12]. While PVP is readily soluble in [HOC_2MIm] BF_4 (>5%), less than 0.5% of PVP is dissolvable in 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm] BF_4). This unique solubility makes [HOC_2MIm]BF_4 a suitable medium for the synthesis of Rh nanoparticles in conjunction with the use of PVP as costabilizer (Figure 7). Because of the intrinsic immiscibility between [HOC_2MIm]BF_4 and the product, ethylbenzene, the Rh nanoparticle-IL system could be easily recovered, and its stability was also demonstrated to be reliable.

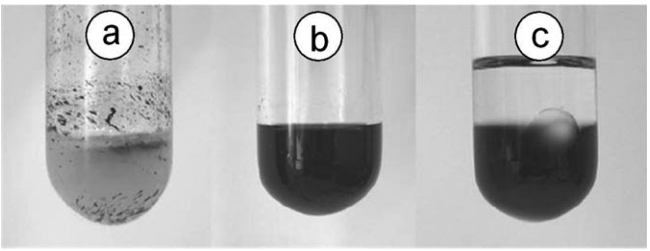
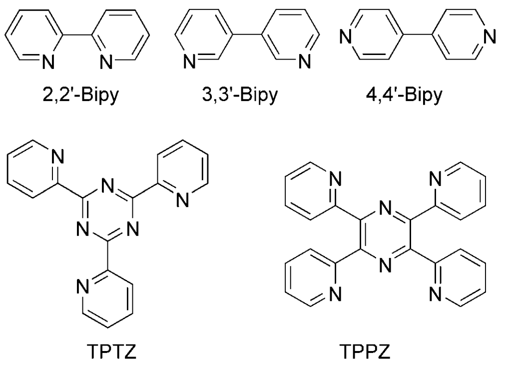


Figure 7. Photographs of Rh nanoparticles dispersed in (**a**) [EMIm]BF_4, (**b**) [HOEMIm]BF_4, and (**c**) [HOEMIm]BF_4 after hydrogenation of styrene (from X. Yang, N. Yan, Z. Fei, R. M. Crespo-Quesada, G. Laurenczy, L. Kiwi-Minsker, Y. Kou, Y. Li, P. J. Dyson, *Inorg. Chem.* **2008**, *47*, 7444–7446.[93] Reproduced by permission of The American Chemical Society).

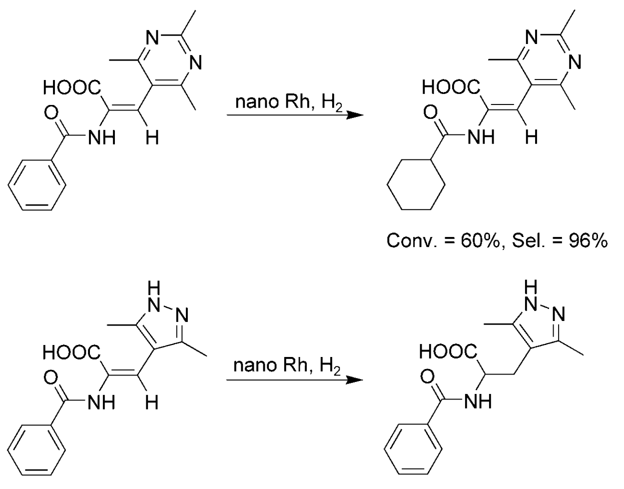
The second strategy is to modify the skeleton of PVP in order to make it soluble in IL. A great success has been achieved in Kou's group, which has prepared an IL-like copolymer, poly(NVP-*co*-[BVIm]Cl) [(**n**), Scheme 13].[94] As already demonstrated, (**n**) is readily soluble in many ILs. Particularly, rhodium nanoparticles protected by the copolymer were shown to catalyze the hydrogenation of benzene with a record total turnover (TTO) of 20,000. Other alkyl-substituted arenes such as phenol, 4-*n*-propylphenol, 4-methoxyphenol, and benzyl alcohol were also investigated, and in the most cases, partial hydrogenation products were obtained in addition to substituted cyclohexanes.[95] Because the Rh nanoparticles can endure comparatively forcing conditions, faster reaction rates and higher conversions were obtained compared with the hydrogenation reactions catalyzed by nanoparticles protected only by imidazolium ILs.

Quite recently, an alternative approach to the above-mentioned polymer-based strategies for preparation of Rh nanoparticles using [BMIm]PF_6 as solvents has been developed by Roucoux,[96] who adopts a simple polynitrogen ligand, 2,2′-bipyridine, as stabilizer and sodium borohydride ($NaBH_4$) as reducing agent for rhodium trichloride. The obtained Rh nanoparticles, which possess a size range around 2.0 nm, can be stored in the air without any agglomeration over several months. In the hydrogenation of styrene, the Rh nanoparticles showed interesting activities and selectivities. A mixture of ethylbenzene and ethylcyclohexane in a ratio of 2/3 could be obtained in [BMIm]PF_6 with 100% of styrene conversion after 15 h reaction at 80 °C in the presence 40 bar H_2 and 1 mol% Rh nanoparticles catalyst. It should be noted that, under the reaction conditions, the hydrogenation of N-donor chelating agents was not observed. Further investigations revealed that steric stabilization effect of 2,2′-bipyridine seems more pronounced in [BMIm]PF_6 compared with its coordination effect for the Rh nanoparticles. In addition, replacing 2,2′-Bipy with 3,3′-Bipy and 4,4′-Bipy further increases the reactivities in the conversions of styrene to ethylcyclohexane (Scheme 14).[97] This can be explained by decreased steric hindrance on the surface of Rh nanoparticles arising from the use of 3,3′-Bipy and 4,4′-Bipy, which might interact with the Rh metal through a monodentate coordination mode. On the basis of these results, it was finally found that a simple monocoordination of the single N-donor ligand, pyridine, is sufficient to increase the activity of Rh nanoparticles without any precipitation in ILs. In order to further increase the catalytic activity and improve the product selectivity to the full hydrogenated product, the same authors applied two commercial and relatively complex polynitrogen ligands, TPTZ and TPPZ, to stabilize Rh nanoparticles that were prepared in [BMIm]PF_6 by reduction (Scheme 14).[98] As expected, compared with the results obtained in the bipyridine systems, a significant selectivity improvement was observed with TPTZ-stabilized Rh nanoparticles under identical conditions while styrene was completely converted. A TEM investigation revealed that the Rh nanoparticles have an average diameter of 4 nm, which is twice that of 2,2′-Bipy-protected particles (2 nm). The selectivity to ethylcyclohexane reached up to 94%. The improvement both on activity and selectivity can be explained by (i) the presence of an additional nitrogen atom in TPTZ, which leads to a more coordinating system in a considered stabilizing pattern; (ii) TPTZ has relatively obvious steric hindrance as compared to 2,2′-Bipy, this could probably lead to an increased access of the substrate to the metal surface because of a decrease in the amount of TPTZ around the nanoparticles.



Scheme 14. Some ligands applied to the stabilization of metal nanoparticles in ILs.

