

Catalytic Applications of Metal Nanoparticles in Imidazolium Ionic Liquids

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Abstract: Metal nanoparticles (MNPs) with a small diameter and narrow size distribution can be prepared by H₂ reduction of metal compounds or decomposition of organometallic species dissolved in ionic liquids (ILs). MNPs dispersed in ILs are catalysts for reactions under multiphase conditions. These soluble MNPs possess a pronounced surfacelike rather than single-site like catalytic properties. In other cases the MNPs are not stable and tend to aggregate or serve as reservoirs of mononuclear catalytically active species.

Keywords: heterogeneous catalysis • ionic liquids • nanostructures • supramolecular chemistry • transition metals

Introduction

Metal nanoparticles (MNPs) with 1–10 nm in diameter have unique properties that result from their inherent large surface-to-volume ratio and quantum size effects.^[1] The density of states in the valence and conductive bands of these materials decreases with reduced size, down to a few hundred atoms, and the electronic and magnetic properties change dramatically.^[2] Metal nanoparticles are only kinetically stable and consequently nanoparticles that are freely dissolved in solution must be stabilized in order to prevent their agglomeration, that is, from diffusing together and coalescing that eventually leads to the formation of the bulk metal, which is thermodynamically favored.^[3] The stabilization of soluble MNPs may be achieved by the use of stabilizing agents that may provide electronic and/or steric protection.^[4] Moreover, the stabilizing agents play also an impor-

tant role in the control of the MNPs diameter, shape, and size distribution, and also of the surface properties.^[5] In this respect, the catalytic activity and selectivity of soluble-metal-particle catalysts depends not only on the relative abundance of different types of active sites, but also on the concentration and type of stabilizers present in the medium.^[6] For example, good capping ligands—which stabilize robust nanocrystals with very narrow size distributions—are almost inactive catalysts for the hydrogenation reactions;^[7] in contrast, MNP-containing stabilizers that bind less strongly to the metal surface than other anions generate higher catalytic activity.^[8] Quaternary ammonium salts are one of the most popular and investigated classes of stabilizing agents for soluble transition-metal nanoparticle catalysts.^[4,9–11] It is assumed that the stabilization in these cases is essentially due to the positive charge on the metal surface which is ultimately induced by the adsorption of the anions on to the coordinatively unsaturated, electron-deficient, and initially neutral metal surface,^[12] similar to the classic, anion-based, DLVO (Dergaugin–Landau–Verwey–Overbeek)-type Coulombic repulsion model.^[13] However, imidazolium ionic liquids (ILs; Figure 1) differ from classical

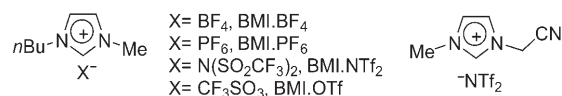


Figure 1. Examples of imidazolium ionic liquids used in the preparation of transition-metal NPs.

salts, since they possess pre-organized structures mainly through hydrogen bonds that induce structural directionality, as opposed to classical salts in which the aggregates display charge-ordering structures.

In particular, the structural organization of 1,3-dialkylimidazolium salts displays a typical trend: they form in the solid state an extended network of cations and anions connected together by hydrogen bonds.^[14,15] The monomeric unit always consists of one imidazolium cation surrounded by at least three anions and in turn each anion is surrounded

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by at least three imidazolium cations. The three-dimensional arrangement of the imidazolium ionic liquids is generally formed through chains of the imidazolium rings that generates channels in which the anions are generally accommodated as chains (Figure 2).^[16]

