Immobilization of molecular catalysts in supported ionic liquid phases

Charlie Van Doorslaer, a Joos Wahlen, a Pascal Mertens, a Koen Binnemans b and Dirk De Vos *a

Received 19th January 2010, Accepted 18th March 2010
DOI: 10.1039/c001285h

In a supported ionic liquid phase (SILP) catalyst system, an ionic liquid (IL) film is immobilized on a high-surface area porous solid and a homogeneous catalyst is dissolved in this supported IL layer, thereby combining the attractive features of homogeneous catalysts with the benefits of heterogeneous catalysts. In this review reliable strategies for the immobilization of molecular catalysts in SILPs are surveyed. In the first part, general aspects concerning the application of SILP catalysts are presented, focusing on the type of catalyst, support, ionic liquid and reaction conditions. Secondly, organic reactions in which SILP technology is applied to improve the performance of homogeneous transition-metal catalysts are presented: hydroformylation, metathesis reactions, carbonylation, hydrogenation, hydroamination, coupling reactions and asymmetric reactions.

Introduction

Ionic liquids (ILs) are organic salts with low melting points and very low vapour pressures. 1–3 Their non-volatile nature is one of the main motives to explore them as alternatives for volatile organic solvents. 4 Depending on their composition, ILs can dissolve or reject organic compounds. Since ILs are ionic and polar, they are excellent media to hold charged or polar catalyst species like transition-metal complexes. 5–11 In analogy to the well-established supported aqueous-phase catalysis, 12–13 ILs have recently been introduced for the immobilization of homogeneous catalysts. 14–16

In a supported ionic liquid phase (SILP) catalyst system, an IL film is immobilized on a high-surface area porous solid (e.g., silica) and the homogeneous catalyst is dissolved in the IL layer. The resulting catalyst is a solid, with the active species being solubilized in the IL phase and behaving as a homogeneous catalyst. Typically, there is no direct interaction between the support’s surface and the homogeneous catalyst.

SILPs allow a more efficient utilization of the IL and the catalyst since the IL’s surface area is increased relative to its volume and the substrate can readily diffuse to the catalyst. In contrast, operation under classical liquid/liquid biphasic conditions requires larger amounts of ILs and the IL’s high viscosity may cause mass-transfer limitations. The latter is particularly important for gas-phase reactions, since ILs generally display a limited solubility for gases such as H 2, O 2 and CO. SILP catalysis combines the most attractive features of homogeneous catalysis like high activity and selectivity with benefits of heterogeneous catalysts such as large interfacial reaction areas and ease of product separation. Indeed, the reaction products can be recovered from the organic phase, while the catalyst remains immobilized in the SILP. Therefore, SILP catalysis has potential for efficient catalyst recycling and might enable the application of fixed-bed reactor technology to homogeneous catalysis. Some reviews about this interesting topic have already appeared. 17–19 Wasserscheid et al. focused in a microreview on the hydroformylation of propene. 17 In another review they tackle the use of SILP technology in catalytic and separation technologies. 19 Gua and Li deal with solid-based...
heterogeneous catalytic systems that have been developed with the aid of ILs. Thus, topics like the use of solid catalysts in ILs, metal nanocatalysts in ILs and the preparation of heterogeneous catalysts in ILs, can be found in this reference. In previous reviews, various aspects of the immobilization of transition-metal complexes in a SILP have only partially been covered. Clear trends can be discerned now in the preparation procedures of the respective SILP catalysts with regard to choice of catalyst, IL and support. Moreover, as the body of experimental work grows, it is now possible to make quantitative comparisons between homogeneous, heterogeneous and biphasic systems. Therefore the present review focuses on recent developments in the immobilization of molecularly defined catalysts in SILPs.

Firstly, general aspects of SILP catalysis are discussed. These include the preparation of SILP catalysts and the choice of the homogeneous catalyst, ionic liquid, support, and reaction conditions. Next, the use of SILP catalysis is illustrated with examples from hydroformylation, metathesis, carbonylation, hydrogenation, hydroamination, C–C coupling and various enantioselective reactions.

**General considerations**

Catalysts, ILs and solid supports can be combined in various ways. An overview is presented in Scheme 1. In this review, catalysts are denoted SILP catalysts (SILPCs) if the support is loaded with a separate IL phase (Type 1). The IL is deposited on the support as a multilayer and acts as an immobilizing medium for the catalyst, behaving as a homogeneous catalyst. The most straightforward procedure for the preparation of a Type 1 SILPC (Type 1a, catalyst/IL/support) is via simple impregnation of the IL on a support’s surface. Prior to the impregnation step, the metal and the ligand are dissolved in the IL phase. In a different approach (Type 1b, catalyst/IL/support), the surface of the support is first modified with a monolayer of covalently anchored IL fragments. Next, additional IL and the catalyst are impregnated on the modified support.

In Type 2 catalysts, the IL is directly anchored to the support via covalent anchoring, forming a monolayer of IL fragments. This can be achieved by grafting a functionalized IL fragment on a preformed support or by sol–gel synthesis. According to our definition, the resulting solid catalysts are in fact no “immobilized ionic liquid phase catalysts”, since there is no separate IL phase supported on the solid. The IL in this case should rather be considered as a covalently anchored ligand. In this approach (Type 2, catalyst–IL-support + IL-support), IL fragments are first covalently anchored to a support via the organic cation, and part of the anion is then ion-exchanged with anionic catalyst species (e.g., [WO₄]²⁻, [SnCl₅]), [PdCl₄]²⁻, [NiCl₄]²⁻, [CuCl₄]²⁻, [AlCl₄]⁻, [SnCl₄]),. In this context, it should be noted that earlier reported catalytic systems with immobilized quaternary ammonium moieties and ion-exchanged metal catalysts are nowadays more popularly called supported ionic liquid catalysts (SILCs). Anchoring via the anionic part of the IL is also possible. Alternatively, the catalyst or ligand is incorporated in the IL fragment via covalent binding.

In a third strategy (Type 3, IL/catalyst-support), an IL is impregnated on the surface of classical heterogeneous catalysts such as covalently anchored

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**Pascal Mertens**

Pascal Mertens (born 1980) obtained his Masters degree in Applied Bioscience and Engineering at the Catholic University of Leuven (K.U.Leuven, Belgium) with a thesis on colloidal gold catalysts in alcohol oxidation at the Centre of Surface Chemistry and Catalysis. He also completed his doctoral research with a dissertation on colloidal metal catalysts in liquid phase redox reactions. His research interests involve selective transformations in the synthesis of fine chemicals and pharmaceuticals.

**Koen Binnemans**

Koen Binnemans (born 1970) obtained his M.Sc. (1992) and Ph.D. (1996) in Chemistry at the Catholic University of Leuven. In the period 1999–2005, he was a postdoctoral fellow of the Fund for Scientific Research Flanders (Belgium). He did postdoctoral work with Prof. Jacques Lucas (Rennes, France) and Prof. Duncan W. Bruce (Exeter, U.K.). In 2000, he received the first ERES (European Rare-Earth and Actinide Society) Junior Award.

From 2002 until 2005, he was (part time) associate professor. Presently, he is professor of chemistry at the Catholic University of Leuven. His current research interests are metal-containing liquid crystals (metallomesogens), lanthanide-mediated organic reactions, lanthanide spectroscopy, luminescent molecular materials, and ionic liquids.

