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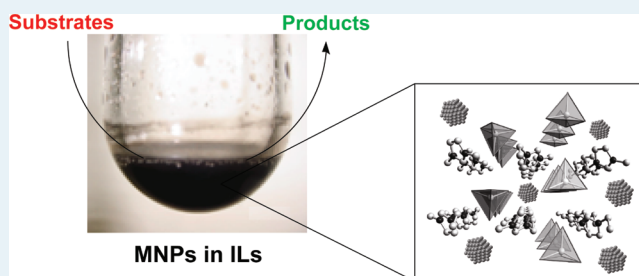
Transition Metal Nanoparticle Catalysis in Ionic Liquids

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ABSTRACT: The main “molecular” physicochemical aspects involved in the catalytic applications of “soluble” transition metal nanoparticles in ionic liquids are used to explain their properties. In particular, a special view on the concepts of coordination catalysis is used to describe the properties of these nanoscale catalysts in solution as well as their scope and limitations in multiphase catalysis.

KEYWORDS: ionic liquids, nanoparticles, catalysis, supramolecular chemistry, imidazolium salts



1. INTRODUCTION

Ionic liquids (ILs) are currently among the most investigated fluids for chemistry in solution.¹ Indeed, the modular physicochemical properties of the majority of these liquids, such as density; viscosity; ionic mobility; hydrophobicity; and miscibility with other organic and inorganic ionic, molecular, or macromolecular compounds, associated with their very low vapor pressure and nonflammability render these materials ideal media for various transformations in solution.² Indeed, since their early days, modern ionic liquids (Figure 1), especially

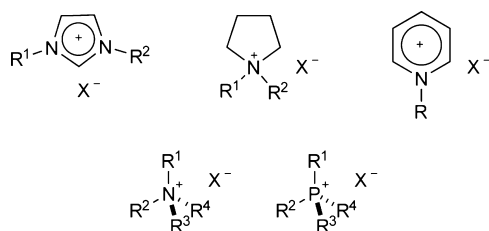


Figure 1. Examples of ILs based on imidazolium, pyrrolidinium, and pyridinium cations and quaternary ammonium or phosphonium salts (R are usually alkyl groups and X are weak coordinating anions such as BF₄, PF₆, N(SO₂CF₃)₂, OAc, etc.).

those based on the 1,3-dialkylimidazolium cation, have been extensively used as immobilizing agents for transition metal catalyst precursors^{3,4} since they allow facile product separation and catalyst recycling.^{5,6}

The unique properties of these liquids are a direct result of their structural organization in both condensate and gas phases. Indeed, ILs cannot be regarded as merely homogeneous solvents^{7,8} because they form extended networks of hydrogen bonds and dispersive forces with polar and nonpolar nanodomains; thus, they are, by definition, “supramolecular” fluids.⁹ Therefore, ILs are better described as hydrogen-bonded and dispersive force-bonded polymeric supramolecules of the type

$[(\text{DAI})_m(\text{X})_{m-n}]^{n+}[(\text{DAI})_{m-n}(\text{X})_m]^{n-}$ (where DAI is the 1,3-dialkylimidazolium cation and X is the anion).¹⁰ This structural pattern is a general trend for both the solid and liquid phases, and is maintained to a large extent even in the gas phase.^{9,11–13}

In fact, imidazolium-based ILs (Figure 2) display a higher degree of 3-D structural organization than the other ILs in view

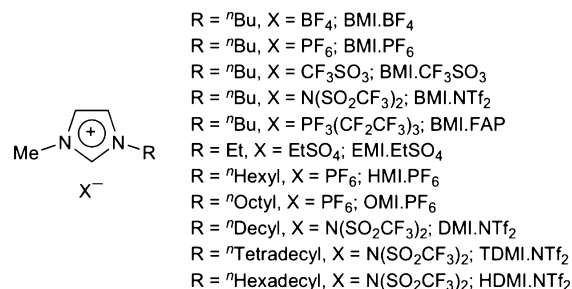


Figure 2. Examples of ILs based on 1-alkyl-3-methylimidazolium cation.

of the presence of a virtually rigid and planar ring and the presence of at least three acid hydrogen sites on the imidazolium cation that strengthen the directionality of hydrogen bonds and other weak forces. This structural organization of ILs has been used as an “entropic driver” (the so-called “IL effect”) for the preparation of a plethora of well-defined and extensively ordered nanoscale structures, either in the bulk phase or at the gas/vacuum interface, in particular, the application as a suitable medium for the synthesis of “soluble” transition metal nanoparticles that may be regarded as soluble forms of heterogeneous catalysts.

Received: October 11, 2011

Revised: December 14, 2011

Published: December 16, 2011

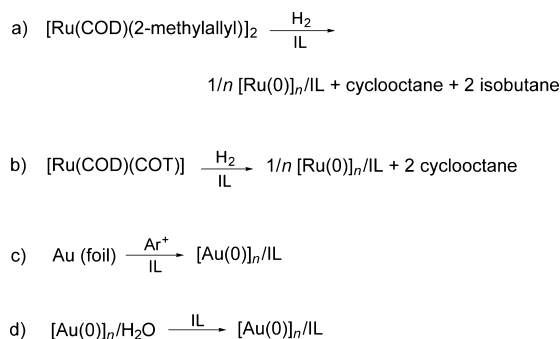
Indeed, several catalytic systems based on transition metal nanoparticles immobilized in ILs have been developed in recent years for hydrogenation, oxidation, and C–C coupling reactions under both single-phase and multiphase conditions. In fact, there are some quite recent outstanding reviews on the preparation, characterization, and use (including in catalysis) of soluble metal nanoparticles in ILs.^{14–16} In fact, a critical review discussing structural aspects and surface properties of MNPs in ILs and two other reviews focusing on catalytic reactions, a general concept article together with one describing C–C cross-coupling reactions in ILs catalyzed by Pd MNPs, have been reported. However, none of these reviews have discussed in detail the catalytic process itself in this media. Other interesting revisions have been done in the field of transition metal nanoparticles, including general considerations on their stabilization modes and catalytic properties.^{17,18}

The main goal of this perspective is to present and discuss the main recent achievements and the limitations of catalysis by transition metal nanoparticles in ILs. Particular attention is paid to describing these nanomaterials as “soluble” analogs of heterogeneous catalysts in which the same concepts of coordination catalysis can be applied to explain the properties of these catalysts, such as how ligands can induce and control selectivity and activity.

2. METAL NANOPARTICLES IN ILs

Soluble and stable transition metal NPs can be easily prepared in ILs by the following methods: (a) simple reduction of M(I), M(II), M(III), or M(IV) compounds dissolved in ILs; (b) decomposition of organometallic complexes in the formal zero oxidation state dissolved in ILs; (c) bombardment of bulk metal precursors with deposition onto ILs; and (d) phase transfer of preformed NPs in water or organic solvents to ILs (Scheme 1).

Scheme 1. Examples of Metal Nanoparticle Synthesis



The two first methods (a and b) are the most simple and are used to access a series of different sizes and shapes of metal nanoparticles since they involve the simple reaction of a metal compound precursor dissolved in an IL in the presence of a reducing agent, such as hydrogen.¹⁹ In general, irregular spherically shaped metal nanoparticles 2–10 nm in size are obtained by these two methods.

The size and shape of these prepared MNPs depends on several aspects, such as the reaction conditions (temperature, metal concentration, time, etc.), the type of metal precursor and reducing agent, and the nature of the ionic liquid. However, there is evidence indicating that the relative size of MNPs is directly related to the volume of the nanoregion (polar and

nonpolar domains) of the IL. Indeed, ionic metal precursors tend to be dissolved in the polar IL domain, and thus, the size is directly related to the volume of the anion of the imidazolium-based IL.^{20–22}

On the other hand, neutral metal precursors tend to be concentrated in the IL nonpolar domain, and thus, the size of MNPs increases with the augmentation of the *N*-alkyl side chain of the imidazolium cation.^{23–26} The third method, based on metal sputtering, is one of the cleanest since only the metal and the IL are used.^{27,28} In these cases, the size and shape of MNPs depends mainly on the surface structural organization of the IL and the current used during the process.^{29,30} The size of the MNPs increases with an augmentation in the current and also with the concentration of the nonpolar domains at the IL interface with the vacuum. The fourth method is particularly interesting since well-defined sizes and shapes of nanoparticles can be prepared in water³¹ or organic solvents³² using well-established procedures; these can then be transferred to the ionic liquid for the desired catalytic application. Noteworthy, other routes for the preparation of nanostructured particles in ILs can also be mentioned, such as by plasma reduction,^{33–36} electrochemical process,^{37–40} and microwave irradiation,^{41–47} and they can be classified as variants of methods a and b; that is, reduction and decomposition, respectively, of metal compounds.

Although is still an open issue, it is usually assumed that the surface of at least small MNPs is electron-deficient, and thus, the electron-rich species present in the media will interact preferentially. In the case of MNP in ILs, the metal surface usually has several species, such as oxides, hydrides, carbenes, and residual ligands from the metal precursors, etc.; that is, it is never clean. Indeed, direct evidence of the interaction of a nonfunctionalized ionic liquid with the metal nanoparticle surface has been obtained by *in situ* TEM,⁴⁸ XPS,⁴⁹ SERS,⁵⁰ and H/D exchange reactions.⁵¹ Indeed, these experiments indicated that the IL interacts with the metal surface as aggregates rather than as isolated ions. In addition, recent theoretical studies suggest that metallic nanoparticles in ionic liquids are preferentially surrounded by the charged moieties of ions, with an interface layer that is one ion thick.⁵² Therefore, the stabilization mechanism of MNPs in ILs is probably not due to an electrostatic double layer, since both cations and anions are present in contact with the surface.

In addition, labeling experiments, using either D₂ or deuterated imidazolium-based ILs, and MNP formation studies point out the presence on the metal surface of *N*-heterocyclic carbenes (NHCs) as at least transient species and probable hydrides.^{51,53–55} Note that recent studies via ESI(+)-MS also indicate that, when imidazolium-based ionic liquids are employed in solutions, even under relatively “neutral” conditions, relatively stable NHCs are most likely to be formed.⁵⁶ Therefore, the presence of such species in imidazolium IL is most probably inevitable; hence, their participation should always be considered in catalytic processes performed in imidazolium ILs.