In order to heterogenize Rh nanoparticles onto a solid, some efforts have been made in ILs recently. For example, Rh nanoparticles (*ca.* 4 nm) dispersed in [BMIm]BF_4 could be encapsulated within a silica network by means of the sol-gel method. The obtained heterogeneous Rh nanoparticles can be used as efficient catalysts for the hydrogenation of olefins.[99] It is well known that the presence of compressed CO_2 can, sometimes, significantly alter physicochemical properties of common organic salts, such as depression of melting point. Inspired by these facts, most recently, Parvulescu and Leitner[100] developed an effective method for the preparation of Rh nanoparticles in a biphasic system composed of commonly used organic salts, such as [Bu_4N]Br, [Hex_6N]Br and [Oct_4N]Br, and $scCO_2$. Although the operational temperatures are lower than the standard melting points of these organic salts, the reduction of the Rh complex, [Rh(acac)$(CO)_2$], to Rh nanoparticules can be carried out in the "artificial" IL phase because of a synergistic melting point depression of the organic salts with $scCO_2$. After venting of CO_2, the generated Rh nanoparticles were embedded in a solid phase of organic salts. Benefitting from the stabilizing effect of ammonium salts on metal nanoparticles, the Rh nanoparticles were stable and very active for the hydrogenation of cyclohexene and benzene. Particularly, Rh nanoparticles with small particle size and narrow size distribution (1.4 ± 0.3 nm), which were prepared in [Oct_4N]Br, showed a very high TOF, 35,700 h^{-1}, in the hydrogenation of cyclohexene. It should be emphasized that this method to prepare Rh nanoparticles also presents another advantage concerning the removal of organic by-products generated from the Rh complex, which can be extracted into $scCO_2$ phase, and subsequently brought out from the system. Moreover, the Rh nanoparticles embedded in ammonium salts also exhibited distinctive activity and selectivity for the selective hydrogenation of (*E*)-2-(benzoylamino)-2-propenoic acids, which cannot be achieved by using homogeneous Wilkinson's catalyst and commercial Rh/Al_2O_3 as catalysts (Scheme 15).



Scheme 15. Selective hydrogenation of (*E*)-2-(benzoylamino)-2-propenoic acids.

4.3 Pt Nanoparticles

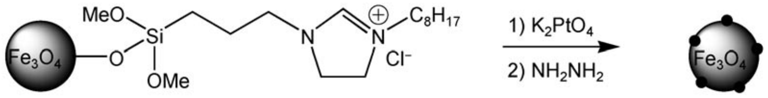
Kou's IL-like copolymer, (**n**) (Scheme 13), is also capable of protecting Pt nanoparticles in [BMIm]BF_4.[59] The Pt nanoparticles obtained by means of reduction with ethylene glycol had average particles sizes of about 1.7 ± 0.4 nm, and exhibited an outstanding activity and selectivity for the hydrogenation of *o*-chloronitrobenzene using [BMIm]BF_4 as solvent. Although the size of the recycled Pt nanoparticles was slightly increased to 2.3 ± 0.4 nm, the activity remained high. Finally, a high TTO of >25,900 was obtained after three cycles of use. It should be noted that [BMIm]BF_4, here, is also important as it is advantageous not only for product separation and catalyst recycling, but also for selectivity improvement.

Alper and his co-workers described a method to support Pt nanoparticles on magnetite nanoparticles by using IL as a key surface modifier.[101] Magnetite-supported ILs play two functions here, (i) absorbing the Pt salt (K_2PtCl_4) onto the surface of magnetite *via* ion exchange and (ii) stabilizing Pt nanoparticles after the reduction of Pt(II) by hydrazine (Scheme 16). The supported Pt nanoparticles were applied to the catalytic hydrogenation of alkynes in which *cis*-alkenes were selectively produced, and in the hydrogenation of α,β-unsaturated aldehydes where the allyl alcohols were obtained as the exclusive products. In the course of the reactions, the Pt-magnetite nanocatalyst could be well dispersed in the medium like a homogeneous species since it is a nano system. After the reactions, the catalyst can be easily separated by applying an external magnetic field and recycled. Therefore, this magnetite-supported Pt nanoparticles catalyst strategically combined the advantages of both homogeneous and heterogeneous catalysts together.

4.4 Ru Nanoparticles

Ru nanoparticles are recognized as powerful catalysts for the oxidation of alcohols or the hydrogenation of unsaturated organic groups. In order to obtain stable, recyclable and active Ru nanoparticles catalysts, much effort has been made to achieve their immobilization onto a solid support. In this context, ILs have also been examined. For example, *nanocrystalline magnesium oxide* (NMO), which is purely ionic and has a three-dimensional polyhedral structure containing high surface concentrations of edge/corner and various exposed crystal planes, has been used to entrap Ru(III) after pretreatment with a basic IL, choline hydroxide (CH).[102] The final Ru nanoparticles were obtained after the following hydrogen treatment. The resulting materials showed good activity, stability and recyclability for the aerobic oxidation of alcohols and the transfer hydrogenation of carbonyl compounds. CH, here, not only acts as a surface functionalizing agent but also stabilizes the metal nanoparticles.[103] This was confirmed by a comparative experiment using NMO-Ru (without CH) as catalyst, in which an extensive leaching of Ru was observed during the catalyst recycling. Another basic IL, [TMG]TFA, is also capable of stabilizing Ru nanoparticles very well in conjunction with the use of a layered material, montmorillonite, as support.[104] The prepared catalyst showed a catalytic activity for the hydrogenation of benzene to cyclohexane that is comparable or superior to that of Ru cluster-based catalysts. The real advantage comes in the recycling of the catalyst, whereby the catalyst kept its original activity for up to five runs. Detailed investigations about the catalysts revealed that a synergistic effect between montmorillonite support and IL [TMG]TFA might be responsible for their high activity and good stability.[105]

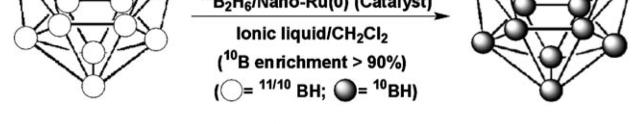
Recently, Dupont and his co-workers[105] prepared well-dispersed Ru nanoparticles, which have narrow size distributions between 2.1 nm and 3.5 nm, in various ILs, including [BMIm] NTf_2, [BMIm] BF_4, [DMIm] NTf_2 [1-*n*-decyl-3-methylimidazolium *N*-bis-(trifluoromethanesulfonyl)imidate] and [DMIm] BF_4, by reduction of [Ru(COD)(2-methylallyl)$_2$] using H_2



Scheme 16. Supporting Pt nanoparticles onto magnetite nanoparticles by using IL as a key surface modifier.

under mild conditions. The Ru nanoparticles in ILs were then used in the liquid-liquid biphasic hydrogenation of arenes, where the Ru nanoparticles obtained in ILs containing the less coordinating anion, NTf_2, were found to be more robust than those from some BF_4-based ILs. Particularly, the catalyst-IL phase can be reused several times without a significant loss in catalytic activity. Kou's IL-like polymer, (**n**), has also been applied to the preparation of Ru nanoparticles, and the obtained Ru catalyst showed an acceptable activity in the hydrogenation of carbon monoxide.[106] Ru nanoparticles could also be prepared by a very simple method based on the *in situ* reduction of a commercially available precursor, ruthenium dioxide, under mild conditions (75 °C and hydrogen pressure 4 atm) in imidazolium ILs.[107] The obtained Ru nanoparticles showed excellent activity in the hydrogenation of arenes, and total turnovers (TTO) of 2,700 Ru^{-1} were obtained for the conversion of benzene to cyclohexane under solvent-free conditions. In order to improve the stability and recyclability of Ru nanoparticles, the authors also conducted the reaction in a biphasic system composed of $[BMIm]PF_6$ and an organic phase. Although the TTO was decreased to 1200 Ru^{-1}, the Ru nanoparticles, here, could be reused up to 17 times, indicating the great stability of $[BMIm]PF_6$.

