NJC

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c4nj01440e

Green synthesis and catalytic properties of palladium nanoparticles for the direct reductive amination of aldehydes and hydrogenation of unsaturated ketones

Mahmoud Nasrollahzadeh

Received (in Montpellier, France)
26th August 2014,
Accepted 8th September 2014

DOI: 10.1039/c4nj01440e

www.rsc.org/njc

This paper reports on the synthesis and use of palladium nanoparticles as heterogeneous catalysts for the reductive amination of aldehydes and hydrogenation of unsaturated ketones. This method has the advantages of high yields, simple methodology and easy work up. The catalyst can be recovered and reused several times without significant loss of catalytic activity.

Introduction

Amines are valuable intermediates in the synthesis of pharmaceutically important compounds. There are several methods for the preparation of amines. Among various methods for the synthesis of amines, direct reductive amination of carbonyl compounds is very attractive in organic synthesis because ketones and aldehydes can be transformed directly into the corresponding primary or secondary amines, with the most common reducing agents such as sodium cyanoborohydride and sodium triacetoxyborohydride or molecular hydrogen in the presence of a platinum-triad catalyst.[1] The use of sodium cyanoborohydride and sodium triacetoxyborohydride has as drawback the formation of toxic byproducts (HCN and NaCN) or the use of corrosive acetic acid.

The field of nanotechnology is an active area of research in modern materials science. In the present century, nanotechnology has drawn attention in various fields such as electronics, chemical, biotechnology, bioanalytics and other industries.[2] Metal nanoparticles have been used widely in recent years due to their unique electronic, optical, mechanical, magnetic and chemical properties which differ greatly from the bulk substances.[3] These special and unique properties could be attributed to their small dimensions and large surface areas.

In nanotechnology, palladium nanoparticles are the most promising ones. Palladium nanoparticles (Pd NPs) have been widely used during the past few years as homogeneous or heterogeneous catalysts in organic synthesis. Generally, the homogeneous catalysis suffers from some difficulties in catalyst separation from the reaction mixture and recyclability.[4] However, there is an example on catalyst recovery by distillation of a reaction mixture.[5] Moreover, the homogeneous palladium catalysts tend to lose their catalytic activity because of Pd metal aggregation.[4] These problems are of environmental and economic concern in large-scale syntheses.[6] To overcome this problem, palladium nanoparticles are generally dispersed on polymer or inorganic supports which makes the system heterogeneous.[7]

The green synthesis techniques are generally synthetic routes that utilize relatively nontoxic solvents such as water, biological extracts, biological systems and microwave assisted synthesis.[8] Green synthesis of NPs has several advantages over chemical synthesis, such as simplicity, cost effectiveness as well as compatibility for biomedical and pharmaceutical applications.

Typically the gum consists of volatile oil, water soluble gum (polysaccharides), lipophilic terpenes and insoluble matter. Polysaccharides are abundant in neutral sugars and are composed of galactose, arabinose, xylose and D-glucuronic acid.[9] There is a considerable interest in the use of naturally occurring polymers, in particular those of polysaccharides as supports to achieve high-performance and environmentally friendly catalysts that are chemically stable and are biodegradable.[10]

Recently our group described the synthesis of palladium(0) nanoparticles as heterogeneous catalysts by Sour Cherry tree gum (stabilizing/reducing agent) and their applications in Sonogashira coupling reactions.[11] Due to the importance of amines and hydrogenation of olefinic double bonds in the synthesis of pharmaceuticals and functional materials and in continuation of our efforts to develop environmentally friendly synthetic methodologies,[12] we report convenient methodologies for the reductive amination of aldehydes and hydrogenation of unsaturated ketones in the presence of gum stabilized palladium nanoparticles as recyclable heterogeneous catalysts that are air and moisture stable and highly active.