Interesting, elegant NMR studies have demonstrated that, at least for Ru, nanoparticles prepared under hydrogen in ILs or organic solvent show the presence of surface hydrides.^{55,57} XPS analysis of the isolated MNPs usually shows the presence of an oxide layer and the presence of anionic species or ligands interacting with the metal surface.^{21,58–62} All these species are responsible for the relative stability of metal nanoparticles in nonfunctionalized ILs and may be considered as ligands/

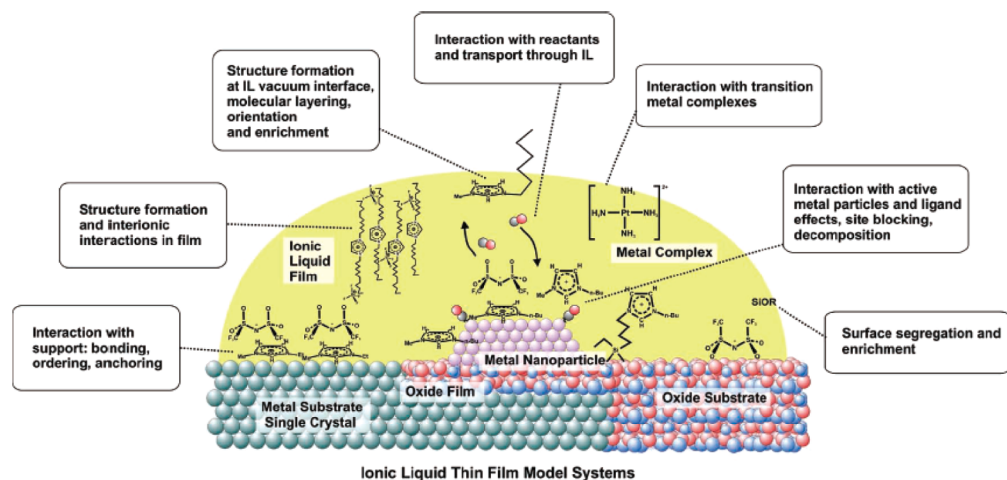
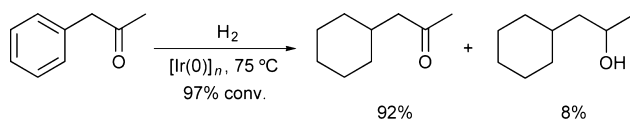


Figure 4. General aspects involved in SCILL materials. Reprinted with permission from ref 76 (copyright Wiley-VCH Verlag GmbH & Co. KGaA).

this case, the NPs display surface-like catalytic properties rather than homogeneous-like properties since the aromatic rings are preferentially reduced on aromatic derivatives (Scheme 2).⁷⁸

Scheme 2. Selectivity of the Hydrogenation of Benzylmethylketone Catalyzed by Ir MNPs⁷⁸



Moreover, the influence of substituents on the rate constant of the hydrogenation of monoalkylbenzenes by isolated MNPs can be rationalized in terms of the Taft rule. The results clearly showed that the reaction constants for alkyl-substituents can be expressed by steric factors and are independent of any other nonsteric factors.⁷⁹ It has been suggested that bulky alkylbenzene substituents for transition metal nanoparticles, akin to the classical heterogeneous hydrogenation reactions, lower the overall hydrogenation rate, implying a more disturbed transition state compared with the initial state of the hydrogenation reaction (in terms of the Horiuti–Polanyi mechanism).⁸⁰

4. ACTIVE SITES OF METAL NANOPARTICLES IMMOBILIZED IN IONIC LIQUIDS

It is obvious that in organometallic catalysis, 1 mol of the catalyst has 1 mol of single active catalytic sites (single-site catalysts). Opposite to this, in supported metal catalysts, the particles are generally assumed to present a broad size and shape distribution (multisite catalysts). The surface of a dispersed metal catalyst is composed of a number of different types of atoms, which are distinguished by the number and geometry of their neighboring atoms (Figure 5).⁸¹ Therefore, the determination of metal sites where catalytic processes occur is still one of the key questions in heterogeneous catalysis. These sites are usually distinctly different from the sites where strong bonding of atoms and molecules takes place, accompanied by low reactivity and slow conversion. It is assumed that the catalytic process is predominant at high metal coordination sites since the more bulklike the site, the greater the probability of electron-state fluctuations, which participate catalytically in the breaking and formation of chemical bonds

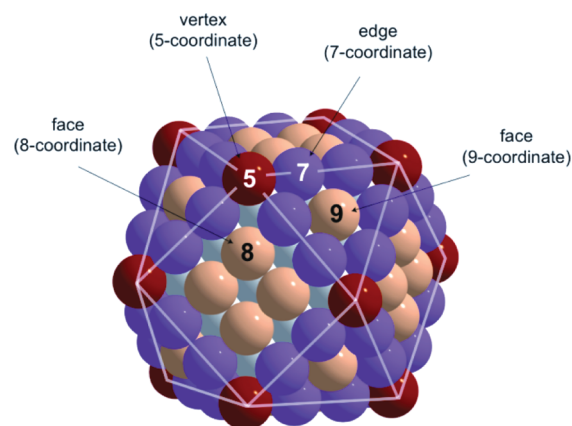


Figure 5. Types of atoms usually present on a nanoparticle metal surface. Reprinted with permission from ref 86 (copyright Wiley-VCH Verlag GmbH & Co. KGaA).

and yield a high turnover. Experimentally, the number of active atoms is determined by means of chemisorption of a model substrate, such as hydrogen, oxygen or carbon monoxide.^{82,83}

In the case of IL-soluble nanoparticle-based catalysts,^{14,84,85} the situation for the determination of active sites is also complicated.⁸⁶ As for classical heterogeneous catalysts, for soluble metal nanoparticles, only a small fraction of the metal atoms are active, mainly those on the particle surface (Figure 5).

However, in contrast to heterogeneous catalysis, there is no straightforward or general experimental method to titrate the number of active sites for soluble metal nanoparticles. Note that the hydrogenation of benzene can be used as a benchmark test to check if the metal nanoparticles possess heterogeneous-like or homogeneous-like catalytic properties, since this reaction is unlikely to be promoted by single metal catalysts.^{87–89}

For IL-soluble metal nanoparticles,¹⁴ four limiting situations can be described: (i) the soluble metal nanoparticle is surrounded only by weak coordinating agents/ligands, and all surface atoms are available for catalysis either by direct coordination or by displacing the stabilizing agents/ligands; (ii and iii) only a fraction of the surface atoms are available for catalysis in cases that the nanoparticle is stabilized by relatively strong coordinating agents such as (ii) functional groups present on the ionic liquid or (iii) ligands akin to the metal

coordination compounds or classical supported heterogeneous catalysts in which parts of the metal catalyst are blocked by the interaction with the support; and finally, (iv) the nanoparticle is just a reservoir of monometallic catalytic active species akin to classical homogeneous catalysis.

In the first case, it can be assumed that in a soluble metal nanoparticle, only the surface atoms are active for catalysis, although in some cases, other metal atoms can participate in the activation processes, such as in the hydrogenation reaction by nanocatalysts. This is most probably the case of metal nanoparticles prepared and used in catalysis in nonfunctionalized ILs. In these cases, the nanoparticle surface is not clean, but the (stabilizing) species are present, such as oxides or hydrides, when the metal nanoparticle is prepared under hydrogen and transient NHCs derived from the imidazolium cation, which can be easily displaced by the incoming reagents. Thus, the activity and selectivity can be ascribed to the size and shape of the metal nanoparticle, the species formed by interaction with the substrates, or both. Nevertheless, there is not a single systematic study on the direct influence of the coordination strength of the ionic species on the metal surface. Particularly, it appears that in the higher catalytic activity observed with Pt MNPs in BMI·BF₄ can be ascribed to the presence of highly uncoordinated anion compared with those reactions performed in ILs containing more coordinating anions (PF₆ and CF₃SO₃).⁵⁸ It is clear that more in-depth and systematic investigations of the subject as well as in the influence of nanoparticles size and shape are a needed.

In the second limiting situation, the IL “soluble” nanoparticle possesses extra-stabilizing agents, such as functionalized ILs^{90,91} or even ligands (Figure 6). In these cases, the ligand effect is

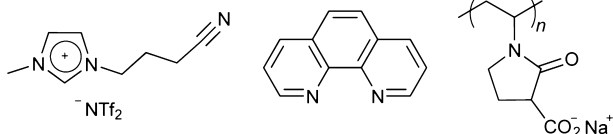


Figure 6. Examples of functionalized IL, phenanthroline and PVP-derived ligand.^{91–93}

predominant and the catalytic activity and selectivity probably follows a similar type of influence exerted by the same ligands in classical organometallic catalysis. It is likely the ligands are preferentially attached to the low-coordination metal sites that are the most reactive areas of the nanoparticle surface (atoms at the corners and edges, Figure 5),⁸⁶ and thus, the catalytic reaction should occur at the exposed face atoms. There are several examples in which the ligand indeed induces higher nanoparticle stability and increases catalytic activity and selectivity, as compared with the reactions performed in nonfunctionalized ILs and in the absence of ligands.^{91–94}

In other cases, the soluble metal nanoparticles are just a reservoir of soluble active catalytic species. In these cases, only small fractions of more active surface atoms are removed from the metal nanoparticle to generate the soluble monometallic catalytic active species, and therefore, the maximum number of active sites is defined by the atoms on the metal surface. This is typically the case in C–C coupling reactions (Heck and Suzuki type, for example) promoted by Pd nanoparticles in ILs.³² The same behavior was observed in the solvent-free hydroformylation of alkenes by Rh nanoparticles.⁹⁵

5. HYDROGENATION REACTIONS

5.1. MNPs in Nonfunctionalized ILs. The hydrogenation of alkenes and arenes by transition metal nanoparticles is the most investigated catalytic reaction in ILs. It is probable that one of the first examples involving hydrogenation catalysis by MNPs in ILs could be related to the case of biphasic cyclohexene hydrogenation in the presence of Rh complexes.³ In particular, when [Rh(COD)₂]BF₄ dissolved in BMI·BF₄ was used as the catalytic phase, it is most probable that in situ-generated Rh MNPs were the effective catalyst of this transformation, although no discussion regarding this possibility was mentioned.