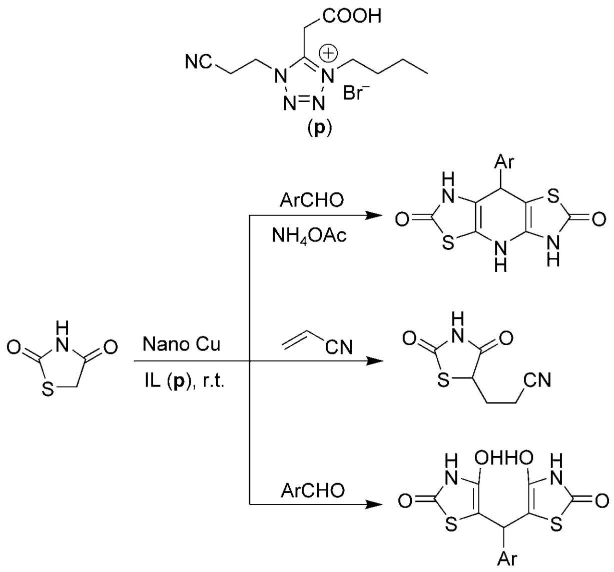
The transfer of ready made Ru nanoparticles into IL phases can be an alternative way for investigating catalysis of Ru nanoparticles with IL. For example, Ru nanoparticles with uniform size (2∼4 nm), which were prepared *via* reduction of [CpRuCp*RuCp*] PF_6 ($Cp^* = C_5Me_5$) in ethylene glycol, have been successfully transferred into an IL, trihexyltetradecylphosphonium dodecylbenzenesulfonate ([THTdP] DBS).[108] The Ru nanoparticles in [THTdP] DBS were found to be capable of catalyzing a novel isotope exchange reaction between ^{10}B-enriched diborane and natural abundant $B_{10}H_{14}$, which produces highly ^{10}B-enriched decaborane(14) product with >90% yield (Scheme 17). It should be noted that this strategy not only represents the first example of a catalytic isotope exchange reaction between ^{10}B-enriched diborane and $B_{10}H_{14}$, but also offers a straightforward route for the synthesis of ^{10}B-enriched decaborane(14) which is highly useful for clinical purposes.



Scheme 17. Catalytic ^{10}B–^{11}B isotope exchange.

4.5 Cu Nanoparticles

A new IL, (**p**), (Scheme 18), has been synthesized and utilized to make Cu nanoparticles starting from $Cu(NO_3)_2$ by treatment with sodium borohydride. The as-prepared Cu nanoparticles were then applied to a series of reactions of thiazolidine-2,4-dione including carba-Michael reactions, condensation between thiazolidine-2,4-dione and aromatic aldehydes and three-component reactions of thiazolidine-2,4-dione, aromatic aldehydes and ammonium acetate (Scheme 18).[109] The Cu nanoparticles as well as the IL could be recycled and reused in these reactions without significant loss of catalytic abilities.



Scheme 18. Functionalized IL and the Cu nanoparticles-catalyzed reactions.

4.6 Au Nanoparticles

An NH_2-functionalized IL, 1-(3-aminopropyl)-3-methylimidazolium bromide ($[NH_2$-PMIm] Br, (**k**), Scheme 12), was applied, by Niu and his co-workers, to simultaneously reduce aqueous $HAuCl_4$ and stabilize the resulting gold nanoparticles. With this method, Au nanoparticles with an average diameter of 1.7 nm were obtained, which exhibited good long-term stability.[110] The authors suspect that two factors are essential to form such Au nanoparticles with small sizes: (i) in the presence of the IL, only weak Ostwald ripening occurs, which is mainly responsible for the formation of Au nanoparticles with very small size; (ii) interaction between the NH_2 group of the IL and Au nanoparticles also plays a crucial role in controlling the size and structure of the Au nanoparticles because of the fact that no reduction occurs using a commonly used IL, [BMIm] BF_4, instead of the functionalized IL (**k**).

These IL (**k**) stabilized Au nanoparticles showed better electrocatalytic activity in the reduction of oxygen than similarly prepared Au nanoparticles stabilized by thiol or citrate. While oxygen reduction began at a potential of 0.28 V with an electrode functionalized by Au-IL (**k**), the same reduction began at potentials of −0.51 V and −0.26 V using electrodes functionalized by Au-thiol and Au-citrate, respectively, under the same conditions. Because of the fact that the particle sizes of all Au-IL (**k**), Au-SH and Au-cit are quite similar, the clear difference observed in oxygen reduction indicates that the type of stabilizing group contributes strongly to the catalytic activity. Here, some properties of IL (**k**), such as high conductivity and weak interaction between Au(0) and N, might play a key role in improving the electrocatalytic performance of Au nanoparticles. A thioether-functionalized IL [(**l**), Scheme 12] has been applied to synthesize and stabilize Au nanoparticles in conjunction with the use of [BMIm]PF_6 as solvent. The formed Au nanoparticles possess small and uniform particle sizes ranging from 2.0 nm to 3.6 nm, and exhibit mild activity in the epoxidation of styrene using 3-chloroperoxybenzoic acid as oxidant.[111]

4.7 Ir Nanoparticles

Ir nanoparticles in ILs have been investigated at the very beginning of the studies on metal nanoparticles chemistry with ILs.[112] Recently, a novel IL, trihexyltetradecylphosphonium methanesulfonate ([THTdP][MS]), has been used to stabilize Ir nanoparticles which were prepared by reduction of a precursor hydridoiridium carborane, $(Ph_3P)_2Ir(H)$-(7,8-*nido*-$C_2B_9H_{11}$) (Figure 8). In the presence of auxiliary ligands or bases, the Ir nanoparticles were found to be active catalysts for the C–H borylation of arenes by pinacol borane (HBpin), forming boric acids (Scheme 19). Particularly, a highest yield of 91% was achieved with a TOF of 151.7 h^{-1} in a microwave reactor using a base, tetra(2-pyridinyl)pyrazine, in the presence of [THTdP][MS]. Although the Ir nanoparticle catalyst system is not so effective as homogeneous catalysts as, e.g., the $[Ir(cod)Cl]_2$/2,2′-bipyridine (bipy) system, it has the advantage of being recyclable; the Ir nanoparticle catalyst was reused more than 6 times with less than 0.5% loss of activity.[113]

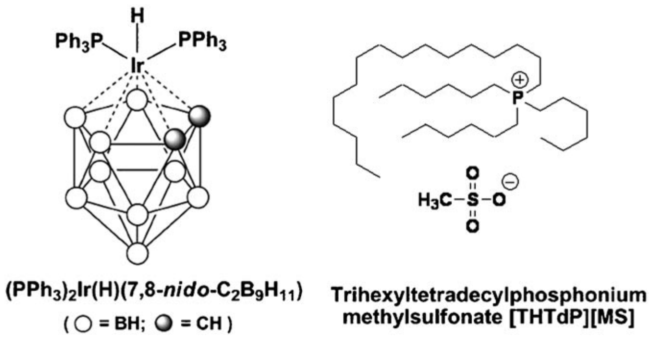
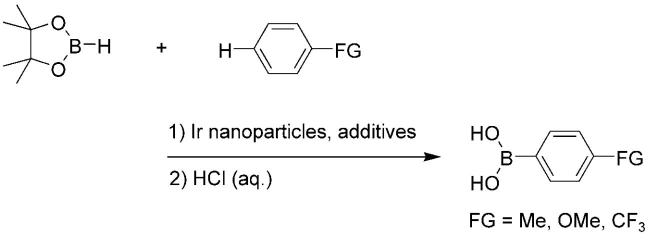


Figure 8. Structures of Ir precursor and used IL (from Z. Yinghuai, K. Chenyan, A. T. Peng, A. Emi, W. Monalisa, L. K.-J. Louis, N. S. Hosmane, J. A. Maguire, *Inorg. Chem.* **2008**, *47*, 5756–5761.[113] Reproduced by permission of The American Chemical Society).



Scheme 19. Ir nanoparticles-catalyzed C–H borylation of arenes by Hbpin.

ILs in catalysis are not always innocent to the catalytic mechanism, and sometimes, paricipate into the catalytic cycles. A recent example clearly demonstrated this possibility. In deuterated imidazolium ILs ([BMI-d_3]NTf_2), D/H exchange reactions at C-2, C-4 and C-5 of the imidazolium cation were observed in the hydrogenation of cyclohexene promoted by classical Ir(I) colloid precursors and Ir nanoparticles. Interestingly, no D/H exchange reaction was observed in the same reaction by Ir bulk metal dispersed in [BMI-d_3] NTf_2.[114] These results suggested that carbene species in this IL participated into the catalytic reaction when the Ir aggregate was used as catalysts.

