Green Chemistry

Cite this: *Green Chem.*, 2011, **13**, 1238

www.rsc.org/greenchem

PAPER

Pd immobilized on amine-functionalized magnetite nanoparticles: a novel and highly active catalyst for hydrogenation and Heck reactions

Fengwei Zhang, Jun Jin, Xing Zhong, Shuwen Li, Jianrui Niu, Rong Li* and Jiantai Ma*

Received 26th November 2010, Accepted 1st March 2011
DOI: 10.1039/c0gc00854k

A palladium-based catalyst supported on amine-functionalized magnetite nanoparticles was successfully prepared by a facile one-pot template-free method combined with a metal adsorption–reduction procedure. The catalyst was characterized by TEM, XRD, XPS, FT-IR and VSM. The catalyst afforded fast conversions for various aromatic nitro and unsaturated compounds, and with a turn-over frequency (TOF) of 83.33 h^{-1} under a H_2 atmosphere in ethanol, even at room temperature. Furthermore, it was found that the catalyst showed a high activity for the Heck reaction, affording over a 93% yield in all the cases investigated. Interestingly, the novel catalyst could be recovered in a facile manner from the reaction mixture and recycled eight times without any significant loss in activity.

Introduction

It is well known that Pd-catalyzed hydrogenation and Heck reactions (the Pd with nanometre-scale dimensions with a high surface area per unit volume) are of significant importance in modern chemical transformations.[1] Recently, the hydrogenation of nitro compounds to amines has become one of the most important chemical reactions because organic amines are essential materials for the production of agrochemicals, dyes, pharmaceuticals, polymers and rubbers.[2] Additionally, much recent work has been directed toward the Heck reaction because it is the most powerful and widely used method to couple alkenes with organic moieties bearing suitable leaving groups, such as halide, triflate or diazonium.[3] The resulting products have found extensive applications as intermediates in the preparation of materials,[4] natural products[5] and bioactive compounds.[6] Unfortunately, the efficient separation and subsequent recycling of homogeneous Pd catalysts remains a scientific challenge. Therefore, developing a facile and expedient approach to separate and recycle homogeneous catalysts is highly desirable. One approach to such an environmentally benign process is based on the development of heterogeneous catalysts because these heterogeneous systems are easy to handle, recover and are "green" processes.[7]

In the last few years, numerous methods have been developed to immobilize palladium on a large variety of solid supports, such as microporous polymers,[8] mesoporous silica,[9] amorphous silica[10] and carbon nanofibers,[11] making it really easy and simple to separate the catalyst from the mixture. Nevertheless, a limited enhancement of catalytic activity was found and attributed to the mass transfer restriction. To improve the rate of the reaction, much attention has been paid to non-porous and small supports because they can effectively decrease the pore diffusion resistance. Very recently, magnetic nanoparticles have emerged as viable alternatives to conventional materials as robust, readily available, high surface area heterogeneous catalyst supports.[12] In particular, much attention has been focused on amine functionalization, since amines are well known to stabilise nanoparticles against aggregation without disturbing their desirable properties and are also recognised to increase their catalytic activity.[13] For example, amine-functionalized magnetic nanoparticles have been employed in a range of organic transformations, showing excellent catalytic activities in oxidation,[14] hydrogenation [15] and C–C coupling reactions.[16] However, a drawback is that the amine-functionalized magnetic catalyst needs further chemical functionalization, and the process is relatively complicated. Therefore, developing a simple and facile approach to obtain amine-functionalized magnetic nanoparticles with a good dispersibility is highly desirable.

Herein, we report a novel and one-pot template-free synthesis of a nano-magnetite-supported, magnetically recyclable and highly active Pd catalyst, and its application in hydrogenation and Heck reactions. To the best of our knowledge, no examples of the one-pot template-free synthesis of an amine-functionalized magnetite nanoparticle-supported Pd catalyst have been reported.

Experimental

Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, >99%) as a single iron source, anhydrous sodium acetate, ethylene glycol, 1,

---

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China.
E-mail: liyirong@lzu.edu.cn;majiantai@lzu.edu.cn; Fax: +86 931 8912311; Tel: +86 931 8912311

6-hexanediamine and ethanol. All chemicals were of analytical grade and used as received without further purification. Deionized water was used throughout the experiments.