**Dirk De Vos**

Dirk De Vos (born 1967) is a full professor at the Catholic University of Leuven. After doctoral research in Leuven and postdoctoral work at Purdue University, he focuses on selective catalytic oxidation, metal–organic frameworks, ionic liquids and in situ spectroscopy and microscopy of working catalysts. His awards include the D. W. Breck Award in Zeolite Science and Technology (1998, together with P. Jacobs and co-workers), the BASF catalysis award (2001), the award of the Flemish scientific foundation (2006), and the IPMI Student Advisor Award (2008).
catalysts,27 or supported transition-metal nanoparticles.28-30 This type of catalyst was recently named “solid catalyst with ionic liquid layer” (SCIL).31 The present review is limited to Type 1 catalysts, for which a SILP is used to immobilize homogeneous catalyst species. For the immobilization of transition-metal nanoparticles, we refer to other reviews, which elaborate this topic more exhaustively.18-19

Homogeneous catalyst

A prerequisite for the industrial application of SILP catalysis is that the homogeneous catalyst has an inherently stable catalytic performance, guaranteeing a long lifetime. In addition, the loss of catalyst into the organic layer containing the products should be negligible. Since ILs are charged and have polar properties, they are well suited to hold ionic or highly polar catalyst species, like ionic metal species (e.g., \([\text{PdCl}_4]^2-\), [WO_4]^{2-}\). On the other hand, the preference of the catalyst for the IL phase can be increased by incorporation of ionic groups in the ligand of the catalyst complex. For instance, phosphine ligands can be modified with anionic sulfonate groups or cationic groups based on guanidinium, imidazolium or pyridinium moieties. This review focuses on molecularly defined catalysts; therefore, the combination of ionic ILs with supported metal catalysts,31 metal nanoparticles33 or supported enzymes34 is not discussed. Regarding the field of applications, the use of SILPs is being studied extensively for the immobilization of rhodium and palladium complexes, since their heterogenization via classical routes (e.g., impregnation or covalent anchoring) has only been developed with limited success. Although less frequently studied in this context, other metals such as Ru, Cu, Mn, Co, Zn or Cr have also been considered for immobilization in SILPs.

Ionic liquid

ILs are often called designer solvents, since their properties – such as density, melting point, viscosity, or miscibility with water or organic solvents – can be fine-tuned by an appropriate choice of anion and cation.1-3 The cations in ILs are mostly large organic cations, like \(N,N^\prime\)-dialkyl-imidazolium, \(N\)-alkylpyridinium, \(N,N\)-dialkylypyrrolidinium, tetraalkylammonium or tetraalkylphosphonium ions. Several cation types can be used for SILP catalysis. Especially the 1-ethyl-3-methylimidazolium (emim), 1-butyl-3-methylimidazolium (bmim) and 1-hexyl-3-methylimidazolium (hmim) ions are often used as the IL’s cationic part. The anions can vary widely, e.g., \(\text{Cl}^-\), \(\text{Br}^-\), \(\text{PF}_6^-\), \(\text{BF}_4^-\), \(\text{CF}_3\text{SO}_3^-\) and \((\text{CF}_3\text{SO}_2)_2\text{N}^-\). Whereas \(\text{Cl}^-\) and \(\text{Br}^-\) yield hydrophilic ILs that are miscible with water, fluorinated anions like \(\text{BF}_4^-\) or \(\text{PF}_6^-\) allow the preparation of hydrophobic ILs immiscible with \(\text{H}_2\text{O}\). The hydrophobicity of ILs with \(\text{BF}_4^-\) depends on the cation’s alkyl chain length. The most widely used IL in SILP applications is 1-butyl-3-methylimidazolium tetrafluoroborate, \([\text{bmim}][\text{BF}_4]\), or the hexafluorophosphate salt, \([\text{bmim}][\text{PF}_6]\). These ILs combine a high solvation power for polar catalyst complexes with a weak coordination strength. This specific combination makes them suitable for reactions with electrophilic catalysts. The major problem is that the \(\text{BF}_4^-\) and \(\text{PF}_6^-\) anions are sensitive to hydrolysis. The resulting HF might cause side reactions or corrosion problems, or the strongly coordinating fluoride ions might poison the transition-metal catalyst by irreversible complexation. Consequently, the application of these ILs is restricted to anhydrous conditions. In this context, it is not surprising that the IL’s water content is an important issue, as the presence of small amounts of water might induce hydrolysis of the metal catalyst or decomposition of the \(\text{BF}_4^-\) or \(\text{PF}_6^-\) anions. Moreover, impurities such as residual halide ions might bind tightly to the transition-metal complex and impede its catalytic activity. Recently, bis(trifluoro-methylsulfonylimide anion \((\text{CF}_3\text{SO}_2)_2\text{N}^-\) has emerged as a popular anion for synthesizing hydrophobic ILs, because the resulting ILs are chemically and thermally more robust. However, disposal of such ILs, e.g., by combustion, is more complicated due to potential HF liberation. General concerns about environmental impact and toxicology associated with ILs involving halogen-containing anions recently led to the introduction of halogen-free ILs as environmentally friendly solvents e.g., imidazolium-based ILs with weakly coordinating anions like alkylsulfates.34 In summary, such low-melting, halogen-free IL systems that combine weak coordination to electrophilic metal centres and low viscosity with high stability to hydrolysis are highly desirable for applications in transition-metal catalysis.

Support

The majority of the supports used in SILP catalysis are porous silica gels with a high surface area of \(300-500\ \text{m}^2\ \text{g}^{-1}\). Thermal pretreatment of the silica gel reduces the number of acidic silanol groups. This can be important for a stable catalyst performance since the silanol groups may react with ligands or catalysts, hereby lowering the actual concentration of the ligand or the catalyst in the IL phase. Mesoporous silica materials (e.g., MCM-41 and MCM-48) and crystalline silica–alumina materials such as zeolites and clays (e.g., montmorillonite) have also been used.35-39 Other inorganic materials (\(\text{Al}_2\text{O}_3\), TiO_2, ZrO_2, etc.) are less frequently used due to their low surface areas and pore volumes. However, under certain conditions alumina might be preferred, since this support shows higher stability at high pH values as compared to

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**Scheme 1** Various catalyst/ionic liquid/support combinations.
SiO₂. A few studies focused on the use of organic polymer materials including poly(diallyldimethylammonium chloride), polystyrene based polymers and chitosan. More advanced supports such as membranes and carbon nanofibers supported on sintered metal fibres have also been used.

Catalyst preparation

The general method for the preparation of SILPCs is impregnation. The catalyst precursor and the ligand are first dissolved in a small amount of a volatile organic solvent (e.g., methanol, acetone, acetonitrile, tetrahydrofuran, dichloromethane and chloroform) that dissolves both the catalyst complex and the IL, and then the IL is added. Next, this solution is mixed with the support material, and upon stirring, the volatile solvent is removed by evaporation under reduced pressure. Alternatively, the homogeneous catalyst and the IL are impregnated on a support that already contains a monolayer of covalently anchored IL fragments. In both cases, the homogeneous catalyst is dissolved in the IL film. The resulting SILPCs are characterized by the nature of the support, the catalytic metal loading, the molar ligand/metal ratio (L/M), the IL loading and the pore filling degree (α). The IL loading is usually defined as the amount of IL relative to the mass of the support (weight percentage), while the pore filling degree α is defined as the volume of the IL divided by the pore volume of the support. Ideally, the IL should form a thin layer on the surface, without completely filling the pores. In general, nitrogen adsorption measurements show that the BET surface area, the total pore volume and the mean pore size of the support decrease upon adsorption of the IL. Most of the SILP catalyst systems described in the literature have IL loadings in the range of 10–25 wt.%, while the metal loadings vary between 0.01–0.2 mmol g⁻¹.

Reaction conditions

SILP catalysis is ideally suited for gas-phase reactions since no problems regarding catalyst leaching or washing out of the IL are encountered if the reaction products are not too polar. In addition, several ILs show high thermal stability and low vapour pressure, and are therefore excellent media for reactions at elevated temperatures at which conventional solvents would evaporate or decompose. On the other hand, liquid-phase reactions require careful tuning of the polarities of all reaction constituents in order to prevent leaching of the catalyst or the IL. Application of a SILPC in liquid-phase conditions supposes extremely low solubility of the IL in the liquid reactant/product mixture. Physical removal of the IL film from the support by mechanical forces should also be prevented. The SILPC can be used in solvent-free conditions, with the reagents and products forming a separate organic layer. Alternatively, an additional solvent may be used. This solvent contains the reagents and the products and should be immiscible with the IL phase to prevent leaching of the IL from the surface of the support. Obviously, the solvent should not dissolve the catalyst to any extent. For this purpose, non-polar solvents such as alkanes (e.g., n-hexane, n-heptane, n-dodecane) are commonly used. Slightly more polar solvents are toluene and dichloromethane. On the other hand, water, ethanol, or 2-propanol should be used in combination with hydrophobic ILs (e.g., containing BF₄⁻ or (CF₃SO₂)₂N anions), although even in this case, limited extraction of the IL and the catalyst in the solvent is difficult to avoid. Supercritical carbon dioxide (scCO₂) has recently been introduced as an organic solvent. Although scCO₂ shows good solubility in some ILs, the reverse is not the case, with no detectable IL solubilization in the scCO₂ phase. scCO₂ reduces the viscosity of the IL and thus improves the solubility and mass transport of permanent gases. Disadvantages are the high investment and operating costs and the limited solvating ability of scCO₂ compared with classical organic solvents.