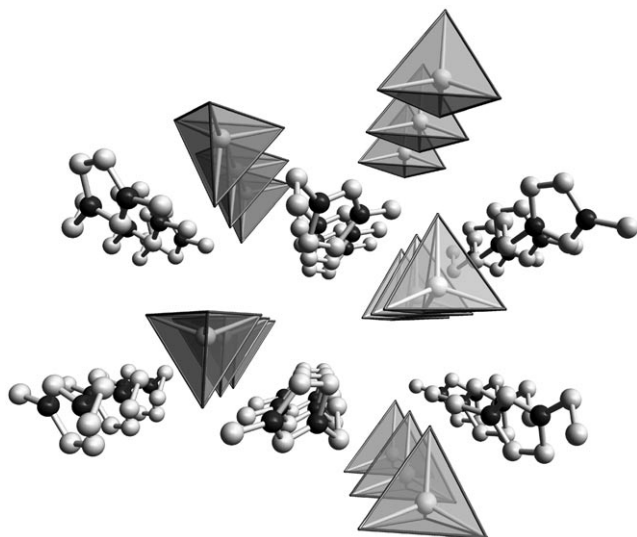


Figure 2. A three-dimensional simplified schematic view of the arrangements of 1-ethyl-3-methylimidazolium cation associated with a tetrahedral anion showing the channels formed.

These ILs structures can adapt or are adaptable to many species, as they provide hydrophobic or hydrophilic regions^[17,18] and a high directional polarizability. This is one of the special qualities of imidazolium ILs that differentiates them from the classical ion aggregates of which ion pairs and ion triplets are widely recognized examples. This structural organization of ILs can be used as “entropic drivers” for spontaneous, well-defined, and extended ordering of nanoscale structures.^[19] Indeed, the unique combination of adaptability towards other molecules and phases plus the strong hydrogen-bond-driven structure makes ionic liquids potential key tools in the preparation of a new generation of chemical nanostructures.

We were among one of the first groups to recognize these properties and used imidazolium ionic liquids as a template, stabilizer, and solvent for the synthesis of a plethora of transition-metal nanoparticles.^[20] The transition-metal nanoparticles dispersed in these fluids are stable and active catalysts for some reactions in multiphase conditions. The catalytic properties (activity and selectivity) of these soluble metal nanoparticles indicate that they possess a pronounced surfacelike (multi-site) rather than single-site-like catalytic properties. In other cases the metal nanoparticles are not stable and tend to aggregate/agglomerate or serve as simple reservoirs for mononuclear catalytically active species. The main goal of this paper is to demonstrate the utility of imidazolium ionic liquids as a template, stabilizer, and immobilizing agent for catalytic transition-metal nanoparticles. It is

worth mentioning that the purity, in particular the water and halide contents,^[21] of the imidazolium ILs play important role in the MNP chemistry, since these impurities may influence the stability and catalytic properties of the material.^[22]

Preparation and Characterization of MNPs in ILs

Transition-metal NPs are easily prepared by: 1) controlled decomposition of organometallic compounds in the formal zero oxidation state such as $[\text{Pt}_2(\text{dba})_3]$,^[23] $[\text{Ru}(\text{cod})(\text{cot})]$,^[24] or $[\text{Ni}(\text{cod})_2]$ ^[25] (dba = dibenzylideneacetone, cod = 1,5-cyclooctadiene, and cot = 1,3,5-cyclooctatriene) dispersed in ILs; 2) chemical reduction (usually with hydrogen or a hydride source) of transition-metal compounds such as $[\text{Pd}(\text{acac})_2]$ ^[26] (acac = acetylacetonate), $[\text{Ir}(\text{cod})\text{Cl}]_2$, RhCl_3 ,^[27] and RuO_2 ^[28] dispersed in the ILs and 3) simple transfer of the freshly prepared MNP in water or “classical” organic solvents to the ILs.^[29] Alternatively, in situ laser radiation may be used to induce the fragmentation of relatively large MNPs dispersed in ILs into smaller particles with a narrow size distribution.^[30]

The formation of the nanoparticles from methods 1) and 2) apparently follows the autocatalytic mechanism developed by Finke and co-workers^[31,32] that basically involves two steps: nucleation and surface growth. In various cases these IL colloidal mixtures can be used directly as catalysts or they may be isolated and used as powders in solventless conditions (the substrates/products are per definition the solvent) or re-dispersed in the ILs (see below).