Synthesis of amine-functionalized magnetite nanoparticles (Fe_3O_4-NH_2)

Amine-functionalized magnetite nanoparticles were synthesized *via* the versatile solvothermal reaction reported by Li.[17] Typically, a solution of 6.5 g 1,6-hexanediamine, 2.0 g anhydrous sodium acetate and 1.0 g $FeCl_3 \cdot 6H_2O$ as a ferric source in 30 mL ethylene glycol was stirred vigorously at 50 °C to give a transparent solution. The solution was then transferred into a Teflon-lined autoclave and maintained at 200 °C for 6 h. The magnetite nanoparticles were then thoroughly rinsed with deionized water and ethanol to effectively remove the solvent and unbound 1,6-hexanediamine, and then vacuum dried at 50 °C to obtain a black powder for further use. During each rinsing step, the nanoparticles were separated from the supernatant by using a magnetic force.

Loading of Pd on amine-functionalized magnetic nanoparticles (Fe_3O_4-NH_2–Pd)

500 mg of as-synthesised Fe_3O_4 samples were first dispersed in a 50 mL ethanol solution under ultrasonication for 0.5 h. The formed black suspension was ultrasonically mixed with 3.0 mM of a $PdCl_2$ solution for 1 h, then an excess 0.01 M $NaBH_4$ solution was slowly dropped into the above mixture with vigorous stirring. After 2 h of reduction, the products were obtained with the help of a magnet, washed thoroughly with deionized water and then dried in a vacuum at room temperature overnight. The weight percentage of Pd in the Fe_3O_4-NH_2–Pd, as determined by atomic absorption spectroscopic (AAS) analysis, was 8.43 wt%.

Fe_3O_4-NH_2–Pd catalyst for hydrogenation reaction

In a typical experiment, 1 mmol of the reagent was dissolved in 5 mL ethanol with 20 mg of catalyst under a H_2 atmosphere. The reaction process was monitored by thin layer chromatography (TLC). After the reaction, the catalyst was separated by a small magnet placed at the bottom of the reaction vessel, and the conversion was estimated by GC (P.E. AutoSystem XL) or GC-MS (Agilent 6,890N/5,973N). Thereafter, the catalyst was washed three times with ethanol and dried at room temperature for the next cycle. The catalytic reactions were repeated, and even after 5 cycles, there was no deterioration in the catalytic efficiency.

Fe_3O_4-NH_2–Pd catalyst for the Heck reaction

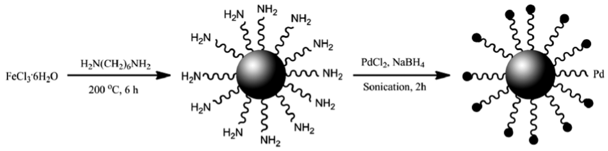
For Heck coupling reactions, 0.5 mmol of the aryl halides, 0.6 mmol of styrene or n-butyl acrylate, and 0.6 mmol of K_2CO_3 were taken into 5 mL of *N*-methyl-2-pyrrolidone (NMP). The amount of catalyst used in each reaction was 32 mg, and the reaction mixture was refluxed at 130 °C. The reaction process was monitored by thin layer chromatography (TLC). After completion of the reaction, the mixture was cooled to room temperature, separated by magnetic decantation, the resultant residual mixture diluted with 20 mL H_2O, followed by extraction twice (2 × 15 mL) with ethyl acetate. The organic fraction was dried over $MgSO_4$, the solvents evaporated under vacuum and the residue redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GC or GC-MS analysis. Yields were calculated against the consumption of the aryl halides. After the first cycle of the reaction, the catalyst was recovered with the help of a magnet, successively rinsed with NMP, distilled water (to remove excess of base) and ethanol, and dried at room temperature ready for the next cycle.

Characterization

FT-IR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrometer with a DTGS detector, and samples were measured with KBr pellets. XRD measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-Kα radiation as the X-ray source in the 2θ range of 10–80°. The size and morphology of the magnetic nanoparticles were observed by a Tecnai G2 F30 transmission electron microscopy and samples were obtained by placing a drop of a colloidal solution onto a copper grid and evaporating the solvent in air at room temperature. X-Ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 instrument and the C_{1S} line at 292.1 eV was used as the binding energy reference. Magnetic measurements of Fe_3O_4-NH_2 and Fe_3O_4-NH_2–Pd were investigated with a Quantum Design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from −15 to 15 kOe.

Results and discussion

The process for the preparation of the catalyst Fe_3O_4-NH_2–Pd is schematically described in Scheme 1. First, amine-functionalized magnetite nanoparticles were synthesized by a facile one-pot solvothermal synthetic strategy. Second, Pd(0) nanoparticles were immobilized on amine-functionalized magnetic nanoparticles through the reduction of $PdCl_2$ by $NaBH_4$ with the assistance of ultrasound radiation. Briefly, magnetite particles were first prepared by a one-pot method and then immobilized Pd(0) on the surface of the magnetite nanoparticles (amine groups on the surface of nanoparticles act as a robust anchor and avoid Pd leaching).