In fact, the hydrogenation of alkenes can be used as a reaction probe to follow the formation of metal nanoparticles from the reduction of the metal center²¹ or decomposition⁵⁸ of transition metal compounds. It is interesting to note that the MNPs in ILs usually behave as typical homogeneous-like catalysts for the hydrogenation of alkenes. Indeed, a strong dependence of the rate of hydrogenation on the structure of the alkene and the observed rate constants decrease in the order mono- > di- > tri- > tetra-substituted double bonds (Figure 7),

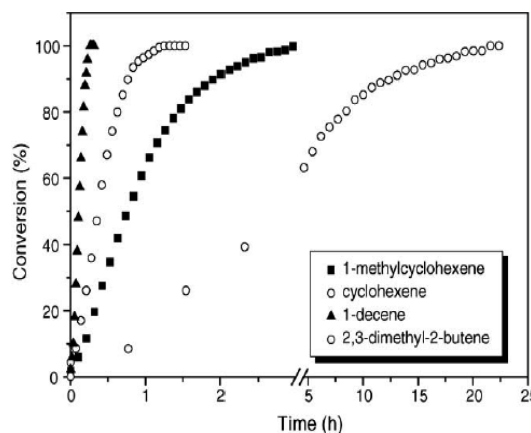
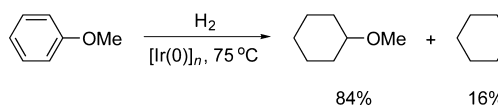


Figure 7. Dependence of the rate of hydrogenation on the structure of the alkene. Reprinted with permission from ref 66 (copyright Elsevier).

a reactivity order clearly related to the increase in steric demand of the substituted alkenes.⁶⁶ A similar trend is characteristic of classical homogeneous (single-site) catalysts.⁹⁶

Conversely, MNPs in ILs or in solvent-free conditions usually behave as heterogeneous-like catalysts in the hydrogenation of arenes. In fact, the hydrogenation of arenes containing functional groups (anisole, for example) by Ir MNPs occurs with the reduction of the aromatic ring and concomitant hydrogenolysis of the C–O bond (Scheme 3). The hydrogenolysis step is a typical reaction promoted by classical heterogeneous catalysts.⁹⁷

Scheme 3. Hydrogenation of Arenes Containing Functional Groups Catalyzed by Ir MNPs in Solvent-Free Conditions⁹⁷



Ir MNPs have been shown to be effective catalysts in the hydrogenation of several carbonyl compounds in ILs or in

Table 2. Examples of Catalytic Reactions Promoted by MNPs in ILs^a

entry	reaction	metal	ionic liquid	substrate	product	conv. (%)/sel. (%) ^b	ref
1	hydrogenation	Ir	BMI·PF ₆	cyclohexanone	cyclohexanol	100/100	78
2			solvent-free	1-phenyl-propan-2-one	1-cyclohexyl-propan-2-one/1-cyclohexyl-propan-2-ol	97/92:8	
3	hydrogenation	Ru	BMI·PF ₆	1-hexene	hexane	>99/100	99
4	hydrogenation	Ru	BMI·NTf ₂	toluene	methylcyclohexane	85/100	74
5				<i>o</i> -xylene	1,2-dimethylcyclohexane	32/100	
6 ^c	hydrogenation	Ru	BMI·NTf ₂	1,3-cyclohexadiene	cyclohexene	66/97	102
7 ^d						83/80	
8	hydrogenation	Ir	BMI·BF ₄	cyclohexene	cyclohexane	100/100	108
9	hydrogenation	Ru				95/100	46
10	hydrogenation	Pt	BMI·PF ₆	cyclohexene	cyclohexane	100/100	48
11				benzene	cyclohexane	46/100	
12				2,3-dimethyl-but-1-ene	2,3-dimethylbutane	82/100	
13	hydrogenation	Pd	BMI·PF ₆	acetophenone	1-phenylethanol	98/90	111
14		Rh				41/69	
15 ^e	hydrogenation	Rh	solvent-free	cyclohexene	cyclohexane	100/100	112
16 ^e				benzene	cyclohexane	100/100	
17	hydrogenation	Ru	(BCN)MI·NTf ₂	benzonitrile	(<i>E</i>)- <i>N</i> -benzylidene-1-phenylmethanamine	70/100	91
18	hydrogenation	Pd	(BCN)MI·NTf ₂	3-hexyne	(<i>Z</i>)-3-hexene	100/92:4:4 ^f	90
19	hydrogenation	Rh	BMI·NTf ₂ /BIHB·NTf ₂	toluene	methylcyclohexane	100/100	63
20			BMI·NTf ₂ /bipy			68/100	
21			BMI·NTf ₂ /BIMB·(NTf ₂) ₂			18/100	
22	hydrogenation	Rh	BMI·PF ₆ /2,2'-bipy	styrene	ethylbenzene/ethylcyclohexane	100/40:60	62, 121
23			BMI·PF ₆ /3,3'-bipy			100/0:100	
24			BMI·PF ₆ /4,4'-bipy			100/0:100	
25			BMI·PF ₆ /2,2'-bipy	cumene	isopropylcyclohexane	10/100	
26			BMI·PF ₆ /4,4'-bipy			100/100	
27			BMP·NTf ₂ /3,3'-bipy	styrene	ethylbenzene/ethylcyclohexane	100/0:100	
28	hydrogenation	Rh	BMI·PF ₆ /TPTZ	styrene	ethylbenzene/ethylcyclohexane	100/4:96	123
29			BMI·PF ₆ /TPPZ			100/70:30	
30			BMI·PF ₆ /2,2'-bipy	anisole	methoxycyclohexane/ cyclohexanone	100/77:23	
31			BMI·PF ₆ /2,2'-bipy	<i>o</i> -cresol	2-methylcyclohexanol/2-methylcyclohexanone	30/52:48	
32			BMI·PF ₆ /2,2'-bipy	<i>m</i> -cresol	3-methylcyclohexanol/3-methylcyclohexanone	100/61:39	
33	hydrogenation	Pd	BMI·PF ₆ /Phen	1,3-cyclohexadiene	cyclohexene	95/100	92
34 ^g	hydrogenation	Pd	BM ₂ I·PF ₆	cyclohexene	cyclohexane	100/100	127
35 ^g				styrene	ethylbenzene	100/100	
36 ^g	hydrogenation	Pd	BM ₂ I·PF ₆	cinnamaldehyde	3-phenyl-propionaldehyde/3-phenyl-propan-1-ol	97/84:16	61
37 ^g				cyclohex-2-enone	cyclohexanone	100/100	
38	hydrogenation	Pt	(C ₂ OH)MI·BF ₄ /PVP or IL-like copolymer	4-chloro-2-nitrophenol	2-amino-4-chlorophenol	100/99	124
39	hydrogenation	Rh	BMI·BF ₄ /poly[NVP-co-VBIM-Cl]	ethylbenzene	ethylcyclohexane	100/>99	129
40	hydrogenation	Rh	(C ₂ OH)MI·PF ₆ /PVP	styrene	ethylbenzene/ethylcyclohexane	99.7:0 ^h	131
41	hydrogenation	Pd	BMI·PF ₆ /TBAB	1-((2-allylphenoxy)methyl)benzene	1-((2-propylphenoxy)methyl)benzene	98	126
42	hydrogenation	Pd	SILP (TMGL-MS)	cyclohexene	cyclohexane	100/100	133
43				1,3-cyclohexadiene	cyclohexene	98/100	
44	hydrogenation	Pd	SILP ((TESP)MI·NO ₃ -SiO ₂)	cinnamaldehyde	hydrocinnamaldehyde	100	134
45			SILP ((TESP)MI·PF ₆ -SiO ₂)			100	
46	hydrogenation	Pt	SILP (CSIL-Fe ₃ O ₄)	diphenylacetylene	<i>cis</i> -stilbene/ <i>trans</i> -stilbene	100/95:5	137
47				cinnamaldehyde	3-phenylprop-2-en-1-ol	99/99	
48	hydrogenation	Pd	SILP (fIL-SbF ₆ -MWCNTs)	<i>trans</i> -stilbene	1,2-diphenylethane	100/100	139
49 ⁱ	hydrogenation	Pd	SILP (fMWCNTs)	(<i>E</i>)-4-phenyl-but-3-en-2-one	4-phenyl-butan-2-one	76/100	140
50	Mizoroki-Heck	Pd	BBI·Br/BBI·BF ₄	iodobenzene/ethyl acrylate	ethyl cinnamate	87 ^h	149