The structures of the MNPs either dispersed in the ionic liquids or after isolation have been studied by using various techniques, such as X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (EXAFS), small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and X-ray diffraction (XRD).

The XRD of the MNPs isolated from the ILs have been used to check the crystalline nature of the material and to estimate the mean diameter by means of the Debye–Scherrer equation by using Rietveld’s refinements. The mean diameters of these isolated materials have also been determined by TEM and usually are quite close to those obtained with the nanoparticles dispersed in the ILs (see below). More interesting results have been obtained from the XPS analysis of the isolated MNPs of nanoparticles prepared in ionic liquids containing the PF_6 and BF_4 anions;^[24,26,28,33] in most of these cases M–O and M–F contributions are observed. The contribution of the M–F component is more pronounced in the case of PF_6 anion than for BF_4 anion. The F 1s, P (in the case of PF_6), and B (in the case of BF_4) contributions are also observed in the XPS spectra.^[33] These results clearly indicate that even relatively low coordinating anions such as PF_6 and BF_4 coordinate with the metal surface. Moreover, XPS experiments indicate that the MNP surface is more susceptible to oxidation in air than the bulk metal and that this oxide layer may also be a significant source of stability of the metal nanoparticles.^[34] It is noticea-

ble that after Ar⁺ sputtering almost all of these surface-bound species are removed (Figure 3). Indeed, XPS spectra after sputtering displays mainly the M–M component at the 4f region, demonstrating that only the external surface metal atoms are bound to F and O.^[24,26,30,33,35]

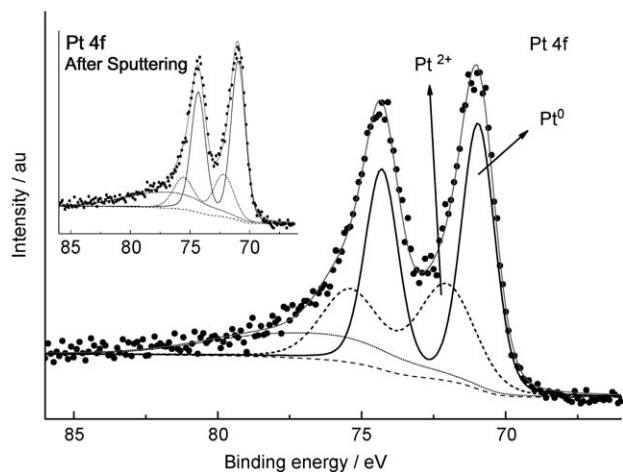


Figure 3. X-ray photoelectron spectra of the Ir 4f region for Pt⁰ nanoparticles prepared in BMI·BF₄ before and after (inset) Ar⁺ sputtering. The Ar⁺ sputtering eliminates the outmost layers of the particles and therefore resulting in the Pt 4f region with mainly Ir–Pt bond component.

Inasmuch as most of the 1,3-dialkylimidazolium ionic liquids have extremely low vapor pressure^[36–38] and relatively high viscosity at room temperature,^[39–42] in situ TEM^[23,43] and XPS^[44]—which require high vacuum—could be performed with the MNPs dispersed in ILs.^[37] The size and shape determined by this TEM in situ technique are the same as that obtained with the isolated nanoparticles which were mixed with an epoxy resin distributed between two silicon wafer pieces.^[23] More interestingly, detailed analysis of the Pt⁰ nanoparticles dispersed in the ionic liquids, shows a rather strong fluctuation of the contrast density. These contrast density fluctuations are characteristic of amorphous substances, offering strong evidence for the interaction features of the ionic liquid with the Pt⁰ nanoparticles.^[23]