Selected examples

1. Olefin hydroformylation

Rhodium complexes are the most effective catalysts for olefin hydroformylation under mild conditions (100 °C, 15 bar CO/H₂). Typically, Rh(CO)₂(acac) (acac = acetylacetonate) is used as the catalyst precursor and a phosphine ligand is added to favour the formation of linear over branched aldehydes (n/iso-aldehyde ratio). Since the heterogenization of Rh catalysts via classical routes (e.g., impregnation or covalent anchoring) has only been achieved with limited success, the Rh complex immobilization in supported liquid phases emerged as an alternative.

Liquid-phase hydroformylation in batch reactors. The hydroformylation of 1-hexene was one of the first reactions carried out with a homogeneous catalyst immobilized in a SILP (Scheme 2). Initially, the hydroformylation was performed with Rh-monophosphine complexes (Scheme 3, 1). As support a [1-butyl-3-(3-triethoxysilyl-propyl)-4,5-dihydroimidazolium][BF₄] or [PF₆] modified dehydrated silica gel (474 m² g⁻¹) was used (Scheme 4).

The resulting SILP catalyst ([Rh]/IL/IL-SiO₂) activity of the SILPC (TOF = 3900 h⁻¹) was almost three times higher compared to the biphasic IL system (Table 1). This improvement was attributed to a higher concentration of the active Rh species at the interface and the generally larger interface area of the solid support in comparison with the biphasic system. The selectivity (n/iso aldehyde ratio = 2.4) was comparable for both systems. Note that the homogeneous system is still significantly more active (Table 1), which is probably due to mass transfer limitations, caused by the lower solubility of the gases in the IL. However the IL introduction enables the recycling of the catalytic system. Although the active Rh species are insoluble in the organic medium, at high aldehyde concentrations [bmm][BF₄] partially dissolved in the organic phase which led to rhodium complex leaching (Rh loss = 2 mol%). This was solved by keeping the aldehyde concentration below 50 wt.% and increasing the phosphine concentration in the IL. Note that the Rh leaching could still be minimized.
Scheme 3 Classical ligands and ionic liquid tagged ligands in SILP catalysis (1 sulfonated monophosphine ligands; 2 ionic liquid-tagged Pd complex; 3 monophosphine ligands containing ionic guanidinium or sulfonate groups; 4 [1,1,3,3-tetramethylguanidinium][lactate] (TMGL); 5 imidazolium-tagged bis(oxazoline) ligand; 6 (S)-BINAP ligand; 7 triphenylphosphine; 8 the bisphosphine ligand sulfoxantphos; 9 5,5¢-isopropylidenebis[(4R)-4-phenyl-4,5-dihydro-1,3-oxazole]; 10 (S,S)-Mn(III) salen chloride; 11 dimeric (R,R)-Cr(III) salen complex).

Scheme 4 Covalently anchored imidazolium fragments on silica gel.

Table 1 Comparison of the catalytic performance of SILP, homogeneous, and biphasic catalytic systems in the liquid-phase hydroformylation in batch reactors

<table>
<thead>
<tr>
<th>S</th>
<th>Catalytic system</th>
<th>L/Rh</th>
<th>n/i</th>
<th>TOF/h⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td>SILP/[bmim][BF₄]-tppts-Rh</td>
<td>10</td>
<td>2.4</td>
<td>3900</td>
<td>41</td>
</tr>
<tr>
<td>C6</td>
<td>Biphasic/[bmim][BF₄]-tppts-Rh</td>
<td>10</td>
<td>2.2</td>
<td>1380</td>
<td>41</td>
</tr>
<tr>
<td>C6</td>
<td>Homog/PPh₃-Rh</td>
<td>10</td>
<td>2.6</td>
<td>24000</td>
<td>41</td>
</tr>
<tr>
<td>C6</td>
<td>Biphasic/TMGL-TPTS-Rh</td>
<td>5</td>
<td>3.8</td>
<td>82</td>
<td>42</td>
</tr>
<tr>
<td>C6</td>
<td>SILP/TMGL-TPTS-Rh/MCM-41</td>
<td>5</td>
<td>3.0</td>
<td>389</td>
<td>42</td>
</tr>
<tr>
<td>C6</td>
<td>SILP/TMGL-TPTS-Rh/SiO₂</td>
<td>5</td>
<td>2.1</td>
<td>87</td>
<td>42</td>
</tr>
</tbody>
</table>

* S = substrate, C6 = 1-hexene. * L/Rh = ligand to Rh molar ratio. * n/i = normal/iso aldehyde ratio. * TOF is defined as mol (aldehyde) per mol (Rh) per hour.

A related Rh-monophosphine based system was prepared using a mesoporous MCM-41 silica (1041 m² g⁻¹) as the support and [bmim][BF₄], [bmim][PF₆] or [1,1,3,3-tetramethylguanidinium][lactate] (TMGL) as ILs (Scheme 3, 4). In the hydroformylation of 1-hexene, the MCM-41 catalyst (tppts/Rh = 5) was more active than a similarly prepared silica gel catalyst (Table 1). The highest activity (TOF = 389 h⁻¹, n/isoo = 3) was obtained with a 15 wt.% TMGL loading. The n/iso aldehyde ratio increased with increasing TMGL loading and tppts/Rh molar ratio. This system is nearly 5 times more active than the corresponding biphasic system (Table 1). The catalyst was reused 5 times without a drop in activity or selectivity, and the Rh content in the organic phase was below the AAS detection limit. In the hydroformylation of higher olefins, the activity of the SILP catalyst decreased with increasing olefin chain length.

Gas- and liquid-phase hydroformylation in fixed-bed reactors. In a further development, the hydroformylation was studied in continuous-flow fixed-bed reactors. Rh complexes with mono- or bisphosphine ligands were used as the catalysts. The gas-phase propene and liquid-phase 1-octene hydroformylation have first been carried out using a SILPC comprised of silica (298 m² g⁻¹), [bmim][PF₆] and ionic Rh-monophosphine complexes (0.2 wt.% Rh loading) (Scheme 3, 4). In the continuous-flow hydroformylation of propene at 120°C, it was observed that catalysts containing the NORBO-CS₃ ligand were significantly more active than the guanidinium-based analogues (Table 2, entries 3 and 4). However, the SILPC were less active compared to the heterogeneous catalyst (Table 2, entry 1). With respect to the ligand/Rh ratio, the
catalyst activity of the SILPs showed an optimum at L/Rh = 11.3 (Table 2, entry 2). Furthermore, the selectivity obtained using both SILP catalysts was in the usual range obtained for Rh-monophosphine catalysts, i.e., n/i < 2.8 and independent of \( \alpha \). Very low n/i ratios and activities were obtained for SILPCs with L/Rh ratios of 2.9 (entries 3 and 4). This indicates that under these conditions, the catalytically active complexes are ligand-free complexes interacting with the support. The poor solubility of CO/H\(_2\) in [bmim][PF\(_6\)] suggested that the catalyst suffered from gas mass-transfer limitations. ICP-AES analysis of outlet samples taken at steady state conversion demonstrated negligible Rh leaching (< 0.7%, below detection limit).

