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## ARTICLE

# Efficient Palladium and Ruthenium Nanocatalysts Stabilized by Phosphine Functionalized Ionic Liquid for Selective Hydrogenation

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The Pd and Ru nanoparticles were synthesized in ionic liquid by using tri(m-sulfonyl)triphenyl phosphine 1-butyl-2,3-dimethyl-imidazolium salt ([BMMIM]<sub>3</sub>[tppt]) as a stabilizing agent. The well-dispersed Pd and Ru NPs with mean diameters of 2.4 nm and 1.7 nm were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). It was demonstrated that [BMMIM]<sub>3</sub>[tppt] stabilized Pd and Ru NPs displayed high activity and excellent selectivity in the hydrogenation of functionalized olefins, aromatic nitro compounds and aromatic aldehydes. The Pd and Ru NPs showed better catalytic performance than corresponding commercially available Pd/C and Ru/C catalysts. The present catalytic system could be easily reused at least six times without significant decrease in activity and selectivity.

## Introduction

The application of transition-metal nanoparticles (NPs) has attracted great interest because these NPs act as highly efficient catalysts in both scientific research and industrial application in recent years<sup>1-3</sup>. It is well-known that the high catalytic activity of nanocatalysts attributes to their large surface-to-volume ratios and quantum size effects<sup>4</sup>. However, nanocatalysts are thermodynamically not stable because of their high excess surface energy, therefore they have a tendency to form aggregation and/or agglomeration, which lead to catalytic activity decrease. Stabilizing agents<sup>5-11</sup>, such as polymers, quaternary ammonium salts, surfactants and polyoxoanions, can form a protective layer around the surface of NPs through electrostatic stabilization, steric protection and coordination stabilization to maintain high reactivity of transition-metal NPs in various reactions<sup>12,13</sup>.

Ionic liquids which have good thermal stability, low saturated vapour pressure and variable physical and chemical properties are deemed to be ideal media for various transformations<sup>14</sup>. In recent years, the number of reports on ionic liquids as solvents and/or stabilizers to prepare NPs catalysts in various reactions, such as hydrogenation<sup>15</sup>, C-C coupling<sup>16</sup> and oxidation<sup>17</sup>, has been growing. However, traditional simple ionic liquids could not provide effective stabilization, especially in catalytic recycle and severe reaction conditions, NPs form visible bulk species, and activity decrease obviously<sup>18-20</sup>. Functionalized ionic liquids which can provide

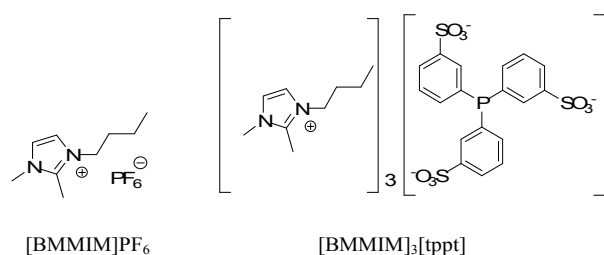
stronger stability than simple ionic liquids are designed to act as efficient stabilizers for NPs<sup>18</sup>. Recently, transition-metal NPs stabilized by N-containing functionalized ionic liquids showed satisfactory performance. Zhao et al.<sup>21</sup> used ionic-liquid-like copolymer stabilized rhodium to catalyse the hydrogenation of benzene and other arenes, high reaction rates and conversions were obtained. Dyson et al.<sup>22</sup> reported polyvinyl pyrrolidone stabilized rhodium nanoparticles were highly soluble in hydroxyl-functionalized ionic liquids, providing an effective and highly stable catalytic system for biphasic hydrogenation. While Dupont<sup>23</sup> found functionalized ionic liquid containing nitrile groups stabilized Ru NPs displayed unusual selectivity towards the hydrogenation of nitrile-containing aromatic compounds.

In this work, Pd and Ru NPs stabilized by novel phosphine-functionalized ionic liquid (PFIL) with characteristic of phosphine ligand as the anion were originally utilized as efficient catalysts in the chemoselective hydrogenation of functionalized olefins, aromatic nitro compounds and aromatic aldehydes. The well-dispersed Pd and Ru NPs were characterized by TEM, XRD and XPS. The Pd and Ru NPs showed better catalytic performance than corresponding commercially available Pd/C and Ru/C catalysts.

## Result and discussion

We chose 1-butyl-2, 3-dimethyl imidazolium hexafluorophosphate ([BMMIM]PF<sub>6</sub>, Scheme 1) rather than 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF<sub>6</sub>)

as the reaction media, mainly because N-heterocyclic carbene might form by C-2 deprotonation or oxidative addition of the C-2-H bond of 1,3-dialkylimidazolium ionic liquids, resulting in the poison of the nanocatalysts and drastic decrease of the catalytic activity and selectivity<sup>24,25</sup>.



Scheme 1. The structures of [BMMIM]PF<sub>6</sub> and [BMMIM]<sub>3</sub>[tppt].

The Pd NPs stabilized by [BMMIM]<sub>3</sub>[tppt] (Scheme 1) were prepared by hydrogenation reduction of Pd(OAc)<sub>2</sub> in [BMMIM]PF<sub>6</sub>. A black powder could be isolated from the obtained Pd NPs by adding acetone and then centrifuging (5000 rpm, 5min). Washed three times with acetone and dried under reduced pressure. The isolated black powder (Pd-1) was characterized by TEM, XRD and XPS methods.

