ARTICLES

July 2010 Vol.53 No.7: 1541–1548 doi: 10.1007/s11426-010-4003-2

Catalytic hydrogenation of aromatic nitro compounds by functionalized ionic liquids-stabilized nickel nanoparticles in aqueous phase: The influence of anions

HU Yu¹, YU YinYin¹, ZHAO XiuGe¹, YANG HanMing^{2*}, FENG Bo¹, LI Huan¹, QIAO YunXiang¹, HUA Li¹, PAN ZhenYan¹ & HOU ZhenShan^{1*}

¹Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, China

²Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission, Ministry of Education, South-Central University for Nationalities, Wuhan 430074, China

Received March 12, 2010; accepted April 27, 2010

Two kinds of nickel nanoparticles (NPs) well-dispersed in aqueous phase have been conveniently prepared by reducing nickel(II) salt with hydrazine in the presence of amino group (-NH₂) functionalized ionic liquids: 1-(3-aminopropyl)-2,3-dimethylimidazolium bromide ([AMMIM][Br]) and 1-(3-aminopropyl)-2,3-dimethylimidazolium acetate ([AMMIM][AcO]). The Ni(0) particles are composed of smaller ones which assemble in a blackberry-like shape. The Ni nanoparticles stabilized with [AMMIM][AcO] are much larger than those stabilized with [AMMIM][Br], and the former unexpectedly give much higher activity in the selective hydrogenation of citral and nitrobenzene (NB) in aqueous phase. The Ni(0) nanocatalysts dispersed in aqueous phase are stable enough to be reused at least five times without significant loss of catalytic activity and selectivity during the catalytic recycles.

functionalized ionic liquid, nickel nanoparticles, aqueous phase, selective hydrogenation

1 Introduction

Ionic liquids (ILs) as a new class of solvents are considered as designer solvents owing to the quasi-infinite number of possible cations and anions combination that can be envisioned. Over the past decade, the application of ILs in catalysis has been of growing interest due to their unique properties [1, 2]. An IL was demonstrated to be able to act as both the catalyst and the solvent in a reaction as early as 1986 [3]. In catalyzed reactions, ILs, as effective alternative solvents, have been designed for immobilizing catalysts, facilitating product isolation and recycling the catalyst system [4]. For example, ILs have played a significant role in stabilizing transition metal complexes [5]. The neoteric solvents have been utilized for the synthesis of nanostructures. Many metal NPs such as Ir, Rh, Ru, Te, Al, Ag, Pt, and Au NPs have been prepared in the presence of ILs [6–13]. In particular, imidazolium ILs have been intensively studied for the formation and stabilization of catalytically active transition-metal NPs due to their high chemical stability, excellent thermal stability and electrochemical stability, as well as a wide liquid range. The pre-organized 'supermolecular' structures of imidazolium ILs can create an external layer around the metal NPs to control the growth of the particle size and affect the mass transfer. However, simple imidazolium ILs could not provide an effective protection to the NPs against aggregation under the catalytic conditions [14]. Therefore, the functionalized ILs have recently been designed for effectively stabilizing metal nanocatalysts

^{*}Corresponding author (email: houzhenshan@ecust.edu.cn; yanghanmin@sina.com)

[©] Science China Press and Springer-Verlag Berlin Heidelberg 2010

[15-17].

Selective hydrogenation of substituted nitrobenzene (NB), being a major challenge for chemists, is commonly used to manufacture aniline and its derivatives, which are significant intermediates for dyes, polyurethanes, pharmaceuticals, explosives, and agrochemicals. The hydrogenation can be performed in organic solvents by using a variety of precious metal catalysts (Pd and Pt) supported on active carbon, polymers and metal oxides which show good catalytic activity even under mild conditions, but the selectivity is unsatisfactory unless the catalysts are modified by other stoichiometric additives or have to be poisoned or tailored to achieve the desired selectivity [18-21]. Besides, most of the reported hydrogenations of nitro compounds with nonprecious nickel nanocatalysts were not very effective, or were carried out in ecological unfavorable organic solvents [22-27]. Arai and Xu's groups have reported that dense phase CO₂ and ILs, compared with conventional organic solvents, have positive effects on selective hydrogenation of nitro compounds over Ni/y-Al2O3 and Raney Ni catalysts, respectively [28, 29]. Considering the high costs of using ILs and dense CO_2 fluid as solvents, as well as the slow mass transfer and limited solubility of H₂ in ILs, researchers aim to develop much more economic, efficient and greener pathways for organic transformations.