Department of Chemistry, Faculty of Science, University of Qom, PO Box 37185-359, Qom, Iran. E-mail: mahmoudnasr81@gmail.com; Fax: +98 25 32103595; Tel: +98 25 32850953

Result and discussion

Pd nanoparticles (Pd NPs) were characterized using powder XRD, SEM, UV-vis and TEM.[11]

Pd nanoparticles stabilized on the surface of Sour Cherry tree gum form a dark brown colored solution in water. The absence of absorption bands for the yellow colored Pd^{II} solution (λ_{max} 415 nm) confirms the complete reduction of Pd ions.[11]

The crystalline structure of the catalyst was confirmed using powder XRD (X-ray powder diffraction) measurements. The X-ray diffraction pattern of Pd NPs is shown in Fig. 1. The X-ray diffraction pattern of Pd nanoparticles encapsulated with Sour Cherry tree gum exhibits five peaks at 20.0°, 28.8°, 40.0°, 46.0°, 50.5° and 66.7°, which could be attributed to Pd NPs synthesized in the presence of a stabilizing agent.[11]

The size and shape of the products were examined by scanning electron microscopy (SEM). Fig. 2 shows typical large-scale SEM images of the as-produced palladium nanosphere. The products are of spherical morphology and have very narrow diameter distributions.

Fig. 3 shows the transmission electron microscopy (TEM) image of Pd nanoparticles. The sizes of Pd nanoparticles are in the range of 2.5 to 15 nm.

Evaluation of the catalytic activity of Pd NPs through the reductive amination of aldehydes

The catalytic behaviour of the Pd NPs was studied for the reductive amination of aldehydes.

For optimization of the reaction conditions, we chose the reaction of benzaldehyde with nitrobenzene in the presence of 1.3 mol% of catalyst as the model reaction, and the effects of the solvent were examined. As shown in Table 1, the reaction was influenced significantly by the solvent employed and based on the reaction yields and environmental consideration the best result was obtained in the case of ethanol (Table 1, entry 6). The optimum conditions were found to be 1.0 mmol of benzaldehyde, 1.2 mmol of nitrobenzene and 1.3 mol% of catalyst in EtOH (5.0 mL) at room temperature under a H_2 atmosphere for 6 h. Increasing the amount of catalyst showed no substantial improvement in the yield (entry 7). An increase in the temperature from room temperature to 40 °C or 60 °C afforded the product in lower yield (Table 1, entries 8 and 9).

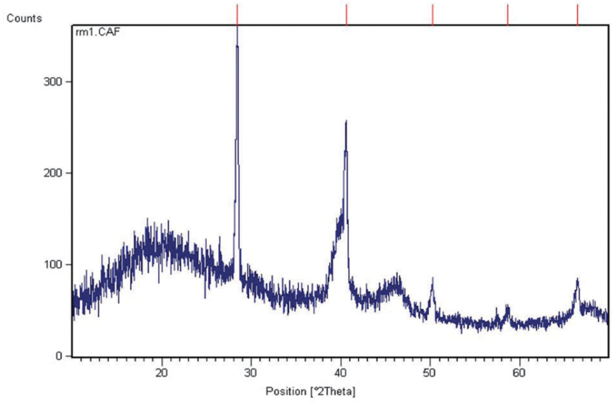


Fig. 1 XRD pattern of Pd nanoparticles.

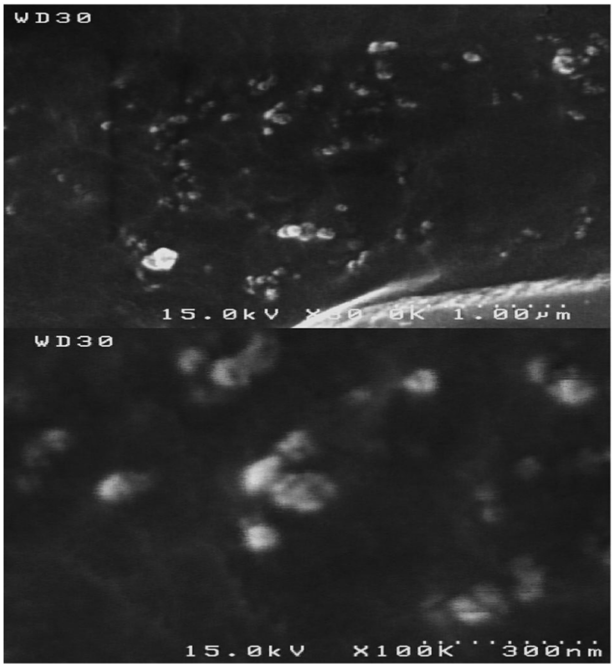


Fig. 2 SEM images of Pd nanoparticles.