TEM was used to confirm the formation of Pd particles and observe dispersal. TEM images and distribution histograms of nearly spherical Pd NPs were displayed in Figure 1, the observation indicated that these particles were well dispersal with an average diameter of 2.4 nm in fresh Pd-1. Furthermore, the Pd NPs after six recycles of styrene hydrogenation were also well-dispersed with an average diameter of 2.76 nm. Size distribution histograms were obtained on a basis of the measurement of 300 particles.

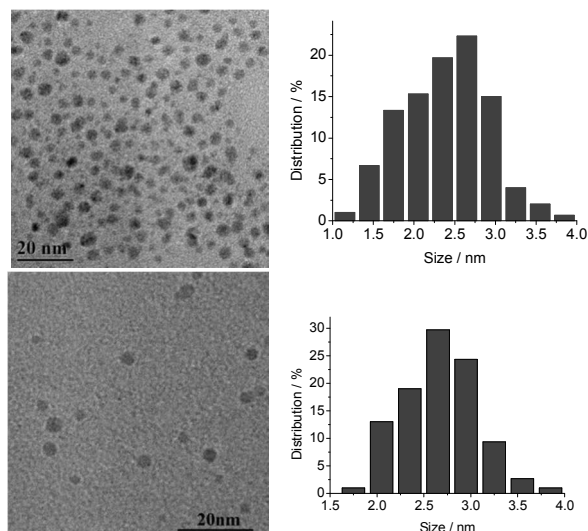


Figure 1. TEM images of Pd-1 before (up) and after (down) six recycles of styrene hydrogenation.

The XRD pattern of Pd-1 (Figure 2) confirmed that the presence of crystalline Pd(0). The most representative

reflections of Pd(0) were indexed as face-centered cubic (fcc) structure. The Bragg reflections at 40.16°, 46.68° and 68.30°, corresponded to the indexed planes of the crystals of Pd(0) (111), (200) and (220).

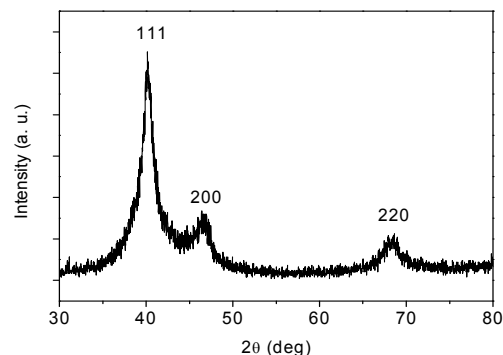


Figure 2. XRD pattern of Pd-1

The surface characteristics of Pd-1 were investigated by XPS (Figure 3). Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> signals, with binding energies of 335.8eV and 341.2eV, were observed respectively. In addition, the main peak of Pd 3d<sub>5/2</sub> shifted 0.8eV higher in binding energy compared to the specimens of the giant clusters of Pd(0) (335.0eV). The XPS observation was consistent with previous literature<sup>26</sup>. We deduced there had a tendency that the electron clouds transferred from Pd(0) particles surface to [BMMIM]<sub>3</sub>[tppt]<sup>27</sup>. On the other hand, the Pd 3d spectrum indicated the presence of two chemical states of Pd at the nanoparticle surface with distinct binding energies; the main contribution was related to Pd (0) (Pd-Pd bonds, Pd<sub>5/2</sub> at 335.8 eV) and the other corresponding to Pd-F bonds (Pd<sub>5/2</sub> at 337.3 eV)<sup>28</sup>.

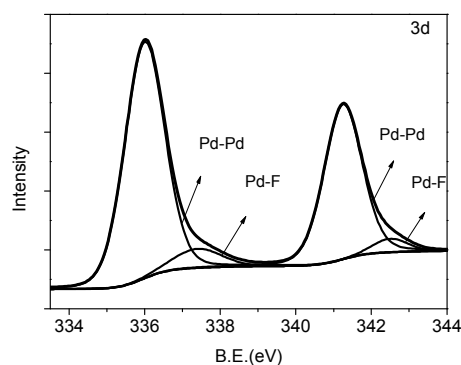
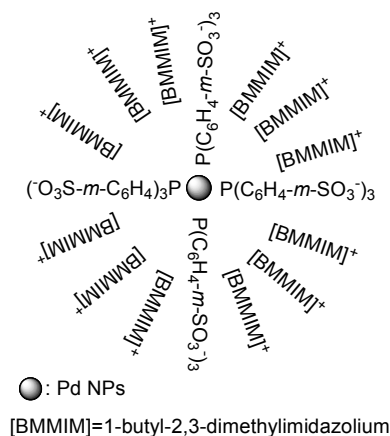
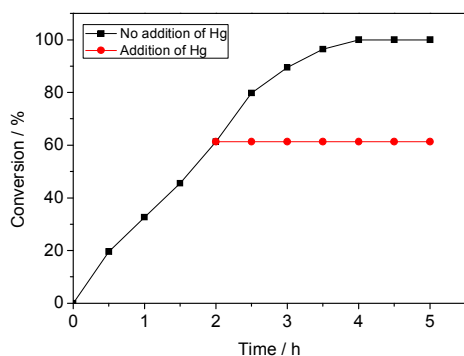


Figure 3. X-ray photoelectron spectra of Pd-1

In short, the results of TEM, XRD and XPS indicated that Pd(II) species were completely reduced to Pd(0) NPs by molecular hydrogenation.