Similarly, Rh-bisphosphine complexes were applied in the continuous-flow gas-phase hydroformylation of propene at 100 °C. The IL [bmim][PF\(_6\)] or the halogen-free [bmim][n-octysulfate] were impregnated on silica gel (298 m\(^2\) g\(^{-1}\)).\(^{4,6}\) The L/Rh ratio and the pore filling degree of the IL had a strong influence on the catalytic performance. Ligand/Rh ratios of 2.5 resulted in rather low activities (TOF = 5.1 h\(^{-1}\)) and unusually low n/i ratios around 2 (entry 6). This is in contrast with analogous reactions performed with the IL free catalyst where high activities were observed even at L/Rh ratios of 2.5 (entry 5). On the other hand, L/Rh ratios of 10 and 20 resulted in much higher activities and n/i ratios up to 23.7 (entries 8–9) (96% linearity). The highest initial activity was obtained in the absence of IL (entry 7), which might be attributed to the formation of surface-bound ligand-free Rh species exhibiting high activities and to the absence of any mass transport limiting factors. As for the reactions with catalysts having a low L/Rh ratio, increased IL loading resulted in decreasing activity. This supports the conclusion that the catalysts are operating under mass-transfer limitation due to the poor gas dissolution rate in ILs.

A breakthrough for SILPCs with improved long-term stability was achieved by thermal pre-treatment of the silica support. These studies contributed significantly to a better understanding of various aspects of SILP catalysis. The improved catalyst was prepared by dispersing Rh(CO)\(_3\)(acac), sulfoxantphos (Scheme 3, 8) and [bmim][n-C\(_8\)H\(_17\)OSO\(_3\)] on a silica gel (304 m\(^2\) g\(^{-1}\)).\(^{4,6,11}\) The resulting partial dehydroxylation of the surface silanol groups proved to be crucial for obtaining SILP catalysts with high stability. This was demonstrated by temperature-programmed desorption of ammonia (NH\(_3\)-TPD) and MAS \(^{29}\)Si NMR spectroscopy. The SILPC was very active and highly selective for the hydroformylation of propene at 100 °C. \( \text{In situ} \) high-pressure IR spectroscopy showed that the rhodium catalyst indeed behaves as a homogeneous catalyst, \textit{i.e.}, a complex dissolved in an IL film on a support. Experiments in the absence of the IL revealed a deactivation of the catalyst within 10 h time-on-stream. Catalysts with low ligand/Rh loadings (L/Rh = 3 and 5) were initially very active but deactivated rapidly while the selectivity dropped to very low n/i ratios. In contrast, with higher ligand loadings the initial catalytic performance was retained for at least 60 h (TOF = 44 h\(^{-1}\), TON = 2600, n/i = 20). FTIR spectroscopy indicated that the deactivation is related to a gradual degradation and removal of the ligand from the catalyst complex. Evidence for the ligand-support interaction was provided by solid state MAS \(^{31}\)P NMR, which showed that the support effect is related to the irreversible reaction of the ligand with the acidic silanol surface groups. Consequently, successful catalyst systems require a relatively large excess of ligand to compensate for the loss caused by surface reactions. The catalyst lifetime exceeded 200 h time-on-stream, with only a slight decrease in activity. Since the selectivity towards n-butanal remained high at around 97%, it was concluded that possibly high-boiling side products (\textit{e.g.}, 2-ethyl-hexanal and 2-ethyl-hexanol from consecutive aldol condensation of the formed product) accumulate in the IL film, thus diluting the effective Rh concentration. Upon exposure of the SILP catalyst to vacuum, these condensation products could be removed and the initial activity was restored, allowing total lifetimes exceeding 700 h. ICP analyses of the exit gas streams showed Rh contents below the 3 ppm detection limit.

The same Rh-sulfoxantphos complex in [bmim][n-C\(_8\)H\(_17\)OSO\(_3\)] on pre-treated silica gel (\( \alpha = 0.1 \), L/Rh = 10) was used for the continuous gas-phase hydroformylation of 1-butene.\(^{42}\) As previously described for propene hydroformylation, the SILP catalyst displayed the typical characteristics of a truly homogeneous catalyst. At 120 °C, the SILPC showed a 2.1-fold higher activity when 1-butene (TOF = 647 h\(^{-1}\)) was used instead of propene (TOF = 308 h\(^{-1}\)) (Table 2, entry 10). The selectivity to \( n \)-aldehydes was also higher for 1-butene (98%) compared to propene (95%). Solubility measurements showed that the difference in solubility between propene and 1-butene in silica-supported [bmim][n-C\(_8\)H\(_17\)OSO\(_3\)] parallels the observed differences in activity well. The same group also carried out the SILP catalyzed hydroformylation of 1-butene in a gradient-free gas-phase reactor. Such Berty-type reactors allowed kinetic studies without artefacts caused by

### Table 2 Comparison of the catalytic performance of SILP and heterogeneous catalysts in the hydroformylation of propene in fixed-bed reactors

<table>
<thead>
<tr>
<th>Catalytic system*</th>
<th>( \alpha )</th>
<th>L/Rh</th>
<th>n/i</th>
<th>TOF, h(^{-1})</th>
<th>Rf</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Heterog/NORBOCS3-Rh-SiO(_2)</td>
<td>0</td>
<td>2.9</td>
<td>1.0</td>
<td>114.8</td>
<td>43</td>
</tr>
<tr>
<td>2 SILP/[bmim][PF(_6)]-NORBOCS3-Rh-SiO(_2)</td>
<td>0.05</td>
<td>11.3</td>
<td>2.0</td>
<td>88.4</td>
<td>43</td>
</tr>
<tr>
<td>3 SILP/[bmim][PF(_6)]-NORBOCS3-Rh-SiO(_2)</td>
<td>0.78</td>
<td>2.9</td>
<td>0.9</td>
<td>38.0</td>
<td>43</td>
</tr>
<tr>
<td>4 SILP/[bmim][PF(_6)]-guanidinium-Rh-SiO(_2)</td>
<td>0.78</td>
<td>2.9</td>
<td>0.9</td>
<td>20.6</td>
<td>43</td>
</tr>
<tr>
<td>5 Heterog/sulfox.-Rh-SiO(_2)</td>
<td>—</td>
<td>2.5</td>
<td>1.7</td>
<td>37.4</td>
<td>44</td>
</tr>
<tr>
<td>6 SILP/[bmim][PF(_6)]-sulfox.-Rh-SiO(_2)</td>
<td>0.49</td>
<td>2.5</td>
<td>2.0</td>
<td>5.1</td>
<td>44</td>
</tr>
<tr>
<td>7 Heterog/sulfox.-Rh-SiO(_2)</td>
<td>—</td>
<td>10.2</td>
<td>16.9</td>
<td>40.8</td>
<td>44</td>
</tr>
<tr>
<td>8 SILP/[bmim][PF(_6)]-sulfox.-Rh-SiO(_2)</td>
<td>0.08</td>
<td>10.0</td>
<td>23.3</td>
<td>37.0</td>
<td>44</td>
</tr>
<tr>
<td>9 SILP/[bmim][PF(_6)]-sulfox.-Rh-SiO(_2)</td>
<td>0.20</td>
<td>20.0</td>
<td>23.7</td>
<td>16.7</td>
<td>44</td>
</tr>
<tr>
<td>10 SILP/[bmim][PF(_6)]-sulfox.-Rh-SiO(_2)</td>
<td>0.1</td>
<td>10.0</td>
<td>18.2</td>
<td>308</td>
<td>48</td>
</tr>
</tbody>
</table>

* Heterog = heterogeneous reaction system (without IL), sulfox = sulfoxantphos ligand. Pore filling degree of support as the ratio IL volume/support porous volume. L/Rh = ligand to Rh molar ratio. n/i = normal/iso aldehyde ratio. TOF is defined as mol (aldehyde) per mol (Rh) per hour. /References.
concentration or temperature gradients. The results showed that at least in this case, there were no mass transport limitations from the gas into the IL phase. Furthermore, the limitation by film or pore diffusion seemed to be negligible.\textsuperscript{9}

**Hydroformylation in supercritical CO\textsubscript{2}**. A further technical advancement was introduced with the use of \textsubscript{sc}CO\textsubscript{2} as the mobile phase. Compared to conventional organic solvents, the hydroformylation reaction in ILs generally suffers from low gas solubility and slow diffusion of the reactive CO/H\textsubscript{2} gases in the ionic medium. A key aspect in this context is to enhance the solubility of the reactants in the IL and to enhance the mass transfer between the gas phase/organic liquid and the IL phase. Swelling with supercritical CO\textsubscript{2} reduces the IL’s viscosity and thus improves the solubility and mass transport of permanent gases. Importantly, although \textsubscript{sc}CO\textsubscript{2} shows good solubility in some ILs, the reverse is not the case, with no detectable IL solubilization in the CO\textsubscript{2} phase.