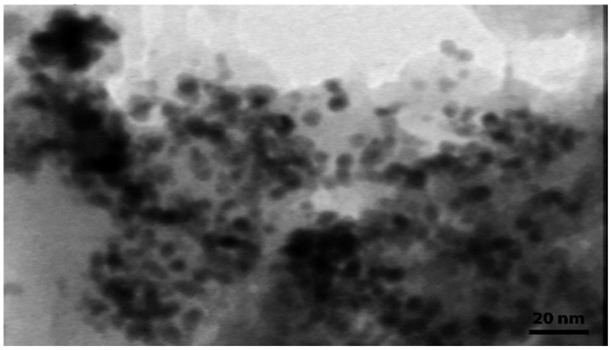


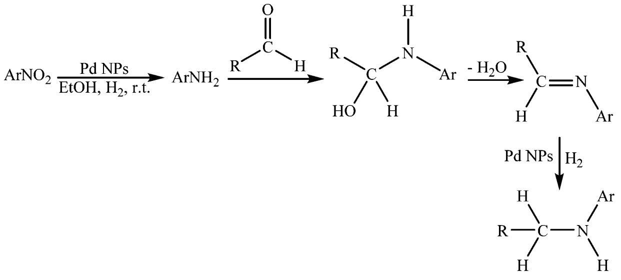
Fig. 3 TEM image of Pd nanoparticles.

Table 1 Optimization of reaction conditions under a H_2 atmosphere[a]

Entry	Catalyst (mol%)	Base	Yield[b] (%)
1	1.3	*s*-BuOH	38
2	1.3	i-BuOH	51
3	1.3	*n*-BuOH	81
4	1.3	i-PrOH	75
5	1.3	MeOH	92
6	1.3	EtOH	92
7	2.0	EtOH	92
8	1.3	EtOH	78[c]
9	1.3	EtOH	32[d]

[a] Reaction conditions: 1.0 equiv. of benzaldehyde, 1.2 equiv. of nitrobenzene, 1.3 mol% of catalyst and 5.0 mL of solvent, room temperature, 6 h. [b] Isolated yield. [c] At 40 °C. [d] At 60 °C.

Optimization of the experimental conditions led to one-pot reaction with 92% yield (Table 1). These conditions (two step



Scheme 1 Reaction steps and intermediates proposed in the reductive amination of aldehydes.

method) involve the following procedure: the initial quantitative reduction of nitrobenzene with hydrogen (1 atm) in the presence of Pd NPs (step 1); the addition of benzaldehyde and the subsequent hydrogenation of the resulting imine under one atmosphere (Scheme 1). Further investigations on the mechanism of reaction are in progress in our laboratory.

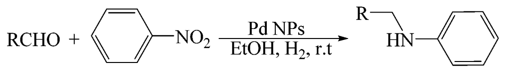
As reported by Sreedhar and coworkers, when the reductive amination of benzaldehyde with nitrobenzene was performed in the presence of traditional heterogeneous catalysts, such as Pd–SiO$_2$ and Pd–TiO$_2$, the nitrobenzene was reduced to the corresponding amine moderately, but the hydrogenation of *in situ* generated imine did not proceed even after 24 h.[13] On the other hand, using 10% Pd/C as catalyst, the same reaction gave, after 6 h, only 20% yield of the product.[13] The enhanced activity of Pd NP catalysts over other supported palladium catalysts screened results from the high surface area and strong hydrogen-trapping property of palladium nanoparticles compared to bulk palladium.[14]

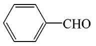
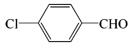
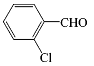
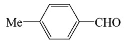
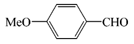
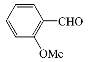
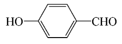
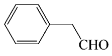
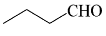
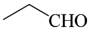
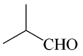
Upon optimization of reaction conditions, the scope of the protocol was subsequently extended to a range of substituted benzaldehyde and nitroarenes as substrates (Table 2). The electron-neutral, electron-rich and electron-poor benzaldehyde reacted with nitrobenzene very well to generate the corresponding products in good to excellent yields under the standard reaction conditions.

Aliphatic aldehydes were also used for the one-pot reductive amination with Pd NPs. The reaction gave satisfactory yields for aliphatic aldehydes (Table 2, entries 8–11).