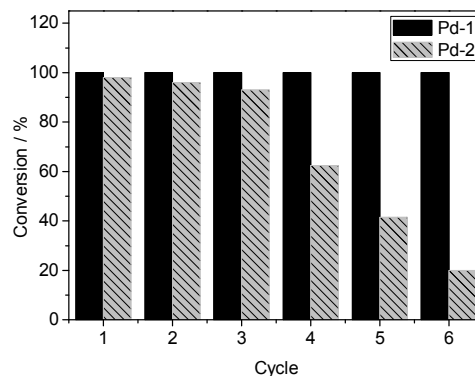
The effect of [BMMIM]<sub>3</sub>[tppt] in catalyst is noteworthy. Due to the strong coordination capacity of the anion of [BMMIM]<sub>3</sub>[tppt], Pd NPs were well dispersed and highly stable in catalytic hydrogenation. On the basis of these results, it was deduced that the [P(C<sub>6</sub>H<sub>4</sub>-m-SO<sub>3</sub>)<sub>3</sub>]<sup>-</sup> ions formed a layer around the surface of the Pd NPs, leading

Figure 4. The PFIL ([BMMIM]<sub>3</sub>[tppt]) stabilized/modified Pd nanoparticlesFigure 5. Reaction profile for the hydrogenation of styrene and Hg<sup>0</sup> poisoning test of Pd-1. catalyst Pd-1 (2.5×10<sup>-3</sup>mmol), substrate/Pd=250, [BMMIM]PF<sub>6</sub> (1mL), 1MPa initial hydrogen pressure, 45 °C.

to a sphere of negative charge, and then the cation of [BMMIM]<sub>3</sub>[tppt] became arranged as an outer layer for charge conservation (Figure 4). Recently, several groups have demonstrated ionic liquids possess self-organized structures, which can create an external layer around the surface of the metal NPs to protect them from aggregation<sup>29-31</sup>.

Initially, we chose styrene as a model substrate to explore the catalytic performance of Pd-1. Figure 5 showed the effect of the conversion versus time. The hydrogenation of styrene produced only ethylbenzene in the test. It was found that the conversion increased linearly with time, showing no induction period, proving that this catalyst did not convert into other catalytically active species. Furthermore, in order to ascertain the involvement of metallic Pd in the hydrogenation reactions, mercury-poisoning experiments were run as they could selectively poison metal nanoparticles, by forming an amalgam with mercury, to help distinguish between homogeneous and heterogeneous catalysts<sup>32</sup>. An excess of Hg<sup>0</sup> (300 equiv) was added to the reaction mixture after 2h (about 60%

conversion) and then the catalytic system was performed under standard hydrogenation conditions. The catalytic activity was completely suppressed and no catalytic activity was observed even though the catalytic system had been vigorously stirred with Hg<sup>0</sup> for another 3h. All the results above strongly support proposal that the reaction progresses under heterogeneous catalysis rather than homogeneous catalysis.

Figure 6. Recyclability of Pd-1 and Pd-2 in hydrogenation of styrene. catalyst Pd (2.5×10<sup>-3</sup>mmol), substrate/Pd=250, [BMMIM]PF<sub>6</sub> (1mL), 1MPa initial hydrogen pressure, 45°C. The hydrogenation of styrene produced only ethylbenzene in the test.

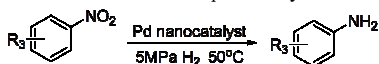
In order to investigate the recyclability of catalysts and the stabilization effect of [BMMIM]<sub>3</sub>[tppt] to Pd NPs, both Pd-1 and Pd NPs with no addition of [BMMIM]<sub>3</sub>[tppt] in the preparation (Pd-2) were tested in the hydrogenation of styrene (Figure 6). After the hydrogenation, diethyl ether was added to extract products, and then the catalysts were washed with diethyl ether three times and further treated under vacuum for the next run. It was found that the catalyst Pd-1 could be reused at least six times without significant decrease in activity. However, the activity of Pd-2 diminished dramatically after the third cycle. The recyclability results demonstrated the remarkable performance of Pd-1 catalyst and the strong stabilization effect of [BMMIM]<sub>3</sub>[tppt] to Pd NPs.

Before the chemoselective hydrogenation of olefins, we chose hexane and cyclohexene as substrates to test the catalytic performance of Pd-1. The results showed that complete conversion could be achieved in 8h and 5h respectively. We further investigated chemoselective hydrogenation of various olefins (Table 1). Pd-1 dispersed in [BMMIM]PF<sub>6</sub> showed excellent chemoselectivity in the hydrogenation of various

Table 1. Chemoselective hydrogenation of various olefins by nanocatalyst Pd-1<sup>a</sup>.

Entry	Substrate	Product	t./h	Conv.(%) <sup>b</sup>	Sel. (%)
1	styrene	ethylbenzene	4	100	100
2	ethyl acrylate	ethyl propionate	4	99	100
3	4-phenyl-3-buten-2-one	4-phenyl-2-butanone	15	100	100
4	1,5-cyclooctadiene	cyclooctane	15	100	100

<sup>a</sup> Reaction conditions: Pd-1 (2.5×10<sup>-3</sup>mmol), substrate/Pd=250, [BMMIM]PF<sub>6</sub> (1mL), 1MPa initial hydrogen pressure, 45 °C. <sup>b</sup> GC yield.