As an alternative solvent, water has attracted extraordinary attention because it is inexpensive and environmentally benign. It could offer the easy approach for separation of organic reagents from catalysts which were immobilized in aqueous phase [30-32]. From the viewpoint of green chemistry, the immobilization of nanocatalysts in an aqueous solution immiscible with the product phase (organic phase) represents an almost ideal combination of homogeneous and heterogeneous reaction processes. Therefore, the development of the functionalized imidazolium IL-stabilized NPs especially dispersed in aqueous phase has become one of the hot research topics in recent years [13, 33-38]. Enlightened by the numerous advantages of nanocatalysts in aqueous phase, we attempted to develop a new hydrophilic, easily prepared amino-functionalized imidazolium IL, 1-(3-aminopropyl)-2,3-dimethylimidazolium acetate [AMMIM][AcO], as a ligand to stabilize nickel NPs. Based on our previous study [39], the catalytic performance of [AMMIM][Br]stabilized nano-sized nickel(0) particles has been demonstrated to be superior than that of conventional Raney nickel for hydrogenation reactions in aqueous phase. We further examined the effect of ionic liquid anions on catalytic hydrogenation. First, the reaction kinetics for the hydrogenation of NB over two nanocatalysts has been investigated by choosing aqueous hydrogenation of NB as a model reaction, and then the reason why the as-synthesized nanocatalysts showed different catalytic performance was analyzed via various methods. Finally, the superior catalyst has been extended to the selective hydrogenation of various substituted nitro aromatic compounds and its lifetime has been examined.

2 Experimental

2.1 Reagents and instruments

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen. The solvents were all of reagent grade and distilled from appropriate drying agents under a nitrogen atmosphere prior to use. Nickel acetate tetrahydrate (\geq 98.0%) and aqueous hydrazine (80 wt.%) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. The water-soluble Ni NPs stabilized with amino group functionalized ILs and Blank-Ni catalyst were prepared by a chemical reduction method as shown in Figure 1 [39].

The structural properties were examined by X-ray diffraction (XRD, D/MAX 2550 VB/PC), N2 adsorptiondesorption (BET, ASAP 2020) and transmission electron microscopy (TEM, JEOL JEM 2010). The inductively coupled plasma atomic emission spectrometer (ICP-AES) analyses of Ni contents for [AMMIM][Br]-Ni and [AMMIM][AcO]-Ni were performed on a Varian ICP-710ES instrument. A Perkin Elmer Pyris Diamond was used for the thermogravimetric analysis (TGA). TGA measurements of the nickel NPs were performed under high-purity nitrogen purge (100 mL/min) by heating the sample to 700 °C at a rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 spectrometer. Nonmonochro Al Ka radiation was used as a primary excitation. The binding energies were calibrated with the C_{1s} level of adventitious carbon (284.8 eV) as the internal standard reference.



Figure 1 Structure illustration of the functionalized IL stabilized nickel catalysts: [AMMIM][Br]-Ni, [AMMIM][AcO]-Ni and Blank-Ni.

2.2 General procedure of hydrogenation

The stainless steel autoclave containing previously prepared Ni(0) catalyst (0.053 mmol) re-dispersed in 2 mL water was charged with the corresponding substrate (2.65 mmol), and then hydrogen was admitted into the system to the desired pressure. The reaction was conducted by stirring the mixture for a desired time at the setting temperature. After the reaction, the autoclave was cooled with ice-bath and then hydrogen was carefully vented. The products were separated from the catalyst by simple extraction with diethyl ether and identified by GC-MS, followed by quantitative analysis using a GC 112A with a FID detector equipped with a HP-5 column (30 m, 0.25 mm i.d.) and a flame ionization detector. The products of hydrogenation of p-Nitrophenol were analyzed by HPLC (Agilent 1200 series equipped with Eclipse XDB-C18 column).