As already discussed pure 1,3-dialkylimidazolium ionic liquids^[45] are best described as hydrogen-bonded polymeric supramolecules of the type $\{[(\text{DAI})_x(\text{X})_{x-n}]^{n+}[(\text{DAI})_{x-n}(\text{X})_x]^{n-}\}_n$ in which DAI is the 1,3-dialkylimidazolium cation and X the anion.^[46,47] Depending on the type of the anion and the alkyl side chains the imidazolium IL may display relatively long-range order that increases with the number of carbon atoms of the *N*-alkyl side chain. Indeed, SAXS analysis of Pt⁰, Ni⁰, and Ir⁰ nanoparticles dispersed in ILs indicated the formation of a layer surrounding the MNPs. This protective layer is probably composed of semi-organized supramolecular aggregates of the type $\{[(\text{DAI})_x(\text{X})_{x-n}]^{n+}[(\text{DAI})_{x-n}(\text{X})_x]^{n-}\}_n$ on the metal surface.^[33,35,48] More interestingly, TEM, SAXS, and EXAFS studies of Ni NPs prepared in 1-alkyl-3-methylimidazolium (alkyl = *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-tetradecyl, and

n-hexadecyl) ILs indicate a reduction in the mean diameter (Figure 4), a narrowing of the size distribution, and an increase of the shape regularity of the MNPs with an increase

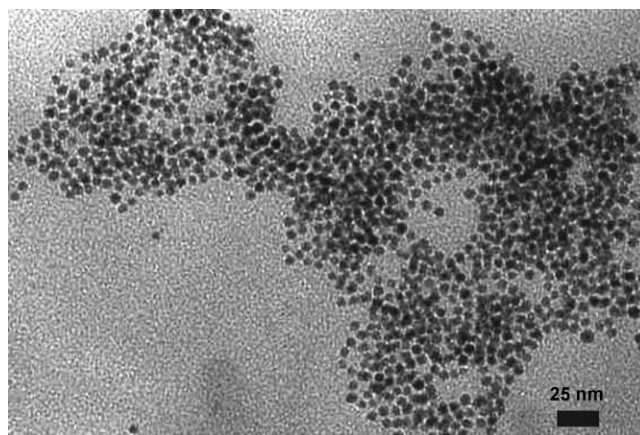
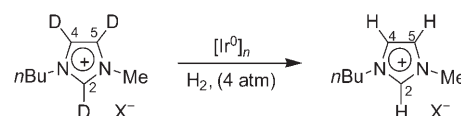


Figure 4. Part of TEM micrographs of Ni nanoparticles (5.1 ± 0.9 nm) dispersed in 1-methyl-3-*n*-tetradecylimidazolium *N*-bis(trifluoromethanesulfonyl) imidate IL.^[25]

in length of the alkyl side chain, that is, with the increase of the range order of the salt (templatelike effect of the IL).^[25]

In a similar vein, evidence has been recently reported for the formation of ordered three-dimensional structures (cage-type) in solutions around a cationic palladium compound in a thin film of supported ionic liquid.^[49] Using D₂ and ²H NMR spectroscopy in the formation of Ir⁰ nanoparticles from the reduction of [Ir(cod)(MeCN)₂]⁺ in BMI·NTf₂ (BMI = 1-butyl-3-methylimidazolium NTf₂ = bis(trifluoromethylsulfonyl)imide)/acetone and Proton Sponge (1,8-bis(dimethylamino)naphthalene), Finke and co-workers have detected the intermediacy of surface-ligand-coordinated *N*-heterocyclic carbenes. The Ir⁰-nanoparticle-catalyzed H/D exchange, in which deuterium incorporation in the 2-H and 4-H positions of the imidazolium occurs only after an induction period.^[50] The kinetics are well-fit by the analytical equations corresponding to the autocatalytic mechanism that is diagnostic of nanocluster formation. Moreover, it was also independently observed that the D/H exchange only occurs after the formation of Ir⁰ nanoparticles and the D/H exchange occurs preferentially at the less acidic C-4 and C-5 imidazolium positions in the reaction of [Ir(cod)Cl]₂ in deuterated BMI·NTf₂ with molecular hydrogen (Scheme 1).^[51]