Table 2. Chemoselective hydrogenation of aromatic nitro compounds by Pd-1<sup>a</sup>


Entry	Substrate	Product	T(h)	Conv. (%) <sup>b</sup>	Sel. (%)
1	nitrobenzene	aniline	12	100	100
2 <sup>c</sup>	nitrobenzene	aniline	12	100	98
3 <sup>d</sup>	nitrobenzene	aniline	12	80	95
4	<i>p</i> -nitrotoluene	<i>p</i> -toulidine	12	100	100
5	<i>m</i> -nitrotoluene	<i>m</i> -toluidine	12	92	100
6	<i>p</i> -chloronitrobenzene	<i>p</i> -chloroaniline	8	100	100
7	<i>o</i> -chloronitrobenzene	<i>o</i> -chloroaniline	10	100	100
8	<i>p</i> -fluoronitrobenzene	<i>p</i> -fluoroaniline	12	97	100
9	<i>o</i> -nitroacetophenone	<i>o</i> -aminoacetophenone	12	100	100
10	<i>m</i> -nitroacetophenone	<i>m</i> -aminoacetophenone	12	100	100
11	<i>p</i> -nitroanisole	<i>p</i> -anisidine	12	38.4	100
12	<i>o</i> -nitroanisole	<i>o</i> -anisidine	12	22.4	100

<sup>a</sup> Reaction conditions: catalyst Pd ( $2.5 \times 10^{-3}$  mmol), substrate/Pd=200, [BMMIM]PF<sub>6</sub> (1 mL), 5 MPa initial hydrogen pressure, 50 °C. <sup>b</sup> GC yield. <sup>c</sup> 10% Pd/C (2.66 mg). <sup>d</sup> Pd NPs with no addition of [BMMIM]<sub>3</sub>[tppt] in the preparation (Pd-2).

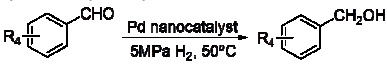
functionalized olefins. The fact that styrene and ethyl acrylate (Table 1, entries 1-2) exhibited higher activity than hexane and cyclohexene indicated the catalytic hydrogenation was apparently affected by the steric effect and the electronic effect. Furthermore, 4-phenyl-3-buten-2-one and 1, 5-cyclooctadiene (Table 1, entries 3-4), could be completely converted into the corresponding saturated C-C single-bond compounds with the aromatic ring and carbonyl group remained.

Selective hydrogenation of substituted nitrobenzene to corresponding aniline is still a significant reaction and challenge for chemists, since aniline and its derivatives are important intermediates for dyes, polyurethanes, pharmaceuticals, explosives and agrochemicals<sup>33, 34</sup>. As in Table 2, Pd-1 catalytic system was very active and exclusively selective towards hydrogenation of the nitro group (Table 2, entry 1). While commercial Pd/C catalyst acted as the heterogeneous catalyst, chemoselectivity to aniline was 98% (Table 2, entry 2). Additionally, Pd-2 showed an unsatisfactory conversion of 80% and 95% chemoselectivity to aniline (Table 2, entry 3). Pd-2

catalytic species formed black particles visible to naked eyes after the hydrogenation. The results testified that traditional ionic liquid ([BMMIM]PF<sub>6</sub>) could not provide effective stabilization for Pd NPs. The scope of the substrates was also tested. The aromatic nitro compounds bearing different substituent groups (-CH<sub>3</sub>, -Cl, -F, -C=O) (Table 2, entries 4-10) did not show significant influence

on the activity and selectivity during the hydrogenation. Furthermore, dehalogenation was not detected in the process of hydrogenation. However, considering substrates with a methoxy substituent, the activity was sharply decreased (Table 2, entries 11-12). The results revealed that Pd-1 showed promising activity for chemoselective hydrogenation of nitrobenzene and its derivatives, which was not apparently affected by the steric effect, but possibly by the electric effect.

Aromatic alcohols are important intermediates in pharmaceuticals, flavors, fragrances, chemical intermediates and photographic chemicals<sup>35</sup>. We further applied Pd-1 in the challenging chemoselective hydrogenation of aromatic aldehydes. Benzaldehyde was selected as the model substrate and relatively low conversion of 27.5% was obtained (Table 3, entry 1). The conversion of commercial catalyst Pd/C was 24% (Table 3, entry 2). Water is an attractive alternative to traditional organic solvents, because it is cheap, readily available, nontoxic, non-flammable and safe to environment.

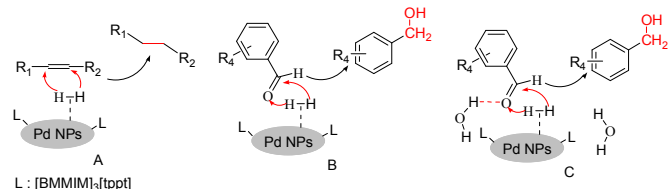
Table 3. Chemoselective hydrogenation of aromatic aldehydes catalyzed by Pd-1<sup>a</sup>.