Scheme 1 Preparation of palladium nanoparticles supported on amine-functionalized magnetite nanoparticles.

Fig. 1a shows the typical TEM image of Fe_3O_4-NH_2 nanoparticles prepared by the versatile solvothermal reaction. As can be seen from the image, the average diameter of the as-synthesized spherical particles was about 35 nm and nearly monodisperse. The TEM image in Fig. 1b shows that the Fe_3O_4-NH_2–Pd catalyst didn't change considerably after attachment of the palladium onto the surface of the magnetic nanoparticles. From Fig. 1b, it can also be concluded that the palladium particle size distribution was centered at 8.9 nm. Meanwhile, the figure also

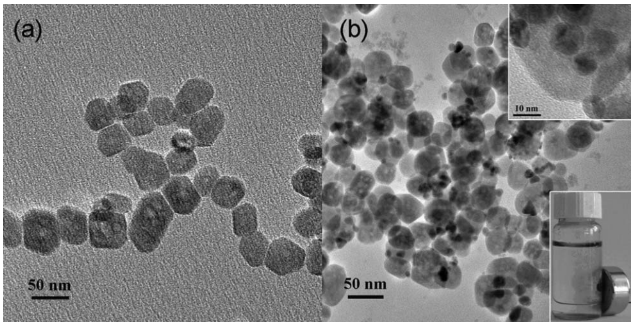


Fig. 1 TEM images of (a) Fe_3O_4-NH_2 and (b) Fe_3O_4-NH_2–Pd (the upper right image in Fig. 1b is the HRTEM image).

shows the photograph of the catalyst being pulled magnetically (shown in the inset of Fig. 1b).

Unambiguous evidence of palladium particles on Fe_3O_4-NH_2 is provided *via* X-ray powder diffraction analysis (XRD). The XRD pattern of Fe_3O_4-NH_2 shows characteristic peaks of magnetite nanoparticles, and the sharp and strong peaks confirm the products are well crystallized. The XRD results reveal their high crystallinity, which is coincident with the results reported by Li.[17] Fig. 2b shows that apart from the original peaks, the appearance of the new peaks at 2θ = 40.1, 46.5 and 68.0 are attributed to the Pd species. The results from XRD imply that the Pd nanoparticles have been successfully immobilized onto the surface of the magnetic nanoparticles. The average crystallite size, calculated using Scherrer's equation, is about 12.8 nm and the crystallite size nearly matches with the average particle size seen in the HRTEM analysis.

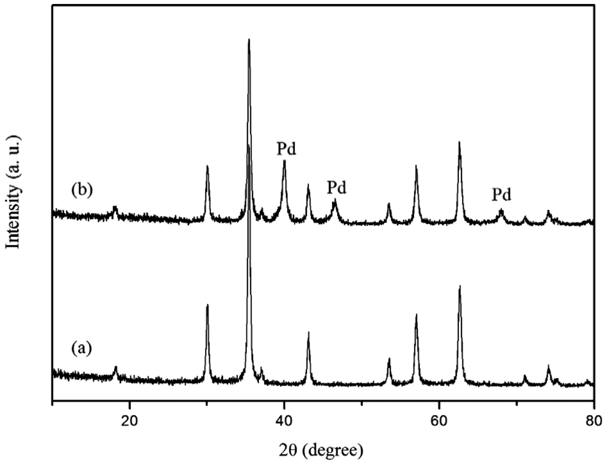


Fig. 2 XRD patterns of (a) Fe_3O_4-NH_2 and (b) Fe_3O_4-NH_2–Pd.

Fig. 3 presents XPS elemental survey scans of the surface of the Fe_3O_4-NH_2–Pd catalyst. Peaks corresponding to oxygen, carbon, nitrogen, palladium and iron are clearly observed. To ascertain the oxidation state of the Pd, X-ray photoelectron spectroscopy (XPS) studies were carried out. In Fig. 4, the Pd binding energy of Fe_3O_4-NH_2–Pd exhibits two strong peaks centered at 340.6 and 335.3 eV, which are assigned to Pd $3d_{3/2}$ and Pd $3d_{5/2}$, respectively. However, only after close inspection can one find another weak peak, appearing at 336.8 eV (Pd $3d_{5/2}$). The results from XPS reveal that the Pd(0) exists as two types of species, the first being larger Pd nanoparticles >10 nm having a binding energy of 335.3 eV[18] and the second corresponding to smaller Pd particles with a binding energy of 336.8 eV.[19]