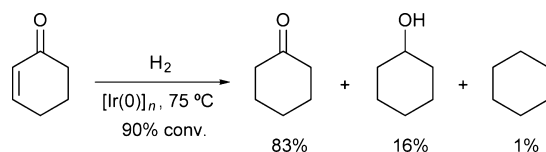
Table 2. continued

entry	reaction	metal	ionic liquid	substrate	product	conv. (%)/sel. (%) ^b	ref
51	Mizoroki–Heck	Pd	TBAB/TBAA	chlorobenzene/Styrene	coupling product	88 ^j	152
52				<i>p</i> -CH ₃ O-chlorobenzene	coupling product	95 ^j	
53	Mizoroki–Heck	Pd	amine-functionalized IL	bromobenzene/ <i>n</i> -butyl acrylate	coupling product	25	160
54	Mizoroki–Heck	Pd	TBAB/TBAA	bromobenzene/ <i>n</i> -butyl acrylate	coupling product	>99	161
55 ^k	Suzuki–Miyaura	Pd	THeptAB	chlorobenzene/ Phenylboronic acid	coupling product	98	165
56	Suzuki–Miyaura	Pd	BMI·PF ₆	bromobenzene/ phenylboronic acid	coupling product	100	166
57 ^l	Suzuki C–C coupling	Pd	BMI·PF ₆ /N ligand	1-Br-4-(CF ₃)benzene/ phenylboronic acid	coupling product	79/73:26 ^m	167
58 ^l	Suzuki C–C coupling	Pd	BMI·PF ₆ /N ligand	bromobenzene/ phenylboronic acid	coupling product	56 ^h	168
59 ⁿ	Sonogashira	Pd	solvent-free	iodobenzene/ phenylacetylene	coupling product	100	170
60	Stille	Pd	THeptAB	chlorobenzene/ tributylphenylstannane	coupling product	75	165
61	Stille	Pd	C ₃ CNPy·NTf ₂	iodobenzene/ tributylphenylstannane	coupling product	49	114
62	Ullmann	Pd	TBAA	bromobenzene	homocoupling	95	176
63 ^o	Ullmann	Pd	(C ₄ SO ₃ H)BI·HSO ₄	chlorobenzene	homocoupling	100	177
64	Ullmann	Pd	OMI·BF ₄	iodobenzene	homocoupling	99	179
65	methoxycarbonylation	Pd	BMPy·PF ₆ /PVP	iodobenzene	methylbenzoate	83	180
66 ^p	borylation	Ir	THTdp·MS	benzene/pinacolborane	phenylboronic acid	47 ^h	181
67	hydrosilylation	Pt	BPY·BF ₄	1-hexadecene/siloxane B9800	organosilicon product	85	182
68	hydrodehalogenation	Pd	TBAB/TBAA	chlorobenzene	benzene	>99	183
69	isotope exchange	Ru	THTdp·DBS	decaborane	¹⁰ B-decaborane	90	187
70	Fischer–Tropsch	Ru	BMI·BF ₄ /poly[NVP-co- VBIMX]	CO	hydrocarbons	75	193

^aFor detailed reaction conditions, see the original references. ^bDetermined by GC analysis. ^cRu MNPs 1.1 nm in diameter. ^dRu MNPs 2.9 nm in diameter. ^eRh MNPs immobilized in a tetraalkylammonium salt matrix. ^f*cis*-Alkene/*trans*-alkene/alkane. ^gThe additional ligand BM₂(DPA)I·PF₆ was used to stabilize the Pd MNPs. ^hIsolated yield (%). ⁱThe additional ligand 4-(3-phenylpropyl)pyridine was used to stabilize the MNPs. The Pd MNPs were previously prepared in BMI·PF₆. ^j*E/Z* ratio is >98:2. ^kIn the presence of Bu₄NOH. ^lIn the presence of water. ^mCross-coupling product/dehalogenated product = 73:26. ⁿMNPs previously prepared in the IL 1-methyl-3-(2'-mercaptoacetoxyethyl)imidazolium chloride. ^oIn the presence of supercritical carbon dioxide. ^pIn the presence of tetra-2-pyridinylpyrazine.

solventless conditions (entries 1 and 2, Table 2).^{78,98} As expected, cyclohexanone hydrogenation in IL requires more time to complete the conversion due to the characteristic biphasic nature of catalysis, which can be a mass-controlled process. However, the system could be reused up to 15 recharges without a loss of catalyst activity. Moreover, in some cases, significant amounts of the hydrogenolysis product are observed in solventless conditions, which can be attributed to the heterogeneous behavior of the catalyst. Interestingly, highly selective hydrogenation of the aromatic ring over the carbonyl group is also observed, depending on the substrate type (Scheme 4).

Scheme 4. Hydrogenation of Carbonyl Compounds without Solvent Catalyzed by Ir MNPs Prepared in an IL⁷⁸



Although long reaction times are needed in biphasic catalysis using ILs, the possibility of recovering and reusing the catalyst several times is an attractive aspect of these molten salts. In

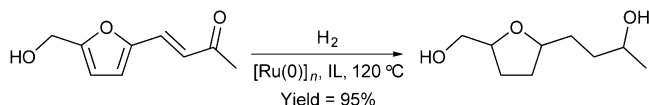
addition, the lifetime of MNPs is often improved when they are immobilized in ILs, and oxidation is inhibited to a large extent. In fact, Ru MNPs dispersed in classical imidazolium ILs remained active during 1-hexene hydrogenation, even after 17 recycles (entry 3, Table 2).⁹⁹ Poisoning tests using Hg and CS₂ confirmed the presence of Ru(0) as the true hydrogenation catalyst. However, it is important to note that, in some cases, the Hg test alone is only an indication for the involvement of heterogeneous species, since this poisoning test relies on the formation of an amalgam with colloidal metal, although poisoning of molecular metal(0) cannot be excluded. Indeed, the Hg poisoning test can confirm a homogeneous catalytic system but not a heterogeneous one.¹⁰⁰

Arene hydrogenation was also successfully employed as a chemical probe to confirm the presence of heterogeneous-like metal(0) species on the formation of Ru MNPs from the reduction of a Ru(II) precursor promoted by an imidazolium IL containing NTf₂ anion without additional reducing agents.⁵⁴ The hydrogenation of arenes was chosen as an appropriate procedure since it is likely that heterogeneous species are the true catalysts for this reaction.⁸⁹ In particular, 95% conversion of toluene was observed for Ru MNPs generated in HM₂I·NTf₂, which is a strong indication of heterogeneous catalysis. Similarly, pregenerated Ru MNPs in different

imidazolium ILs were applied as the catalytic phase in biphasic hydrogenation of substituted arenes (entries 4 and 5, Table 2).⁷⁴ Analogous to what is usually observed with isolated MNPs,⁷⁹ the catalytic tests indicated that arene hydrogenation by Ru MNPs in ILs was to a great extent sensitive to the steric effect imposed by alkyl groups on the aromatic ring.

Ru(0) nanoparticles in ILs are also quite effective catalysts for the selective hydrogenation of biomass-derived substrates (Scheme 5).¹⁰¹

Scheme 5. Selective Hydrogenation of Biomass-Derived Substrates in ILs¹⁰¹



The understanding of the real effect of MNP size on the activity of catalytic reactions is another attractive point. Indeed, the activity of Ru MNPs in BMI·NTf₂ was dependent on their size, in particular, for 1,3-cyclohexadiene hydrogenation, which could be considered as a “structure-sensitive reaction” (entries 6 and 7, Table 2).¹⁰² In this case, larger particles (2.9 nm) showed the best activity during diene hydrogenation, but the selectivity to cyclohexene was lower compared with small MNPs (1.1 nm). This enhancement in activity promoted by large Ru MNPs in 1,3-cyclohexadiene hydrogenation is most likely related to the appropriate number of neighboring surface sites that facilitate π -bond coordination and activation of the conjugated diene. On the other hand, selectivity is explained on the basis of the type of active sites, which can be quite different, depending on the particle size. In fact, small MNPs have sites located mainly at the vertex and edge positions, providing only a single C=C coordination with further selective formation of alkene, whereas large particles tend to exhibit active sites at facial regions, which facilitate planar double C=C interactions and full diene hydrogenation (Figure 8). The absence of MNP

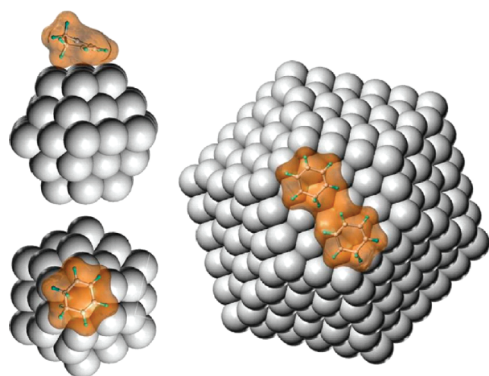


Figure 8. Simulation of 1,3-cyclohexadiene interacting with hcp Ru MNPs with diameters of 1.3 (left) and 2.8 nm (right). Reprinted with permission from ref 102 (copyright Elsevier).

size effect observed in cyclohexene hydrogenation (“structure-insensitive reaction”) is acceptable since olefins can easily coordinate at small or large metal surfaces.

The type of metal precursor and the nature of the IL used in the preparation of MNPs with different sizes is an important aspect, since it can influence their activity in catalytic reactions. Recent investigations have revealed that the activity of Ir MNPs

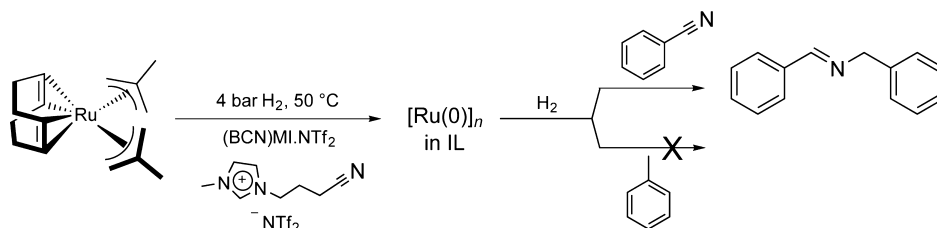
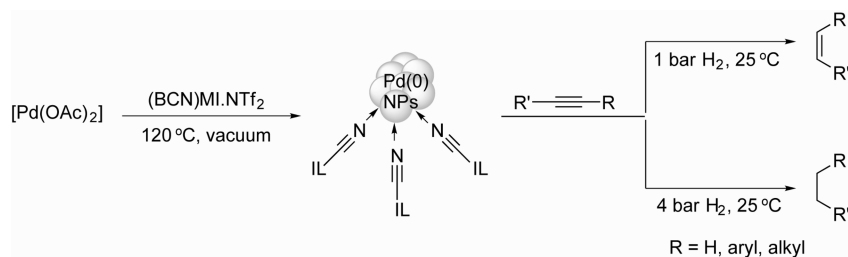
in cyclohexene hydrogenation in the same IL is almost twice as fast for MNPs prepared from an ionic Ir(I) precursor compared with MNPs synthesized using a neutral Ir(I) precursor.²² This fact is probably related to (i) the smaller size presented by MNPs generated from the ionic precursor [Ir(COD)₂]₂BF₄ (1.9 nm in BMI or DMI·BF₄), which provides a greater surface area; or (ii) a negative effect due to the presence of residual chloride that can coordinate on the metal surface of particles prepared from [Ir(COD)Cl]₂ (2.5 nm in BMI·BF₄ and 3.6 nm in DMI·BF₄). The possibility of chloride poisoning is a suitable explanation for this significant difference in activity, since, as described elsewhere,¹⁰² olefin coordination may not be the rate-limiting pathway in these cases.