The conversion was estimated by GC. In all cases, the conversion of reactions is very high (>90%). It was observed that in all of these reactions there was no formation of any byproducts. Aliphatic aldehydes gave excellent yield of the desired products because the imine intermediate formed is unstable and is readily converted into the product by hydrogenation. In fact, the aliphatic imine intermediates are readily hydrogenated to the product, and the hydrogenation of the carbonyl group is not competitive with the reduction of the nitro or imine groups. On the other hand, in the case of aromatic aldehydes, though the imine intermediate formed is quite stable, it can undergo backward reaction to form aldehyde and amine, resulting in a competition between hydrogenation and backward reaction that leads to a decrease in yield.

Table 2 Reductive amination of different aldehydes with nitrobenzene under a H$_2$ atmosphere[a]

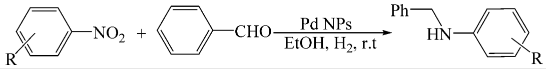


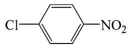
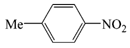
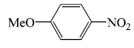
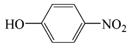
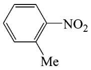
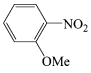
Entry	Aldehyde	Time (h)	Yield[b] (%)
1		6	92 (88)[b]
2		6	90
3		6	85
4		7	92
5		8	90
6		8	81
7		6	86
8		8	91
9		6	93
10		6	96
11		6	98

[a] Yields are after work-up. [b] Yield after the 4th cycle.

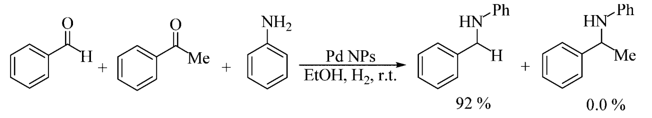
Then, the generality of the Pd NPs was examined by extending the benzaldehyde reaction to a series of different nitroarenes. In all cases, the experimental results show that the all the reactions proceeded smoothly under optimized conditions to produce the respective products in good yields (Table 3). As shown in Tables 2 and 3, the steric hindrance of the substituent did not influence the product yield in the reductive amination of aldehydes using

Table 3 Reductive amination of different aldehydes with nitrobenzene under a H$_2$ atmosphere



Entry	Nitrobenzene	Time (h)	Yield[a] (%)
1		6	81
2		6	89
3		6	89
4		6	77
5		6	85
6		6	90

[a] Yields are after work-up.



Scheme 2 Selective reductive amination of aldehyde.

the Pd nanoparticles (Table 2, entries 3 and 6 and Table 3, entries 5 and 6).

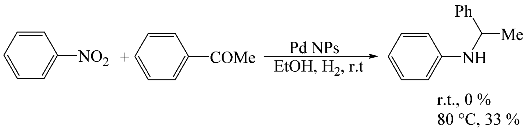
As shown in Scheme 2, the reported method is highly selective for the preparation of amines from aldehydes, and the reductive amination of aldehydes in the presence of ketones, by this method, gives only secondary amines of the aldehydes.

Generally, aromatic ketones are poor substrates for reductive amination protocols.[15] Acetophenone as a ketone was also used for the one-pot reductive amination with Pd NPs. Scheme 3 shows the results obtained for reactions carried out using acetophenone with nitrobenzene at room temperature and 80 °C. The result is, however, interesting because acetophenone has shown to be an inert or a difficult substrate in some reported reductive amination reactions.[15]

Compared with the other literature studies on the reductive amination of aldehydes,[16] the notable features of our method are:

- The reaction system is simple;
- The reaction was performed under mild conditions at room temperature;
- Elimination of toxic reagents and homogeneous catalysts;
- Wide substrate scope and generality;
- Toxic and expensive ligands are not needed;
- The use of ethanol as a green solvent;
- The yields of the products are high;
- The procedure is ''green'' and easy, requiring H_2 as a clean reagent and avoiding any excess of hazardous reducing agent (borohydrides, hydrazine);
- The use of plant extract as an economic and effective alternative represents an interesting, fast and clean synthetic route for the large scale synthesis of Pd nanoparticles;
- The catalyst is versatile and highly selective;
- No surfactant, capping agent, and/or template were used in this method for the synthesis of the Pd NPs;
- The reactions are relatively more environmentally friendly with easy and efficient recyclability of the catalyst;
- According to the UV-vis results, the synthesized Pd NPs by this method are quite stable and can be kept under inert atmosphere for several months.