4.8 Ag Nanoparticles

The controlled synthesis of defined and stable Ag nanoparticles, which are very important catalysts for epoxidation of olefin, is of crucial importance. The syntheses of Ag nanoparticles from AgX_n salts with hydrogen suffer from the formation of the strong acid HX (X = Cl, NO_3, BF_4, PF_6, CF_3SO_3), which leads to an acidic reaction medium and destabilizes the nanoparticles. Recently, Janiak and his co-workers presented an elegant method, which involves the use of *N*-butylimidazole as scavenger and [BMIm] BF_4 as solvent, for the preparation of Ag nanoparticles with a narrow size distribution by reduction with H_2 (Figure 9). Importantly, the size of formed Ag nanoparticles increases linearly with increase of the molec-

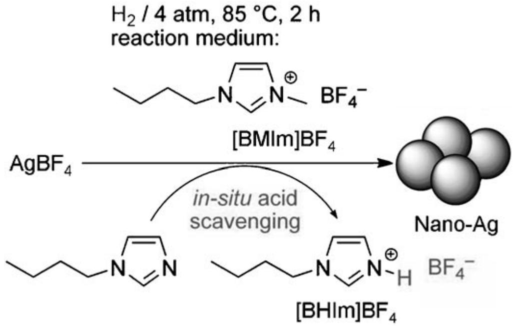


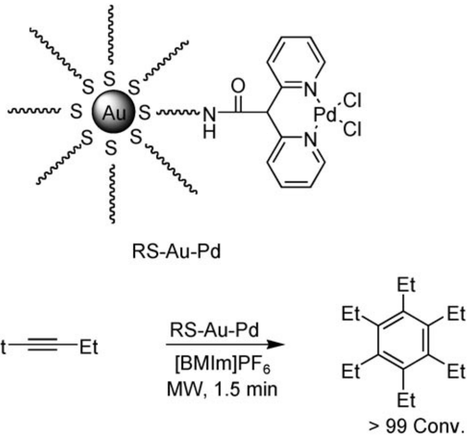
Figure 9. Formation and stabilization of Ag nanoparticles by H_2 reduction of $AgBF_4$ using *N*-butylimidazole as scavenger (from E. Redel, R. Thomann, C. Janiak, *Inorg. Chem.* **2008**, *47*, 14–16. [115] Reproduced by permission of The American Chemical Society).

ular volume of the IL anion, indicating the potential ability of ILs to tune the size of Ag nanoparticles.[115]

4.9 Bimetallic Nanoparticles

Catalysis with bimetallic nanoparticles is also of great interest as the particle size, composition and structure can offer the ability to tune the activity, and also in many cases, the selectivity of catalysts. Scott et al. found that although the IL [BMIm] PF_6 is not a good solvent for the preparation of bimetallic nanoparticles, it did prove to be a good carrier for ready-made PVP-stabilized Au-Pd bimetallic nanoparticles in methanol.[116] Phase transfer of the nanometal particles from methanol to [BMIm] PF_6 did not cause a significant change in the particle size. Subsequent tests on their catalytic activity in hydrogenations of allylic alcohol, *trans*-cinnamaldehyde and 3-hexyn-1-ol showed that both activity and selectivity of the reactions could be tuned by varying the composition of the bimetallic particles. While nanoparticles with high Pd loadings exhibited the highest activity, pure Au nanoparticles showed no activity at all. Although water was also found to play the same role as that of IL, the real advantage of IL system comes in recycling of the catalyst. Owing to the negligible volatility of the IL, unreacted substrates and products could be easily removed from the IL phase under reduced pressure. The recovered catalyst solution showed only a very little change in catalytic activity in the next run.[117]

Metal nanoparticles could also be used as supports of organometallic complexes to form inorganic/organic hydrid metal nanoparticles for catalysis in ILs. Owing to the high surface area and unique solubility in homogeneous solutions of nanoparticle supports, the obtained immobilized bimetallic nanocatalysts are normally characterized by competitive activity with the corresponding homogeneous counterparts and easy recycling. A recent example is the immobilization of palladium(II) complexes, by means of chelation of the surface-bound dipyridyl groups, onto gold nanoparticles which are stabilized with octanethiolate and have core diameters of 3.9–4.7 nm (Scheme 20).[118] These Au NPs-bound interphase Pd(II) species were demonstrated to be highly effective catalysts, in [BMIm]PF_6 under microwave irradiation conditions, for [2+2+2] alkyne cyclotrimerization reactions to give highly congested benzene rings with fairly good selectivity.



Scheme 20. An Au NPs-bound interphase Pd(II) catalyst and its use in cyclotrimerization reactions of alkynes.

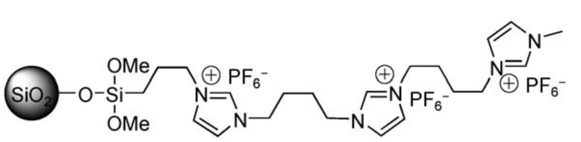
4.10 Other Metal Nanoparticles

The preparation of Ni nanoparticles in ILs was explored by a few groups in order to check whether ILs can improve the performance or not.[119] As expected, Ni nanoparticles prepared in [BMIm]PF_6 showed not only good stability but also relatively high activity in the hydrogenation of styrene to ethylbenzene compared with those prepared in water.[120]

5 Catalysis over Supported Metal Complexes through ILs

Anchoring of cations of IL onto a solid material offered an attractive opportunity to researchers for immobilizations of metal-containing anionic species by means of replacing the counteranions. This method is very useful because of the fact that there are many anionic metal-containing catalysts in practical synthesis. For example, perruthenates and polyoxometalates are active for the oxidation of hydrocarbons; some of chloroaluminates and chloroferrates are Lewis acids that can catalyze many organic transformations. Although this strategy is not new, it has attracted much attention because of the ease of design and high efficiency. One of the recent examples is the immobilization of the perruthenate anion with a silica-supported imidazolium IL.[121] The resulting materials are capable of catalyzing the aerobic oxidation of alcohols in conjunction with the use of $scCO_2$ as reaction medium. The reaction rate is very high and the corresponding rate constant, obtained from integrated pseudo-first order plots, is $k = 2.87 \times 10^{-2}\,\text{min}^{-1}$. This ultrafast reaction rate addresses, thus, the problem posed by the low efficiency (TOF) of many Ru-based catalysts. $scCO_2$ might play a key role in the mass transport of substrates and products during the reaction, because it is able to dissolve both the alcoholic substrate and O_2, thus, by contacting with the the powdered sol-gel entrapped catalyst, it spills the reactants into the pores where the oxidative dehydrogenation takes place. After the reaction, $scCO_2$ can also extract the products away from the pore surface (Figure 10). It should be noted that IL fragments, here, not only act as a key linker for the immobilization of RuO_4^-, but also play the role of a solubilizing agent to accelerate substrate/product dissolution and thus the reaction rate.

With an analogous electrostatic attachment strategy, immobilizations of polyoxometalate anions have also been explored.[122] Many catalysts containing anions such as $[W_2O_3(O_2)_4]^{2-}$, $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ and $[PMo_{10}V_2O_{40}]^{5-}$, have been prepared by using an imidazolium-grafted silica or resin as supports, and the obtained materials were examined in the selective oxidation of sulfide to sulfoxides and sulfones or of alcohols to carbonyl compounds in conjunction with the use of H_2O_2 as oxidant.[123,124] The activities and product selectivities were generally comparable to those of the homogeneous analogues, demonstrating that the homogeneous catalysis could be heterogenized successfully. The good catalytic performance and ease of catalyst recovery and reuse raise the prospect of using this strategy for immobilizations of homogeneous oxidation catalysts.[125] In order to improve the catalyst loading, Wei and his co-workers[126] developed a novel SiO_2-IL that contains three covalently bonded imidazolium cations in a single site of the SiO_2 surface (Scheme 21). Treatment of Wei's SiO_2-IL with $K_2[(W(=O)(O_2)(H_2O))_2(\mu\text{-}O)]\cdot 2H_2O$ in water generated a solid material, which can be used as an efficient catalyst for the dihydroxylation of olefins.