3 Results and discussion

3.1 Properties of Ni catalysts

The water-soluble Ni NPs stabilized with amino group functionalized ILs and Blank-Ni catalyst were prepared by a chemical reduction method as shown in Figure 1 [39]. As shown in Figure 2, the XRD patterns of the isolated Ni(0) particles ([AMMIM][Br]-Ni and [AMMIM][AcO]-Ni) confirmed the presence of crystalline Ni(0) and the absence of NiO or Ni(OH)₂. Both of the Bragg reflections at ca. 44.5°, 51.8°, and 76.4° corresponded to the indexed planes of the crystals of Ni(0) (111), (200), (220).

The aqueous dispersions of the fresh [AMMIM][Br]-Ni and [AMMIM][AcO]-Ni NPs were placed as thin films in two carbon coated copper grids and characterized by TEM analyses. As shown in Figure 3, both of the two micrographs



Figure 2 X-ray diffraction pattern of the isolated Ni(0) NPs. (a) [AMMIM][Br]-Ni and (b) [AMMIM][AcO]-Ni. The peaks are labelled with the hkl of the planes for the corresponding Bragg angles.



Figure 3 TEM images and histograms of (a) [AMMIM][Br]-Ni and (b) [AMMIM][AcO]-Ni nanocatalysts.

displayed a complex, blackberry-like morphology and very good dispersity in aqueous phase. It was noteworthy that each particle was an aggregate of smaller particles, which might result from the magnetic interaction between Ni NPs [40]. The [AMMIM][Br]-Ni NPs with the average diameter of about 35 nm were aggregates of smaller particles with the average diameter of 6.4 nm; however, the [AMMIM][AcO]-Ni NPs with much larger average diameter of about 53 nm were composed of smaller particles of about 12.1 nm in diameter and the crystal lattice of the metal NPs was clearly observable. From the TEM images (Figure 3), these NP-aggregates demonstrated the presence of interstices among the small particles and the BET surface area of [AMMIM][Br]-Ni was 114.5 m²/g, much higher than that of [AMMIM][AcO]-Ni $(80.1 \text{ m}^2/\text{g})$ as shown in Table 1. This might result from the much smaller average particle size of [AMMIM][Br]-Ni. However, both of these two nanocatalysts owned larger surface area than the Blank-Ni catalyst $(13.0 \text{ m}^2/\text{g})$.

On the basis of TGA analysis as shown in Figure 5, the organic contents of the Ni NPs were determined to be 24.5% for the [AMMIM][Br]-Ni and 23.6% for the [AMMIM][AcO]-Ni within the range of the temperature studied (100–700 °C). The Ni contents of the two NPs were 72.5% and 74.2% by the ICP-AES analysis (Table 1).

It was found that the bulk molar ratios of Ni to IL for the [AMMIM][AcO]-Ni and [AMMIM][Br]-Ni catalysts were



Figure 4 The image of the Blank-Ni catalyst by an optical microscope. A large amount of bulk Ni aggregates was observed.



Figure 5 TGA curves of two nanocatalysts.

11.4 and 11.8, respectively. These results showed that after the step of purification, the whole amount of the remaining functionalized ILs in the Ni nanocatalysts kept almost at the same level. Additionally, the decomposition of the IL ([AMIMIM][Br]) remaining on Ni catalyst occurred between ca. 190 °C and 320 °C, and the degradation of [AMIMIM]-[AcO] on Ni catalyst occurred between ca. 260 °C and 400 °C, which indicated slightly higher thermal stability of [AMIMIM][AcO] than that of [AMIMIM][Br].

Figure 6 shows the XPS characterization results of the fresh-prepared [AMMIM][Br]-Ni and [AMMIM][AcO]-Ni catalysts. The two spectra had basically similar profiles, both indicating the existence of a few atomic layers of Ni²⁺ species on NPs surface and the absence of NiO or Ni(OH)₂ as demonstrated in our previous report [39]. However, the Ni_{2p3/2} binding energy of [AMMIM][Br]-Ni catalyst was 0.64 eV higher than that of [AMMIM][AcO]-Ni catalyst as shown in Table 1, which was possibly induced by the stronger nucleophilic characteristic of the bromide anion compared with acetate anion, so the electron cloud was more likely apt to transfer from the surface Ni atoms to Branions. Besides, as the XRD data and TEM results did not show the presence of nickel oxide or hydroxide particles or a core-shell structure (metal-oxide), both of the XPS results indicated the existence of a few atomic layers of Ni²⁺ species on NPs surface as observed by Couto's and Win-