The generation of MNPs in ILs based on a simple thermal decomposition of metal carbonyl compounds is also very attractive, since the only byproduct is CO gas, which is rapidly expelled from the medium due to its low solubility in IL.^{103–105} This method avoids the presence of undesired ligands that could interact with the MNP surface, playing an important role in further catalytic activities. As an example, MNPs in ILs prepared using their respective metal carbonyl precursors^{46,106–108} proved to be effective materials as hydrogenation catalysts. In fact, cyclohexene was successfully hydrogenated in the presence of Rh, Ir,¹⁰⁸ and Ru⁴⁶ MNPs dispersed in BMI·BF₄ (entries 8 and 9, Table 2). Moreover, control experiments with CS₂ confirmed that Ru MNPs possess preferential heterogeneous-like properties. Notably in this particular case, the significant increase in activity after recycling was probably related to (i) the generation of more active sites due to the continuous surface modification that is an expected process in heterogeneous catalysis; or (ii) the formation of active Ru-NHC species.

However, the addition of small amounts of an imidazolium IL apparently poisoned the activity of Ir MNPs in the case of acetone hydrogenation.¹⁰⁹ Isotope labeling studies demonstrated the formation of NHCs in situ that could be considered herein as the most probable surface poisoning ligand of Ir MNPs. In fact, these NHC species were detected after the formation of Ir MNPs⁵³ or during cyclohexene hydrogenation catalyzed by Ir MNPs in deuterated ILs.⁵¹

Pt MNPs prepared in ILs⁵⁸ are also suitable catalysts for the hydrogenation of substituted olefins and aromatic compounds in either biphasic or solventless media (entries 10–12, Table 2).⁴⁸ Similarly to Ir MNPs,⁶⁶ the catalytic activity decreases with the increase in steric bulk on the olefin C=C bond. In addition, these Pt MNPs prepared in BMI·PF₆ showed no ability to selectively hydrogenate dienes to alkenes, in contrast to other selective systems based on platinum salts.¹¹⁰ Moreover, Ni nanoparticles composed of a metallic Ni core and a NiO cap dispersed in IL are quite active catalysts for cyclohexene hydrogenation.²⁵

The combination of an IL and supercritical carbon dioxide was employed as an efficient route to MNP preparation and product separation after hydrogenation reactions.¹¹¹ Indeed, Rh and Pd MNPs prepared in an imidazolium IL or in a quaternary ammonium salt were able to catalyze the hydrogenation of acetophenone with good selectivities in 1-phenylethanol (entries 13 and 14, Table 2). Although Pd MNPs immobilized in THA·Br are inactive, those particles stabilized in BMI·PF₆ proved to be the best recyclable catalytic system. An interesting ability to generate CO₂-induced melting ILs was explored for the synthesis of Rh MNPs and their application in hydrogenation tests.¹¹² After gas release, the incorporated Rh MNPs

Scheme 6. Selective Hydrogenation of Benzonitrile Catalyzed by Ru MNPs Prepared in a Nitrile-Functionalized IL⁹¹Scheme 7. Hydrogenation of Alkynes Tuned by Variable Hydrogen Gas Pressure^a

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on a tetraalkylammonium salt matrix were successfully applied for both cyclohexene and benzene hydrogenation (entries 15 and 16, Table 2). In general, under solvent-free conditions, the catalyst matrix was partially miscible in the substrates. Moreover, amino acid derivatives could also be selectively reduced at its olefinic or aromatic moieties, depending on the substrate structure.

5.2. MNPs in Functionalized ILs. The development of functionalized ILs has arisen as an important strategy to maintain the attractive properties of general ILs but also to essentially improve their ability to interact with classical organic solvents, substrates, and several inorganic materials.¹¹³ In contrast to early reports in which only the cation was modified for a desired application, new studies have focused on the synthesis of ILs containing both functionalized cations and anions. In fact, these functionalized ILs have been widely used as reaction media for chiral induction, electrolytes, lubricants, surface modification, and synthesis of stable MNPs. Among all the possible applications of these versatile ILs, the preparation and stabilization of small-sized MNPs is of our interest herein. Although some studies have been demonstrated using modified pyridinium or pyrrolidinium cations,^{114,115} imidazolium ILs bearing a functional moiety (bipy, $-\text{NR}_2$, $-\text{CN}$, $-\text{SR}$) attached to the alkyl side chain of the cation is far the most investigated system for this purpose.^{116–120} As mentioned previously, it is known that these functionalized salts can provide enhanced stabilization of NPs compared to nonfunctionalized analogues.

In this context, Ru MNPs (2.2 nm) prepared in a nitrile-functionalized IL display unusual selectivities toward the hydrogenation of nitrile-containing aromatic compounds (entry 17, Table 2).⁹¹ Indeed, Ru MNPs dispersed in (BCN)MI·NTf₂ ((BCN)MI = 1-butyronitrile-3-methylimidazolium) exclusively hydrogenate nitrile groups instead of arenes, which are typically hydrogenated by Ru MNPs in nonfunctionalized ILs⁷⁴ (Scheme 6). It is likely that in these systems, the nitrile group of the IL is strongly coordinated to the Ru metal surface, which allows access of only the nitrile moiety of the substrate to the nanoparticle surface, thus avoiding arene coordination. Therefore, it is possible to

modulate the selectivity of the catalyst simply by the presence of a functionalized IL.

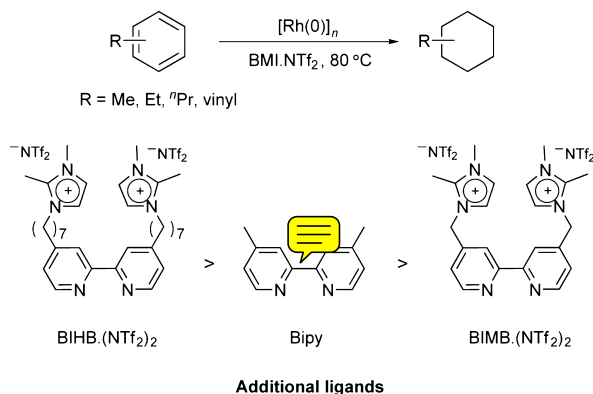
The selective hydrogenation of alkynes to (Z)-alkenes catalyzed by Pd MNPs (7.3 nm) stabilized in (BCN)MI·NTf₂ was also recently reported.⁹⁰ Remarkably, 3-hexyne was partially hydrogenated to the corresponding olefin without any trace of isomerized byproduct (entry 18, Table 2). This absence of isomerization indicates that Pd MNPs possess typical behavior with surfacelike (multisite) catalytic properties. Most surprisingly, depending on the hydrogen pressure, it is possible to tune the selectivity toward alkenes or alkanes (Scheme 7). These results are probably quite related to the low hydrogen gas solubility in IL and mass transfer/diffusion limitations. It is expected that, at low pressure, there is a minimal amount of hydrogen dissolved in the IL, affording the alkene product; in contrast, increasing the gas pressure results in more hydrogen present in the IL phase to yield total hydrogenation (alkane).

5.3. MNPs with Additional Stabilizing Ligands in ILs.

Additional stabilizing ligands are another suitable strategy for enhanced MNP stabilization in ILs. Extra protective agents, such as N-donor ligands,^{62,63,92,121–123} polymers,^{124,125} or quaternary ammonium salts¹²⁶ have been used to increase the stability of MNPs in ILs during the catalytic process. There are several lines of evidence indicating that the ligands interact with the surface of MNPs dispersed in ILs. For example, the coordination of imidazolium-functionalized bipyridine compounds on the surface of Rh MNPs in BMI·NTf₂ has been demonstrated by NMR experiments.⁶³ Furthermore, the catalytic activity in the biphasic hydrogenation of arenes was strongly influenced by the stabilizer employed and followed the trend shown in Scheme 8.

It is noteworthy that Rh MNPs protected by BIHB·(NTf₂)₂ (BIHB = 4,4'-bis-[7-(2,3-dimethylimidazolium)heptyl]-2,2'-bipyridine) ligands are considerably more active than the system containing bipyridine as a stabilizer. On the other hand, MNPs stabilized by BIMB·(NTf₂)₂ (BIMB = 4,4'-bis[(1,2-dimethylimidazolium)methyl]-2,2'-bipyridine), with a shorter alkyl chain between the imidazolium functionality and the

Scheme 8. Hydrogenation of Arenes Catalyzed by Rh MNPs Stabilized by N Ligands in ILs (top) and the Activity Observed for the Different Ligands Used (bottom)⁶³



pyridine, present the lowest activity (entries 19–21, Table 2). The reduced activity of the Rh MNP/BIMB·(NTf₂)₂ system can be explained by the weaker interaction between the ligand and the metal surface. This result is probably related to the minor distance between the imidazolium cation and the bipy group, which induces negative effects on MNP stabilization, such as electron withdrawing, undesirable proximity of positive charges to the MNP surface and steric hindrance.

Similarly, a monofunctionalized bipyridine ligand was also designed to allow good stabilization of Rh MNPs in BMI·PF₆.¹²² In fact, the particles in solution remained stable even after hydrogenation of substituted arenes. Different bipyridine ligands (2,2'-, 3,3'-, 4,4'-bipyridine) and their influence on arene hydrogenation were evaluated in various ILs.⁶² XPS analysis of the isolated Rh MNPs/2,2'-bipyridine prepared in BMI·PF₆ showed the presence of nitrogen atoms, which could be most likely attributed to the surface bonded ligand and not to the remaining IL, since independent analyses of Ir MNPs have not shown nitrogen signals due to the imidazolium group.²¹ In the present case, the different activities and selectivities observed in the hydrogenation of substituted aromatic compounds were justified by an explanation based on bipyridine coordination modes. The best selectivities for styrene hydrogenation in BMI·PF₆ were obtained with Rh MNPs stabilized with 3,3'- and 4,4'-bipyridine (entries 23 and 24, Table 2). This can be explained by a monodentate coordinated mode of 3,3'-, 4,4'-bipy to the metal surface (Figure 9), which decreases steric hindrance and allows access of the substrate, thus increasing activity and selectivity. In contrast, 2,2'-bipyridine hindered the MNP surface, limiting access of the substrate and resulting in lower activity and selectivity.