These advantages make the present method to be considered as a convenient alternative method for the reductive amination of aldehydes. These advantages make this methodology attractive for the development of large-scale industrial synthesis.



Scheme 3

Evaluation of the catalytic activity of Pd NPs through the hydrogenation of unsaturated ketones

Due to the importance of hydrogenation of olefinic double bonds in the synthesis of natural products, pharmaceuticals, and functional materials, we next turned our attention to applying Pd NPs to the hydrogenation of unsaturated ketones. The desired products are obtained in good yields.

We initially selected hydrogenation of (*E*)-chalcone as a model reaction. Among the various solvents (H_2O, MeOH, PhMe and EtOH) tested in the presence of Pd NPs, EtOH led to significant conversion. The best result was obtained with chalcone (1.0 mmol), Pd NPs (1.3 mol%) and EtOH (5 mL) at room temperature under a hydrogen atmosphere, which gave the product in an excellent yield (93%). We have examined the hydrogenation of different unsaturated compounds on the surface of palladium nanoparticles to afford the saturated products in good to excellent yields and the results are presented in Table 4. The enhanced activity of Pd NPs over other supported palladium catalysts screened results from the high surface area and strong hydrogen-trapping property of palladium nanoparticles compared to bulk palladium.

In hydrogenation of unsaturated compounds, we do believe that the selective reduction of the C=C double bond takes place at room temperature. The catalyst is versatile and highly selective. The selectivity of the reactions is very high. The reaction is believed to occur by selective addition of molecular hydrogen, generated *in situ*, on the carbon–carbon double bond. The molecular hydrogen reacts efficiently with the carbon–carbon double bond of unsaturated compounds to yield the corresponding saturated products in high yields.

Table 4 shows that Pd NPs can catalyze chemoselective reduction of C=C in the presence of the NO_2 group (entry 9). Reduction of NO_2 did not occur even after the reaction time was extended to 8 h. Our control experiments with this substrate showed that hydrogenation with Pd/C (under same reaction conditions with respect to time and Pd content in the catalyst) led to reduction of both nitro and C=C moieties (entry 10 in Table 4).

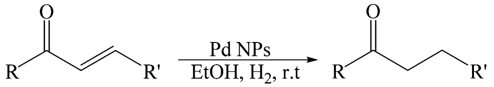
For the further investigation of the selectivity of the reaction, we attempted to reduce acetophenone under the same conditions in ethanol (Table 4, entry 11). No further hydrogenation of acetophenone was observed in ethanol even within 20 h, which confirmed the selectivity of this method.

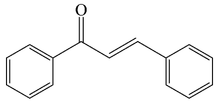
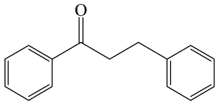
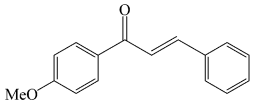
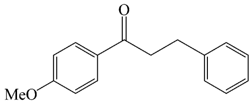
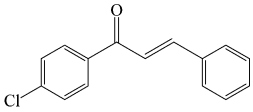
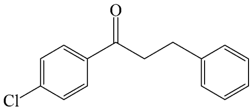
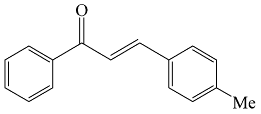
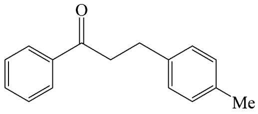
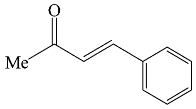
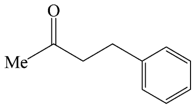
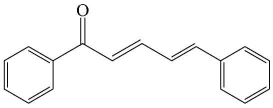
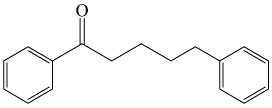
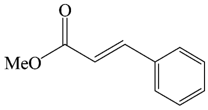
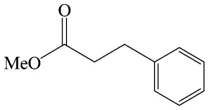
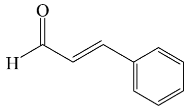
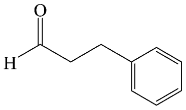
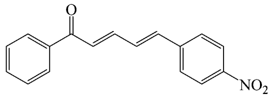
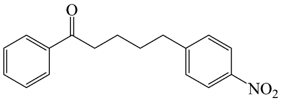
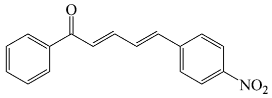
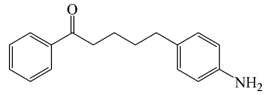
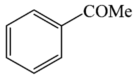
After removal of the solvent and purification, the products were characterized by melting points, elemental analysis (CHN), IR, ^1H NMR and ^{13}C NMR. All of the products are known and were identified by comparison of their physical and spectral data with those of authentic samples. All melting points were compared satisfactorily with those reported in the literature.