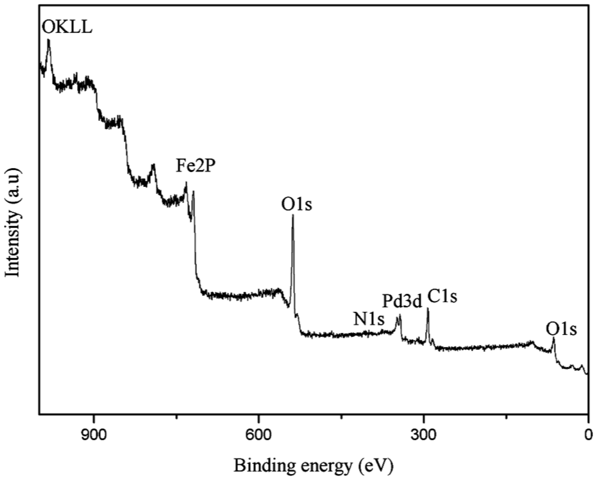


Fig. 3 XPS spectrum of the elemental survey scan of Fe_3O_4-NH_2–Pd.

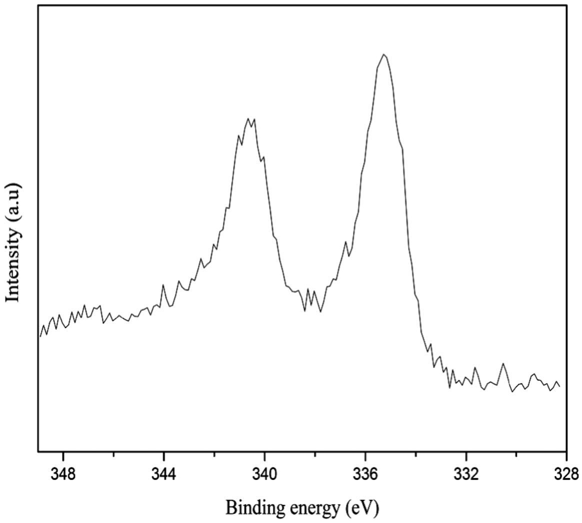


Fig. 4 XPS spectrum of the Fe_3O_4-NH_2–Pd showing Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies.

We also measured the Fourier transform infrared (FTIR) spectra of Fe_3O_4-NH_2 and Fe_3O_4-NH_2–Pd. Fig. 5a shows the IR spectrum of Fe_3O_4-NH_2, indicating that plenty of 1,6-hexanediamine molecules are immobilized on the surface of the nanoparticles.[20] The peaks at 1043, 1618, 3420 and around 2845–2929 cm^{-1} correspond to C–N stretching, N–H deformation and C–H stretching models of the alkyl chain, respectively.[21] The major peaks for the palladium-based catalyst in Fig. 5b can be assigned as follows: 3420 cm^{-1} (N–H stretching vibration), 1557 cm^{-1} (N–H deformation vibration) and 1402 cm^{-1} (C–H symmetric blending vibration). The IR spectrum of the palladium-based catalyst demonstrates that almost no change occurs after immobilization of palladium on the magnetite nanoparticle surface.

Magnetization curves revealed the superparamagnetic behavior of the magnetic nanoparticles. The hysteresis loops of Fe_3O_4-NH_2 and Fe_3O_4-NH_2–Pd are shown in Fig. 6. It can be seen that the magnetic saturation values of these are 71.0 and 60.7 emu g^{-1}, respectively. The decrease of the saturation magnetization

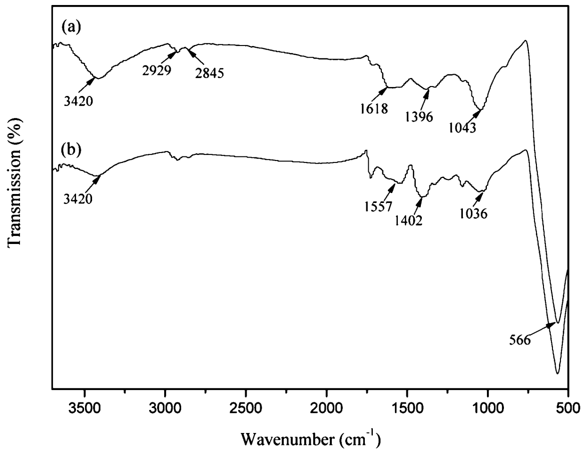


Fig. 5 FT-IR spectra of (a) Fe_3O_4-NH_2 and (b) Fe_3O_4-NH_2–Pd.