Entry	Substrate	Co-solvent <sup>b</sup>	Product	Time (h)	Con. (%) <sup>c</sup>	Sel. (%)
1	benzaldehyde	-	phenylmethanol	19	27.5	100
2 <sup>d</sup>	benzaldehyde	-	phenylmethanol	19	24	100
3	benzaldehyde	H <sub>2</sub> O	phenylmethanol	19	100	100
4 <sup>d</sup>	benzaldehyde	H <sub>2</sub> O	phenylmethanol	19	93	100
5 <sup>e</sup>	benzaldehyde	H <sub>2</sub> O	phenylmethanol	19	40	100
6	<i>p</i> -methylbenzaldehyde	H <sub>2</sub> O	<i>p</i> -tolylmethanol	40	100	100
7	<i>p</i> -chlorobenzaldehyde	H <sub>2</sub> O	<i>p</i> -chlorobenzylalcohol	45	99	100
8	<i>m</i> -chlorobenzaldehyde	H <sub>2</sub> O	<i>m</i> -chlorobenzylalcohol	48	85.1	100
9	<i>o</i> -chlorobenzaldehyde	H <sub>2</sub> O	<i>o</i> -chlorobenzylalcohol	48	97	100
10	<i>o</i> -methoxybenzaldehyde	H <sub>2</sub> O	<i>o</i> -methoxybenzylalcohol	48	78.5	100

<sup>a</sup> Reaction condition: catalyst Pd ( $2.5 \times 10^{-3}$  mmol), substrate/Pd=1:50, [BMMIM]PF<sub>6</sub> (1 mL), 5 MPa initial hydrogen pressure, 50 °C. <sup>b</sup> co-solvent (1 mL) was introduced. <sup>c</sup> GC yield. <sup>d</sup> 10% Pd/C (2.66 mg). <sup>e</sup> Pd NPs with no addition of [BMMIM]<sub>3</sub>[tppt] in the preparation (Pd-2).



When water was introduced to catalytic system, the activity of Pd-1 sharply increased to 100% (Table 3, entry 3). The conversion of commercial Pd/C catalyst also increased to 93% (Table 3, entry 4). However, Pd-2 showed unsatisfied conversion of just 40% (Table 3, entry 5). Some representative examples are listed in Table 3 for the chemoselective hydrogenation of aromatic aldehydes catalyzed by Pd-1 in a mixture solvent of H<sub>2</sub>O and [BMMIM]PF<sub>6</sub>. The catalytic system showed good activity and selectivity to corresponding aromatic alcohols (Table 3, entries 6-10).



Scheme 2. Proposed intermediates for olefins and aromatic aldehydes hydrogenation catalyzed by Pd-1.

Based on the obvious difference in catalytic activity during the chemoselective hydrogenation of olefins and aromatic aldehydes (Table 1, Table 3), the hydrogenation intermediates are proposed and shown in Scheme 2. In comparison with the chemoselective hydrogenation of olefins (Scheme 2, A), the chemoselective hydrogenation of C=O in aromatic aldehydes (Scheme 2, B) is less thermodynamically preferable. So, the olefins exhibited much higher hydrogenation activity than aromatic aldehydes. Additionally, the results in Table 3 have clearly shown that water plays a promotional role in the hydrogenation of aromatic aldehydes to aromatic alcohols. We speculate that C=O not only interacts with palladium, but it also forms the hydrogen bond with water (Scheme 2, C). As a result, the hydrogen bond between C=O and water improves the activity of Pd-1 for the hydrogenation of aromatic aldehydes to aromatic alcohols.

On the basis of the above results, we examined the use of Ru NPs as active species and extended the application scope of PFIL stabilized transition-metal NPs catalytic system. The Ru nanocatalyst was prepared by hydrogenation reduction of RuO<sub>2</sub> hydrate in [BMMIM]PF<sub>6</sub> at 75 °C for 4h. A black powder could be isolated from the obtained Ru NPs by adding acetone and then centrifuging (5000 rpm, 5min). Washed three times with acetone and dried under reduced pressure. The obtained black species (Ru-1) were characterized by TEM, XRD and XPS methods.

TEM analysis was

displayed in Figure 7, the metal particle size distribution was estimated from the measurement of about 300 particles. These particles displayed a monomodal size distribution and the average diameter was 1.7 nm. In comparison with Pd NPs, Ru NPs were significantly smaller. This phenomenon could be explained that Pd NPs can easily form aggregation, especially in severe reaction conditions<sup>18</sup>.

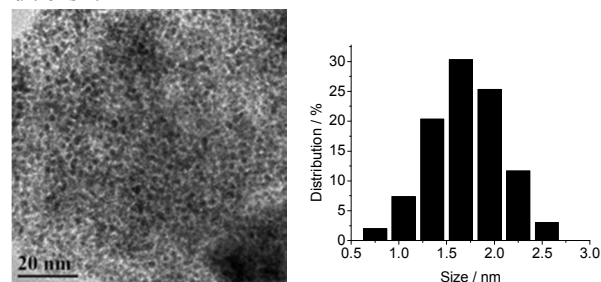


Figure 7. TEM image of Ru-1

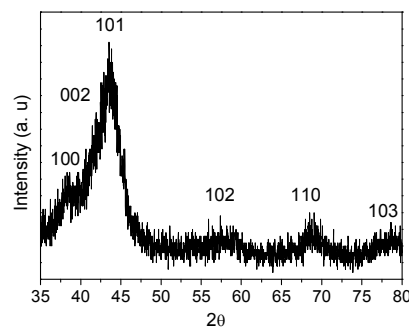


Figure 8. X-ray diffraction pattern of isolated Ru-1

XRD analysis indicated that the solid consists of metal particles of hexagonal close packed (hcp) ruthenium (Figure 8). The Bragg reflections at 38.41°, 42.03°, 43.79°, 58.13°, 69.06°, 78.44° corresponded to the indexed planes of (hcp) crystals of Ru (0): (100), (002), (101), (102), (110), (103) respectively.

Table 4. Chemoselective hydrogenation of aromatic nitro compounds by Ru-1<sup>a</sup>.