The D/H exchange only occurs after the complete consumption of the alkene and no D-incorporated alkane was detected, indicating that the coordinated NHC carbene is



Scheme 1.

easily displaced by the alkene and that these carbenes are less strongly bound to the metal surface than observed in mononuclear metal compounds.^[52]

These results strongly suggest that the imidazolium cations react with the nanoparticle surface preferentially as aggregates of the type $\{[(\text{DAI})_x(\text{X})_{x-n}]^n+[(\text{DAI})_{x-n}(\text{X})_x]^{n-}\}_n$ (in which DAI is the 1,3-dialkylimidazolium cation and X the anion) rather than as isolated imidazolium cations.

Catalytic Reactions

It is worth noting that classical molecular transition-metal clusters have been used in ILs for hydrogenation reactions. In particular, the air and moisture stable system $[\text{BMI}\cdot\text{BF}_4]/[\text{Ru}_4(\eta^6\text{-C}_6\text{H}_6)_4][\text{BF}_4]$ has been used for the multiphase hydrogenations of arenes.^[77]

Transition-metal NPs dispersed in imidazolium ionic liquids are active catalysts for various reactions (Table 1) such as the hydrogenation of alkenes, arenes, and ketones. In

most of these cases, the catalytic reactions are typically multiphase systems in which the MNPs, dispersed in the ILs, form the denser phase and the substrates and product remains in the upper-phase; hence the ionic catalytic solution is easily recovered by simple decantation.^[39]

In the hydrogenation of simple alkenes the recovered ionic dispersion can be re-used several times without any significant loss in catalytic activity, as observed with IL-dispersed Ir^0 , Rh^0 , Pt^0 , and Ru^0 NPs. However, in the case of aromatic compounds and ketones some metal NPs tend to aggregate with loss of their catalytic activity such as Rh^0 in the hydrogenation of benzene^[78] and Ir^0 in the reduction of ketones.^[60] However, these NPs are more stable in the hydrogenation reactions when dispersed in the ionic liquids than in solventless conditions. Note that aromatics, ketones, and alcohols are much more soluble in the ionic liquids than the alkenes and alkanes.^[79] Therefore, aromatic and functionalized compounds probably wash-out the protective ionic liquid species from the metal surface, thereby facilitating the aggregation/agglomeration process that eventually

Table 1. Examples of catalytic reactions performed with MNPs in ILs.