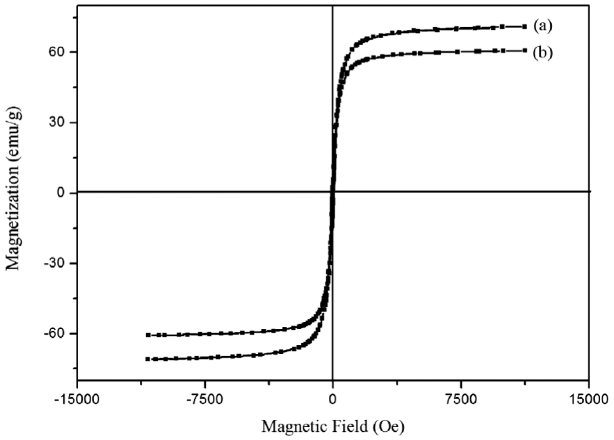


Fig. 6 Room temperature magnetization curves of (a) Fe_3O_4-NH_2 and (b) Fe_3O_4-NH_2–Pd.

suggests the presence of some palladium particles on the surface of the magnetic supports. Even with this reduction in the saturation magnetization, the catalyst can still be efficiently separated easily from the solution with the help of an external magnetic force.

Catalyst testing for hydrogenation reactions

Initially, the catalytic activity of Fe_3O_4-NH_2–Pd was tested for the hydrogenation of a variety of aromatic nitro and unsaturated compounds to their corresponding products. The reactions were carried out in ethanol at room temperature and under a 1 atm pressure of H_2. Detailed observations of all the reactions are given in Table 1. We observed that the catalyst was very active for the hydrogenation reaction under such mild conditions, since the amine groups are known to enhance the catalytic activity of Pd. As shown in Table 1, the hydrogenation reaction could be completed within 45 min, except for 1-nitronaphthalene and *trans*-stilbene, which required for 75 min. This is probably due to the relatively large steric hindrance. Furthermore, the Fe_3O_4-NH_2–Pd catalyst, with a Pd content of 1.6 mol%, afforded a fast conversion of the aromatic nitro and unsaturated compounds to the corresponding products, and the turn-over frequency (TOF) for the hydrogenation reaction was up to 83.33 h^{-1} under mild conditions. A satisfactory yield (>99%) was still obtained even after the catalyst had been reused ten times. The recyclability of the catalyst can be attributed to the efficient stabilisation of the active Pd species by the amine groups on the magnetite surface. In contrast, commercial 10% Pd/C was used to catalytically hydrogenate nitrobenzene; it demanded at least 2 h to complete the reaction, whereas the Fe_3O_4-NH_2–Pd completed the reaction in no more than 1 h with a relatively low Pd loading under similar experimental conditions.

After completion of the reaction, the catalyst was recovered in a facile manner from the reaction mixture by using a permanent magnet. The magnetic property of the nanoparticles facilitated the separation of the catalyst while ensuring redispersion of the particles in the solvent for further use. Moreover, the Pd content (8.29 wt%) of the recovered Fe_3O_4-NH_2–Pd catalyst remained just about the same as the fresh catalyst, indicating that Pd leaching was negligible.

Catalyst testing for the Heck reaction

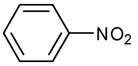
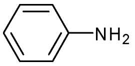
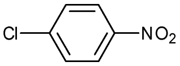
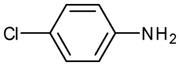
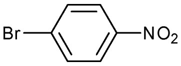
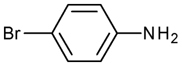
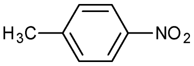
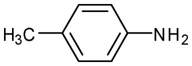
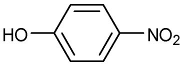
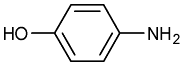
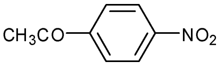
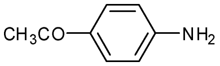
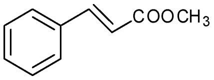
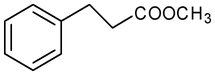
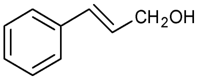
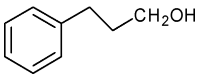
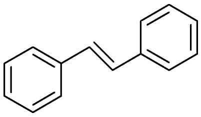
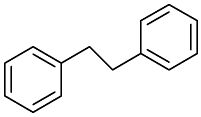
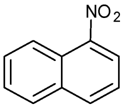
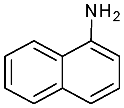
Having demonstrated that the Fe_3O_4-NH_2–Pd catalyst was highly effective for the hydrogenation reaction, its activity was also investigated for the Heck reaction. Table 2 displays the results of the Heck reaction of aryl halides with styrene or n-butyl acrylate. A range of activities were observed from 93 to >99% yields, depending on the nature of the aryl bromo and iodo derivatives. For both styrene and n-butyl acrylate, shorter reaction times were observed for 4-bromonitrobenzene and 4-bromoacetophenone (Table 2, entries 3, 4, 8 and 9), however, longer reaction times were observed for bromobenzene (Table 2, entries 1 and 6). When using iodobenzene and styrene as substrates, the reaction afforded almost a 100% yield (Table 2, entry 5). The results show that electron-withdrawing substituents enhance the coupling product formation, while electron-donating groups have a negative influence on the reaction process.