Catalyst recyclability

The work-up procedure is straightforward due to the heterogeneous nature of the catalyst. To evaluate the reusability of Pd NPs, the catalyst after completion of the reaction was separated (Table 2, entry 1) and was washed with ethanol, dried in

Table 4 Hydrogenation of different compounds under a H_2 atmosphere[a]



Entry	Substrate	Product	Time (h)	Yield[b] (%)
1			6	94
2			6	91
3			5	90
4			6	90
5			6	93
6			6	92
7			5	94
8			7	82
9			6	92
10			6	91[c]
11		No reaction	20	0

[a] Reaction conditions: 1.0 equiv. of the substrate, 1.3 mol% of the catalyst and 5.0 mL of EtOH, room temperature. [b] Isolated yield. [c] Control experiment using 10% Pd/C.

vacuum and the recycled catalyst was saved for the next reaction. The recycled catalyst could be reused four times with no loss of activity. Thus, the nanocatalyst is stable during the reductive amination of aldehydes. The reusability of the catalyst was also studied for the hydrogenation of unsaturated ketones under the present reaction conditions. The catalytic activity did not decrease considerably after four catalytic cycles (Fig. 4). These results further confirmed the high recyclability of the catalyst.

Conclusion

In summary, we have established that the Pd NPs are a highly efficient, stable and recyclable catalyst for the reductive amination

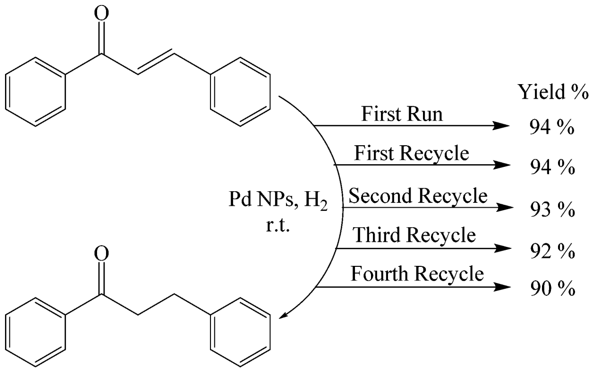


Fig. 4 Reusability of Pd NPs for the hydrogenation of (*E*)-chalcone.

of aldehydes and hydrogenation of unsaturated ketones. The present method has the advantages of readily available starting materials, straightforward and easy work-up procedures, elimination of homogeneous catalysts, mild reaction conditions, high yields, tolerance for a wide variety of functionality, and excellent reusability of the catalyst.

Experimental

High-purity chemical reagents were purchased from the Merck and Aldrich chemical companies. All materials were of commercial reagent grade. Melting points were determined in open capillaries using a BUCHI 510 melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer at 400 and 100 MHz, respectively. FT-IR spectra were recorded on a Nicolet 370 FT/IR spectrometer (Thermo Nicolet, USA) using pressed KBr pellets. The element analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer carried out on Perkin-Elmer 240c analyzer. X-ray diffraction (XRD) measurements were carried out using a Philips powder diffractometer type PW 1373 goniometer (Cu Kα = 1.5406 Å). The scanning rate was 2° min^{-1} in the 2θ range from 10 to 80°. Scanning electron microscopy (SEM) was performed on a Cam scan MV2300. Transmission electron microscopy (TEM) was recorded on a JEOL JSM 100CX. XRD was recorded on a Bruker D8 XRD instrument SWAX.