For the hydroformylation of 1-octene, a SILP catalyst was prepared by supporting Rh(CO\textsubscript{2})(acac), 3-(diphenylphosphino)benzenesulfonate 1-propyl-3-methyl-imidazolium salt (L/Rh = 10) and [1-octyl-3-methyl-imidazolium][NTf\textsubscript{2}] on silica gel (322 m\textsuperscript{2} g\textsuperscript{-1}).\textsuperscript{8} High activities were obtained (TOF up to 800 h\textsuperscript{-1}) and proved stable for at least 40 h. The corresponding aldehydes were produced with an n/iso ratio of 3. The IL loading had little effect on the reaction rate. This observation suggests that using the supercritical fluid, diffusion is not rate limiting. An additional advantage of the supercritical fluid is that it prevents catalyst fouling by extracting aldol condensation products from the IL layer. Leaching levels measured by ICP-MS tended to start high (2–4 ppm) in the first fractions, but dropped to 0.5 ppm later on.

### 2. Olefin metathesis

A solution of the first generation Grubbs Ru catalyst and [hmim][PF\textsubscript{6}] was impregnated on amorphous alumina. The Ru-SILP catalyst (0.03 mmol Ru g\textsuperscript{-1}) was effective for multiple olefin metathesis reactions like macrocyclizations and dimetrazines.\textsuperscript{8} The activity of the SILPC was dependent on the solvent choice: whereas in polar solvents no reaction occurred, the reaction proceeded well in aromatic hydrocarbons. For diethyl diallylmalonate metathesis in benzene the TON number reached 154 (82% yield).

ICP analysis of the hydrocarbon layer revealed no Ru leaching from the SILP catalyst. However, upon recycling, a moderate activity decrease was observed: 82% yield in 1 h upon first use vs. 70% yield in 2 h after the 5th recycle.

### 3. Methanol carbonylation

The [bmim][Rh(CO\textsubscript{2})I\textsubscript{2}] IL was prepared by stirring the dimeric catalyst precursor [Rh(CO\textsubscript{2})I\textsubscript{2}] with an excess of [bmim][I] in methanol.\textsuperscript{9} Subsequently, silica gel (304 m\textsuperscript{2} g\textsuperscript{-1}, dried at 500 °C) was added to this solution and next the volatile solvent was evaporated. The SILP catalyst was used for the continuous gas-phase carbonylation of a mixture of methanol and methyl iodide (75:25 wt.%) with CO at 180 °C. At low gas space velocity, complete conversion of methanol was obtained with a TOF for the desired acetyl products (acetic acid and methyl acetate) of 76.5 h\textsuperscript{-1}. The selectivity towards the ester was high (Scheme 5). Li et al. remarked that the process design of the fixed bed SILPC requires a smaller reactor size than the current technology in order to obtain the same productivity, which makes the SILPC carbonylation concept potentially interesting for technical applications.

### 4. Carbonylation of amines and nitrobenzene to ureas

A modified sol–gel synthesis procedure was used for the incorporation of [1-alkyl-3-methylimidazolium][BF\textsubscript{4}] and a metal-phosphine complex (Rh, Pd, Ru, or Co) into the pores or cavities of a silica material.\textsuperscript{9} The silica precursor (tetraethyl orthosilicate), the IL, and the metal complex were mixed with a HCl solution in aqueous ethanol. After ageing at 60 °C, the solid was dried at 150 °C. N\textsubscript{2} adsorption measurements after removal of [bmim][BF\textsubscript{4}] and TEM and XRD analysis showed that the silica gel matrix is amorphous and non-uniformly mesoporous with pore sizes of 5–11 nm. Whereas the ethyl- and butyl-substituted ILs could be washed out in refluxing acetone, ILs with larger molecular sizes such as decyl- and hexadecyl-substituted ILs were retained more firmly. It was proposed that these ILs are retained in the cavities of the silica gel by physical confinement or encapsulation. FT-Raman spectroscopy showed that the confinement of the IL resulted in unusual changes in the symmetry and coordination geometry of the ILs. The resulting SILPCs (0.11 wt.% Rh, 35 wt.% IL) were tested in the carbonylation of amines and nitrobenzene to ureas. In the carbonylation of aniline and nitrobenzene, the highest catalytic activity was observed for the Rh(PPh\textsubscript{3})Cl catalyst immobilized in [1-decyl-3-methylimidazolium][BF\textsubscript{4}] on silica (Scheme 6).

The enhanced catalytic activity compared to homogeneous IL carbonylation systems was ascribed to the effect of the high local concentration of IL containing the metal complex due to its confinement in the silica gel matrix. Upon reuse, the SILPC showed reduced activity and the Rh content of the catalyst was slightly lower than in the first reaction. The Rh and Pd SILPCs were also active in the oxidative carbonylation of aniline to methyl N-phenyl-carbamate in methanol at 135 °C and 50 bar CO/O\textsubscript{2}.

### 5. Hydrogenation

The catalytic reduction of unsaturated bonds with molecular hydrogen is an important transformation in the industrial production of fine and bulk chemicals. Typical catalysts are transition-metal complexes based on Ru, Rh, Ir, Pd or Pt. Most applications of
SILP catalysis in this field concern the immobilization of Rh-phosphine complexes for the hydrogenation of C=C double bonds. In this respect, the tunability of the solvation properties of ILs might offer interesting opportunities for selective hydrogenation reactions, e.g., in the partial hydrogenation of dienes.

The Rh complex [Rh(norbornadiene)(PPh3)2][PF6] and [bmm][PF6] were impregnated on silica gel (289 m2 g−1). The IL loading was 25 wt.% and the average IL layer thickness was estimated at 0.6 nm. The resulting catalyst was used for the hydrogenation of alkenes like 1-hexene, cyclohexene and 2,3-dimethyl-2-butene at room temperature and 41 bar of H2 in n-heptane as the solvent. In the hydrogenation of 1-hexene, the SILPC showed an enhanced activity in comparison with homogeneous and biphasic IL/heptane reaction systems (Table 3). The enhanced activity of the Rh complex in an IL phase compared to the homogeneous system has been observed and might be explained due to the absence of any coordinating solvent. Therefore, if the catalyst is carried out in an IL medium no coordinating species should be present, in that way leading to easy accessible metal centers and consequently higher reactivities. The improved performance (higher TOF) of the SILP catalytic system with respect to the biphasic IL system was ascribed to a concentration effect: by using a high-surface area support containing only a small amount of IL the concentration of the active rhodium species is significantly increased on the interface in comparison with the biphasic system. The catalyst could be reused 18 times without activity loss. The Rh leaching remained below the detection limit of 33 ppb. SEM and TEM analysis of fresh and spent catalysts indicated no Rh aggregation.

Serp et al. used multiwalled carbon nanotubes (MWCNTs) instead of the commonly used oxide supports as support for the heterogenization of ILs and homogeneous Rh catalysts for the hydrogenation of 1-hexene. CNTs are attractive supports because of inherent advantageous properties such as good mechanical strength, high chemical stability, and large surface area-to-volume ratio. They discovered that the covalent modification of the CNT surface with imidazolium based ionic functionalities is necessary to prevent leaching of the IL film. Ionophilic ligands are indeed known to be better retained in the IL phase compared to the conventional ligands. ILs are after all excellent solvents for other ionic species. One method to prepare a highly “ionophilic” catalyst is to confer a charge to the catalyst. However, there are concerns that charged species react more slowly in ILs than equivalent neutral species, due to a too strong binding between the IL and the metal centre. Therefore, both in SILP and biphasic catalysis, the ionophilicity of the catalyst has been increased by using an ionic ligand. This has been achieved by introduction of IL (ammonium, imidazolium) ponytails in the ligands.

The loading of free flowing IL [bmm][PF6], on these functionalized CNTs can be increased to 55 wt.% without detectable leaching of the IL, compared to 20–30 wt.% on the traditionally employed oxide supports. The Rh/CNT SILPC catalyst exhibits a significantly higher activity (TOF ~ 2850 h−1) than SILPCs supported on oxide supports, including silica (TOF ~ 1400 h−1) or activated carbon (TOF ~ 950 h−1), with full retention of the Rh/IL active phase upon recycling. This higher activity might be partially attributed to a more efficient use of Rh catalyst in the hydrogenation because of the good dispersibility of the CNT support in the reaction mixture which minimizes the mass transport effects.

