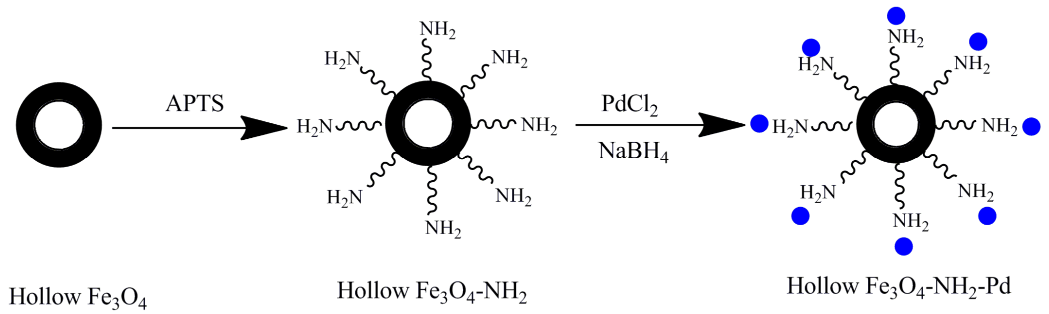
RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances



Scheme 1 Preparation of palladium nanoparticles supported on amine-functionalized hollow Fe_3O_4

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Stabilizing Pd on the surface of amine-functionalized hollow Fe_3O_4 spheres: a highly active and recyclable catalysts for Suzuki cross-coupling and hydrogenation reactions

Peng Wang, Mengmeng Liu, Jianrui Niu, Bing Yuan, Rong Li* and Jiantai Ma*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A palladium-based catalyst supported on amine-functionalized hollow magnetite nanoparticles was successfully prepared by a facil template-free method. The catalyst was characterized by TEM, XRD, FT-IR and VSM. The catalyst afforded fast conversions for various aromatic nitro compounds under a H_2 atmosphere in ethanol even at room temperature. Furthermore, it was found that the catalyst showed a high activity for the Suzuki reactions. Interestingly, the novel catalyst could be recovered in a facile manner from the reaction mixture and recycled five times without any significant loss in activity.

Introduction:

Recently, the development of novel, non-toxic, eco-friendly, recyclable catalytic systems with high efficiency have received a great deal of attention in the research of organic synthesis for environmental and economic reaction.[1] In this regard, surpported metal nanoparticles play an important role in several heterogeneous catalytic reactions for green organic synthesis.[2] Palladium nanoparticles, particularly with dimension smaller than 10 nm, exhibit unexpectedly high catalytic activities toward different type of reactions, a property not displayed in bulk palladium.[3] over the last a few years, numerous methods have been developed to immobilize palladium on solid surpports, such as microporous polymers,[4] carbon nanofibers,[5] silica[6] and mesoporous hollow spheres.[7] Although these metal catalysts proccess implies an extremely high catalytic activity, the separation step becomes a more troublesome issue like centifugation, nanofiltration and precipitation-flocculation. In order to overcome this problem, magnetic nanoparticles that can be easily removed from the reaction mixture using an exernal magnet are particularly attractive.[8]Monodisperse hollow spheres have attracted considerable interest in the past few decades due to their well-definied morphology, uniforom size, low density, large surface area and wide range of potential apllication.[9] Hollow mesoprous structures incorporated with catalytically active nanoparicles (NPS) present powerful catalytic activity and therefore produce promising application as nanoreactors for catalytic reactions.[10] However, the template method is the most commnonly used to synthesis of hollow spheres. But the synthesis is too complex and not green at all. First, the templates must be synthesized, then the template must be eliminated in some way, leaving behind a hollow shell.[8] The designing of a recyclable hollow sphere through a facile one-pot template-free method is still a challenging task in organic synthesis area.

It is well known that Pd-catalyzed hydrogenation and Suzuki coupling reaction are of considerable importance in mordern chemical transformation. The hydrogenation of nitro compounds to amines has become one of the most important chemical reactions, This is due to the fact that amines and their derivatives exist in many biologically active compounds, morever they are relevant intermediates in the synthesis of pharmaceutically active substances, dyes and fine chemicals.[11] Suzuki reaction since the discovery in 1979 by Suzuki has been a very active research topic in organic synthesis. Because of the mild reaction conditions, the strong adaptability, the functional group tolerance, the good reaction yield and low toxicity, the Suzuki reaction is much favored by chemical synthesis workers.[12]

Herein, we report an esay template-free synthesis of a nano-magnetite-surppored, magnetically recyclable and highly active Pd catalyst, and its application in hydrogenation and Suzuki coupling reaction.

Experimental

Synthesis of hollow Fe_3O_4

The hollow Fe_3O_4 NPs were prepared using a published method with a slight modification.[13] 6 mmol of $FeCl_3 \cdot 6H_2O$ and 30 mmol of NH_4Ac were dissolved in 60 ml of EG under magnetic stirring to from a clear solution. Then, the mixture was transferred in a 100 ml Teflon-lined autoclave and maintained at 200℃ for 12h. After the autoclave was cooled down to ambient temperature, the products were obtained by centrifuging and washing with distilled water and ethanol several times, finally, the products were dried in a vaccuum at 60℃ for 8 h.

Synthesis of aminopropyl-modified hollow Fe_3O_4 (hollow Fe_3O_4-NH_2)

The 1.0 g of hollow Fe_3O_4 was carried out by adding 2 mL of aminopropyl trimethoxysilane (APTS) to 200 mL of ethanol. The resulting solution was refluxed for 24 h and then washed with toluene and acetone. The obtained solid material was dried in vacuum at 50 ºC for 24 h.