Synthesis of Pd NPs

Sour Cherry tree Gum was powdered in a Prestige high-speed mechanical blender. Then, 1.0% (w/v) of homogenous gum stock solution was prepared by adding this powder to a reagent bottle containing ultra-pure water and stirring overnight at room temperature. Then this solution was centrifuged to remove the insoluble materials and the supernatant was used for all the experiments. In a typical synthesis of Pd NPs, 10 mL of the gum solution prepared above was added dropwise to 30 mL of 0.001 M aqueous solution of $PdCl_2$ with constant stirring at 80 °C. Reduction of palladium ions (Pd^{II}) to palladium (Pd^0) was completed around 30 min (as monitored by UV-vis).[11] The color of the reaction mixtures gradually changed from transparent yellow to dark brown in 30 min at 80 °C indicating the formation of palladium nanoparticles. Then the colored solution of palladium nanoparticles was centrifuged at 6000 rpm for 30 min to completely disperse.

Typical procedure for the reductive amination of different aldehydes with nitroarenes

Under a hydrogen atmosphere, 1.3 mol% of gum-Pd as a catalyst was suspended in ethanol (3 mL) and stirred for 20 min at room temperature. Then 1.0 mmol of the different aldehydes and 1.2 mmol of nitroarenes dissolved in ethanol (2 mL) were added. The reaction mixture was stirred at room temperature for the specified period of time. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered and the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to give the desired product. All the products are known compounds and the spectral data and melting points were identical to those reported in the literature.[17]

General procedure for the hydrogenation of different unsaturated compounds

Under hydrogen atmosphere, 1.3 mol% of gum-Pd as catalyst was suspended in ethanol (3 mL) and stirred for 20 min at room temperature. Then 1.0 mmol of the reactant dissolved in ethanol (2 mL) was added and the mixture was stirred at room temperature for appropriate time. After completion of the reaction (as monitored by TLC), the catalyst was separated from the reaction mixture and the solvent was removed under reduced pressure, and the residue was subjected to column chromatography to afford pure products. All the products are known compounds and the spectral data and melting points were identical to those reported in the literature.[18]

Acknowledgements

We gratefully acknowledge the Iranian Nano Council and the University of Qom for the support of this work.

References

1 (*a*) V. A. Tarasevich and N. G. Kozlov, *Russ. Chem. Rev.*, 1999, **68**, 55; (*b*) P. N. Grenga, B. L. Sumbler, F. Beland and R. Priefer, *Tetrahedron Lett.*, 2009, **50**, 6658; (*c*) H. O. Kim, B. Carrol and M. S. Lee, *Synth. Commun.*, 1997, **27**, 2505; (*d*) K. Nagaiah, V. N. Kumar, R. S. Rao, B. V. S. Reddy, A. V. Narsaiah and J. S. Yadav, *Synth. Commun.*, 2006, **36**, 3345; (*e*) M. E. Domine, M. C. Hernandez-Soto and Y. Perez, *Catal. Today*, 2011, **159**, 2.
2 M. D. Malinsky, K. L. Kelly, G. C. Schatz and R. P. Van Duyne, *J. Am. Chem. Soc.*, 2001, **123**, 1471.
3 M. C. Daniel and D. Astruc, *Chem. Soc. Rev.*, 2004, **104**, 293.
4 R. B. Bedford, C. S. J. Cazin and S. L. Hazelwood, *Angew. Chem., Int. Ed.*, 2002, **41**, 4120.

5 H. Kimura, K. Matsutani, S.-I. Tsutsumi, S. Nomura, K. Ishikawa, Y. Hattori and M. Itahashi, *Catal. Lett.*, 2005, **99**(3–4), 119.

6 K. Ariga, X. Hu, S. Mandal and J. P. Hill, *Nanoscale*, 2010, **2**, 198.

7 (*a*) C. M. Park, M. S. Kwon and J. Park, *Synthesis*, 2006, 3790; (*b*) L. Yin and J. Liebscher, *Chem. Rev.*, 2007, **107**, 133.

8 (*a*) E. S. Abdel-Halim, M. H. El-Rafie and S. S. Al-Deyab, *Carbohydr. Polym.*, 2011, **85**, 692; (*b*) A. R. Jasbi, *Phytochemistry*, 2006, **67**, 1977; (*c*) S. P. Dubey, M. Lahtinen and M. Sillanpa, *Process Biochem.*, 2010, **45**, 1065.