Comparable results were obtained in the hydrogenation of functionalized aromatic compounds promoted by Rh MNPs in BMI·PF₆ using poly-N-donor ligands based on bipyridine as a protective agent.^{62,121,123} Styrene hydrogenation catalyzed by Rh MNPs stabilized by tetra-2-pyridinylpyrazine (TPPZ) showed low activities compared with ligands such as 2,2'-, 3,3'-, 4,4'-bipyridine, and 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ) (entries 22–24, 28 and 29, Table 2). In the same way, these results can be explained by the different coordination modes obtained with the different ligands employed. A point to note is the ability to form significant amounts of a ketone intermediate when Rh MNPs stabilized by 2,2'-bipyridine are used in the hydrogenation of compounds such as anisole or cresols (entries 30–32, Table 2).

The role of phenanthroline (Phen) as an extra ligand was investigated during the hydrogenation of olefins using Pd MNPs in BMI·PF₆.⁹² Good activities and selectivities (entry 33, Table 2) were obtained for diene hydrogenation, and the Pd MNPs/IL system could be reused many times without a loss of activity. In the same context, Pd MNPs (5–6 nm) stabilized by a 2,2'-dipyridylamine-functionalized IL ligand (BM₂(DPA)-I·PF₆; BM₂(DPA)I = 2,3-dimethyl-1-[3-N,N-bis(2-pyridyl)-propyl-amido]imidazolium) was employed as an efficient catalyst for the biphasic hydrogenation of olefins in BM₂I·PF₆ (entries 34 and 35, Table 2).¹²⁷ Both temperature and Pd concentration play an important role for MNP stabilization and catalytic activity. Independently of the ligand (BM₂(DPA)I·PF₆ or 2,2'-bipyridineamine), cyclohexene hydrogenation is practically prevented in the case of BMI·PF₆, attributed most likely to the presence of σ -donating N-heterocyclic carbenes in the medium that can strongly interact with the generated MNP surface, can inhibit the reduction of the Pd(II) precursor to the active Pd(0) species, or both. Moreover, this catalytic system demonstrated high selectivity for C=C bond hydrogenation when α,β -unsaturated aldehydes/ketones were tested (entries 36 and 37, Table 2).⁶¹

Ligands based on tetraalkylammonium salts are commonly applied for enhanced stabilization of MNPs in ILs. In particular, Pd MNPs prepared in the presence of tetrabutylammonium bromide (TBAB) as a capping agent and then dispersed in BMI·PF₆ showed good efficiency and selectivity in hydrogenation reactions (entry 41, Table 2).¹²⁶

Polymers are another class of ligands extensively used for MNP stabilization. These compounds provide electronic stabilization by binding weakly to the NP surface, but they mainly provide steric protection. Poly(*N*-vinyl-2-pyrrolidone) (PVP) is the most commonly used polymer for MNP stabilization due its capacity to act as a ligand and to provide steric protection for the particle. However, the solubility of PVP in ILs is limited, and there are, at least in principle, two

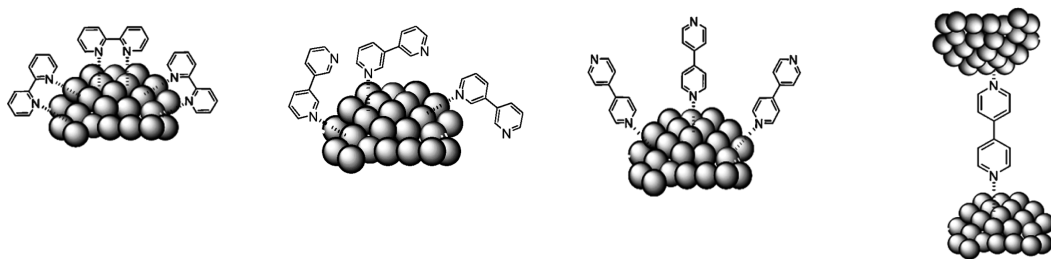


Figure 9. Representation of bipyridine coordination modes in MNPs. Reprinted with permission from ref 62 (copyright American Chemical Society).

methodologies to solve this problem: (i) modification of the PVP by introducing imidazolium units into the polymer chain; or (ii) using functionalized ILs, which can dissolve PVP. Some examples using PVP or an IL-like copolymer (functionalized PVP) as additional ligands are the selective hydrogenation of chloronitro arene compounds into aromatic chloroamines using Pt MNPs in ILs^{124,128} and olefin or arene hydrogenation using Rh MNPs^{125,129,130} (entries 38 and 39, Table 2). In addition, PVP-stabilized rhodium NPs provide an effective and highly stable catalytic system in hydroxyl-functionalized ILs for styrene hydrogenation¹³¹ (entry 40, Table 2). Bimetallic nanoparticles capped with PVP have also been used for the hydrogenation of various substrates in imidazolium ILs.¹³² The activities and selectivities can be controlled by the Au/Pd ratio, with maximum activities obtained with an Au/Pd ratio of 1:3.

5.4. MNPs/SILP Catalysis. MNPs immobilized in supported ILs have emerged as alternative materials for catalytic reactions. Combining the advantages of classical heterogeneous supports, so-called SILP (supported ionic liquid phase) catalysis also provides the elimination/reduction of mass-transfer limitations and gives access to more robust/recyclable catalysts with easy separation after reactions. It is noteworthy that there is a difference between the SCILL and SILP concepts. In SCILL, the classical heterogeneous catalysts are coated with a thin IL layer, which can modify their properties and catalytic performance. On the other hand, the SILP concept involves the use of an IL layer on the solid support or IL molecules covalently attached to the support surface to immobilize transition metal catalysts. In particular, Pd MNPs (1–2 nm) synthesized in molecular sieves containing an IL layer were successfully employed in alkene hydrogenation (entries 42 and 43, Table 2).¹³³ Moreover, these materials showed superior catalytic activity in cyclohexene hydrogenation when compared to a biphasic system.⁹²

Silica gel modified by ILs can be used as a support for Pd MNPs (2–10 nm), as well.¹³⁴ In this case, the Pd-supported catalyst selectively hydrogenates cinnamaldehyde to hydrocinnamaldehyde (entries 44 and 45, Table 2). In the same context, Pd MNPs stabilized by active carbon cloth in the presence of an IL layer were suitable catalysts for cinnamaldehyde and citral hydrogenation.¹³⁵ Although high selectivity for C=C hydrogenation was observed for the cinnamaldehyde reaction yielding hydrocinnamaldehyde, citral hydrogenation can afford dihydrocitronellal and citronellal as the main products, depending on the IL and conditions used. Interestingly, parahydrogen-induced polarization (PHIP) was detected in the gas phase hydrogenation of propyne catalyzed by Pd MNPs supported in activated carbon fibers modified with ILs.¹³⁶ The replacement of normal H₂ by enriched para-H₂ gas causes a significant increase in the intensity of the polarized propylene signals in the NMR spectrum. However, in a classical Pd-supported catalyst without an IL, the effect was not considerable. Thus, it was concluded that the presence of an IL plays a crucial role in the formation of PHIP in the hydrogenation process.

Magnetite NPs modified using a dihydroimidazolium-based IL have proven to be an appropriate support for Pt MNPs (~2 nm).¹³⁷ Notably, the hydrogenation of alkynes preferentially affords alkenes, and only the carbonyl group is reduced in the case of α,β -unsaturated aldehydes (entries 46 and 47, Table 2). These results may be a consequence of the distinct steric/electronic effects caused by the support in each reaction. New hybrid membranes composed of Rh (4.8 nm) or Pt (3 nm)

MNPs, IL, and cellulose acetate have also been developed.¹³⁸ Compared with biphasic IL systems, these membranes showed better catalytic activities and stability for cyclohexene hydrogenation.

Multiwalled carbon nanotubes functionalized by ILs are other interesting supports for MNP immobilization purposes. Indeed, the reduction of a Pd(II) precursor affords Pd MNPs that are deposited in situ in the IL-X-MWCNTs (X is the imidazolium counterion) support.¹³⁹ The system based on the SbF₆ anion demonstrates the best activity in *trans*-stilbene hydrogenation to 1,2-diphenylethane (entry 48, Table 2). The previous preparation of Pd MNPs/with or without L (L = 4-(3-phenylpropyl)pyridine) in an IL followed by a simple deposition on MWCNTs modified with imidazolium groups (fMWCNTs) afforded a suitable hydrogenation catalyst.¹⁴⁰ In particular, (*E*)-4-phenyl-but-3-en-2-one was selectively hydrogenated at C=C by Pd MNPs/L-fMWCNTs, even at 30 °C, using heptane as the solvent (entry 49, Table 2). In this case, the catalytic activities were quite dependent on the IL used for MNP preparation, the presence of additional ligands, and the reaction conditions. Furthermore, this type of catalyst was also successfully employed in a sequential Heck coupling/hydrogenation process.

In general, SILP catalysis commonly provides better results than conventional biphasic systems, since the key drawbacks of biphasic IL systems such as mass transfer limitations and low gas solubility are significantly reduced in this case.

6. C–C COUPLING REACTIONS

Currently, carbon–carbon coupling reactions have received much attention as one of the most important and investigated processes in catalysis.^{141–143} To promote these transformations, Pd-based catalysts are usually employed due to the superior activity of Pd compared with other metals. In particular, Pd MNPs stabilized in ILs have become a very attractive alternative recyclable catalyst phase for C–C bond formation purposes.^{15,144,145} Herein, a few examples will be briefly described to demonstrate the potential applicability of these nanostructures in ILs as efficient catalysts in several C–C coupling reactions, such as Mizoroki–Heck, Suzuki–Miyaura, Sonogashira, Stille, and Ullmann.