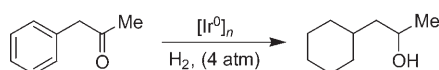
Entry	Reaction	Catalyst	Ionic liquid ^[a]	Ref.
1	alkene and diene hydrogenation	Pd	BMI-PF ₆	[53]
			BMI-PF ₆ /TBA-Br	[54]
			BMI-PF ₆	[55]
			BMI-BF ₄ , BMI-PF ₆	[26]
			TMGL immobilized in molecular sieves ^[a,b]	[56]
		Pt	BMI-PF ₆	[23]
			BMI-PF ₆	[55]
			BMI-PF ₆ /BMI-BF ₄	[35]
			Rh	[55]
			Ru	[24, 28, 57]
2	arene hydrogenation	Rh	BMI-PF ₆	[20, 33, 58]
			BMI-BF ₄	[27, 59]
		Pt	BMI-PF ₆	[23]
			Ru	[24, 57]
		Ir	BMI-BF ₄ , BMI-PF ₆ , BMI-Otf	
			BMI-PF ₆	
			BMI-PF ₆	[27]
			BMI-PF ₆	[60]
			Ru	[61]
			Rh	[62]
3	ketone hydrogenation	Pd	TBA-Br	[63–66]
			BMI-PF ₆	[67]
		Ir	TBA-Br, BMPyrr-NTf ₂	[68]
			IL layer immobilized in silica ^[c]	[69]
			ThepA-Br, TBA-Br	[70]
			BMI-PF ₆ , BMI-Cl	[71]
			Bpy-X, CNC ₃ Py-X (X = Cl, PF ₆ , BF ₄ , NTf ₂)	[72]
			ThepA-Br	[71]
			BMI-NTf ₂ , NCC ₃ MI-NTf ₂	[73]
			BMI-PF ₆	[70]
4	cellobiose hydrogenation	Pd	BMI-X or BMPy-X (X = PF ₆ , BF ₄ , Cl)	[74]
			pyridinium/imidazolium based ILs	[75]
			BMI-PF ₆	[70]
			BMI-X or BMPy-X (X = PF ₆ , BF ₄ , Cl)	[74]
5	alkenes hydroformylation	Pd	BMI-PF ₆	[70]
			BMI-PF ₆	[70]
6	Heck reactions	Pd	BMI-PF ₆	[70]
			BMI-PF ₆	[70]
7	Suzuki C–C coupling	Pd	BMI-PF ₆	[70]
			BMI-PF ₆	[70]
8	Stille C–C couplings	Pd	BMI-PF ₆	[70]
			BMI-PF ₆	[70]
			BMI-PF ₆	[70]
			BMI-PF ₆	[70]
			BMI-PF ₆	[70]
			BMI-PF ₆	[70]
9	Sonogashira C–C couplings	Pd	BMI-PF ₆	[70]
			BMI-PF ₆	[70]
10	methoxy carbonylations	Pd	BMI-PF ₆	[70]
			BMI-PF ₆	[70]
11	hydrosilylations	Pt	BMI-PF ₆	[70]
			BMI-PF ₆	[70]
12	methanol oxidation	Pt/Ru	BMI-BF ₄	[76]

[a] Abbreviations: TMGL = tetramethyl guanidinium lactate; TBA-Br = tetrabutyl ammonium bromide; BMPyrr-NTf₂ = butyl-methyl pyrrolidinium *N*-bis(trifluoromethanesulfonyl) imidate; ThepA-Br = tetra-heptyl ammonium bromide; BPy = butyl pyridinium cation; NCC₃Py-X = *N*-butyronitrile pyridinium cation; NCC₃MI-NTf₂ = 1-butyronitrile-3-methyl imidazolium *N*-bis(trifluoromethanesulfonyl) imidate and BMPy = 1-butyl-4-methyl pyridinium cation; Otf = triflate. [b] The nanoparticles were immobilized in molecular sieves with the TMGL. [c] A palladium carbene complex is anchored on a silica matrix and under the reaction conditions Pd nanoparticles are formed in the ionic liquid layer.

leads to the formation of the bulk metal with consequent loss of their catalytic activity. The stability and evolution of the size and shape of the MNPs can be easily followed by in situ TEM analysis of the ionic catalytic dispersion before and after catalysis.^[67]

The hydrogenation of simple alkenes by Ir⁰ nanoparticles dispersed in ILs depends on steric hindrance at the C=C double bond^[58] and follows the same trend observed with classical iridium complexes in homogeneous conditions, that is, the reaction follows the order: terminal > disubstituted > trisubstituted > tetrasubstituted.^[80] Interestingly, the alkene hydrogenation process by the Ir⁰ nanoparticles in BMI-PF₆ follows the classical monomolecular surface reaction mechanism $v = k_c K[S]/1 + K[S]$ (k_c = kinetic constant and K = adsorption constant). The reaction rate is a mass controlled process below hydrogen pressure set < 4 atm. The reaction under hydrogen pressures ≥ 4 atm is zero order with respect to hydrogen and the reaction rate depends only on the olefin concentration in the ionic liquid phase.^[52] The hydrogenation reaction constants of alkylbenzenes by Ir⁰, Rh⁰ and Ru⁰ MNPs prepared in the imidazolium ILs can be expressed by steric factors and are independent of any other non-steric factors.^[81] The presence of bulky alkylbenzene substituents for transition-metal, NP-mediated hydrogenation reactions lower the overall hydrogenation rate, implying a more disrupted transition state compared to the initial state of the hydrogenation in terms of the Horiuti–Polanyi mechanism.^[82]

The hydrogenation of ketones containing aryl groups such as benzylmethylketone by Ir⁰ nanoparticles is highly selective towards the reduction of the aromatic ring (Scheme 2).^[60] The high selectivity is a strong indication of the preferential coordination of the aromatic ring to the metal surface rather than the ketone moiety.