The Wilkinson catalyst [Rh(PPh3)3][Cl] and [bmm][PF6] were mixed with the organic polymer poly(diallyl-dimethylammonium chloride). The resulting SILPC (5 mol Rh g−1) was used for the selective hydrogenation of 2-cyclohexen-1-one to cyclohexanone and 1,3-cyclooctadiene to cyclooctene at 30 °C and 5 bar of H2 in diethyl ether as the solvent. The authors claim that the SILPC showed similar activity and selectivity compared to the homogeneous reaction system in CH2Cl2, and the activity was higher compared to a conventional biphasic IL/ether system, which is probably due to improved mass transfer between the SILP and the substrate containing solvent phase. However it should be noted that upon water addition to the homogeneous reaction the reaction rate increased significantly (TOF = 15 h−1), compared to a TOF of 9 h−1 for the SILP system. The introduction of the IL is nevertheless advantageous because of the reusability of the SILPC without loss of activity. AAS spectroscopy showed no traces of Rh in the organic layer.

Sintered metal fibers (SMFs) were used as structured supports for the [bmm][BF4] IL containing the homogeneous catalyst precursor [Rh(norbornadiene)Cl], triphenylphosphine (Scheme 3, 7) and HBF4. The SMFs were first coated with a layer of carbon nanofibers (CNF) or zeolite ZSM-5 to increase the specific surface area of the support and to favour a homogeneous coverage by the IL. The coating of a thin film of IL on this support ensured a full use of the catalyst without mass transfer limitations. The resulting SILPC system (0.06 wt.% Rh, 12 wt.% IL) was used for the gas-phase hydrogenation of 1,3-cyclohexadiene to cyclohexene at 60 °C in a fixed-bed tubular reactor. The catalysts were only active in the presence of acid (e.g., HBF4 or H3PO4) and the optimal molar ratio acid/IL was 0.5. In the absence of acid, the catalyst rapidly decomposed, thereby yielding metallic Rh. Based on 1H NMR spectroscopy, Rh(H2)Cl(PPh3)3 was proposed as the catalytically active species. The amount of PPh3 was also important; a PPh3/Rh ratio of 8 resulted in a high activity (TOF up to 285 h−1), a very high selectivity (> 96%) towards cyclohexene and an acceptable stability during 6 h on stream.

6. Hydroamination

Supported hydroamination catalysts were prepared by impregnation of the metal complexes [Rh(1,1'-bis(diphenylphosphino)ferrocene)(2,5-norbornadiene)][ClO4], [Pd(dpdpf)] [(CF3SO3)2], [Cu2(C6H5CH3)][(CF3SO3)2] or Zn(CF3SO3)2 and the IL [1-ethyl-3-methylimidazolium] [CF3SO3] on a diatomaceous earth support. Before, the diatomaceous earth (10 m2 g−1) was washed with acid and silylated with Me3SiCl. The resulting
catalysts were tested in the addition of 4-isopropylaniline to phenylacetylene in n-heptane as the co-solvent. The reaction yields the enamine which in situ isomerizes to the corresponding imine (Scheme 7). At 98 °C, the highest initial activity was observed for the supported palladium catalyst (TOF = 4.3 h⁻¹, 0.1 wt.% Pd, 18.8 wt.% IL). The other supported metal complexes showed much lower activities. Details on the extent of the metal leaching or the recyclability of the SILPCs were not reported.

Ammonium hydroxide addition product was the only product apart from some styrene oligomerization products. The highest activity was observed for the SILPCs containing more polar 1-alkyl-3-methylimidazolium based ILs (ethyl > butyl > hexyl). The initial TOF for the most active material was 33.3 h⁻¹. The same activity was observed under biphasic IL/heptane conditions, suggesting the absence of diffusion limitation across the liquid–liquid phase-boundary. The catalytic activity increased with increasing IL amount. The amount of Pd leached into the reaction solution was below 1 μmol L⁻¹. The temperature dependence was explored in a fixed-bed reactor. Aniline conversion started at 150 °C and the catalytic activity increased exponentially with temperature to reach a maximum at approximately 240 °C. At this temperature, the steady-state conversion of 65% corresponds with a TOF of 200 h⁻¹. In the kinetic regime (T < 240 °C), the selectivity to N-(1-phenylethyl)aniline was 100% below 180 °C and decreased steadily at higher temperatures. Above 250 °C, the conversion decreased as the thermodynamic limit of the reaction was encountered. In the thermodynamic regime (T > 240 °C), the selectivity to N-(1-phenylethyl)aniline (44%) was the same for all SILPCs and nearly temperature independent.

7. Pd-catalyzed coupling reactions

Palladium is an excellent catalyst for various selective C–C coupling reactions. It is not always clear whether the reaction is catalyzed by molecularly defined palladium species or by in situ formed palladium nanoparticles. In some cases, these nanoparticles are stabilized in ILs and the resulting catalyst systems have shown excellent performance.28 On the other hand, if palladium-catalyzed reactions are carried out in 1,3-dialkylimidazolium based ILs as the solvent, palladium might react with the imidazolium cation forming a metal carbene complex.26 This is due to the relatively high acidity of the H atom in the 2-position of a 1,3-dialkylimidazolium ion. The latter can be deprotonated (e.g., by basic ligands or by basic reactants) to form a metal-carbene complex. In these cases, the IL acts a ligand precursor.

C–C coupling reactions. Pd(OAc)₂ and [bmim][PF₆] were impregnated on amorphous silica (600–700 m² g⁻¹). The SILP catalyst (0.25 mmol Pd g⁻¹) was used for the Mizoroki–Heck reaction between iodo-benzene and cyclohexyl acrylate with tri-n-butylamine (2 equiv.) as the base.43 In order to prevent removal of the IL layer from the silica surface, the reaction was carried out in n-dodecane as the co-solvent. At 150 °C, the TON and TOF numbers reached 68 400 and 8000 h⁻¹ respectively (96% yield). Upon reuse of the catalyst, the catalytic activity slightly decreased after two recycles. This might arise from fouling of the silica surface with the formed n-Bu₃NH, which is insoluble in n-dodecane. This problem could be solved by washing the catalyst with dilute aqueous NaOH after each run. ICP analysis of the hydrocarbon layer showed that 0.24% of the Pd dissolved from the SILPC.

In a related study, Pd(OAc)₂ and [bmim][PF₆] were immobilized on reversed-phase silica gels such as aminopropylated or N,N-diethylaninopropylated silica.44 Using the N,N-diethylaminopropylated silica gel, the Mizoroki–Heck reaction between iodo-benzene and cyclohexyl acrylate was carried out in water as the solvent and tri-n-butylamine as the base (Scheme 9). At 100 °C, the reaction was faster than in n-dodecane as the solvent and the use of water eliminated the need for a washing step to remove the
ammonium iodide from the surface. The catalyst could be reused 5 times without loss of catalytic activity. Pd leaching into the aqueous layer was 1.1 ppm after the first run (ICP). Normal phase silica resulted in the removal of the IL from the silica surface and leaching of palladium. At low Pd loadings (0.043 mmol g\(^{-1}\)), TON and TOF numbers reached 1 600 000 and 71 000 h\(^{-1}\) respectively.

A similar catalyst system was used for the Suzuki–Miyaura coupling of aryl halides with arylboronic acids. Pd(OAc)\(_2\) and [bmim][PF\(_6\)] were impregnated on N,N-diethyldiathanopro-pylated alumina.\(^{65}\) Alumina was preferred over silica owing to its higher stability in aqueous basic reaction conditions.

The coupling reaction between \(p\)-bromoacetophenone and phenylboronic acid proceeded very fast in the presence of K\(_2\)CO\(_3\) (2 equiv.) at room temperature in 50\% aqueous ethanol as the solvent (Scheme 10). The catalyst was reused up to five times with 95\% average yield, though the catalytic activity gradually decreased upon recycling. At low Pd loadings (0.02–0.025 mmol g\(^{-1}\)), TON and TOF numbers amounted to 2 000 000 and 30 000 h\(^{-1}\) respectively. At higher loadings (0.25–0.3 mmol g\(^{-1}\)), Pd leaching was observed.