Scheme 21. SiO_2-immobilized IL with multilayers.

Another example related to this strategy is the immobilization of a typical catalyst for the dihydroxylation of olefins, osimium tetraoxide (OsO_4^{2-}), onto an imidazolium-grafted polystyrene resin.[127] Different with previous silica supports, OsO_4^{2-} species only existed in the surface of polymer. The dihydroxylation of olefins proceeded very well over this polymer-IL-OsO_4 system in the presence of *N*-methylmorpholine *N*-oxide (NMO, a co-oxidant). The catalyst was proved to be recoverable and reusable, but unfortunately, with a slight leaching of Os species.

Silica or resin-immobilized dialkylimidazolium chloride ILs have been used to incorporate $AlCl_3$ and

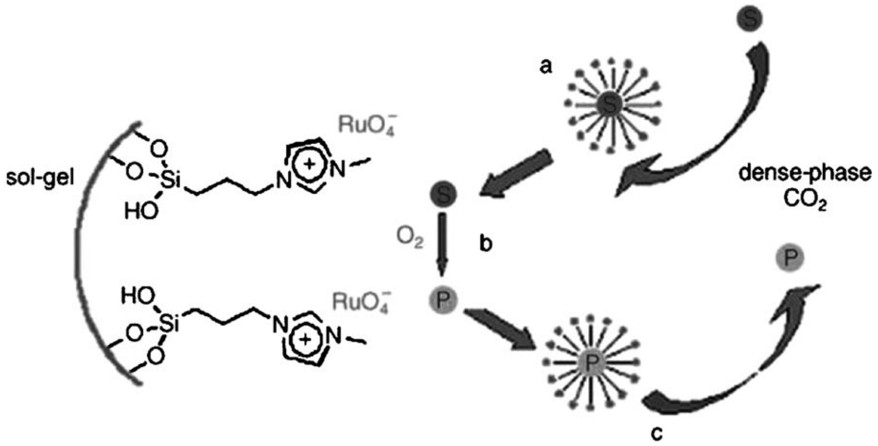
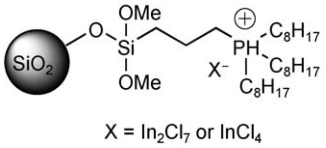


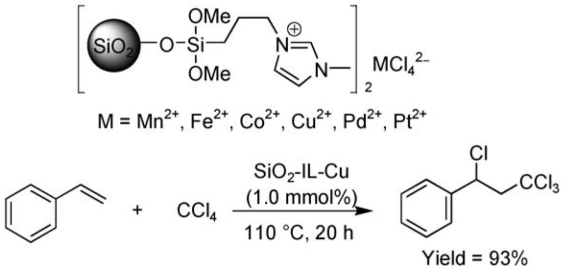
Figure 10. Illustration of the transport, reaction, and adsorption/desorption steps of the oxidation process. The dense phase CO_2 dissolving the substrate (**a**) spills its content into the catalyst tethered to the IL moiety where (**b**) the catalytic process takes place. Then, (**c**) the highly diffusible dense phase CO_2 carries the product back into solution (from R. Ciriminna, P. Hesemann, J. J. E. Moreau, M. Carraro, S. Campestrini, M. Pagliaro, *Chem. Eur. J.* **2006**, *12*, 5220–5224.[121] Reproduced by permission of Wiley-VCH and the authors).

$FeCl_3$ which can act as Lewis acid catalysts for many organic reactions, such as Friedel–Crafts acylation and alkylation reactions,[128] Diels–Alder addition,[129] and ring-opening of propylene oxide with methanol to form propylene glycol methyl ether.[130] By employing these solid-supported catalysts in organic reactions, it is expected that the neutralization procedure and the consequent formation of waste by-products rising from the use of homogeneous Lewis acid catalyst can be avoided. These advantages have been fully represented in a recent report in which an $FeCl_3$-based-IL was immobilized on mesoporous silica of the MCM-41 type *via* a two-step process involving the synthesis of 1-trimethoxysilylpropyl-3-methylimidazolium chloride-$FeCl_3$ and the subsequent grafting of the IL onto siliceous MCM-41.[131] In comparison with the homogeneous counterpart, [BMIm]Cl-$FeCl_3$, the obtained catalyst showed a much higher efficiency in the Friedel–Crafts benzylation reaction. More importantly, such an immobilized IL could be reused without a significant loss of catalytic activity. Another advantage of this method is that the catalytic activities of these solids can be tuned, to some extent, by means of controlling the ratio of metal to imidazolium cation. It is particularly important in the case of a reaction sensitive to the strength of the acid, for example, the liquid-phase *tert*-butylation of phenol with isobutene. This has been particularly elucidated recently by means of using a covalently grafted silica with a phosphonium IL which uses $InCl_3$ as precursor of the anion, as the catalyst (Scheme 22).[132] With the aid of an FT-IR analysis using pyridine as probe molecule, it was found that the In-IL modified silica [In-IL(Phos)/SiO_2] material behaves like a pure Lewis solid acid, and that the acidity increased with an increase of temperature. In the liquid-phase *tert*-butylation of phenol with isobutene, this solid showed, at maximum, a phenol conversion of about 80% with 60% selectivity to the di-*tert*-butylated product, 2,4-di-*tert*-butylphenol (2,4-DTBP). ICP-AES analysis of the solid proved a molar ratio P/In = 1:1.8 suggesting the formation of polymetallic species that should be mainly responsible for the Lewis acidity. The use of In-IL(Phos)/SiO_2 for a second reaction cycle provided almost similar rates of product accumulation in the reaction mixture as were seen in the first cycle, demonstrating the good recyclability of the catalyst.



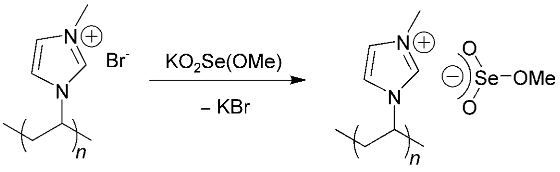
Scheme 22. In-IL(Phos)/SiO_2.

A silica-immobilized nickel-containing IL, SiO_2-$[MIm]_2$ $[NiCl_4]$, was found to be an efficient catalyst for Suzuki cross-coupling reactions between aryl chlorides and arylboronic acids. In this system, pretreatment of the catalyst with base and addition of triphenylphosphine to the reaction system are crucial. Furthermore, SiO_2-$[MIm]_2$ $[NiCl_4]$ was reusable, albeit with a slightly decreased yield, whereas the homogeneous counterpart bis(1-*n*-butyl-3-methyl-imidazolium) tetrachloronickelate ($[BMIm]_2$ $[NiCl_4]$) is difficult to separate from the reaction products.[133] Recently, the Kharasch addition reaction of tetrachloromethane to styrene has also been studied using a series of metal salts which were incorporated with imidazolium-grafted silica materials as the counteranions. Among all the salts screened, Cu(II)-integrated silica-IL showed the best result for the model reaction (Scheme 23).[134]



Scheme 23. Kharasch addition reaction of tetrachloromethane to styrene over SiO_2-IL catalysts.

