

Highly Selective Hydrogenation with Ionic Liquid Stabilized Nickel Nanoparticles

He-yan Jiang¹ · Si-shi Zhang¹ · Bin Sun¹

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Abstract

Nickel nanoparticles (Ni NPs) were conveniently synthesized from the reduction of nickel(II) salt with NaBH₄ or hydrazine in the presence of the ionic liquid 1-butyl-2,3-dimethylimidazolium (S)-2-pyrrolidinecarboxylic acid salt. UV/Vis spectroscopy, thermogravimetric analysis, and X-ray photoelectron spectroscopy were employed to characterize the interaction between the metal and the ionic liquid. The face-centered cubic structure of the Ni NPs(0) was confirmed by X-ray diffraction characterization. Transmission electron microscopy images revealed well-dispersed Ni particles of approximately 5.1 nm in average diameter. The ionic liquid immobilized Ni NPs were employed as highly efficient catalysts in chemoselective hydrogenation of quinoline and relevant compounds, as well as aromatic nitro compounds under mild reaction conditions. The Ni NPs can be efficiently recovered and reused.

Graphical Abstract



Keywords Chemoselective hydrogenation · Nanoparticles · Ionic liquids · Quinoline · Nickel

1 Introduction

Metal nanoparticles have received boost interest in recent years, which stems from their application in such fields as medicine, sensing, and catalysis [1-5]. Metal nanoparticles are thermodynamically not stable due to their high excess surface energy, therefore they have a tendency to aggregate unless they are stabilized. Stabilizing species, such as polymers, solid supports or ionic liquids with specific stabilizing groups, can adhere to the metal surface through either electrostatic, van der Waals or covalent interactions, which provide stability to the nanoparticles through electrostatic or steric repulsion between neighbouring particles [6–10]. By now, ionic liquid-stabilized metal nanoparticles were assessed as catalytic materials, mostly in olefins or arenes hydrogenation [11–16].

1,2,3,4-Tetrahydroquinoline as well as relevant compounds are crucial structure that exists in various pharmacologically related therapeutic agents and biologically active natural products [17–24]. Straightforward hydrogenation of quinoline and relevant compounds is regarded as the most economical way to access 1,2,3,4-tetrahydroquinoline and analogous compounds [17–24]. Both homogeneous and

He-yan Jiang orgjiang@163.com

Key Laboratory of Catalysis Science and Technology of Chongqing Education Commission, Chongqing Key Laboratory of Catalysis and New Environmental Materials, College of Environmental and Resources, Chongqing Technology and Business University, Chongqing 400067, China

heterogeneous catalytic reactions have been widely investigated in the chemoselective hydrogenation. However, these studies were generally focused on nobel-metal catalytic process on the basis of Pd, Rh, Ru, Pt or Ir etc. [17–24], and the reaction temperatures were always high (> 80 °C). The development of easily available and relatively abundant-metal catalysts is of high importance from the viewpoint of practical use. In this work, we originally report the highly chemoselective catalytic hydrogenation of quinoline as well as relevant compounds with ionic liquid (1-butyl-2,3-dimethylimidazolium (*S*)-2-pyrrolidinecarboxylic acid salt ([BMIM][Pro])) stabilized nickel nanoparticles (Ni NPs) under mild conditions.