Entry	Substrate	Product	T(h)	Conv.(%) <sup>b</sup>	Sel. (%)
1	nitrobenzene	aniline	1.5	100	100
2 <sup>c</sup>	nitrobenzene	aniline	1.5	49	100
3 <sup>d</sup>	nitrobenzene	aniline	1.5	4.6	100
4 <sup>e</sup>	nitrobenzene	aniline	2.5	100	100
5	<i>p</i> -nitrotoluene	<i>p</i> -toluidine	2	100	100
6	<i>m</i> -nitrotoluene	<i>m</i> -toluidine	4	100	100
7	<i>p</i> -chloronitrobenzene	<i>p</i> -chloroaniline	4	100	100
8	<i>o</i> -chloronitrobenzene	<i>o</i> -chloroaniline	4	100	100
9	<i>p</i> -fluoronitrobenzene	<i>p</i> -fluoroaniline	4	100	100
10	<i>p</i> -nitroanisole	<i>p</i> -anisidine	4	100	100
11	<i>o</i> -nitroanisole	<i>o</i> -anisidine	4	100	100
12	<i>o</i> -nitroacetophenone	<i>o</i> -aminoacetophenone	4	100	100

<sup>a</sup> Reaction conditions: catalyst Ru (17.75×10<sup>-3</sup>mmol), [BMMIM]PF<sub>6</sub> (1ml), substrate/Ru=200, inner hydrogen pressure 5MPa, 60 °C. <sup>b</sup> GC yield. <sup>c</sup> Ru/C (5%wt, 36mg). <sup>d</sup> No addition of [BMMIM]<sub>3</sub>[tppt] in preparation of Ru NPs. <sup>e</sup> Catalyst Ru (2.5×10<sup>-3</sup>mmol), 50 °C.

XPS analysis revealed the surface composition of Ru NPs. Ru 3d<sub>5/2</sub> and 3d<sub>3/2</sub> signals with binding energies of 280.0 eV and 284.8 eV were observed, which was consistent with Ru(0)<sup>36</sup>.

We selected nitrobenzene as standard substrate to explore the performance of Ru-1 catalyst. The results revealed that Ru-1 nanocatalyst showed high activity and chemoselectivity in the hydrogenation of nitrobenzene (Table 4, entry 1). However, the catalytic activity of commercial Ru/C catalyst was only 49% (Table 4, entry 2). When there was no addition of [BMMIM]<sub>3</sub>[tppt] in the preparation of Ru NPs (Ru-2), the Ru-2 catalyst displayed a very poor conversion of only 4.6% (Table 4, entry 3). Ru-2 species formed black particles visible to naked eyes after the hydrogenation. The above results demonstrated that Ru-1 nanocatalyst was more efficient than commercial Ru/C catalyst in chemoselective hydrogenation of nitrobenzene in [BMMIM]PF<sub>6</sub> (Table 4, entries 1 vs 2). The catalytic performance of Ru-2 revealed the strong stabilization effect of [BMMIM]<sub>3</sub>[tppt] to Ru NPs (Table 4, entries 1 vs 3). Since the percentage of Ru in Ru-1 catalyst is higher than the percentage of Pd in Pd-1 catalyst (Table 4, entry 1 vs Table 2, entry 1), it is necessary to clarify whether the high catalytic activity of Ru-1 is owing to the high concentration of active metal. Under the same reaction conditions with Pd-1 in Table 2, Ru catalyst with the same mole loading to Pd-1 was also tested in the hydrogenation of nitrobenzene (Table 4, entry 4). Nitrobenzene could be completely hydrogenated to aniline in 2.5 h. However, 12 hours was needed for Pd-1 to achieve the complete hydrogenation (Table 2, entry 1). Substituted nitrobenzenes were also investigated over Ru-1 in [BMMIM]PF<sub>6</sub>. The substrates were completely converted to corresponding anilines within 4h (Table 4, entries 5-12). The results revealed that Ru-1 showed promising activity for chemoselective hydrogenation of nitrobenzene and its derivatives, which was not apparently affected by the steric effect and the electric effect.

## Conclusion

In summary, highly dispersed Pd and Ru NPs were prepared in [BMMIM]PF<sub>6</sub> by using PFIL ([BMMIM]<sub>3</sub>[tppt]) as the stabilizer. These metal NPs catalysts showed excellent catalytic activity and chemoselectivity in the challenging hydrogenation of alkenes, aromatic nitro compounds and aromatic aldehydes. These Pd and Ru NPs showed better catalytic performance than commercially available Pd/C and Ru/C catalysts. The present catalytic system could be easily reused at least six times without significant decrease in activity and selectivity. Additional work is currently in progress in this and related areas.

## Experimental Section

**Materials:** palladium acetate, ruthenium dioxide hydrate, 10% Pd/C, 5% Ru/C, and triphenylphosphine were purchased from Adamas Reagent Co. Ltd., various substrates and all other materials were obtained from Aladdin. The purity of H<sub>2</sub>, N<sub>2</sub> and air were 99.99%. All manipulations involving air sensitive materials were carried out by using standard Schlenk line

techniques under an atmosphere of nitrogen and all solvents were dried by standard methods prior to use. [BMMIM]PF<sub>6</sub> was prepared according to previously reported procedure<sup>37</sup>. Tris(3-sulfophenyl)phosphine trisodium salt (Na<sub>3</sub>[TPPTS]) was synthesized according to literature<sup>38</sup>. The phosphine functionalized ionic liquid [BMMIM]<sub>3</sub>[tppt] was synthesized according to the literature<sup>29</sup>.