Scheme 2.

It is interesting to note that MNPs in simple imidazolium ILs tend to agglomerate/aggregate after the hydrogenation reactions. However, more stable catalytic systems in ILs can be obtained by the use of additive ligand or polymeric stabilizers. For example, immobilizing Rh⁰ NPs in polymeric ionic liquids such as poly[(*N*-vinyl-2-pyrrolidone)-co-(1-vinyl-3-alkylimidazolium halide)] copolymers. Rhodium nanoparticles stabilized by the ionic copolymer showed high lifetime and activity in arene hydrogenation reactions.^[59] Stable alkenes hydrogenation catalysts based on Pt⁰, Pd⁰, and Rh⁰ nanoparticles stabilized by poly(*N*-vinyl-2-pyrrolidone) (PVP) have been also prepared by simple ethanolic reduction of the corresponding metal halide salts immobilized in BMI-PF₆.^[55] Other extra stabilizing agents, such as carbon, montmorillonite (MMT) or mesoporous SBA-15, have been used to improve the stability of MNPs in ionic liquids.^[83,84] The nanoparticle/ionic liquid/extra stabilizer

combination usually exhibits excellent synergistic effect that enhance the activity and durability of the catalyst for the hydrogenation of olefins. For example, bimetallic Pt-Ru/C nanoparticles of around 2.5–3.5 nm prepared by reduction of H₂PtCl₆, RuCl₃, and Vulcan XC-72 carbon black dispersed in BMI-BF₄ display high electrocatalytic activity for methanol oxidation.^[76]

Another highly interesting approach consists of the use of ligands on the metal surface akin to classical mononuclear organometallic chemistry. For example, Pd⁰ nanoparticles in “classical” ILs such as BMI-PF₆ tend to agglomerate after the hydrogenation of alkenes.^[26] However, phenanthroline-protected palladium nanoparticles in this IL are very active and selective for the hydrogenation of olefins, and the nanoparticles/IL system could be reused several times without a loss of activity.^[53] Moreover, elegant investigations by Dyson and co-workers on functionalized ILs^[85,86] such as imidazolium or pyridinium salts with the nitrile functional group attached to the alkyl side demonstrated that the ILs could act as both solvent and ligand for metal-catalyzed reactions.^[87] For example, Pd⁰ NPs immobilized in both *N*-butylpyridinium and nitrile-functionalized ILs show good catalytic activity for the Stille coupling reactions, but recycling and reuse is considerably superior in the nitrile-functionalized ionic liquid.^[72]

One of the most interesting applications of transition-metal NPs dispersed ILs is the possibility of tuning the selectivity of the reaction, since in these multiphase catalytic processes the primary products can be extracted during the reaction thereby modulating the product selectivity (modifying the different substrates and the solubility of the reaction products with the catalyst containing phase). For example, 1,3-butadiene is at least four times more soluble in BMI-BF₄ than butenes, therefore the selective partial hydrogenation could be performed by Pd⁰ nanoparticles embedded in the ionic liquid (selectivities up to 72% in 1-butene were achieved at 99% 1,3-butadiene conversion). The amounts of butane (fully hydrogenated 1,3-butadiene) and *cis*-2-butene products are marginal and the butenes formed do not undergo an isomerization process, indicating that the soluble Pd⁰ nanoparticles possess a pronounced surfacelike rather than single-site like catalytic properties. In a similar way the solubility difference of benzene and cyclohexene (maximum of 1% cyclohexene concentration is attained at 4% of benzene concentration in BMI-PF₆) was used for the hydrogenation of benzene to cyclohexene with a 39% selectivity at low benzene conversions by Ru⁰ NPs dispersed in BMI-PF₆.^[24] Although the maximum yield of 2% in cyclohexene is too low for technical applications, it represents a rare example of partial hydrogenation of benzene by soluble transition-metal NPs.^[88]