An IL-tagged Pd(t) complex (Scheme 3, 2) and [bmim][PF\(_6\)] were immobilized on silica or on a polymeric imidazolium salt. As described earlier for the hydrogenation reactions, the introduction of a more “ionophilic” ligand is expected to induce here as well a positive effect on the Pd leaching from the SILPC.\(^{66}\) Alternatively, the polyvinyl imidazolium salt was prepared inside the megapores of Raschig rings.\(^{66}\) The immobilized catalysts (26 \(\mu\)mol Pd g\(^{-1}\) silica or 5 \(\mu\)mol Pd g\(^{-1}\) ring) were used for the Mizoroki–Heck coupling reaction between \(p\)-iodoacetophenone and \(\text{tert-}1,3\)-butylacrylate in toluene as the co-solvent. The reaction was carried out at 150 °C using triethylamine (2 equiv.) as the base. Although Pd leaching was about 5\% after the first run (ICP-MS analysis), the catalysts could be reused up to 10 times without loss of activity. STEM measurements showed the presence of Pd nanoparticles that remain on the polymeric surface of the spent catalysts. Strictly speaking this catalyst is not a pure SILP catalyst, since Pd nanoparticles are deposited on the support during the reaction.

The Pd(t1) complexes in the above mentioned Heck and Suzuki coupling reactions are expected to serve as a “dormant species” (pre-catalysts) that are not involved in the real catalytic cycle but are a source of colloidal Pd(0) which also can show catalytic activity at low concentrations. It was suggested that the leached and soluble palladium species do not follow the proposed Pd(t1)/Pd(t4) catalytic cycle. This has severe consequences regarding the claimed recyclability of these systems: the immobilized Pd(t1) complexes are reusable catalyst if, and only if, the \textit{in situ} produced Pd(0) species remain wholly with the support and do not freely leach into solution.\(^{67}\)

**Allylic substitution reactions.** The biopolymer chitosan was used as a support for Pd(OAc)\(_2\), tppts and [bmim][BF\(_4\)] or [bmim][PF\(_6\)]. Chitosan consists of D-glucosamine units with a small amount of N-acetyl-D-glucosamine units. The resulting catalyst was used for the allylic substitution between morpholine and (\(E\))-1,3-diphenyl-3-acetoxyprop-1-ene at room temperature (Scheme 11). After reaction, the product was separated from the IL phase by extraction with diethyl ether.

The SILPC system could be recycled and reused at least 10 times without any decrease in activity. Except for the first cycle, in which the amount of palladium leached was 9\%, the detected Pd levels by ICP-MS in the ether phase after product extraction were very low.

**8. Asymmetric reactions**

Asymmetric metal complexes are often used as molecular catalysts to introduce chirality in the synthesis of enantiopure organic compounds like pharmaceuticals or agrochemicals. In particular, transition-metal complexes with chiral P- or N-donor ligands provide high enantioselectivities. Classical strategies for the immobilization of chiral metal complexes include cross-linking with (in)organic groups and covalent attachment to solid supports. However, these methods require chemical modification of the ligand and/or the support and the obtained enantioselectivity and activity values are not seldom inferior compared to their homogeneous analogues. These limitations might be overcome by using a supported IL as the solvent phase for dissolving the chiral catalyst. In that case, even commercially available ligands and catalysts can be used.

**Asymmetric hydrogenation.** For the asymmetric \(\beta\)-ketoester hydrogenation a SILPC was prepared by mixing the chiral [Ru(S-BINAP)][Cl] \(\text{(} S\text{-BINAP} = (S)-2,2'\text{-bis(diphenylphosphino)-1,1'\text{-binapthalene}}\) (Scheme 3, 6), [bmim][PF\(_6\)] and poly(diallyldimethammonium chloride). The resulting catalyst (10 \(\mu\)mol Ru g\(^{-1}\)) was applied in the asymmetric hydrogenation of methyl acetooacetate to methyl hydroxybutrate in 2-propanol as the co-solvent (Scheme 12). The SILPC was less active compared to the homogeneous catalyst in
2-propanol but showed higher activity compared to homogeneous biphasic conditions in IL/2-propanol. Importantly, the high enantioselectivity of the homogeneous catalyst was maintained in the SILP system. The supported Ru catalyst was reused once without loss of activity and no traces of Ru were observed in the organic layer.

The asymmetric acetonophene hydrogenation was studied using SILPCs containing Ru- or Rh-BINAP complexes and phosphonium-based ILs supported on a modified silica gel. As the reaction requires basic pH conditions, the silica beads were first impregnated with K₂CO₃ or K₃PO₄. Phosphonium-based ILs were used because of their stability at high pH. In a typical catalyst synthesis, the Rh precursor [Rh(1,5-cyclooctadiene)₂][CF₃SO₃] was first stirred with (R)-BINAP in CH₂Cl₂. Next, tetradecyl(trihexyl) phosphonium decanoate and the base-promoted silica gel (141 m² g⁻¹) were added and the volatile solvent was removed in vacuo.

The asymmetric hydrogenation of acetonophene was carried out at 50 °C and 50 bar of H₂ in n-hexane as the solvent. The activity of the supported Rh catalysts was comparable to the homogeneous analogues. Ru catalysts showed high initial activity and moderate enantioselectivity, but deactivated rapidly. At 90% conversion, the above-mentioned supported Rh catalyst (11 mmol Rh g⁻¹, 12 wt.% liquidic onic) showed a selectivity towards 1-phenylethanol of 70% and an enantiomeric excess of 30%. The main side reaction was the phenyl ring saturation, leading to 1-cyclohexyle thanone and 1-cyclohexylethanol. A filtration test proved that no catalytically active Rh species leached to the hexane phase. In methanol as the solvent, the homogeneous Rh catalysts were highly selective for the reduction of the carbonyl group but showed no stereoselectivity. Apparently, the interactions between acetophenone and the chiral phosphine ligand are enhanced in the SILP. As already proposed in recent reports on imidazolium salts, a strong broadening of the molecules around the substrate-catalyst adducts. The formation of these solvent cages was indicated by a strong broadening of the MAS ¹H and ³¹P NMR signals of the supported ILs. Within the restricted space of the solvent cage, the preferred binding mode of acetophenone to the metal centre would be different from that in classical solvents such as methanol. A model was proposed in which acetophenone preferentially binds to the metal complex via simultaneous π-π-coordination of both the carbonyl and the phenyl group. Improved stereoselection is obtained, as the π-π-coordinated acetophenone has to fit tightly into the pocket formed by the 4 phenyl groups of the chiral BINAP ligand.

Recently, the chiral Ru complex (PPh₃)₂[RuCl₂(PPh₃)](S,S)-2,3-diphenylpiperidinediamine) was synthesized and immobilized in [bmim][BF₄] confined on the surface of 1-methyl-3-(3-triethoxysilylpropyl)imidazolium tetrafluoroborate modified mesoporous materials MCM-48, MCM-41, SBA-15 and amorphous SiO₂ (0.6 mmol IL g⁻¹:0.2 mmol Ru g⁻¹). In 2-propanol, the prepared heterogeneous catalysts showed high activity and enantioselectivity in the asymmetric hydrogenation of acetophenone. All 4 catalysts could be used 4 times without observable decrease in conversions and ee values, while the SiO₂-based catalyst still maintained high conversion and ee values even in the fifth run. This might be due to the larger pore size and complex structure in SiO₂ particles, which is more effective to avoid channel blockage in the recycling experiments. The total turnover number (TON) of catalyst IL/1-SiO₂/a (in which the chiral Ru complex a and the [bmim][BF₄] IL were adsorbed onto 1-methyl-3-(3-triethoxysilylpropyl)imidazolium tetrafluoroborate (1) modified SiO₂) after five catalytic runs (ca. 1000) was much higher than that of the homogeneous catalyst (200). To investigate the possible synergistic interaction between the two kinds of ILs, the catalyst IL/M48/a (in which the chiral Ru complex a and the [bmim][BF₄] IL were directly adsorbed onto unmodified MCM-48) and 1-M48/a (without adsorbed ionic liquid [bmim][BF₄]; imidazolium based IL 1 modified M48) were also evaluated. Both catalysts showed comparable catalytic activity (>99% conversion) to that of IL/1-M48/a, however, they presented a much lower conversion (<10%) when reused for the second run. This indicated that the synergistic interaction between the two kinds of ILs in the heterogeneous catalyst can significantly enhance the stability of active species.