Table 1 Characterization results of the fresh [AMMIM][Br]-Ni and [AMMIM][AcO]-Ni nanocatalysts

Samples	[AMMIM][Br]-Ni	[AMMIM][AcO]-Ni	Blank-Ni
Ni particle size (nm)	6.4 ^{a)}	12.1 ^{a)}	bulk particles b)
BET area (m ² /g)	114.5	80.1	13.0
Mass loss (wt%) ^{c)}	24.5	23.6	-
Ni loading (wt%) ^{d)}	72.5	74.2	_
Bulk Ni/IL molar ratio e)	11.8	11.4	-
Binding energy of $Ni_{2p3/2} (eV)^{f}$	856.10	855.46	852.1 ^{g)}

a) See Figure 3; b) see Figure 4; c) obtained from TGA analysis; d) measured by ICP-AES analysis; e) obtained on the basis of TGA and elemental analyses; f) detected by XPS analysis; g) see ref. [41].

nischofer's groups [42, 43]. We again demonstrated that the Ni(0) surface composition was dominated by adsorbed Ni²⁺-[AMMIM][Br]/[AcO] complexes in the present system which devoted to the high stability of the two nanocatalysts towards bulk oxidation and aggregation during the reaction.

3.2 The influence of IL anions on the activities of Ni nanocatalysts

First, we examined two nanocatalysts for selective hydrogenation of α , β -unsaturated double bond of citral and the results are shown in Table 2. It was found that both Blank-Ni catalyst and [AMMIM][Br]-Ni were almost unreactive for selective hydrogenation of C=C double bond under mild conditions (1.0 MPa H₂ pressure and 60 °C) (Table 2, entries 1 and 4), while [AMMIM][AcO]-Ni nanocatalysts demonstrated good reactivity and selectivity for selective hydrogenation of α,β -unsaturated double bond under the same reaction conditions (Table 2, entry 3). The [AMMIM]-[Br]-Ni and Blank-Ni catalysts solely displayed activity under increasing H₂ pressure (3.0 MPa) and at higher reaction temperature (70 °C) (Table 2, entries 2 and 5), although the former is much more active for the conversion of citral. As a result, the activity for selective hydrogenation of citral decreased in the following order: [AMMIM][AcO]-Ni > [AMMIM][Br]-Ni > Blank-Ni, which was attributed to much higher BET surface area of [AMMIM][AcO] or [AMMIM][Br]-stabilized Ni nanocatalysts as shown in Table 1.

Encouraged by the good activity and selectivity obtained by using [AMMIM][AcO]-Ni as a catalyst for selective hydrogenation of citral, we extended the current catalyst to selective hydrogenate NB and its derivatives. Figure 7 shows the evolution of product distribution with time in selective hydrogenation of NB in water over [AMMIM]-[AcO]-Ni and [AMMIM][Br]-Ni nanocatalysts. In general, the basic profiles of (a) and (b) in Figure 7 were very similar. Both of the two catalysts were active and selective towards hydrogenation of NB to aniline (AN) as the sole product as long as more time was given. The [AMMIM]-[AcO]-Ni nanocatalysts were much more active and only needed 3 h to completely convert NB into AN, while the [AMMIM][Br]-Ni nanocatalysts needed almost 4 h to achieve full conversion, which was in agreement with previous results for selective hydrogenation of citral.

From the above TGA and elemental analyses, the amounts of the two functionalized ILs coordinated on the surface of nanocatalysts kept almost at the same level. As the larger Ni NPs in [AMMIM][AcO]-Ni (12.1 nm) had unexpected higher catalytic activity in both selective hydrogenation of citral and NB than [AMMIM][Br]-Ni catalyst (6.4 nm), we proposed that the worse performance of the [AMMIM][Br]-Ni nanocatalysts was mainly due to the stronger nucleophilic characteristic of the bromide anion (in accordance with the previous XPS analyses), which hampered the absorption of the substrate molecules on the catalytic center compared with that of AcO⁻ anion, and thus induced a decrease of the activity.



Figure 6 XPS spectra of Ni_{2p} for (a) [AMMIM][Br]-Ni and (b) [AMMIM][AcO]-Ni nanocatalysts.