2 Experimental

2.1 Materials

All manipulations were performed using standard Schlenk line techniques under N₂. Nickel acetate tetrahydrate was from Aldrich. Other reagents were analytical grade. H₂ purity was over 99.99%. Ionic liquids were prepared in accordance with published procedure [25, 26]. [BMIM] [OAc]: ¹HNMR (300M, CDCl₃), δ 0.93–1.29 (m, 5H), 1.69-1.85(m, 5H), 2.73(s, 3H), 3.90(s, 3H), 4.19-4.35 (m, 2H), 7.99–8.27 (m, 2H). ¹³C NMR, δ 10.9, 12.9, 18.5, 24.3, 31.5, 35.1, 49.5, 120.9, 123.3, 136.8, 175.6. HRMS: calcd. for C₀H₁₇N₂⁺ 153.1392 [M]⁺, found 153.1393; calcd. for C₂H₃O₂⁻ 59.0139 [M]⁻, found 59.0136. [BMIM][Pro]: ¹HNMR (300M, CDCl₃), δ 1.03–1.25 (m, 5H), 1.54–1.62 (m, 2H), 1.69-1.85(m, 4H), 2.73(s, 3H), 2.81-2.97 (m, 2H), 3.32 (m, 1H), 3.63 (s, 1H), 3.93(s, 3H), 4.22-4.38 (m, 2H), 7.79–7.87 (m, 2H). 13 C NMR, δ 12.6, 25.3, 15.1, 29.6, 31.5, 35.5, 44.0, 46.4, 54.9, 61.8, 120.5, 122.7, 135.9, 174.0. HRMS: calcd. for C₉H₁₇N₂⁺ 153.1392 [M]⁺, found 153.1399; calcd. for $C_5H_8NO_2^-$ 114.0561 [M]⁻, found 114.0554. Raney Ni was synthesized in terms of literature [27]. Products were analyzed by GC with FID detector and HP-5 column (30 m \times 0.25 mm). Hydrogenation products were identified by GC-MS, NMR and HRMS.¹ UV/Vis spectra were recorded on a Varian Cary 500 spectrophotometer. A Perkin-Elmer Pyris Diamond was used in the current study for the thermogravimetric analysis (TGA). TGA analyses of the separated Ni catalysts were carried out with highpurity nitrogen purge (100 mL min⁻¹). X-ray diffraction (XRD) measurement was performed in a D/MAX 2550 VB/ PC with a graphite crystal as monochromator. The transmission electron microscopy (TEM) analyses were performed in a JEOL JEM 2010 transmission electron microscope operating at 200 kV with nominal resolution of 0.25 nm.

2.2 Synthesis of Nickel Nanoparticles

Nanocatalysts **1**, **3** or **5** (Scheme 1) preparation: typically, Ni NPs stabilized by ionic liquids were synthesized by dissolving Ni(OAc)₂·4H₂O (0.132 g, 0.53 mmol) in water (30 mL), then ionic liquids (1.06 mmol) were introduced. The solution color changed from light green to blue in the period of ionic liquids addition. The color change is a strong electron transfer indication between nickel(II) acetate and ionic

¹ *Aa*: ¹HNMR (300M, CDCl₃), *δ* 1.90–1.95 (m, 2H), 2.70–2.76 (m, 2H), 3.20–3.25 (m, 2H), 3.69 (s, 1H), 6.38–7.10 (m, 4H). ¹³C NMR, *δ* 22.2, 26.8, 41.5, 114.9, 117.0, 121.6, 126.0, 129.6, 144.9. HRMS: calcd. for C₉H₁₁N [M+H]⁺ 134.0970, found 134.0966. *Ba*: ¹HNMR (300M, CDCl₃), *δ* 1.26 (s, 3H), 1.54–1.65 (m, 1H), 1.90–1.93 (m, 1H), 2.75–2.86 (m, 2H), 3.36–3.45 (m, 1H), 3.73 (s, 1H), 6.49–6.58 (m, 2H), 6.96–7.02 (m, 2H). ¹³C NMR, *δ* 22.6, 26.7, 30.3, 47.2, 114.1, 117.0, 121.2, 126.7, 129.2, 144.9. HRMS: calcd. for C₁₀H₁₃N [M+H]⁺ 148.1126, found 148.1125. *Ca*: ¹HNMR (300M, CDCl₃), *δ* 1.23 (s, 3H), 1.53–1.63 (m, 1H), 1.87–1.91 (m, 1H), 2.74–2.85 (m, 2H), 3.37–3.45 (m, 1H), 3.69 (s, 1H), 6.47–6.54 (m, 2H), 6.95–7.03 (m, 2H). ¹³C NMR, *δ* 21.5, 26.8, 30.1, 47.0, 114.3, 117.9, 121.9, 126.6, 129.6, 143.8. HRMS: calcd. for C₁₀H₁₃N [M+H]⁺ 148.1126, found 148.1118. *Da*: ¹HNMR (300M, CDCl₃), *δ* 1.23–1.27 (m,