Asymmetric aldol reactions. The organocatalyst L-proline has been supported on silica gels modified with a monolayer of covalently anchored ILs, with or without additionally adsorbed IL. An active and selective SILP catalyst was obtained by the impregnation of L-proline and [bmim][BF₄] or [1-butyl-4-methylpyridinium] [BF₄] on silica gel (453 m² g⁻¹) which was previously modified with [1-(3-triethoxysilyl-propyl)-2,3-dimethylimidazolium][BF₄] or [1-(3-triethoxysilylpropyl)-4-methylpyridinium][BF₄] respectively. The BET surface area, the BJH average pore diameter and the cumulative pore volume of the materials decreased slightly upon covalent attachment of IL fragments and a further steep decrease of these parameters was observed upon impregnation with additional IL. In the asymmetric aldol reaction between acetone and benzaldehyde, the yield and enantioselectivity obtained with the modified silica gel with additional IL were comparable with those obtained under homogeneous conditions in DMSO as the solvent. The physically adsorbed IL did not have any effect on the e.e. values. Impregnation of L-proline and IL on silica without covalently anchored IL fragments resulted in decreased yields and low enantioselectivities. The imidazolium-based SILPCs were recycled three times in the aldol condensation between p-nitrobenzaldehyde and acetone with limited activity or enantioselectivity losses. However, starting from the fifth run, lower yields were observed. According to NMR measurements, no proline leaching was observed. Regeneration of the catalytic materials was possible by methanol washing, drying, and recharging with L-proline.

For the asymmetric Mukaiyama aldol condensation, a SILPC was prepared by impregnation of Cu(OTf)₂, an imidazolium-tagged bis(oaxazoline) ligand (Scheme 3, 5) and [emim][NTf₂] on silica (20 m² g⁻¹). Alternatively, Cu, ligand and IL were impregnated on a support that already contained a monolayer of covalently anchored imidazolium fragments. The resulting catalysts were applied in the asymmetric Mukaiyama aldol condensation of 1-phenyl-1-trimethylsiloxyethene and methyl pyruvate in diethyl ether as the co-solvent (Scheme 13).

The SILPC systems were less active than the homogeneous catalyst in IL but at least as active as the homogeneous analogue.
in CH₂Cl₂. The unmodified silica impregnated with [emim][NTf₂] was efficiently recycled and gave stable conversions and enantioselectivities over 5 reaction runs. Ligand leaching was below the detection limit. Analysis of the solvent phase after extraction showed that IL leaching into the ether layer was below the 1 ppm detection limit of suppressed ion chromatography. The activity drop after the fifth run was ascribed to aggregation of silica particles.

**Asymmetric ring opening of epoxides.** A dimeric \((R,R)\)-Cr(III) salen complex (Scheme 3, 11) and [bmim][PF₆] were impregnated on silica and the resulting SILPC was used for the asymmetric ring opening of epoxides, in batch and fixed-bed reactors.\(^{72}\) The SILPC showed enhanced activity and selectivity compared to a related supported catalyst prepared by conventional impregnation in the absence of an IL.

Under continuous-flow operation, the asymmetric ring opening of 1,2-epoxyhexane with TMSN₃ in \(n\)-hexane resulted in 51% conversion and an e.e. value of the epoxide of 94%. The cumulative TON over three runs amounted to 314 and the overall leaching was only 0.7% (Scheme 14).

![Scheme 14 Asymmetric ring opening of epoxides.](image)

**Asymmetric epoxidation of olefins.** The IL fragment [1-(3-trimethoxysilylpropyl)-3-methyl-imidazolium][PF₆] was covalently anchored to mesoporous MCM-48 silica and the IL-modified material was impregnated with additional [bmim][PF₆] and a chiral substituted (5S,5S)-Mn(III) salen chloride complex (Scheme 3, 10).\(^{73}\) The immobilized catalyst (0.2 mmol Mn g\(^{-1}\)) was used for the asymmetric epoxidation of unfunctionalized olefins in CH₂Cl₂ as the solvent using a mixture of \(m\)-chloroperbenzoic acid and \(N\)-methylmorpholine-N-oxide as the oxidant at 0 \(°\)C. For olefins like 1-phenyl-1-cyclohexene, the SILPC showed higher e.e. values compared to the homogeneous catalyst. The immobilized catalyst could be reused 3 times without loss of activity or selectivity. NMR and ICP-AES measurements showed no leaching of IL or Mn-salen complex.

**Asymmetric cyclopropanation of olefins.** The asymmetric cyclopropanation of olefins with ethyl diazoacetate was carried out using a SILPC prepared by impregnation of CuCl, 5,5'-isopropylidenediisobenzofuran-4(4R)-4-phenyl-4,5-dihydro-1,3-oxazole (Scheme 3, 9) and [bmim][PF₆] on a laponite clay (370 m² g\(^{-1}\)) (Scheme 15).\(^{74}\) Compared to homogeneous reaction conditions, the SILPCs showed much lower yields. However, the supported catalyst showed interesting variations in the cis/trans- and enantioselectivities. As an example, the cyclopropanation of styrene changed from a preference for the \((1S,2S)\)-trans isomer in bulk solution to the \((1R,2S)\)-cis isomer in the supported IL film. These variations were strongly dependent on the thickness of the IL film and the support’s nature. A decrease of the IL loading led to a decrease in yield and cis/trans selectivity. Remarkably, upon reuse the yield increased and the enantioselectivity increased for trans-isomers, whereas for the cis-isomers, the enantioselectivity tended to zero or was even reversed, albeit with low values. Only layered solids with negative layer charges (e.g., clays) displayed this behaviour. It was proposed that the close proximity to the surface of the support results in a restricted rotational mobility of the bis(oxazoline)-copper complexes.

**Scheme 15 Asymmetric cyclopropanation of styrene with ethyl diazoacetate.**

Conclusions

Supported ionic liquid phase (SILP) catalysis combines the advantages of homogeneous and heterogeneous catalysis. Amongst the most attractive features are the high activity and selectivity, the ease of product separation, and the efficient catalyst recycling. Compared to biphasic reaction conditions, SILP catalysis allows a more efficient utilization of the ionic liquid and the catalyst. Summarizing, these properties make this technology very attractive for future applications. However, as the field of SILP catalysis has only developed relatively recently, some limitations remain and significant progress is still to be expected. For instance, whereas application of SILP catalysis in gas-phase processes is quite straightforward, liquid-phase reactions require tuning of all reaction constituents’ polarities in order to prevent leaching of the catalyst or the ionic liquid. It is generally accepted that ionophilic ligands, typically prepared by introduction of IL (ammonium, imidazolium) ponytails in the ligands, are superior to the conventional ligands, concerning catalyst leaching. This is particularly relevant for reactions in which highly polar reaction products are formed. In that case, limited extraction of the ionic liquid and the catalyst into the polar product phase seems difficult to avoid. Furthermore, a more fundamental understanding of various aspects of SILP catalysis is lacking, for example the support’s influence on activity and selectivity of the catalyst, the precise interaction of the ionic liquid with the support, and the issue of mass transfer in supported ionic liquid phases. In addition, the nature of the active species in SILP catalysis should be studied in more detail. Therefore, detailed mechanistic studies need to be performed to investigate SILP catalysis for specific transformations. Additionally, the basic kinetics of SILP catalysis should be studied more thoroughly. Finally, prior to industrial use, the performance of SILP catalysts must be superior to that of the...
existing catalytic systems, both with respect to activity, selectivity and recyclability.

Acknowledgements

Financial support from the K.U. Leuven (project IDO/05/005 CECAT grant and CASAS Methusalem grant) and from the IWT (SBO-project “Materials processing in ionic liquids” and PhD fellowship of CVD) is acknowledged.

Notes and references