Ionic polymers derived from 1-methyl-3-vinylimidazolium bromide ([MVIm]Br) and 1-ethyl-3-vinylimidazolium bromide ([EVIm]Br) have been utilized to ionically incorporate the methylselenite anion (Scheme 24). These polymer-supported heterogeneous catalysts exhibited a reasonably high activity for the oxidative carbonylation of aniline. Unfortunately, the catalyst recycling showed that selenite leaching, which is detrimental for practical applications, was observed although the supported catalyst can be reused at least five times.[135] On the other hand, IL-embedded silica has also been used to immobilize an analogous methylselenite species, and the formed solid can be further used as an active catalyst for synthesis of methyl phe-

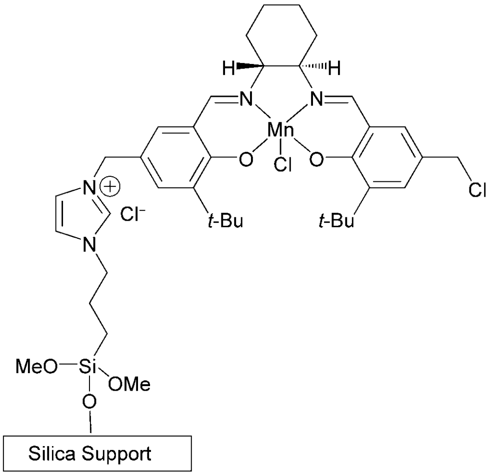


Scheme 24. Incorporation of the methylselenite anion to the ionic polymer.

nylcarbamate by oxidative carbonylation of aniline.[136]

It was well known that triflate salts could be immobilized into silica-based materials by means of ionic interactions between salt and surface hydroxy groups. On the basis of this fact, Coman and his co-workers developed an MCM-41-supported scandium triflate [$Sc(OTf)_3$] doped with surface-grafted ILs starting from MCM-41-supported ILs.[137] The catalysts were tested in the acylation of amines and sulfonamides, and high activity and good selectivity were obtained. Remarkably, a synergistic effect between the IL and the Sc salt was found in acylation of aliphatic amines. While nearly quantitative conversions of amines were obtained with MCM-41-IL-Sc, only small amounts of substrates were converted by using MCM-41-IL or MCM-41-Sc as catalysts. Furthermore, recycling the catalyst, MCM-41-IL-Sc, was not accompanied by any leaching of IL or metal triflate. Moreover, incorporation of gadolinium triflate [$Gd(OTf)_3$] with an imidazolium cationic fragment-doped polymer, poly(styrene-co-{1-[(4-vinylphenyl)methyl]-3-methylimidazolium} tetrafluoroborate) [(**o**), Scheme 13], resulted in a heterogeneous Lewis acid catalytic system [PS-IL-Gd-$(OTf)_3$], which was demonstrated to be capable of catalyzing Michael additions of amines and thiols to α,β-unsaturated esters and acrylonitrile.[138] Although analogous catalytic activity was also obtained with a polystyrene-supported $Gd(OTf)_3$ [PS-$Gd(OTf)_3$] material, the real advantage of IL-containing system comes in recycling of catalyst. While PS-$Gd(OTf)_3$ is soluble in the reaction mixture, PS-IL-$Gd(OTf)_3$ performs as a solid catalyst due to its insolubility in the reaction mixture. Therefore, the catalytic system could be easily recycled and following reuse experiments showed that PS-IL-$Gd(OTf)_3$ could be reused at least 3 times without significant loss of its acativity.

An ionic polymer which contains a quaternary ammonium acetate fragment was proved to be a suitable solid support for the immobilization of CuI.[139] In Huisgen's 1,3-dipolar cycloaddition of azides and terminal alkynes, the obtained CuI-immobilized compound showed negligible leaching of CuI, providing 1,4-disubstituted 1,2,3-triazoles in good yields. An alternative strategy to the above-mentioned immobilization by means of anionic exchange is to design the imidazolium cation of the IL to be a linker of the catalytically active center. In this case, imidazolium cations were covalently bonded to both sides of the support and the metal catalyst, thus more like an anchor which was used to covalently immobilize the metal species onto the surface of the support. Although the preparation of the catalyst is relatively difficult compared with the anionic method, it benefited from the ionic properties of the surface attributed to the presence of imidazolium salts. The thus obtained catalyst showed somewhat enhanced activity or selectivity. For example, the activity of an SBA-15 immobilized-chiral salen Mn(III) catalyst for the asymmetric epoxidation of olefin could be significantly improved by using imidazolium cation as a key linker, and a high TOF, 2.78×10^{-2} s, was obtained for the epoxidation of styrene and α-methylstyrene (Scheme 25).[140] Furthermore, these immobilized catalysts were stable and could be easily recycled at least five times.

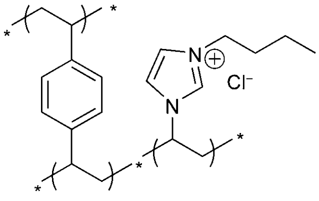


Scheme 25. Immobilization of chiral salen-Mn(III) by using an imidazolium salt as the linker.

6 Catalysis of Supported ILs

6.1 Fixation of Carbon Dioxide over Solid Supported ILs

Although the cycloaddition of CO_2 to epoxides to produce cyclic carbonates has been extensively studied with ILs,[141] homogeneous IL systems suffer from either low catalytic efficiency (TOF) or high energy consumption for recycling of the IL catalyst and separation of the carbonate product, therefore, the design of highly effective heterogeneous IL catalysts is still desirable. Han and his co-workers[142] prepared a completely insoluble polymer-supported IL by co-polymerization of [BVIm]Cl and a cross-linker, divinylbenzene (DVB) (Scheme 26). This PSIL catalytic system not only shows comparable or even better catalytic activities for the cycloaddition of CO_2 to pro-

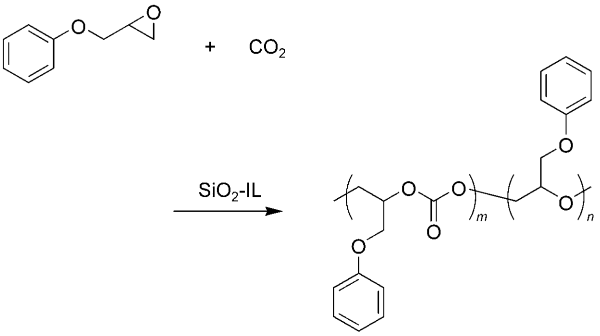


Scheme 26. Copolymer of [BVIm]Cl and DVB.

pene oxide than those of homogeneous counterparts ([BMIm]Cl or [VBIm]Cl), but also enables recovery of the catalyst by filtration because of the inherent insolubility of the PSIL solid in the product (propene carbonate, PC). Another advantage of the solid PSIL was that it showed a relatively higher TOF value ($>70\ h^{-1}$) compared with other solid-supported IL systems such as silica-immobilized imidazolium ILs[143] or molecular sieve-immobilized choline chloride/urea systems.[144] Functionalization of the imidazolium cation, which being anchored onto a polystyrene resin, with a hydroxy group was found to be effective for enhancement of the catalytic activity in the cycloaddition of CO_2 to epoxides.[145] Despite these advantageous aspects, this copolymer-supported IL catalyst system has to face some problems such as high price and lack of information about the biocompatibility which is quite important from the environmental point of view. In this regard, the molecular sieve-immobilized choline chloride/urea systems exhibited a great potential to address these problems owing to their relatively low cost and biodegradable properties. However, the low efficiency of this system, unfortunately, restricts its practical applications.