Footnote 1 (continued)

³H), 1.53-1.60 (m, 1H), 1.93-1.99 (m, 1H), 2.79-2.86 (m, 2H), 3.39-3.48 (m, 1H), 3.60 (s, 1H), 6.45-6.51 (m, 2H), 6.93-7.00 (m, 2H). ¹³C NMR, δ 20.5, 26.9, 31.3, 49.5, 115.8, 119.1, 121.6, 126.9, 129.8, 145.3. HRMS: calcd. for C₁₀H₁₃N [M+H]⁺ 148.1126, found 148.1127. Ea: ¹HNMR (300M, CDCl₃), δ 2.99–3.06 (m, 2H), 3.81– 3.90 (m, 2H), 7.21–7.36 (m, 4H). 13 C NMR, δ 29.9, 70.6, 109.3, 120.8, 124.6, 126.9, 127.3, 160.3. HRMS: calcd. for C₈H₈O [M+H]⁺ 121.0653, found 121.0648. *Fa*: ¹HNMR (300M, CDCl₃), δ 3.33–3.45 (m, 4H), 7.19–7.29 (m, 4H). ¹³C NMR, δ 33.9, 36.6, 122.5, 124.3, 124.8, 127.5, 139.0, 142.2. HRMS: calcd. for C₈H₈S [M+H]⁺ 137.0425, found 137.0421. Aniline: ¹HNMR (300M, CDCl₃), δ 3.55 (S, 2H), 6.60–7.02 (m, 5H). ¹³C NMR, δ 115.4, 119.7, 119.9, 129.6, 130.0, 148.1. HRMS: calcd. for C₆H₇N [M+H]⁺ 94.0657, found 94.0651. m-Methylaniline: ¹HNMR (300M, CDCl₃), & 2.52 (S, 3H), 3.46 (S, 2H), 6.47–6.56 (m, 2H), 6.97–7.11 (m, 2H). ¹³C NMR, *b* 21.4, 112.2, 115.9, 119.5, 129.1, 140.1, 146.5. HRMS: calcd. for C_7H_9N [M+H]⁺ 108.0813, found 108.0810. *p*-Methylaniline: ¹HNMR (300M, CDCl₃), δ 2.23 (S, 3H), 3.51 (S, 2H), 6.49–6.58 (m, 2H), 6.95–7.05 (m, 2H). ¹³C NMR, δ 20.7, 115.2, 115.3, 127.5, 129.6, 129.9, 144.9. HRMS: calcd. for $C_7H_0N [M+H]^+$ 108.0813, found 108.0818. o-Methoxyaniline: ¹HNMR (300M, CDCl₃), δ 3.69 (S, 3H), 3.75 (S, 2H), 6.65–6.76 (m, 4H). ¹³C NMR, δ 55.2, 110.7, 114.9, 118.3, 121.1, 136.6, 147.6. HRMS: calcd. for C7H9NO $[M+H]^+$ 124.0762, found 124.0763. *p-Methoxyaniline*: ¹HNMR (300M, CDCl₃), *b* 3.45 (S, 3H), 3.60 (S, 2H), 6.60–6.69 (m, 4H). ¹³C NMR, δ 55.5, 110.6, 115.0, 118.8, 121.1, 136.5, 147.5. HRMS: calcd. for C₇H₉NO [M+H]⁺ 124.0762, found 124.0766. p-Fluoroaniline: ¹HNMR (300M, CDCl₃), δ 3.69 (S, 2H), 6.45–6.96 (m, 4H). ¹³C NMR, δ 116.8, 117.0, 117.2, 118.0, 146.7, 154.2. HRMS: calcd. for $C_6H_6FN [M+H]^+$ 112.0563, found 112.0569. *o-Chloroaniline*: ¹HNMR (300M, CDCl₃), δ 3.93 (S, 2H), 6.66–6.72 (m, 2H), 7.02– 7.20 (m, 2H). ¹³C NMR, δ 115.8, 115.9, 118.9, 127.5, 129.3, 142.2. HRMS: calcd. for $C_6H_6FN [M+H]^+$ 128.0267, found 128.0261. *p-Chloroaniline*: ¹HNMR (300M, CDCl₃), δ 3.60 (S, 2H), 6.55–6.70 (m, 2H), 7.00–7.16 (m, 2H). 13 C NMR, δ 116.2, 118.0, 122.4, 128.7, 129.0, 145.2. HRMS: calcd. for C₆H₆FN [M+H]⁺ 128.0267, found 128.0270.