The recyclability of Fe_3O_4-NH_2–Pd was further investigated because the recyclability of the heterogeneous catalyst is one of the most important issues for practical applications. We therefore turned attention to the reusability of our Pd catalyst. As shown in Table 3, the catalyst was recycled in the Heck coupling of 4-bromonitrobenzene with styrene. It is worth noting that the catalyst gave a complete conversion of 4-bromonitrobenzene, an over 95% yield was achieved within 10 h under each cycle and without a significant loss of activity. Furthermore, the catalyst could be easily separated magnetically from the reaction mixture, washed three times with ethanol and finally dried for the next run. The results further confirmed the high recyclability of Fe_3O_4-NH_2–Pd.

Conclusions

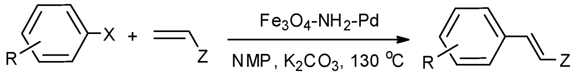
In the present study, a nanosized Fe_3O_4-NH_2–Pd catalyst with a high magnetic responsivity and excellent dispersibility was prepared through a facile one-pot template-free strategy combined with a metal adsorption–reduction procedure. In this system, the novel magnetite nanomaterials play two important roles: one is in increasing the stability of the nanoparticles, because of their surface amino groups, and the other in immobilizing Pd by means of coordination. On the basis of the above-mentioned

Table 1 Hydrogenation of various substrates using Fe_3O_4-NH_2–Pd as the catalyst[a]

Entry	Substrate	Product	t/min	Yield (%)
1			45 45 120 120	>99 >99[b] >99[c] 97[d]
2			45	>99
3			45	92
4			45	96
5			45	>99
6			45	98
7			45	92
8			45	99
9			75	98
10			75	97

[a] Reaction conditions: 20 mg catalyst; 1 atm H_2; 1 mmol substrate; 5 mL solvent. [b] Yield after 5 runs. [c] Hydrogenation with 20 mg of 10% Pd/C. [d] Hydrogenation with 1.6 mol% Pd/C.

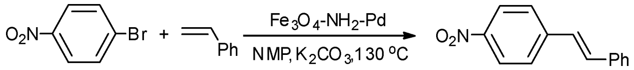
Table 2 Heck reactions in the presence of Fe_3O_4-NH_2–Pd[a]



Entry	R	X	Z	t/h	Yield[b] (%)
1	H	Br	Ph	24	96
2	4-Me	Br	Ph	24	93
3	4-NO_2	Br	Ph	10	>99
4	4-COMe	Br	Ph	10	>99
5	H	I	Ph	10	>99
6	H	Br	$CO_2{}^nBu$	24	98
7	4-Me	Br	$CO_2{}^nBu$	24	96
8	4-NO_2	Br	$CO_2{}^nBu$	10	>99
9	4-COMe	Br	$CO_2{}^nBu$	10	>99
10	H	I	$CO_2{}^nBu$	10	>99

[a] The reaction was carried out with 0.50 mmol of aryl halides, 0.6 mmol of styrene (or n-butyl acrylate), 0.6 mmol of K_2CO_3, 5 mol% Pd with respect to the aryl halides and 5 mL of NMP under an N_2 atmosphere. [b] Determined by GC or GC-MS.