Well-defined and in-situ-prepared Pd⁰ nanoparticles in ionic liquids have been reported to promote C–C coupling reactions such as Heck and Suzuki processes (Table 1, entries 6–9). In most cases, however, the Pd⁰ nanoparticles are simple reservoirs of homogeneous Pd⁰ catalytically active species akin to those observed with phosphane-free palladi-

um catalysts precursors,^[89–91] such as simple Pd^{II} compounds^[92] or palladacycles.^[93,94] It is highly probable that in these cases the Heck coupling reaction proceeds through the oxidative addition of the aryl halide on the nanoparticles surface, and the oxidized Pd species thus formed are detached from the surface and enter into the main catalytic cycle.^[95] The Pd⁰ formed in the main catalytic cycle, after β -hydride and reductive elimination steps, can either continue in the catalytic cycle or fall back to the nanoparticle reservoir.^[67]

The same behavior was observed in the hydroformylation of olefins catalyzed by Rh⁰ nanoparticles prepared in BMI·PF₆.^[62] Aldehydes were generated preferentially when 5.0 nm Rh⁰ nanoparticles were used in the hydroformylation of 1-alkenes. Although small nanoparticles also generate catalytically active species the chemoselectivity decreases compared to those performed with 5.0 nm nanoparticles. In contrast, the large-sized nanoparticles (15 nm) produce only small amounts of aldehydes similar to that observed with a classical heterogeneous Rh/C catalyst precursor. TEM, XRD, IR, and NMR experiments indicate that these Rh⁰ nanoparticles degraded under the reaction conditions into catalytically active, soluble mononuclear Rh–carbonyl species.

Conclusions

In summary transition-metal NPs in imidazolium ILs are probably stabilized by protective layers of discrete supramolecular $\{[(\text{DAI})_x(\text{X})_{x-n}]^n + [(\text{DAI})_{x-n}(\text{X})_x]^n\}_n$ species through the loosely bound anionic moieties and/or NHC carbenes together with an oxide layer when present on the metal surface. These loosely surface-bound protective species are easily displaced by other substances present in the media. This on the one hand is responsible to some extent for their catalytic activity, but on the other hand explains their relatively low stability that leads to aggregation/agglomeration and eventually to the bulk metal. Therefore the stability and the catalytic activity of transition-metal NPs in imidazolium ionic liquids are also highly influenced by coordinative strength of the aggregates with the metal surface and the type and nature of the substrates/products.

Moreover, transition-metal NPs dispersed in these fluids are stable and active catalysts for reactions in multiphase conditions. The catalytic properties (activity and selectivity) of these soluble metal nanoparticles indicate that they possess a pronounced surfacelike (multi-site) rather than single-site like catalytic properties. In other cases the metal nanoparticles are not stable and tend to aggregate or alternatively they serve as simple reservoirs of mononuclear catalytically active species. However, the ionic liquid provides a favorable environment for the formation of metal nanoparticles with, in most cases, a small diameter and size distribution under very mild conditions. Alternatively, these nanoparticles can be used in conjunction with other stabilizers or easily transferred to other organic and inorganic sup-

ports to generate more stable and active catalysts. The nanoparticle/ionic liquid/stabilizer combination usually exhibits an excellent synergistic effect that enhances the activity and durability of the catalyst. Furthermore, only a few simple ionic liquids have been used so far for the formation of nanoparticles for catalysis using classical synthetic methods. Therefore, the use of task specific ILs may provide stronger stabilizing fluids for the metal nanoparticles without losing their catalytic properties. Moreover, the use of other transition-metal nanoparticle synthetic methods such as electrochemical reductions in ILs may provide other nanomaterials with differentiated catalytic properties.

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