Scheme 1 Synthesis of ionic liquid stabilized Ni NPs

liquids, which was verified by UV/Vis spectra. The solution was stirred for another 5 h at 25 °C. Sodium borohydride (0.018 g) addition led to the reduction of Ni ions. The color of the solution immediately turned black after the addition of sodium borohydride. The solutions were kept at 25 °C for 1 h to ensure the completion of the reaction. Ni NPs isolation for TEM, XRD, X-ray photoelectron spectroscopy (XPS), TGA analysis and catalytic experiments was attained by centrifuging (5000 rpm for 15 min), washing with ethanol (3 × 20 mL) and drying under vacuum. Furthermore, Ni catalyst was also prepared in the absence of ionic liquid for the control experiment.

Nanocatalysts **2** or **4** (Scheme 1) preparation: typically, Ni NPs stabilized by ionic liquids were synthesized by dissolving Ni(OAc)₂·4H₂O (0.132 g, 0.53 mmol) in water (30 mL), then ionic liquids (1.06 mmol) were introduced. The solution was stirred for another 5 h at 25 °C, NaOH (0.106 g) and N₂H₄·H₂O (1 mL) were introduced into the solution at 90 °C. A dark-brown mixture was obtained in 10 min. Ni NPs isolation for TEM, XRD, XPS, TGA analysis and catalytic experiments was attained by centrifuging (5000 rpm for 15 min), washing with ethanol (3×20 mL) and drying under vacuum.

2.3 General Procedure for the Heterogeneous Chemoselective Hydrogenation

In the stainless steel autoclave, ionic liquid-stabilized Ni (0.053 mmol) and appropriate substrate were dispersed in ethanol (2 mL). Autoclave was sealed and purged with H_2 five times. Reaction timing began after the system heated to predetermined temperature. Hydrogenation products were

separated by centrifugation and decantation of the nanoparticles after reaction completion.

3 Results and Discussion

3.1 Characterization of Ni NPs

The synthetic route of the ionic liquids [BMIM][Pro] and 1-butyl-2,3-dimethylimidazolium acetic acid salt ([BMIM] [OAc]) stabilized Ni NPs **1–5** is displayed in Scheme 1. For comparison, both NaBH₄ and hydrazine were utilized as reducing agents herein. Ni NPs were prepared through the reduction of Ni(OAc)₂ in the presence of 2.0 equivalents of ionic liquids. Additionally, Ni catalyst was also prepared in the absence of ionic liquid for the control experiment.

Ethanol solutions of [BMIM][Pro]-Ni 1, $Ni(OAc)_2$, [BMIM][Pro], and $Ni(OAc)_2$ -[BMIM][Pro] were measured by UV/Vis spectroscopy. Ionic liquid-Ni 1–5 were also characterized by TEM, XPS, XRD and TGA.

The UV/Vis spectra of [BMIM][Pro]-Ni 1, Ni(OAc)₂, [BMIM][Pro], and Ni(OAc)₂-[BMIM][Pro] in ethanol exhibited surprising differences in both intensity and wavelength in 300-800 nm region (Fig. 1). There has no evident absorption for [BMIM][Pro]-Ni 1 in this region (Fig. 1a). The absorption peaks of Ni(OAc)₂ were 394 and 720 nm (Fig. 1b), and the absorption peaks of [BMIM][Pro] were 322 and 631 nm (Fig. 1c). UV/Vis spectra of Ni(OAc)₂-[BMIM][Pro] complex was comparable to the parent [BMIM][Pro] according to the transition energy. However, the absorption peaks of [BMIM][Pro] at 631 nm and Ni(OAc)₂ at 394 and 720 nm disappeared (Fig. 1, inset), and the absorption peak of [BMIM][Pro] at 322 nm showed an obvious hypsochromic shift about 17 nm with the introduction of Ni(OAc)₂ (Fig. 1d). The disappearance of absorption peaks and the hypsochromic shift imply the occurrence of electron transfer between [BMIM][Pro] and Ni(OAc)₂.