In order to further improve the catalytic efficiency of the immobilized ILs, Xia and his co-workers[146] added extra metallic salts, for example, $ZnCl_2$ and $ZnBr_2$, to the reaction system, and surprisingly, a high TOF, 2712^{-1}, for the cycloaddition of CO_2 to propene oxide, was obtained based on an amorphous silica-supported imidazolium IL. As a typical case of a solid catalyst, this SiO_2-IL-$ZnCl_2$ system can be recovered directly by filtration, and the recovered solid catalyst also showed high catalytic efficiency in the next run, indicating the high efficiency and good stability of this system. From the viewpoint of practical synthesis, this system might be one of the most promising among all the IL-based catalytic systems for the synthesis of cyclic carbonates from CO_2. Besides these covalent grafting methods, a simple physical absorption of $[BMIm]BF_4$ onto silica was also proved to be capable of offering a recyclable catalyst for the cycloaddition of CO_2 to epoxide.[147]

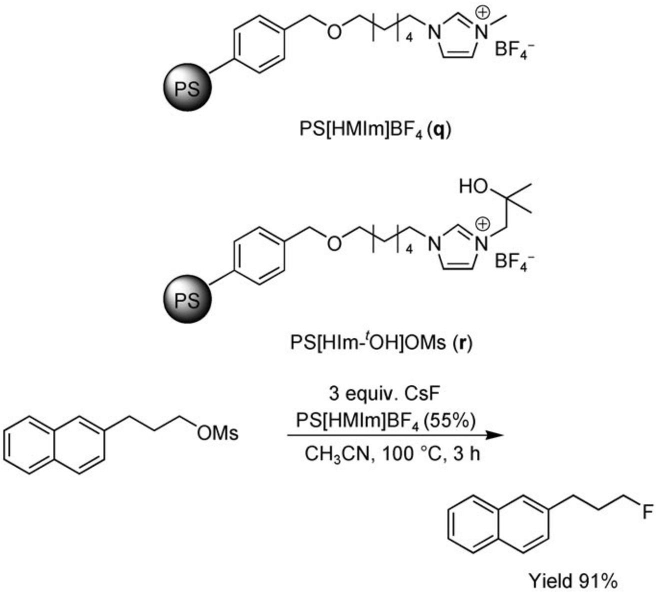
An analogous SiO_2-IL prepared by the sol-gel method was also proved to be an effective heterogeneous catalyst for the solvent-free synthesis of oligomers with carbonate and ether units from phenyl glycidyl ether (PGE) and CO_2 (Scheme 27). The SiO_2-IL materials, here, have very low BET surface areas ($<1\ m^2 g$). The optimum SiO_2-IL, which has a linkage (between the silica matrix and imidazolium cation) composed of four CH_2 units, showed the highest conversion of PGE (94%), the highest carbonate content [$f(CO_2)$] (92%) and average number of the monomer units (712). The SiO_2-IL can be reused for the reaction in up to four consecutive runs without considerable loss of its catalytic activity.[148]



Scheme 27. Copolymerization of epoxide and CO_2 over SiO_2-IL.

6.2 Phase-Transfer Catalysis over Supported ILs

It is known that the imidazolium IL is a kind of ammonium salt which are widely used in phase-transfer catalysis, therefore it is not surprising that the supported imidazolium IL can be used as a phase-transfer catalyst for some organic reactions (Scheme 28).[149] In this context, Chi's group in Inha University, Korea, first demonstrated the feasibility of this application with nucleophilic substitution reactions using a polymer-supported imidazolium IL as catalyst.[150] Chi's catalyst showed a unique activity for thefluorination of alkyl mesylates and alkyl triflate with alkali metal fluorides. For example, the fluorination over an immobilized IL (**q**) catalyst proceeds much faster than that using the same amount of IL as the phase-transfer catalytic system. Furthermore, this immobilized imidazolium catalyst also showed a synergistic effect with the *tert*-alcohol solvent for the flu-



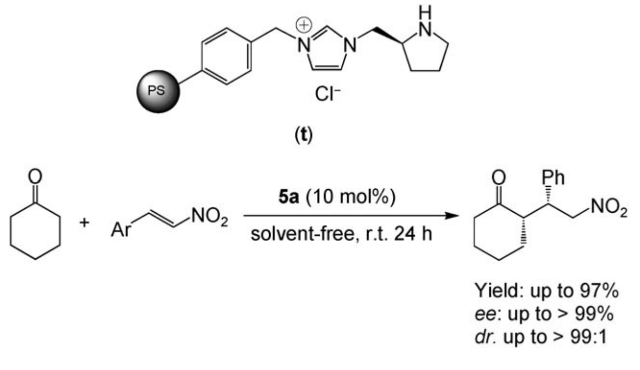
Scheme 28. Chi's supported ILs and their catalyzed fluorination reaction.

orination reactions.[151] For example, the combined PS-$[HMIm]BF_4$/*tert*-amyl alcohol system exhibits not only higher catalytic activity than PS[HMIm] (**q**)/acetonitrile, but also a significantly higher selectivity towards alkyl fluoride than 18-crown-6, which is a well-known catalyst for PTC reactions. Inspired by these results, Chi and his co-workers prepared then a supported imidazolium IL functionalized with a *tert*-alcohol, PS-[Him-^{t}OH]OMs (**r**) (Scheme 28), which shows also high activity for the fluorination of alkyl mesylate.[152]

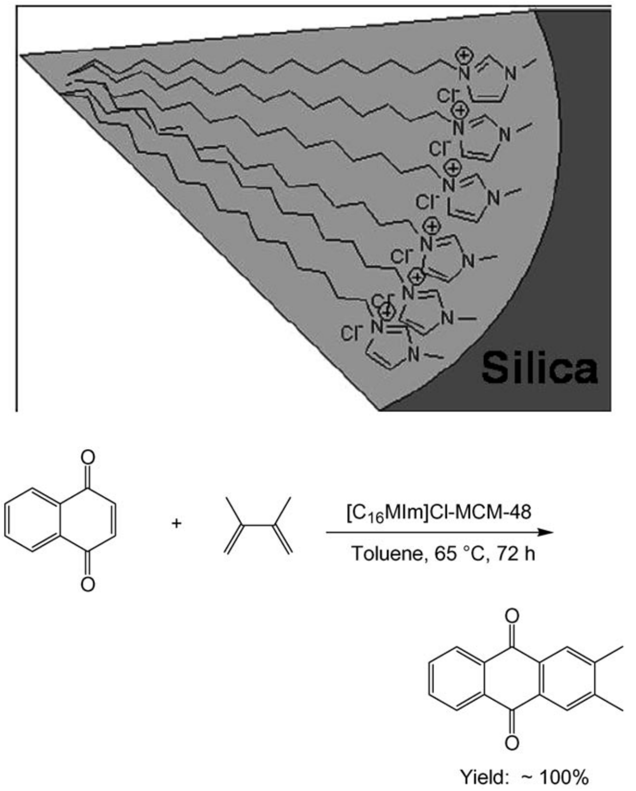
6.3 Organocatalysis with Supported ILs

Recent developments in organocatalysis have shown that these reactions can be advantageously performed in ILs. Among many organocatalysts, proline and its derivatives have attracted enormous attention, and these compounds have recently also been efficiently utilized in ILs. Although performing organocatalytic reactions in ILs offer possibilities for easy catalyst recovery and reuse, the use of solid catalysts is still preferred in practical synthesis owing to the simple product isolation as well as catalyst recycling.[153] Under these considerations, the immobilization of an IL onto a solid can be a good compromise. Recently, a polymer-immobilized pyrrolidine-based chiral IL (**t**) (Scheme 29) was prepared and used as a highly efficient catalyst for the Michael additions of ketones and aldehydes to nitrostyrenes, which afforded the corresponding adducts in good yields (up to 97%), excellent enantioselectivities (up to >99% *ee*) and high diastereoselectivities (up to >99:1 *dr*).[154] Immobilization of chiral ILs opens an attractive way for chemists to overcome the drawbacks of asymmetric catalysis with chiral ILs, such as high price and difficulties of recycling. Indeed, the catalyst (**t**) could be reused at least eight times without any significant loss of its catalytic activity and stereoselectivity.

While much effort has been made for the investigation of supported imidazolium cations, little attention has been paid to the potential effects of the anions on catalyzed reactions in supported ILs. A breakthrough was made recently by Goettman,[155] who found that a supported IL, 1-*n*-cetyl-3-methylimidazolium chloride ($[C_{16}MIm]Cl$) which was used here as template for the synthesis of a mesoporous silica, MCM-48, is able to promote the aromatization of Diels–Alder adducts (Scheme 30). This type of reaction was generally catalyzed by metal-containing species. Interestingly, the non-supported IL was proved to be less active compared with the $[C_{16}MIm]Cl$-MCM-48 system, indicating the presence of synergism between silica and the IL.