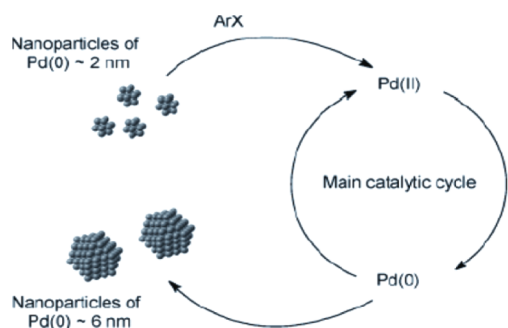
6.1. Mizoroki–Heck Reaction. Generally, the Mizoroki–Heck reaction involves the reaction of an unsaturated halide with olefins in the presence of a base promoted by Pd catalysts. From the point of view of green chemistry, ILs have replaced classical organic solvents, since these molten salts provide a suitable and recyclable medium for the C–C coupling transformation.^{146–148} Moreover, Pd MNPs prepared in ILs or those generated in situ from metal precursors have proven to be outstanding catalysts for the Mizoroki–Heck reaction. However, it is accepted that in most cases, the active catalysts are molecular Pd species detached from the MNP surface.

One of the first reports on the use of ILs and the in situ generation of Pd MNPs in the Mizoroki–Heck process was published 10 years ago.¹⁴⁹ In this case, ILs based on the 1,3-di-*n*-butylimidazolium cation (BBI) proved to be a superior medium for the coupling of iodobenzenes and olefins under ultrasonic conditions, since they enhanced the reaction rate and possibly acted on the stabilization of intermediates (entry 50, Table 2). Tetraalkylammonium salts can also be used as stabilizing agents for the preparation of MNPs. In fact, Pd MNPs immobilized in TBAB were successfully applied in the reaction of bromoarenes with substituted olefins.^{150,151} The

coupling of arylchlorides with deactivated olefins can be envisaged as further evidence of the high activity provided by the Pd MNPs/TBAB system (entries 51 and 52, Table 2).¹⁵²

Interesting insights into the mechanism and role of Pd MNPs dispersed in BMI·PF₆ during the reaction of aryl halides and *n*-butyl acrylate have been described in detail.³² Experimental analyses (TEM and ICP-AS) support the initial predictions that Pd MNPs in an IL act as a reservoir for the molecular catalytically active Pd species. Indeed, it is assumed that the reaction starts through the oxidative addition of iodoarene on the nanoparticle surface, thus forming oxidized Pd species, which detach from the surface and then enter into the main catalytic cycle. After β -hydride and reductive elimination steps, the formed zerovalent Pd can either continue in the catalytic cycle or return to the nanoparticle reservoir (Scheme 9).

Scheme 9. Catalytic Cycle Proposed for the Mizoroki–Heck Reaction Promoted by Pd MNPs in ILs^a



^aReprinted with permission from ref 32 (copyright American Chemical Society).

Additional mechanistic investigations employing palladacycles precursors in Mizoroki–Heck reactions have come to similar conclusions, in which the real active species is likely to be Pd(0) generated in situ.¹⁵³ On the basis of a physical separation method, it was possible to demonstrate the presence of the probable catalytically active Pd atoms detached from the surface of MNPs.^{154,155} In fact, Pd(0) atoms or ions are formed in solution, depending on the conditions employed (with or without aryl halide).

The presence of such Pd(0) species (MNPs 0.8–1.6 nm in diameter) was elegantly demonstrated by in situ XAFS measurements during the coupling reaction in ILs.¹⁵⁶ It is observed in many cases that MNPs are generated in situ and stabilized by the ligands or protective agents present in the medium;^{157–159} however, it is believed that these MNPs act as a reservoir for the catalytically active Pd species. In additional studies, the Mizoroki–Heck reaction between bromobenzene and *n*-butyl acrylate promoted by Pd MNPs in an amine-functionalized IL gave only low conversion (entry 53, Table 2).¹⁶⁰ Also, under the related conditions, the agglomeration of MNPs into undesired bulk particles was verified.

In addition to the use of MNPs directly dispersed in ILs, supported MNPs have garnered attention as alternative materials for Mizoroki–Heck coupling in ILs. For example, Pd MNPs deposited on chitosan are an effective and recyclable heterogeneous catalyst for the coupling reaction of aryl halides and *n*-butyl acrylate in an IL such as TBAB (entry 54, Table 2).¹⁶¹ It is noteworthy that this system is not active in the presence of an imidazolium-based IL.

6.2. Suzuki–Miyaura Reaction. Without doubt, the Suzuki–Miyaura reaction is among the most important and studied process for C–C coupling.^{162–164} In fact, the reaction of aryl halides with boronic acid derivatives allows the formation of biaryl compounds, which is a key pathway in the chemical industry, mainly for the synthesis of pharmaceutical drugs. In this context, the development of MNPs immobilized in ILs has attracted much interest in this area. Indeed, Pd MNPs stabilized in tetraalkylammonium-based ILs are suitable systems employed in the coupling of several aryl halides and boronic acids.¹⁶⁵ The best results were obtained using tetrabutylammonium hydroxide as the base and an IL containing a longer side chain (THeptAB; THeptA = tetraheptylammonium), which provided enhanced stabilization of the MNPs (entry 55, Table 2). Star-like shaped Pd MNPs in BMI·PF₆ proved to be a highly active catalyst phase for the reaction of bromobenzene and phenylboronic acid, in which total conversions were achieved in short reaction times (entry 56, Table 2).¹⁶⁶ Moreover, the isolated palladium powder was not active in the reaction, suggesting that only MNPs stabilized in the IL were active in the Suzuki–Miyaura process. These results highlight the role of the IL in providing a suitable medium for the stabilization of MNPs and the occurrence of the reaction.

Pd MNPs generated in situ from their respective metal precursors have also been observed in ILs. Although the use of a P-containing ligand apparently avoids the formation of MNPs, it was observed that MNPs formed in the presence of a N ligand during the coupling reaction of substituted bromoarenes and phenylboronic acid in BMI·PF₆ (entry 57, Table 2).¹⁶⁷ Quite similarly, Pd MNPs were also responsible for the activity detected in coupling reactions performed in ILs and in the presence of functionalized ligands derived from norborn-5-ene-2,3-dicarboxylic anhydride (entry 58, Table 2).¹⁶⁸ In this case, it was discussed that the occurrence of Pd MNPs is required in order to obtain an active system in ILs.

One interesting approach based on the use of IL-modified poly(*p*-phenylene) microspheres as a support for Pd MNPs and their subsequent use in a heterogeneous Suzuki–Miyaura reaction was described.¹⁶⁹ In fact, the combination of MNPs/IL provides a positive effect on catalyst activity and stability.

6.3. Sonogashira Reaction. The Sonogashira reaction is based on the coupling of aryl halides and substituted alkynes promoted by transition metal catalysts. Unfortunately, only a few examples on the application of the Sonogashira reaction using MNPs in ILs have been reported. In some cases, the IL was employed only for the preparation of the MNPs, and such materials were further applied as heterogeneous catalysts. As an example, metallic Pd nanowires were synthesized in a thiol-functionalized IL using a seed-growth method in the presence of a gold solution (seeds).¹⁷⁰ The coupling of phenyl iodide and phenyl acetylene was successfully performed, where total substrate conversions were reached (entry 59, Table 2). Investigations into the stability of a palladacycle complex in different solvents revealed its decomposition and concomitant generation of MNPs in BMI·PF₆.¹⁷¹ Although the same complex was relatively stable in another IL (BM₂I·PF₆), the IL systems were not considered as appropriate media for the Sonogashira reaction, and the poor activity could be explained due to the poor solubility of the base.

6.4. Stille Reaction. The Stille reaction is another interesting tool in synthetic organic chemistry.^{172,173} As observed in classical coupling systems, the presence of MNPs

has also been checked in the Stille transformation. In this way, Pd MNPs dispersed in tetraalkylammonium IL can be a suitable reaction medium for the Stille reaction between aryl halides and tributylphenylstannane in THeptAB (entry 60, Table 2).¹⁶⁵ In fact, this protocol affords a highly active system, which could be used for up to five runs with a small decrease in activity.

A variety of functionalized ILs has been used to promote better MNP stabilization as well as to extend the catalyst lifetime during catalytic reactions. In this context, the catalytic activity of palladium complexes immobilized in alkyl-substituted and nitrile-functionalized pyridinium ILs was tested in the coupling of tributylphenylstannane and iodobenzene (entry 61, Table 2).¹¹⁴ However, the presence of Pd MNPs was identified after the Stille reaction. Moreover, the recycling experiments showed that the functionalized IL was a far superior reaction medium when compared with a nonfunctionalized analog, which may be associated with enhanced stabilization of the formed MNPs in the nitrile–pyridinium IL (corroborated by TEM). Imidazolium-based ILs containing nitrile groups attached on the alkyl side chain were also employed in the Stille reaction.¹⁷⁴ In this case, a detailed study showed the influence of relative coordination strengths of cations and anions on the efficiency of the coupling reaction. Interestingly, MNPs were formed in some cases, and the superior conversion observed for the nitrile-functionalized IL compared with the nonfunctionalized one was assigned to the improved stabilization of MNPs offered by the nitrile IL.

In the same context, further studies employing molecular Pd complexes in the Stille reaction demonstrated the formation of Pd MNPs in both functionalized and nonfunctionalized imidazolium ILs under certain conditions.¹⁷⁵ It is believed that the MNPs act as a reservoir for the active species and that the nitrile functionality of the IL stabilizes the MNPs by interacting with the metal surface. In addition, it was also proposed that functionalized ILs stabilize molecular intermediates via transient coordination of the nitrile group. However, in addition to the role of the nitrile group, ion-pairing effects and the viscosity of the IL are also important aspects that must be considered in C–C coupling reactions.¹¹⁵

6.5. Ullmann Reaction. A simple and convenient method to produce biaryl compounds is the catalytic homocoupling of aryl halides. In this way, the Ullmann reaction is regarded as an important strategy to achieve such compounds. However, the known original method possesses some disadvantages, such as the requirement for large amounts of copper (byproduct waste) and very high temperatures. As a promising alternative, the Pd-catalyzed Ullmann reaction provides access to a suitable process, although the use of reducing agents is required in this case. As an example, the homocoupling of aryl, vinyl, and heteroaryl halides was promoted by Pd MNPs in tetraalkylammonium ILs and in the presence of aldehydes as reducing agents (entry 62, Table 2).¹⁷⁶ In this case, the use of tetrabutylammonium acetate (TBAA) was crucial since it was both the base and the solvent and generated the enolate intermediate that was responsible for Pd reduction. Moreover, TBAA changes the selectivity of this reaction to Ullmann homocoupling; while in the presence of TBAB, the reaction takes place to the Heck product.