**Preparation of Pd-1:** A mixture of 2.5mmolL<sup>-1</sup> Pd(OAc)<sub>2</sub> solution in acetone (1mL), 2.3mg [BMMIM]<sub>3</sub>[tppt] and [BMMIM]PF<sub>6</sub> (1 mL) was stirred at room temperature in a stainless steel autoclave (50 mL) for several minutes, then the solvent was evaporated under vacuum, followed by reduction with molecular hydrogen (0.2 MPa) at 60°C in an oil bath for 20 min which afforded a dark brownish solution that was used directly for the hydrogenation. The percentage of Pd in Pd-1 was 0.26% wt/wt.

**Preparation of Pd-2:** A mixture of 2.5mmolL<sup>-1</sup> Pd(OAc)<sub>2</sub> solution in acetone (1mL), [BMMIM]PF<sub>6</sub> (1mL) were stirred at room temperature in a stainless steel autoclave (50 mL) for several minutes, then the solvent was evaporated under vacuum, followed by reduction with molecular hydrogen (0.2 MPa) at 60°C in an oil bath for 20 min which afforded a dark brownish solution that was used directly for the hydrogenation. The percentage of Pd in Pd-2 was 0.26% wt/wt.

**Preparation of Ru-1:** In a typical experiment the precursor RuO<sub>2</sub> hydrate (3mg, 0.0225mmol), [BMMIM]<sub>3</sub>[tppt] (16.3mg, 0.0225mmol) was dispersed in [BMMIM]PF<sub>6</sub> (1 mL) in a stainless steel autoclave (50 mL), then the flask was purged three times with H<sub>2</sub>, which was pressurized to 4atm with H<sub>2</sub> and heated to 75°C in an oil bath. After stirring for 4h, the reactor was cooled to ambient temperature and carefully vented. A dark solution was obtained that was used directly for the hydrogenation. The percentage of Ru in Ru-1 was 1.7 % wt/wt.

**Preparation of Ru-2:** In a typical experiment the precursor RuO<sub>2</sub> hydrate (3mg, 0.0225mmol), was dispersed in [BMMIM]PF<sub>6</sub> (1 mL) in a stainless steel autoclave (50 mL), then the flask was purged three times with H<sub>2</sub>, which was pressurized to 4atm with H<sub>2</sub> and heated to 75°C in an oil bath. After stirring for 4h, the reactor was cooled to ambient temperature and carefully vented. A dark solution was obtained that was used directly for the hydrogenation. The percentage of Ru in Ru-2 was 1.7 % wt/wt.

**Catalytic hydrogenation:** All hydrogenation reactions were carried out in a 50 mL stainless-steel high pressure reactor with a glass inlet. The stainless-steel reactor containing previously prepared nanoparticles dispersed in ionic liquid [BMMIM]PF<sub>6</sub> was charged with appropriate substrate, then the reactor was flushed three times with molecular hydrogen, H<sub>2</sub> was charged to the desired pressure and heated to optimal temperature and stirred for given time in an oil bath. After the reaction, the reactor was cooled to ambient temperature and carefully vented. The products were extracted with diethyl ether three times and analysed by GC method. For the recycling procedure, the remained diethyl ether in catalytic system was evaporated under vacuum and then the fresh substrate was added for the next recycling in the same conditions. Additionally, it was found

that the amount of leaching from catalyst was negligible by ICP-AES analysis after the catalytic reaction.

**Hg(0) poisoning experiment:** the previously prepared Pd-1 dispersed in [BMMIM]PF<sub>6</sub> was charged with styrene (52.1mg, 0.625mmol) in a 50 mL stainless-steel reactor. The system was flushed three times with H<sub>2</sub>; the reactor was placed in an oil bath at 45°C and in 1MPa H<sub>2</sub> pressure. After stirring for 4h, the reactor was cooled to room temperature and depressurized carefully. The products were extracted three times by diethyl ether and analysed by GC. The remaining products in the catalytic system was evaporated under vacuum, then additional fresh styrene (52.1mg, 0.625mmol) were added into the reactor, the pressure was reestablished to 1MPa and heated to 45°C. After stirring for 2h, the reaction was stopped and elemental Hg was added to the reaction mixture, the reaction system was reestablished in the same conditions (1MPa, 45°C), after stirring for another 2h, the products were extracted with diethyl ether and analysed by GC method.

**Catalyst characterization:** Transmission electron microscopy (TEM) images were obtained with JEM 2010 transmission electron microscopy at 200 kV with a point resolution of 0.23nm. Samples for TEM were prepared by dropping acetate solutions containing the nanoparticles onto carbon-coated Cu grids. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos XSAM 800 spectrometer. The X-ray diffraction (XRD) analysis was performed in a D/MAX 2550 VB/PC using a graphite crystal as monochromator. Products were analyzed by GC instrument with an FID detector and HP-5 column (30 m × 0.25 mm).