9 A. K. Sen, A. K. Das, N. Banerji and M. R. Vignon, *Carbohydr. Res.*, 1992, **223**, 321.

10 V. Polshettiwar and R. S. Varma, *Green Chem.*, 2010, **12**, 743.

11 M. Nasrollahzadeh, M. Maham and M. M. Tohidi, *J. Mol. Catal. A: Chem.*, 2014, **391**, 83.

12 (*a*) M. Nasrollahzadeh, M. Maham, A. Ehsani and M. Khalaj, *RSC Adv.*, 2014, **4**, 19731; (*b*) M. Nasrollahzadeh, A. Rostami-Vartouni, A. Ehsani and M. Moghadam, *J. Mol. Catal. A: Chem.*, 2014, **387**, 123; (*c*) M. Nasrollahzadeh, A. Zahraei, A. Ehsani and M. Khalaj, *RSC Adv.*, 2014, **4**, 20351; (*d*) M. Nasrollahzadeh, A. Ehsani and A. Rostami-Vartouni, *Ultrason. Sonochem.*, 2014, **21**, 275; (*e*) M. Nasrollahzadeh, A. Azarian, A. Ehsani and A. Zahraei, *Tetrahedron Lett.*, 2014, **55**, 2813; (*f*) A. R. Modarresi-Alam, M. Nasrollahzadeh and F. Khamooshi, *Sci. Iran.*, 2008, **15**, 452; (*g*) P. Fakhri, B. Jaleh and M. Nasrollahzadeh, *J. Mol. Catal. A: Chem.*, 2014, **383–384**, 17; (*h*) M. Nasrollahzadeh, A. Ehsani and M. Maham, *Synlett*, 2014, 505; (*i*) M. Nasrollahzadeh, *RSC Adv.*, 2014, **4**, 29089; (*j*) D. Habibi, M. Nasrollahzadeh, L. Mehrabi and S. Mostafaee, *Monatsh. Chem.*, 2013, **144**, 725; (*k*) M. Nasrollahzadeh, F. Babaei, S. M. Sajadi and A. Ehsani, *Spectrochim. Acta, Part A*, 2014, **132**, 423; (*l*) M. Nasrollahzadeh, A. Azarian, A. Ehsani and M. Khalaj, *J. Mol. Catal. A: Chem.*, 2014, **394**, 205.

13 B. Sreedhar, P. Surendra Reddy and D. Keerthi Devi, *J. Org. Chem.*, 2009, **74**, 8806.

14 H. Kobayashi, M. Yamauchi, H. Kitagawa, Y. Kubota, K. Kato and M. Takata, *J. Am. Chem. Soc.*, 2008, **130**, 1828.

15 (*a*) A. F. Abdel-Magid, K. G. Carson, B. D. Harris, C. A. Maryanoff and R. D. Shah, *J. Org. Chem.*, 1996, **61**, 3849; (*b*) B. T. Cho and S. K. Kang, *Tetrahedron*, 2005, **61**, 5725; (*c*) R. Apodaca and W. Xiao, *Org. Lett.*, 2001, **3**, 1745.

16 (*a*) Q. P. B. Nguyen and T. H. Kim, *Tetrahedron*, 2013, **69**, 4938; (*b*) Y.-B. Huang, W.-B. Yi and C. Cai, *J. Fluorine Chem.*, 2010, **131**, 879; (*c*) J. R. Bernardo, S. C. A. Sousa, P. R. Florindo, M. Wolff, B. Machura and A. C. Fernandes, *Tetrahedron*, 2013, **69**, 9145; (*d*) T. Itoh, K. Nagata, A. Kurihara, M. Miyazaki and A. Ohsawa, *Tetrahedron Lett.*, 2002, **43**, 3105; (*e*) M. M. Dell'Annaa, P. Mastrorilli, A. Rizzuti and C. Leonelli, *Appl. Catal., A*, 2011, **401**, 134; (*f*) S. Wei, Z. Dong, Z. Ma, J. Sun and J. Ma, *Catal. Commun.*, 2013, **30**, 40.

17 (*a*) S. Wei, Z. Dong, Z. Ma, J. Sun and J. Ma, *Catal. Commun.*, 2013, **30**, 40; (*b*) B. Sreedhar, P. S. Reddy and D. K. Devi, *J. Org. Chem.*, 2009, **74**, 8806.

18 (*a*) V. K. R. Kumar and K. R. Gopidas, *Tetrahedron Lett.*, 2011, **52**, 3102; (*b*) M. Lakshmi Kantam, T. Parsharamulu and S. V. Manorama, *J. Mol. Catal. A: Chem.*, 2012, **365**, 115.