The Ni NPs were placed on a carbon-coated copper grid for TEM analyses, which was utilized to characterise the nanoparticles obtained and check the mean diameter (Fig. 2). Generally, Ni NPs reduced by NaBH₄ showed better dispersion than nanoparticles reduced by hydrazine (Fig. 2, images 1, 2 versus 3, 4). The TEM image of 5 exhibited a trend toward agglomeration of the particles in the absence of ionic liquids (Fig. 2, image 5). The TEM image of Ni NPs **1** exhibited regular spherical shape and narrow size distribution, with the average diameter of 5.1 nm.

The surface characteristics of Ni NPs 1 were examined by XPS (Fig. 3). Long XPS spectra of Ni NPs 1 confirmed the existense of nickel, nitrogen and carbon, which suggested the existense of the [BMIM][Pro] on the surface of Ni NPs 1. The existense of [BMIM][Pro] in the ligand sphere of nanoparticles was additionally supported by the



Fig. 1 UV/Vis spectra of (*a*) **1**, (*b*) Ni(OAc)₂, (*c*) [BMIM][Pro], and (*d*) Ni(OAc)₂-[BMIM][Pro] complexes in EtOH

TGA curve of [BMIM][Pro]-Ni 1. The degradation of Ni NPs started with elevation of temperature at about 200 °C and lost around 36.0% weight at last during the temperature range 40–800 °C. Nanoparticles prepared by boron hydride reduction are usually contaminated by B, and herein the B contamination was also detected in long XPS.

Ni 2p XPS is also displayed in Fig. 3, The region between 840 and 890 eV was analyzed, the doublet transitions of Ni $2p_{1/2}$ and $2p_{3/2}$ were observed, and the binding energies are 874.0 and 856.1 eV correspondingly. The binding energy of Ni $2p_{1/2}$ was found to be 17.9 eV higher than the binding energy of Ni $2p_{3/2}$. For emission lines of both Ni $2p_{1/2}$ and Ni $2p_{3/2}$, two shake-up satellites could be observed at about 5.8 eV higher in binding energy. For the Ni NPs 1 surface, a significant ratio of metal Ni(0) species ($2p_{3/2}$ binding energy: 852.5 eV [15]) was not detected. However, the XRD data in Fig. 4 did not demonstrate the existence of nickel oxide or



Fig. 2 TEM images of Ni NPs 1, 2, 3, 4 and 5



hydroxide particles. Similiar to some previous report [28], we speculate that Ni nanoparticles herein probably composed of a small cap layer of NiO around a core of Ni metal.

In Fig. 4, the existence of crystalline Ni(0) and the absence of NiO or Ni(OH)₂ in Ni particles **1**, **2** and **3** were demonstrated by the XRD patterns. And the representative Ni(0) reflections were indexed as a face-centered cubic (fcc) structure. The Bragg reflections at 44.48°, 51.82°, and 76.52° match the indexed planes of the crystals of Ni(0) (111), (200) and (220).