Table 3 Recycling of the Fe_3O_4-NH_2–Pd catalyst in a Heck reaction[a]



Run	Yield (%)	Run	Yield (%)
1	>99	5	97
2	>99	6	98
3	99	7	95
4	98	8	96

[a] Reaction conditions: 4-bromonitrobenzene (0.5 mmol), styrene (0.6 mmol), recycled Pd catalyst, K_2CO_3 (0.6 mmol), NMP (5 mL) under an N_2 atmosphere.

properties, the loss of Pd was greatly suppressed during catalytic cycles. The novel catalyst was successfully applied for the first time to hydrogenation and Heck reactions with the fascinating nature of both a high activity and durability.

Acknowledgements

The authors are grateful to the Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization, Gansu Province for financial support.

References

1 (*a*) M. M. Dell'Anna, M. Gagliardi, P. Mastrorilli, G. P. Suranna and C. F. Nobile, *J. Mol. Catal. A: Chem.*, 2000, **158**, 515; (*b*) Y. Zheng, K. Ma, H. Wang, X. Sun, J. Jiang, C. Wang, R. Li and J. Ma, *Catal. Lett.*, 2008, **124**, 268; (*c*) A. J. Amali and R. K. Rana, *Chem. Commun.*, 2008, 4165; (*d*) N. Erathodiyil, S. Ooi, A. M. Seayad, Y. Han, S. S. Lee and J. Y. Ying, *Chem.–Eur. J.*, 2008, **14**, 3118; (*e*) K. C. Nicolaou, A. L. Nold, R. R. Milburn, C. S. Schindler, K. P. Cole and J. Yamaguchi, *J. Am. Chem. Soc.*, 2007, **129**, 1760; (*f*) F. Zhao, K. Murakami, M. Shirai and M. Arai, *J. Catal.*, 2000, **194**, 479; (*g*) A. Biffis, M. Zecca and M. Basato, *J. Mol. Catal. A: Chem.*, 2001, **173**, 249; (*h*) L. Yin and J. Liebscher, *Chem. Rev.*, 2007, **107**, 133.

2 (*a*) B. Chen, U. Dingerdissen, J. G. E. Krauter, H. G. J. Lansink Rotgerink, K. Möbus, D. J. Ostgard, P. Panster, T. H. Riermeier, S. Seebald, T. Tacke and H. Trauthwein, *Appl. Catal., A*, 2005, **280**, 17; (*b*) K. Nomura, *J. Mol. Catal. A: Chem.*, 1998, **130**, 1.

3 R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, London, 1985.

4 L. F. Tietze, G. Kettschau, U. Heuschert and G. Nordmann, *Chem.–Eur. J.*, 2001, **7**, 368.

5 T. Mizutani, S. Honzawa, S. Tosaki and M. Shibasaki, *Angew. Chem., Int. Ed.*, 2002, **41**, 4680.

6 (*a*) B. M. Choudary, S. Madhi, N. S. Chowdari, M. L. Kantam and B. Sreedhar, *J. Am. Chem. Soc.*, 2002, **124**, 14127; (*b*) A. Haberli and C. J. Leumann, *Org. Lett.*, 2001, **3**, 489.

7 (*a*) A. Corma, P. Concepción, I. Domínguez, V. Forné and M. J. Sabater, *J. Catal.*, 2007, **251**, 39; (*b*) B. M. Choudary, S. Madhi, N. S. Chowdari, M. L. Kantam and B. Sreedhar, *J. Am. Chem. Soc.*, 2002, **124**, 14127; (*c*) G. Wei, W. Zhang, F. Wen, Y. Wang and M. Zhang, *J. Phys. Chem. C*, 2008, **112**, 10827; (*d*) N. Jamwal, M. Gupta and S. Paul, *Green Chem.*, 2008, **10**, 999; (*e*) H. Yang, L. Zhang, P. Wang, Q. Yang and C. Li, *Green Chem.*, 2009, **11**, 257; (*f*) N. Erathodiyil, S. Ooi, A. M. Seayad, Y. Han, S. S. Lee and J. Y. Ying, *Chem.–Eur. J.*, 2008, **14**, 3118; (*g*) B. Karimi, S. Abedi, J. H. Clark and V. Budarin, *Angew. Chem., Int. Ed.*, 2006, **45**, 4776; (*h*) T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037; (*i*) H. Wu, Q. Zhang and Y. Wang, *Adv. Synth. Catal.*, 2005, **347**, 1356; (*j*) T. Matsumoto, M. Ueno, N. Wang and S. Kobayashi, *Chem.–Asian J.*, 2008, **3**, 196; (*k*) J. Shin, J. Bertoia, K. R. Czerwinski and C. Bae, *Green Chem.*, 2009, **11**, 1576.