Table 2 Comparison of unreferit catarysis towards selective nyurogenation of citiar in water

Entry	Catalyst	$P_{\rm c}$ (MP ₂)	t (b)	Conv. (%)	Selectivity (%)		
Entry Catalyst	$P_{\rm H2}$ (MPa)	<i>t</i> (II)	Conv. (%) —	citronellal	citronellol	IP ^{b)}	
1 ^{c)}	[AMMIM][Br]-Ni	1.0	5	<3.0	-	-	-
2 ^{d)}	[AMMIM][Br]-Ni	3.0	3	89.6	94.4	5.4	0.2
3 ^{c)}	[AMMIM][AcO]-Ni	1.0	4	88.4	95.6	3.7	0.7
4 ^{c)}	Blank-Ni	1.0	5	<3.0	-	-	-
5 ^{d)}	Blank-Ni	3.0	3	54.8	97.0	2.8	0.2

a) Reaction conditions: Ni (27 mmol L^{-1} atomic nickel), citral/Ni = 50 (molar radio), water (2 mL); b) unidentified products; c) 60 °C; d) 70 °C.



Figure 7 Evolution of species with time during the hydrogenation of NB in water over (a) [AMMIM][Br]-Ni and (b) [AMMIM][AcO]-Ni. (\blacksquare) NB conversion, (\checkmark) AN selectivity, (\bullet) selectivity of NSB and (\blacktriangle) selectivity of AB and byproducts. Reaction conditions: Ni (27 mmol L⁻¹ atomic nickel), substrate/Ni = 50 (molar radio), water (2 mL), H₂ (1.0 MPa), 70 °C.

3.3 Application of [AMMIM][AcO]-Ni in selective hydrogenation of various substituted nitro aromatic compounds

As shown in Table 3, with the superior [AMMIM][AcO]-Ni as the catalyst, almost all the substrates could efficiently convert into the corresponding substituted amino aromatic compounds under mild conditions in aqueous phase except the p-nitrophenol. The methyl- or chloro-substituted NB afforded the corresponding amino aromatic compounds and showed comparable reactivity and selectivity as that of unsubstituted NB, although the chloro-substituted NB had to be performed at a higher temperature (80 °C) possibly because of its higher melting point (Table 3, entries 1–3). The steric hindrance effect did not seem to be the controlling factor during chemoselective hydrogenation of NB substituted by hydroxyl group at either o- or p-position (Table 3, entries 4 and 5). The o-substituted substrate gave much higher reactivity, which was converted completely into the corresponding aniline within 5 h, while the p-substituted substrate could only reach 59% conversion after 9 h. This was possibly induced by the competitive adsorption of the hydroxyl group on the catalytic active center [44] which would prevent the selective hydrogenation of the nitro group. To conclude, [AMMIM][AcO]-Ni catalysts showed promising activity for chemoselective hydrogenation of NB and its derivatives, which was not apparently affected by the steric effect, but possibly by the electric effect.

3.4 The recyclability of [AMMIM][AcO]-Ni

We investigated the recyclability of [AMMIM][AcO]-Ni nanocatalysts using NB as a model compound in aqueous phase. After each run, the products were extracted by liquidliquid extraction with diethyl ether for three times. Then diethyl ether was evaporated in catalytic aqueous phase under vacuum, and the substrate was recharged into the autoclave for the next recycling. It was found that the yield of AN could remain over 99% even if the catalyst has been reused five times as long as enough time is given. Besides, the Ni(0) NPs were found to be stable without the formation of NiO or Ni(OH)₂ from XRD spectrum analysis and still well–dispersed in aqueous phase (Figure 8), as well as with non-detectable loss of Ni by ICP analysis after three recycles.

Table 3 Results of selective hydrogenation of substituted nitro compounds with [AMMIM][AcO]-Ni^{a)}

Entry	Substrate	<i>t</i> (h)	Conv. (%)		Selectivity (%)	
1	NB	-	-	—	aniline	IP ^{b)}
		3	100	_	>99.9	-
2	<i>p</i> -nitrotoluene	-	-	_	4-methylaniline	IP
		3	100	_	99.9	0.1
3	<i>p</i> -chloro nitrobenzene ^{c)}	-	-	aniline	<i>p</i> -chloroaniline	IP
		3	100	0.6	99.2	0.2
4	p-nitrophenol	-	-	_	p-aminophenol	IP
		9	59.0	_	99.9	0.1
5	o-nitrophenol	-	-	_	o-aminophenol	IP
		3.5	57.0	—	99.9	0.1
		5	100	—	99.9	0.1

a) Reaction conditions: Ni (27 mmol L⁻¹ atomic nickel), substrate/Ni = 50 (molar radio), H₂ (1.0 MPa), water (2 mL), 70 °C; b) unidentified products; c) 80 °C.