3.2 Catalytic Hydrogenation

Hydrogenation of quinoline and related compounds is of extensive industrial concern in the manufacture of petrochemicals, fine chemicals as well as pharmaceuticals [17–24]. The chemoselective hydrogenation of quinoline under various reaction conditions is shown in Table 1. In comparison to the Ni NPs prepared with NaBH₄, nanoparticles prepared with hydrazine exhibited rather poor hydrogenation activity (Table 1, entries 1, 3 versus 2, 4). With the TEM in Fig. 2, the difference in hydrogenation activity might reasonably owing to the obviously difference in Ni NPs sizes accompany with the amount of surface exposed Ni atoms between nanoparticles prepared with hydrazine and nanoparticles reduced by NaBH₄. The ionic liquid stabilizer is fairly important in the catalytic system. The hydrogenation brought about 64.0% 1,2,3,4-tetrahydroquinoline yield in the absence of any stabilizer (Table 1, entry 5). In combination with the UV/Vis spectra in Fig. 1, the variation of ionic liquid stabilizers exhibited obvious influence on the electron density as well as the catalytic performance of Ni NPs. Generally, Ni NPs which have better dispersion exhibited higher catalytic activity and chemoselectivity toward 1,2,3,4-tetrahydroquinoline product. Ni NPs 1 exhibited the best performance toward 1,2,3,4-tetrahydroquinoline (Table 1, entry 1). Above results demonstrated that ionic liquid act as both the stabilizer during the preparation of the metal particles and the modifier in the catalytic chemoselective hydrogenation. Furthermore, when the traditional Raney Ni was employed as the catalyst for the chemoselective hydrogenation, low efficiency toward 1,2,3,4-tetrahydroquinoline were obtained (Table 1, entry 6). Considering the presence of ionic liquid on some classical heterogeneous catalysts metal surface might have a profound effect on both activity and selectivity [29], 0.106 mmol [BMIM][Pro] was introduced to Raney Ni during the hydrogenation, however, no obxious change in activity or selectivity was observed (Table 1, entry 7). TOFs were also calculated based on both the overall Ni atoms and the surface exposed Ni atoms [30], and the TOF on the basis of surface exposed Ni atoms could reach as high as 28.8 h⁻¹ in the quinoline hydrogenation.

In heterogeneous chemoselective catalytic reactions, catalytic performance are generally rather sensitive to the solvent employed [31]. The influence of different solvents was studied in Table 2. Briefly, the results illustrated that protic solvent was more effective than aprotic one. However, no clear interrelationship between catalytic performance and solvent polarity was observed in Table 2. EtOH was the most suitable solvent for the reaction, in which the quinoline hydrogenation activity and chemoselectivity were the highest (Table 2, entry 2).

In Table 3, quinoline could be conveniently hydrogenated to 1,2,3,4-tetrahydroquinoline alongwith 99.1% selectivity with Ni NPs 1 in ethanol (Table 3, entry 1). Catalytic



Fig. 4 X-ray diffraction pattern of (a) 1, (b) 2, and (c) 3

Table 1 Optimization of reaction conditions for the chemoselective hydrogenation of quinoline



Entry	Catalyst	Yield (%)	TOF (h ⁻¹) ^a /TOF ₁ (h ⁻¹) ^b	Selectivity (%)		
				Aa	Ab	Ac
1	1	99.0	11.5/28.8 ^c	99.1	0.9	0.0
2	2	0.6	_/_	74.2	25.8	0.0
3	3	97.1	9.6/24.0 ^c	95.6	4.4	0.0
4	4	7.4	0.6/-	99.0	1.0	0.0
5	5	64.0	5.1/-	95.5	4.5	0.0
6	Raney Ni	75.0	6.0/-	90.0	10.0	0.0
7	Raney Ni ^d	73.6	5.9/-	90.5	9.5	0.0

Reaction was carried out at 75 °C. Substrate: in a 2 mL EtOH at [2.1M], PH2: 3.0 MPa. Substrate/Ni=80:1, Raney Ni (0.053 mmol), reaction time: 10 h

^aTOFs were calculated based on the overall Ni atoms

^bTOFs were calculated based on the surface exposed Ni atoms

^cTOFs were calculated based on the 5 h conversions

^d0.106 mmol [BMIM][Pro] was introduced

Table 2 Different solvents on chemoselective hydrogenation	Entry	Solvent	Dielectric	Yield (%)	$TOF(h^{-1})^a/TOF_1$	Selectivity (%)		
of quinoline with Ni NPs 1			constant		$(h^{-1})^{0}$	Aa	Ab	Ac
	1	MeOH	33.6	67.2	5.4/13.4	98.5	1.5	0.0
	2	EtOH	24.3	99.0	11.5/28.8 ^c	99.1	0.9	0.0
	3	iPrOH	19.9	30.0	2.4/6.0	97.3	2.7	0.0
	4	H_2O	80.4	96.3	10.6/26.4 ^c	98.4	1.6	0.0
	5	THF	7.6	6.9	0.5/1.3	99.0	1.0	0.0