8 S. Ogasawara and S. Kato, *J. Am. Chem. Soc.*, 2010, **132**, 4608.

9 (*a*) C. M. Crudden, M. Sateesh and R. Lewis, *J. Am. Chem. Soc.*, 2005, **127**, 10045; (*b*) B. Karimi, S. Abedi, J. H. Clark and V. Budarin, *Angew. Chem., Int. Ed.*, 2006, **45**, 4776; (*c*) B. Karimi, A. Zamani, S. Abedia and J. H. Clark, *Green Chem.*, 2009, **11**, 109; (*d*) P. Wang, Z. Wang, J. Li and Y. Bai, *Microporous Mesoporous Mater.*, 2008, **116**, 400.

10 (*a*) K. Köhler, R. G. Heidenreich, J. G. E. Krauter and J. Pietsch, *Chem.–Eur. J.*, 2002, **8**, 622; (*b*) Y. Ji, S. Jain and R. J. Davis, *J. Phys. Chem. B*, 2005, **109**, 17232.

11 J. hu, J. H. Zhou, T. J. Zhao, X. G. Zhou, D. Chen and W. K. Yuan, *Appl. Catal., A*, 2009, **352**, 243.

12 (*a*) S. Shylesh, V. Schünemann and W. R. Thiel, *Angew. Chem., Int. Ed.*, 2010, **49**, 3428; (*b*) U. Laska, C. G. Frost, G. J. Price and P. K. Plucinski, *J. Catal.*, 2009, **268**, 318.

13 (*a*) S. Mandal, D. Roy, R. V. Chaudhari and M. Sastry, *Chem. Mater.*, 2004, **16**, 3714; (*b*) A. M. White, T. J. Johnson, Koberstein and N. J. Turro, *J. Am. Chem. Soc.*, 2006, **128**, 11356; (*c*) D. Guin, B. Baruwati and S. V. Manorama, *Org. Lett.*, 2007, **9**, 1419; (*d*) L. N. Lewis, *Chem. Rev.*, 1993, **93**, 2693; (*e*) J. Alvarez, J. Liu, E. Roman and A. E. Kaifer, *Chem. Commun.*, 2000, 1151; (*f*) R. M. Crooks, M. Q. Zhao, L. Sun, V. Chechik and L. K. Yeung, *Acc. Chem. Res.*, 2001, **34**, 181; (*g*) R. S. Underhill and G. J. Liu, *Chem. Mater.*, 2000, **12**, 3633; (*h*) D. K. Yi, S. S. Lee and J. Y. Ying, *Chem. Mater.*, 2006, **18**, 2459; (*i*) Y. Li and M. A. El-Sayed, *J. Phys. Chem. B*, 2001, **105**, 8938; (*j*) R. Abu-Reziq, D. Wang, M. Post and H. Alper, *Chem. Mater.*, 2008, **20**, 2544; (*k*) A. F. Thünemann, D. Schütt, L. Kaufner, Ulrich Pison and H. Möhwald, *Langmuir*, 2006, **22**, 2351; (*l*) A. J. Amali and R. K. Rana, *Chem. Commun.*, 2008, 4165.

14 V. Polshettiwar and R. S. Varma, *Org. Biomol. Chem.*, 2009, **7**, 37.

15 (*a*) V. Polshettiwar, B. Baruwati and R. S. Varma, *Green Chem.*, 2009, **11**, 127; (*b*) D. Guin, B. Baruwati and S. V. Manorama, *Org. Lett.*, 2007, **9**, 1419; (*c*) A. J. Amali and R. K. Rana, *Green Chem.*, 2009, **11**, 1781.

16 (*a*) B. Baruwati, D. Guin and S. V. Manorama, *Org. Lett.*, 2007, **9**, 5377; (*b*) Z. Wang, P. Xiao, B. Shen and N. He, *Colloids Surf., A*, 2006, **276**, 116.

17 L. Wang, J. Bao, L. Wang, F. Zhang and Y. Li, *Chem.–Eur. J.*, 2006, **12**, 6341.

18 M. Schildenberger, R. Prins and Y. C. Bonetti, *J. Phys. Chem. B*, 2000, **104**, 3250.

19 K. McEleney, C. M. Crudden and J. H. Horton, *J. Phys. Chem. C*, 2009, **113**, 1901.

20 X. Liu, Q. Hu, Z. Fang, X. Zhang and B. Zhang, *Langmuir*, 2009, **25**, 3.

21 W. Zhou, N. Yao, G. P. Yao, C. H. Deng, X. M. Zhang and P. Y. Yang, *Chem. Commun.*, 2008, 5577.