Figure 8 TEM image of [AMMIM][AcO]-Ni nanocatalysts after three recycles.

These results indicated that the present catalytic system can efficiently immobilize Ni(0) nanocatalysts in aqueous media and keep their high reactivity during catalytic recycles.

4 Conclusions

In summary, two kinds of water-soluble nickel NPs stabilized by amino-functionalized ILs have been prepared. XRD analyses confirmed the fcc structures of two Ni(0) NPs and the absence of NiO or Ni(OH)2. TEM analyses revealed both of the two kinds of smaller Ni(0) particles assembled to give larger, blackberry-like shaped ones, while the Ni(0) NPs stabilized with [AMMIM][AcO] were much larger than those stabilized with [AMMIM][Br] (12.1 vs 6.4 nm). The elemental analysis and TGA have confirmed that the two kinds of Ni(0) NPs contained almost the same amount of ILs on their surface which could protect them from being oxidized in aqueous phase under the reaction conditions. However, the larger particle size of [AMMIM][AcO]-Ni gave higher reactivity towards the selective hydrogenation of citral and NB, which was explained by the stronger nucleophilic characteristic of the bromide anion, compared with the acetate anion. The superior catalyst [AMMIM]-[AcO]-Ni has been employed for the selective hydrogenation of various substituted nitro aromatic compounds in aqueous phase under mild reaction conditions, which has demonstrated good activity and excellent selectivity to the corresponding anilines. The present catalytic system could be reused several times without loss of any catalytic activity and kept high selectivity towards aniline.

This work was supported by the National Natural Science Foundation of China (20773037), East China University of Science and Technology (YJ0142136), and the Commission of Science and Technology of Shanghai Municipality (07PJ14023).