The reaction conditions are the same as in Table 1 except the solvent

^aTOFs were calculated based on the overall Ni atoms

^bTOFs were calculated based on the surface exposed Ni atoms

^cTOFs were calculated based on the 5 h conversions

reaction activity of 2-methylquinoline, 3-methylquinoline or 8-methylquinoline was comparable to quinoline. The hydrogenation chemoselectivity decline in the order of 2-methylquinoline > 3-methylquinoline > 8-methylquinoline (Table 3, entries 2–4). Introducing a methyl group on a quinoline molecule, especially on 3-position of quinoline, clearly improved the decahydroquinoline yield. Interestingly, 8-methylquinoline could be hydrogenated to 5,6,7,8-tetrahydroquinoline with chemoselectivity as high as 22.0% (Table 3, entry 4). For comparison, 2,3-benzofuran and 1-benzothiophene were also examined. 2,3-benzofuran and 1-benzothiophene displayed decreased catalytic activity. 2,3-benzofuran and 1-benzothiophene could be Table 3 Hydrogenation of quinoline and relevant compounds with Ni NPs 1



Entry	Substrate	Yield (%) ^a	$(\delta)^a$ TOF $(h^{-1})^b/TOF_1 (h^{-1})^c$ Selectivity (%)		%)	
				A-Fa	A-Fb	A-Fc
1	А	99.0 (96.0)	11.5/28.8 ^d	99.1	0.9	0.0
2	В	91.0 (81.5)	9.3/23.2 ^d	96.0	4.0	0.0
3	С	80.9 (72.3)	6.5/16.2	90.6	0.0	9.4
4	D	97.7 (71.1)	10.1/25.2 ^d	78.0	22.0	0.0
5	E	59.7 (54.0)	4.6/11.5	100.0	0.0	0.0
6	F	10.8 (9.0)	0.9/2.2	100.0	0.0	0.0

The reaction conditions are the same as in Table 1

^aIsolated yield for A-Ea in brackets

^bTOFs were calculated based on the overall Ni atoms

^cTOFs were calculated based on the surface exposed Ni atoms

^dTOFs were calculated based on the 5 h conversions

hydrogenated toward 2,3-dihydrobenzofuran and 1-thiaindan with 100.0% chemoselectivity (Table 3, entries 5–6).

Chemoselective hydrogenation of aromatic nitro compounds, as a major challenge in modern synthetic chemistry, is widely employed to produce aniline and its analogues [32, 33]. The hydrogenation could be performed employing various noble metal catalysts, such as Rh, Pd, Ir or Pt etc., which exhibited good catalytic activity even under mild reaction conditions. However, most of the reported hydrogenation reactions of nitrobenzene or substituted nitrobenzene with nonprecious Ni nano-metal catalysts were not so efficient. As shown in Table 4, when traditional Raney Ni was utilized in the chemoselective catalytic hydrogenation of nitrobenzene, Raney Ni showed poor activity (Table 4, entry 6). With the high efficient [BMIM][Pro]-Ni 1, all the aromatic nitro compounds except substrates with a methoxy substituent could be converted to the corresponding substituted anilines efficiently with mild reaction conditions (Table 3, entries 9-10). The methylnitrobenzenes and chloronitrobenzenes were hydrogenated to the corresponding substituted anilines with comparable reactivity and chemoselectivity to nitrobenzene. Briefly, [BMIM][Pro]-Ni 1 catalyst exhibited excellent activity for chemoselective hydrogenation of aromatic nitro compounds, which was not obviously influenced by the steric effect, but probably by the electronic effect. TOFs

based on the overall Ni atoms and the surface exposed Ni atoms were also calculated. The TOF on the basis of surface exposed Ni atoms could reach as high as 32.0 h^{-1} in the hydrogenation of aromatic nitro compounds.