The combination of IL and supercritical carbon dioxide emerged as an efficient alternative to promote the Ullmann reaction in the presence of carbon-supported Pd MNPs and aluminum as the reductant.¹⁷⁷ In fact, the homocoupling of aryl chlorides in a Brønsted-acidic IL and ScCO₂ led to satisfactory

results (entry 63, Table 2). In addition, the functionalized IL can replace traditional hydrogen donors with more efficiency and, together with CO₂, provides advantages in terms of product separation and catalyst recycling. Similarly, the same reaction could be promoted by graphene oxide-supported Pd MNPs in HMI-NTf₂/ScCO₂ (HMI = 1-*n*-hexyl-3-methylimidazolium) and aluminum as the reducing agent.¹⁷⁸ In this case, the support containing hydroxyl, carboxylic, epoxy, and aldehyde groups acts as the hydrogen donor.

A simple and interesting electroreductive homocoupling of aryl halides catalyzed by Pd MNPs has also been described (entry 64, Table 2).¹⁷⁹ In particular, the present method avoids the use of common reducing agents, but gives good yields only for aryl bromides and iodides. Moreover, the MNPs were generated in situ in an electrochemical cell, and electron transfer plays a crucial role to close the catalytic cycle. An imidazolium IL (OMI·BF₄; OMI = 1-methyl-3-*n*-octylimidazolium) was added to enhance the electric conductivity and MNP stabilization, and water was used as an additional reagent. According to the kinetics measurements, it was possible to assume that a two-electron oxidation of water closes the catalytic cycle by regenerating Pd(0).

7. FUNCTIONALIZATION/DEFUNCTIONALIZATION, ISOTOPE EXCHANGE AND ENERGY PRODUCTION REACTIONS

The catalytic applications of MNPs in ILs cannot be envisaged as being only for the hydrogenation of unsaturated compounds or cross-coupling processes, but should also be extended to other types of reactions. Indeed, valuable compounds can be obtained by means of functionalization/defunctionalization reactions such as carbonylation, borylation, silylation, and dehalogenation, among others. The carbonylation reaction of alkyl/aryl halides is an efficient method to obtain esters, aldehydes, and related compounds (entry 65, Table 2).¹⁸⁰ Moreover, borylation and silylation processes give easy access to organoboron and organosilicon products (entries 66 and 67, Table 2).^{181,182}

On the other hand, the dehalogenation reaction provides the possibility of transforming undesired dangerous compounds, such as arylchlorides, into less aggressive ones (entry 68, Table 2).¹⁸³ As another example of a defunctionalization process, C–O bond cleavage is an interesting way to generate alcohols or sugar monomers from sugar–polymeric biomass (renewable sources).¹⁸⁴ Quite similarly, Rh MNPs stabilized in BMI-PF₆ proved to be effective catalysts for citral cyclodehydration.¹⁸⁵ The hydrodeoxygenation of lignin-derived phenols into alkanes was also promoted by MNPs in Brønsted-acidic ILs.¹⁸⁶ Some examples of such reactions are summarized in Table 2. Isotope labeling transformations are important tools for obtaining isotope-enriched compounds, which are important in chemical and medical research. In this context, Ru MNPs in ILs were able to catalyze the ¹¹B/¹⁰B exchange between decaborane and ¹⁰B₂H₆, affording enriched ¹⁰B-decaborane, which is interesting in medical applications (entry 69, Table 2).¹⁸⁷

Presently, it is well-known that there is a requirement for the development of clean energy sources. For this reason, catalytic reactions involving hydrogen gas or synthetic fuel production have drawn considerable interest in modern research. Therefore, methods based on the decomposition of water (water splitting), metal hydrides, amino-boranes, and formic acid as well as Fischer–Tropsch synthesis have become remarkable

topics in catalysis. In this view, the use of ILs with Lewis acid character such as $\text{BMI} \cdot \text{InCl}_4$ in the presence of a Sn complex has been reported as a suitable medium for the synthesis of biodiesel from vegetable oils.¹⁸⁸ The alcoholysis reaction of vegetable oils in ILs to produce biodiesel was also performed under acidic and basic conditions or by enzymatic catalysis.^{189,190}

As an example for hydrogen gas generation, the dehydrogenation of dimethylamino-borane catalyzed by Rh MNPs stabilized in a quaternary ammonium salt was achieved in high activity.¹⁹¹ In the same context, ILs containing cyclohexyl moieties attached to the side chain of imidazolium cation can reversibly add 6–12 hydrogen atoms in the presence of Ir MNPs,¹⁹² then these imidazolium-based ILs can be considered as alternative systems for hydrogen-storage devices.

Another important application is the Fischer–Tropsch process, which could be promoted by nanostructured metals in the presence or absence of ILs. In fact, Co MNPs previously prepared in imidazolium ILs were employed as competent catalysts in Fischer–Tropsch synthesis under solvent-free conditions.^{104,105} This reaction was also performed in IL using Ru MNPs protected by an IL-like copolymer in $\text{BMI} \cdot \text{BF}_4$.¹⁹³ Here, the hydrogenation of carbon monoxide with further chain growth affords hydrocarbons with satisfactory catalytic activities (entry 70, Table 2).

8. CONCLUSIONS AND PERSPECTIVES

Doubtless, ILs provide a flexible liquid platform for catalysis by transition metal nanoparticles. Indeed, ILs can act as the “solvent”, stabilizer, ligand, and support for MNPs. It is now possible to design metal nanoparticle catalysts for specific applications, in particular, for the selective hydrogenation of arenes under very mild reaction conditions. In fact, it appears that soluble MNPs in ILs behave as “single-site metal catalysts” for the hydrogenation of alkenes, but as “soluble-like” heterogeneous catalysts for the reduction of arenes or in Fischer–Tropsch synthesis. These MNPs may serve as simple reservoirs of soluble monometallic catalysts for C–C coupling reactions, such as the Heck and Suzuki reactions.

The catalytic activity, selectivity and in particular the stability of MNPs in nonfunctionalized ILs is related mainly to the surface electronic stabilization provided by protective layers of discrete supramolecular imidazolium aggregates, nonpolar imidazolium alkyl side chains, and NHC species as well as surface hydrogen species, together with an oxide layer when present on the metal surface.

The introduction of moieties on the imidazolium side chain, such as N-, O-, and S-containing groups, or ligands (mainly P- and N-containing ligands) provide extra stabilization of MNPs through coordination to the metal surface, which allows for modulating the selectivity of the catalyst, akin to classical organometallic/coordination catalysis.

However, in most cases, the surface-bound protective species are easily displaced by other substances present in the media, which is responsible for their catalytic activity. This also explains their relatively low stability, which leads to aggregation/agglomeration and eventually to the formation of bulk metal. Moreover, NPs can be used in conjunction with other stabilizers such as functionalized ILs and ligands, similar to classical coordination chemistry, generating so-called soluble-like heterogeneous catalysts. ILs are therefore among the premiere “solutions” for the generation of tailor-made soluble nanomaterials for catalysis. In particular, the use of function-

alized ILs and ionophilic ligands open a new window of opportunity for these soluble metal nanoparticles in catalysis, in terms of both selectivity and activity. Most important, ILs can be used as immobilizing agents, and a simple thin film of the ionic liquid is necessary to give the desired properties for the catalytic device (stability, selectivity, etc.), thus significantly reducing the mass-transfer problems usually associated with reactions performed when ILs are used as solvents.

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ACKNOWLEDGMENTS

Thanks are due to the following agencies for financial support: CNPq, CAPES, FAPERGS, TWAS, Humboldt Foundation, INCTCatal, MCT, and PETROBRAS.

ABBREVIATIONS:

BMI = 1-*n*-butyl-3-methylimidazolium; (BCN)MI = 1-butyronitrile-3-methylimidazolium; BIHB = 4,4'-bis-[7-(2,3-dimethylimidazolium)heptyl]-2,2'-bipyridine; BIMB = 4,4'-bis-[(1,2-dimethylimidazolium)methyl]-2,2'-bipyridine; BM₂I = 1-*n*-butyl-2,3-dimethylimidazolium; bipy = bipyridine; BMP = butyl-methylpyrrolidinium; (C₂OH)MI = 1-(2-hydroxy-ethyl)-3-methylimidazolium; Phen = phenanthroline; poly[NVP-co-VBIM.X] = poly[(*N*-vinyl-2-pyrrolidone)-co-(1-vinyl-3-butylimidazolium halide)]; PVP = poly(*N*-vinyl-2-pyrrolidone); TBAB = tetrabutylammonium bromide; TBAA = tetrabutylammonium acetate; TMGL = 1,1,3,3-tetramethylguanidinium lactate; MS = molecular sieves; (TESP)MI = *N*-3-(3-triethoxysilylpropyl)-3-methylimidazolium; C8IL = 1-octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride; TPTZ = 2,4,6-tris(2-pyridyl)-*s*-triazine; TPPZ = tetrapyrrolinepyrazine; fIL = 1-*n*-butyl-3-(3-amidopropyl)imidazolium; MWCNTs = multiwalled carbon nanotubes; BBI = 1,3-di-*n*-butylimidazolium; THeptAB = tetraheptylammonium bromide; C₃CNPY = butyronitrile pyridinium; (C₄SO₃H)BI = 1-(4-sulfobutyl)-3-butylimidazolium; OMI = 1-methyl-3-*n*-octylimidazolium; BMPY = 1-*n*-butyl-4-methyl pyridinium; BPy = *n*-butyl pyridinium; THTdP = trihexyltetradecylphosphonium; DBS = dodecylbenzene sulfonate; PF₆ = hexafluorophosphate; BF₄ = tetrafluoroborate; NTf₂ = *N*-bis-(trifluoromethanesulfonyl)imide

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