- Dupont J, Souza de RF, Suarez PAZ. Ionic liquid (molten salt) phase organometallic catalysis. *Chem Rev*, 2002, 102: 3667–3692
- 2 Muzart J. Ionic liquids as solvents for catalyzed oxidations of organic compounds. *Adv Synth Catal*, 2006, 348: 275–295
- 3 Boon JA, Levisky JA, Pflug JL, Wilkes JS. Friedel-Crafts reactions in ambient-temperature molten salts. J Org Chem, 1986, 51: 480-483
- 4 Rantwijk van F, Sheldon RA. Biocatalysis in ionic liquids. *Chem Rev*, 2007, 107: 2757–2785
- 5 Scheeren CW, Machado G, Teixeira SR, Morais J, Domingos JB, Dupont J. Synthesis and characterization of Pt(0) nanoparticles in imidazolium ionic liquids. *J Phys Chem B*, 2006, 110: 13011–13020
- 6 Dupont J, Fonseca GS, Umpierra AP, Fichtner PFP. Transition-metal nanoparticles in imidazolium ionic liquids: Recycable catalysts for biphasic hydrogenation reactions. J Am Chem Soc, 2002, 124: 4228–4229
- 7 Fonseca GS, Umpierre AP, Fichtner PFP. The use of imidazolium ionic liquids for the formation and stabilization of Ir0 and Rh0 nanoparticles: Efficient catalysts for the hydrogenation of arenes. *Chem Eur J*, 2003, 9: 3263–3269
- 8 Silveira ET, Umpierre AP, Rossi LM, Machado G, Morais J, Soares GV, Baumvol ILR, Teixeira SR, Fichtner PFP, Dupont J. The partial hydrogenation of benzene to cyclohexene by nanoscale ruthenium catalysts in imidazolium ionic liquids. *Chem Eur J*, 2004, 10: 3734–3740
- 9 Zhu YJ, Wang WW, Qi RJ, Hu XL. Microwave-assisted synthesis of single-crystalline tellurium nanorods and nanowires in ionic liquids. *Angew Chem Int Ed*, 2004, 43: 1410–1414
- 10 Endres F, Bukowski M, Hempelmann R, Natter H. Electrodeposition of nanocrystalline metals and alloys from ionic liquids. *Angew Chem Int Ed*, 2003, 42: 3428–3430
- 11 Bhatt AI, Mechler A, Martin LL, Bond AM. Synthesis of Ag and Au nanostructures in an ionic liquid: thermodynamic and kinetic effects underlying nanoparticle, cluster and nanowire formation. J Mater Chem, 2007, 17: 2241–2250
- 12 Scheeren CW, Machado G, Dupont J, Fichtner PFP, Texeira SR. Nanoscale Pt(0) particles prepared in imidazolium room temperature ionic liquids: synthesis from an organometallic precursor, characterization, and catalytic properties in hydrogenation reactions. *Inorg Chem*, 2003, 42: 4738–4742
- 13 Itoh H, Naka K, Chujo Y. Synthesis of gold nanoparticles modified with ionic liquid based on the imidazolium cation. J Am Chem Soc, 2004, 126: 3026–3027
- 14 Umpierre AP, Machado G, Fecher GH, Morais J, Dupont J. Selective hydrogenation of 1,3-butadiene to 1-butene by Pd(0) nanoparticles embedded in imidazolium ionic liquids. *Adv Synth Catal*, 2005, 347: 1404–1412
- 15 Šebesta R, Kmentová I, Toma S. Catalysts with ionic tag and their use in ionic liquids. *Green Chem*, 2008, 10: 484–496
- 16 Hu Y, Yu YY, Hou ZS, Li H, Zhao XG, Feng B. Biphasic hydrogenation of olefins by functionalized ionic liquid-stabilized palladium nanoparticles. *Adv Synth Catal*, 2008, 350: 2077–2085
- 17 Hu Y, Yang HM, Zhang YC, Hou ZS, Wang XR, Qiao YX, Li H, Feng B, Huang QF. The functionalized ionic liquid-stabilized palladium nanoparticles catalyzed selective hydrogenation in ionic liquid. *Catal Commun*, 2009, 10: 1903–1907
- 18 Downing RS, Kunkeler PJ, Bekkum van H. Catalytic syntheses of aromatic amines. *Catal Today*, 1997, 37: 121–136
- 19 Kratky V, Kralik M, Mecarova M, Stolcova M, Zalibera L. Effect of catalyst and substituents on the hydrogenation of chloronitrobenzenes. *Appl Catal A*, 2002, 235: 225–231
- 20 Cárdenas-Lizana F, Gómez-Quero S, Hugon A, Delannoy L, Louis C, Keane M A. Pd-promoted selective gas phase hydrogenation of *p*-chloronitrobenzene over alumina supported Au. *J Catal*, 2009, 262: 235–244
- 21 Han XX, Chen Q, Zhou RX. Study on the hydrogenation of p-chloronitrobenzene over carbon nanotubes supported platinum catalysts modified by Mn, Fe, Co, Ni and Cu. J Mol Catal A, 2007, 277: 210–214
- 22 Nieto-Márquez A, Gil S, Romero A, Valverde JL, Gómez-Quero S, Keane MA. Gas phase hydrogenation of nitrobenzene over acid

treated structured and amorphous carbon supported Ni catalysts. *Appl Catal A*, 2009, 363: 188–198