The recyclability of catalyst is rather critical aspects for practical utilization of catalytic reactions. We studied the reusability of the [BMIM][Pro]-Ni 1 catalyst and compared [BMIM][Pro]-Ni 1 with Raney Ni in the nitrobenzene hydrogenation in EtOH (Fig. 5). The product was separated by centrifugation and decantation of the nanoparticles; EtOH and nitrobenzene were introduced to the reactor for the next recycle. Only aniline product was detected during all the catalytic cycles. ICP-AES analysis demonstrated that the Ni leaching from catalyst 1 was negligible during successive catalyst reuse. [BMIM][Pro]-Ni 1 could be recycled six times with no obvious decrease in catalytic activity (Fig. 5). However, Raney Ni showed poor activity in the nitrobenzene chemoselective hydrogenation. Moreover, Raney Ni encountered 51.1% activity loss through only three subsequent reuse, and was almost inactive after three catalyst reuse. This phenomenon may be attributed to the Raney Ni micropores became blocked by the resulting reaction mixture in successive catalyst reuse [34, 35]. Above results suggested that the [BMIM][Pro]-Ni 1 catalyst was rather stable and active during successive catalyst reuse.

Table 4Aromatic nitrocompounds hydrogenation withNi NPs

Entry	Substrate	Catalyst	Product	Yield (%) ^a	TOF $(h^{-1})^{b}/$ TOF ₁ $(h^{-1})^{c}$
1	Nitrobenzene	1	Aniline	100.0 (95.4)	12.0/30.0 ^d
2	Nitrobenzene	2	Aniline	1.7	0.1/-
3	Nitrobenzene	3	Aniline	100.0	11.2/28.0 ^d
4	Nitrobenzene	4	Aniline	1.0	0.1/-
5	Nitrobenzene	5	Aniline	9.8	0.8/-
6	Nitrobenzene	Raney Ni	Aniline	56.0	4.5/-
7	m-Methylnitrobenzene	1	<i>m</i> -Methylaniline	97.0 (93.6)	9.9/24.8 ^d
8	p-Methylnitrobenzene	1	p-Methylaniline	100.0 (99.0)	10.6/26.4 ^d
9	o-Methoxylnitrobenzene	1	o-Methoxyaniline	11.8 (9.9)	0.9/2.4
10	p-Methoxylnitrobenzene	1	p-Methoxyaniline	26.3 (20.0)	2.1/5.3
11	p-Fluoronitrobenzene	1	p-Fluoroaniline	100.0 (95.5)	12.2/30.4 ^d
12	o-Chloronitrobenzene	1	o-Chloroaniline	100.0 (98.1)	11.7/29.2 ^d
13	p-Chloronitrobenzene	1	<i>p</i> -Chloroaniline	100.0 (97.5)	12.8/32.0 ^d

Reaction was carried out at 75 °C. Substrate: in a 2 mL EtOH at [2.1M], PH_2 : 3.0 MPa. Substrate/Ni=80:1, Raney Ni (0.053 mmol), reaction time: 10 h. Just corresponding amino aromatic products were detected

^aIsolated yield in brackets

^bTOFs were calculated based on the overall Ni atoms

^cTOFs were calculated based on the surface exposed Ni atoms

^dTOFs were calculated based on the 5 h conversions



Fig. 5 Recyclability of [BMIM][Pro]-Ni **1** and Raney Ni catalysts for selective hydrogenation of nitrobenzene. Reaction conditions are the same as in Table 4. Reaction time: 10 h for each run

4 Conclusion

In conclusion, we have demonstrated that the ionic liquid stabilized Ni NPs could catalyze the highly chemoselective hydrogenation of quinoline and relevant compounds under mild conditions. UV/Vis spectroscopy, TGA, XPS and XRD analyses clarified that the ionic liquid was adsorbed on the surface of the Ni NPs. The Ni NPs could be easily recovered and reused 6 times without obvious loss of catalytic activity and chemoselectivity.

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