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## Notes and references

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- H. J. Chen, H. W. Liu, W. S. Liao, H. B. Pan, C. M. Wai, K. H. Chiu and J. F. Jen, *Appl. Catal. B: Environ.*, 2012, **111-112**, 402.
- M. Pumera, S. Sanchez, I. Ichinose and J. Tang, *Sens. Actuators, B*, 2007, **123**, 1195.
- C. X. Xiao, Z. P. Cai, T. W. Wang, Y. Kou and N. Yan, *Angew. Chem. Int. Ed.*, 2008, **47**, 746.
- O. A. Belyakova and Y. L. Slovokhotov, *Russ. Chem. Bull.*, 2003, **52**, 2299.
- C. Pan, K. Pelzer, K. Philippot, B. Chaudret, F. Dassenoy, P. Lecante and M. J. Casanove, *J. Am. Chem. Soc.*, 2001, **123**, 7584.
- J. L. Pellegatta, C. Blandy, V. Colliere, R. Choukroun, B. Chaudret, P. Cheng and K. Philippot, *J. Mol. Catal. A: Chem.*, 2002, **178**, 55.
- J. Schulz, A. Roucoux and H. Patin, *Chem. Commun.*, 1999, 535.
- Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, *Angew. Chem. Int. Ed.*, 2007, **46**, 704.
- W. W. Zhu, H. M. Yang, Y. Y. Yu, H. Li, H. Li, B. Feng and Z. S. Hou, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13492.
- A. Nowicki, V. L. Boulaire and A. Roucoux, *Adv. Synth. Catal.*, 2007, **349**, 2326.
- D. Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem. Int. Ed.*, 2005, **44**, 7852.
- S. Sawoo, D. Srimani, P. Dutta, R. Lahiri and A. Sarkar, *Tetrahedron*, 2009, **65**, 4367.
- K. L. Luska and A. Moores, *Green Chem.*, 2012, **14**, 1736.
- J. D. Scholten, B. C. Leal and J. Dupont, *ACS Catal.* 2012, **2**, 184.
- J. Julis, M. Hölscher and W. Leitner, *Green Chem.*, 2010, **12**, 1634.
- M. H. G. Precht, J. D. Scholten and J. Dupont, *Molecules*, 2010, **15**, 3441.
- N. Jain, A. Kumar and M. S. C. Shive, *Tetrahedron Lett.*, 2005, **46**, 2599.
- K. L. Luska and A. Moores, *Adv. Synth. Catal.*, 2011, **353**, 3167.
- C. W. Scheeren, G. M. achado, S. R. Teixeira, J. Morais, J. B. Domingos and J. Dupont, *J. Phys. Chem. B*, 2006, **110**, 13011.
- X. Yuan, N. Yan, C. X. Xiao, C. N. Li, Z. F. Fei, Z. P. Cai, Y. Kou and P. J. Dyson, *Green Chem.*, 2010, **12**, 228.
- Z. Chen, H. Z. Wang, N. Yan, C. X. Xiao, X. D. Mu, P. J. Dyson and Y. Kou, *J. Catal.*, 2007, **250**, 33.
- X. Yang, N. Yan, Z. F. Fei, R. M. C. Quesada, G. Laurencyzy, L. K. Minsker, Y. Kou, Y. D. Li and P. J. Dyson, *Inorg. Chem.*, 2008, **47**, 17.
- M. H. G. Precht, J. D. Scholten and J. Dupont, *J. Mol. Catal. A: Chem.*, 2009, **313**, 74.
- G. S. Fonseca, J. B. Domingos, F. Nome and J. Dupont, *J. Mol. Catal. A: Chem.*, 2006, **248**, 10.
- L. S. Ott, S. Campbell, K. R. Seddon and R. G. Finke, *Inorg. Chem.*, 2007, **46**, 10335.
- A. Tressaud, S. Khairoun, H. Touhara and N. Z. Watanabe, *Anorg. Allg. Chem.*, 1986, **540**, 291.
- Y. Hu, H. M. Yang, Y. C. Zhang, Z. S. Hou, X. R. Wang, Y. X. Qiao, H. Li, B. Feng and Q. F. Huang, *Catal. Commun.*, 2009, **10**, 1903.
- A. P. Umpierre, G. Machado, G. H. Fecher, J. Morais and J. Dupont, *Adv. Synth. Catal.*, 2005, **347**, 1404.
- K. L. Luska, A. Moores, *Green Chem.*, 2012, **14**, 1736.
- C. W. Scheeren, G. Machado, S. R. Teixeira, J. Morais, J. B. Domingos, J. Dupont, *J. Phys. Chem. B*, 2006, **110**, 13011.
- W. W. Zhu, Y. Y. Yu, H. M. Yang, H. Li, Y. X. Qiao, X. G. Zhao and Z. S. Hou, *Chem. Eur. J.*, 2013, **19**, 2059.
- B. J. Hornstein, J. D. Aiken and R. G. Finke, *Inorg. Chem.*, 2002, **41**, 1625.
- Y. Hu, Y. Y. Yu, X. G. Zhao, H. M. Yang, B. Feng, H. Li, Y. X. Qiao, L. Hua, Z. Y. Pan and Z. S. Hou, *Sci. China Chem.*, 2010, **53**, 1541.
- G. Wienhofer, I. Sorribes, A. Bod-dien, F. Westerhaus, K. Junge, H. Junge, R. Llusar and M. Beller, *J. Am. Chem. Soc.*, 2011, **133**, 12875.
- Y. H. Zhou, J. Liu, X. Y. Li, X. L. Pan and X. H. Bao, *J. Nat. Gas Chem.*, 2012, **21**, 241.



- 36 Y. H. Zhu, W. Effendi, L. P. S. Shirley, Z. Wang, C. Keith, J. A. Maguire, N. S. Hosmane and M. F. Hawthorne, *J. Am. Chem. Soc.*, 2007, **129**, 6507.
- 37 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1988, 1765.
- 38 W. A. Herrmann, G. P. Albanese, R. B. Manetsberger, P. Lappe and H. Bahrman. *Angew. Chem. Int. Ed.*, 1995, **34**, 811.