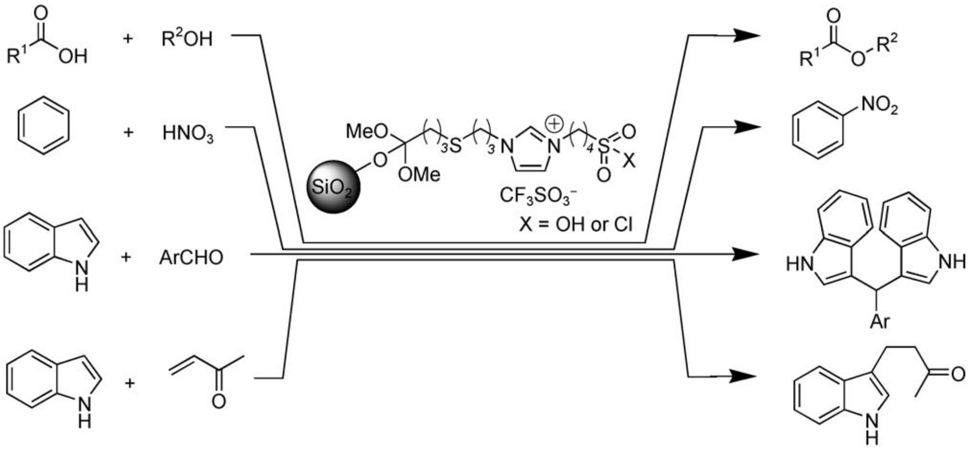


Scheme 29. Supported chiral IL and application in the asymmetric Michael reaction.



Scheme 30. $[C_{16}MIm]Cl$-MCM-48 and its application in the aromatization of Diels–Alder adducts.

Air- and moisture-stable acidic ILs have emerged as powerful catalysts for a series of organic reactions.[156] Despite many advantages such as good catalytic capacity and ease of handling, the applications were restricted by their high price. In order to address this issue, heterogenizing these acidic ILs appears as a promising method. Up to now, two strategies have been utilized for the immobilization of acidic ILs. The first approach was developed by Yokoyama, who has covalently immobilized SO_3H- and SO_2Cl-functionalized ILs onto silica materials, and then tested the obtained solids in many organic transformations including esterification of carboxylic acids with alcohols, nitration of benzene, Michael reaction of indole and



Scheme 31. Some reactions catalyzed by SiO_2-supported SO_3H- or SO_2Cl-functionalized ILs.

condensation between indole and aromatic aldehydes (Scheme 31).[157] This strategy not only combines the advantages of both homogeneous and heterogeneous catalysis, but also introduces, to some extent, ionic properties of the imidazolium salts onto the catalyst surface, thus, making these immobilized systems attractive from the viewpoints of both environmental aspects and catalyst recycling. The second approach involves either physical absorption of functionalized acidic ILs onto SiO_2 or encapsulation with the sol-gel method, offering a solid which is active for esterification between carboxylic acids and alcohols.[158] Another method for immobilization of acidic ILs is also available,[159] however, the catalytic activity seems to be relatively lower compared with Yokoyama's catalysts.

Not only acidic ILs, but also basic ILs have been immobilized by some researchers. For example, Xia and his co-workers[160] reported a resin-supported imidazolium hydroxide which showed a high activity for the hydrolysis to propylene carbonate to 1,2-propylene glycol compared with the homogeneous counterpart, 1-butyl-3-methylimidazolium hydride ([BMIm]OH), which is somewhat unstable on exposure in air. Supporting this basic IL onto resin not only facilitates the work-up procedure, but also offers a good recyclability to this heterogeneous system. Physical absorption of the basic IL onto an acidic support also offers an alternative way for the covalent immobilization of the IL. For example, an amine-based basic IL, Hünig's base-tethered ammonium salt, has been shown to be highly active for Knoevenagel condensations under homogeneous conditions. However, in recycling, degradation of the IL was observed and it was also difficult to remove the product completely by solvent extraction due to solidification of the reaction mixture. Fortunately, the recyclability of this catalyst could be improved by supporting the basic IL onto silica material.[161] Moreover, the effect of the exothermic nature of the reaction will be reduced, to some extent, benefitting form the high heat capacity of silica, which thus minimizes the possibility of degradation of the IL.

6.4 Other Reactions over Solid-Supported ILs

Silica-supported imidazolium ILs have also been used in other reactions.[162] For example, testing these materials as catalysts for the acylation of sulfonamines indicated that they are active and stable for the synthesis of *N*-acylsulfonamines with the reactivity being determined by the surface concentration of IL.[163] Knoevenagel reactions between aromatic aldehdyes and ethyl acetoacetate or malononitrle also proceeded smoothly in the presence of covalently modified silica with IL.[164,165]

7 Preparations of Heterogeneous Catalysts in ILs

Although homogeneous and heterogeneous catalysis with ILs has gained much attention, the preparation of catalysts using IL as solvent or template has been rarely investigated.[166] Up to now, there are only a few reports on the preparations of solid catalytic materials in ILs, and the most of them are related to the use of the IL as a template for the synthesis of a mesoporous material. For example, 1-*n*-cetyl-3-methylimidazolium bromide, $[C_{16}MIm]Br$, has recently been used as both solvent and template for the preparation of spherical aggregates of CeO_2 nanocrystals with nearly monodisperse structure, which can be further utilized as support materials to prepare Cu-based CO conversion catalysts.[167] Furthermore, some ILs have also been used for the preparation of sulfur (S)-doped

TiO_2 nanoparticles which showed promising photocatalytic activity for the degradation of methyl orange.[168]

Functionalization of single-walled carbon nanotubes (SWNTs) with hematin, a water-insoluble porphyrin, was recently realized in $[BMIm]PF_6$ by Ju's group.[169] Hematin can be non-covalently assembled on the surface of SWNTs by π-π interaction in $[BMIm]PF_6$, leading to good dispersion of the SWNTs in the IL and a direct electrochemical response corresponding to the redox couple Fe(III)/Fe(II). The combination of SWNTs and $[BMIm]PF_6$ produces a synergistic effect that accelerates the electron transfer between the redox probe or water-insoluble porphyrin and the electrode. The composite-$[BMIm]PF_6$-modified glassy carbon electrode showed excellent electrocatalytic activity towards the reduction of trichloroacetic acid (TCA) in neutral media due to the synergic effect between SWNTs, $[BMIm]PF_6$, and porphyrin, which led to a highly sensitive and stable amperometric biosensor for TCA with a linear range from 9.0×10^{-7} M to 1.4×10^{-4} M. The detection limit was 3.8×10^{-7} M at a signal-to-noise ratio of 3 with this system.

8 Conclusion

As is clear from this review, IL-based heterogeneous catalysis with solids is a rapidly developing field. It can also be seen from the fact that some new and interesting results appeared during the preparation/publication process of this review.[170] In many cases, the use of IL in solid catalysis enables not only the successful immobilization of homogeneous catalysts but also sufficient minimization of the amount of IL while the efficiency is retained very well. Some results also showed that ILs play a central role for the solid catalysts in achieving either higher activity or better stability. This can be particularly demonstrated by catalysis with metal nanoparticles in the presence of ILs. Despite these promising results, much more research needs to be performed in this area to explore the scope of IL-based solid catalysis. In catalysis with supported ILs, synergistic effects between network of cations/anions and solid or immobilized homogeneous catalysts can be expected to be an effective way to improve the performance in terms of chemical reactivity and selectivity. However, unfortunately, our understanding as to how ILs affect surface reactions and the mass transport phenomena within solid-liquid or solid-liquid-gas systems is limited. This is particularly important in solid-catalyzed processes, and further research needs to address this issue.

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