- 23 Cárdenas-Lizana F, Gómez-Quero S, Keane MA. Clean production of chloroanilines by selective gas phase hydrogenation over supported Ni catalysts. *Appl Catal A*, 2008, 334: 199–206
- 24 Wang C, Qiu J, Liang C, Xing L, Yang X. Carbon nanofiber supported Ni catalysts for the hydrogenation of chloronitrobenzenes. *Catal Commun*, 2008, 9: 1749–1753
- 25 Li H, Lin H, Xie S, Dai W, Qiao M, Lu Y, Li H. Ordered mesoporous Ni nanowires with enhanced hydrogenation activity prepared by electroless plating on functionalized SBA-15. *Chem Mater*, 2008, 20: 3936–3943
- 26 Li H, Zhao Q, Wan Y, Dai W, Qiao M. Self-assembly of mesoporous Ni-B amorphous alloy catalysts. J Catal, 2006, 244: 251–254
- 27 Du Y, Chen H, Chen R, Xu N. Synthesis of *p*-aminophenol from *p*-nitrophenol over nano-sized nickel catalysts. *Appl Catal A*, 2004, 277: 259–264
- 28 Meng XC, Cheng HY, Akiyama Y, Hao YF, Qiao WB, Yu YC, Zhao FY, Fujita S, Arai M. Selective hydrogenation of nitrobenzene to aniline in dense phase carbon dioxide over Ni/γ-Al₂O₃: Significance of molecular interactions. *J Catal*, 2009, 264: 1–10
- 29 Xu DQ, Hu ZY, Li WW, Luo SP, Xu ZY. Hydrogenation in ionic liquids: an alternative methodology toward highly selective catalysis of halonitrobenzenes to corresponding haloanilines. *J Mol Catal A*, 2005, 235: 137–142
- 30 Cornils B. Exciting results from the field of homogeneous two-phase catalysis. Angew Chem Int Ed, 1995, 34: 1575–1577
- 31 Dwars T, Paetzold E, Oehme G. Reactions in micellar systems. Angew Chem Int Ed, 2005, 44: 7174–7199
- 32 Li CJ. Organic reactions in aqueous media with a focus on carbon- carbon bond formations: a decade update. *Chem Rev*, 2005, 105: 3095–3166
- 33 Kim KS, Demberelnyamba D, Lee H. Size-selective synthesis of gold and platinum nanoparticles using novel thiol-functionalized ionic liquids. *Langmuir*, 2004, 20: 556–560
- 34 Schrekker HS, Gelesky MA, Stracke MP, Schrekker CML, Machado G, Teixeira SR, Rubim JC, Dupont J. Disclosure of the imidazolium

cation coordination and stabilization mode in ionic liquid stabilized gold(0) nanoparticles. *J Colloid Interface Sci*, 2007, 316: 189–195

- 35 Zhang SM, Li J, Zhang CL, Wu ZS, Zhang ZJ. Preparation and structural characterization of carboxyl-functional ionic liquid modified Pd nanoparticles. *Chin J Inorg Chem*, 2007, 23: 729–732
- 36 Zhang H, Cui H. Synthesis and characterization of functionalized ionic liquid-stabilized metal (gold and platinum) nanoparticles and metal nanoparticle/carbon nanotube hybrids. *Langmuir*, 2009, 25: 2604–2612
- 37 Wang Z J, Zhang Q X, Kuehner D, Ivaska A, Niu L. Green synthesis of 1–2 nm gold nanoparticles stabilized by amine-terminated ionic liquid and their electrocatalytic activity in oxygen reduction. *Green Chem*, 2008, 10: 907–909
- 38 Dai C, Zhang SM, Li J, Wu ZS, Zhang Z. Preparation and structure characterization of Pd nanoparticles in hydroxyl-functionalized ionic liquids. *Chin J Inorg Chem*, 2007, 23: 1653–1656
- 39 Hu Y, Yu YY, Hou ZS, Yang HM, Feng B, Li H, Qiao YX, Wang XR, Hua L, Pan ZY, Zhao XG. *Chem Asian J*, 2010, 5: 1178–1184
- 40 Ely TO, Amiens C, Chaudret B, Snoeck E, Verelst M, Respaud M, Broto JM. Synthesis of nickel nanoparticles. influence of aggregation induced by modification of poly(vinylpyrrolidone) chain length on their magnetic properties. *Chem Mater*, 1999, 11: 526–529
- 41 Zhao ZF, Wu ZJ, Zhou LX, Zhang MH, Li W, Tao KY. Synthesis of a nano-nickel catalyst modified by ruthenium for hydrogenation and hydrodechlorination. *Catal Commun*, 2008, 9: 2191–2194
- 42 Couto GG, Klein JJ, Schreiner WH, Mosca DH, Oliveira AJA, Zarbin AJG. Nickel nanoparticles obtained by a modified polyol process: synthesis, characterization, and magnetic properties. *J Colloid Interface Sci*, 2007, 311: 461–468
- 43 Winnischofer H, Rocha TCR, Nunes WC, Socolovsky LM, Knobel M, Zanchet D. Chemical synthesis and structural characterization of highly disordered Ni colloidal nanoparticles. ACS NANO, 2008, 2: 1313–1319
- 44 Chen RZ, Wang QQ, Du Y, Xing WH, Xu NP. Effect of initial solution apparent pH on nano-sized nickel catalysts in *p*-nitrophenol hydrogenation. *Chem Eng J*, 2009, 145: 371–376