Loading of Pd on aminopropyl-modified hollow Fe_3O_4 (hollow Fe_3O_4-NH_2-Pd)

500 mg of hollow Fe_3O_4-NH_2 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 mmol of a $PdCl_2$ solution for 1 h, then an excess 0.05 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 catalyst, as determined by atomic absorption spectroscopic (AAS) analysis, was 4.81 wt%. The content of Pd in the hollow Fe_3O_4-NH_2-Pd, as determined by inductive coupled plasma emission spectrometer (ICP) analysis was 4.42 wt% after five cycles.

Typical procedure for hydrogenation reaction

In a typical experiment, 1 mmol of the reagent was dissolved in 5 mL ethanol with 1 mol% 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, and the conversion was estimated by GC (P.E. AutoSystem XL) or GC-MS (Agilent 6,890N/5,973N). The separated catalyst was washed several times with ethanol and dried at room temperature for use in the next time for its reuse.

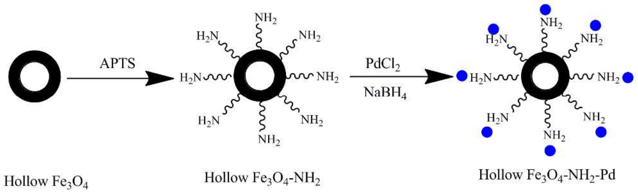
Typical procedure for the Suzuki coupling reaction

In the Suzuki coupling reactions, 0.5 mmol of aryl halides, 0.7 mmol of phenylboronic acid and 1.0 mmol of base were taken into 5 mL of solvent. The amount of catalyst used in each reaction was 10 mg, and the reaction mixture was refluxed at 343K. The reaction process was monitored by thin layer chromatography (TLC), and conversion was estimated by GC after separating the catalyst from the reaction mixture with a magnet. The catalyst was then washed several times with ethanol and dried at room temperature.Yields were calculated against the consumption of the aryl iodides.

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-Ka radiation as the X-ray source in the 2θ range of 10–80°.Thesizeand morphology of the magnetic nanoparticles were observed by a Tecnai G2F30 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. Magnetic measurements of hollow Fe_3O_4-NH_2 and hollow 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 kOe to 15 kOe.

Results and discussion



Scheme 1 Preparation of palladium nanoparticles supported on amine-functionalized hollow Fe_3O_4

The preparation process for the catalyst hollow Fe_3O_4-NH_2-Pd is schematically described in Scheme 1. First, hollow Fe_3O_4 nanoparticles were synthesized by a facile solvothermal sythetic strategy. Second, the functionalization of hollow Fe_3O_4 with APTS. Thirdly, meanwhile palladium chloride was supported on the surface of hollow Fe_3O_4, it reduced to palladium particles with sodium borohydride (amine groups on the surface of nanoparticles act as a robust anchor and avoid Pd leaching)

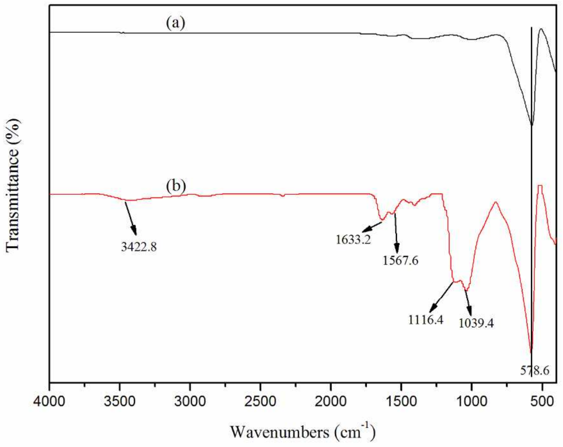


Fig.1 FT-IR spectra of (a) hollow Fe_3O_4 and (b) hollow Fe_3O_4-NH_2

We measured the Fourier transform infrared (FT-IR) spectra of hollow Fe_3O_4 and hollow Fe_3O_4-NH_2. The characteristic peak of Fe_3O_4 at 578.6 cm^{-1} (Fe-O stretching of Fe_3O_4) in Fig.1a was also detected in hollow Fe_3O_4-NH_2 (in Fig. 1b). The major peaks for the hollow Fe_3O_4-NH_2 in Fig. 1b can be assigned as follows: 3422.8 cm^{-1}(C-H stretching vibration), 1633.2 cm^{-1}(N-H deformation vibration) and 1039.4 cm^{-1} (C-N stretching vibration) respectively. Fig.1b shows the IR spectrum of hollow Fe_3O_4-NH_2, indicating that plenty of APTS molecules are immobilized on the surface of nanoparticles.

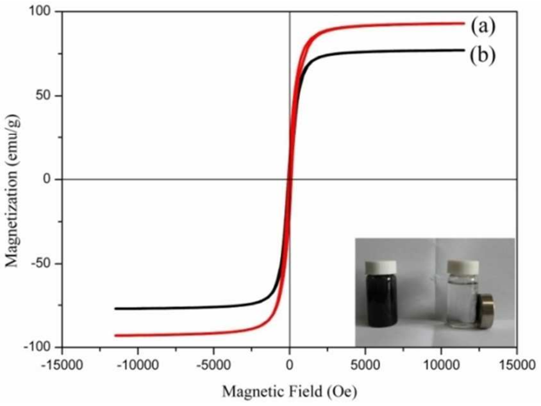


Fig.2 Room temperature magnetization curves of (a) hollow Fe_3O_4 and (b) hollow Fe_3O_4-NH_2-Pd

The magnetic properties of resulting products were investigated with a VSM at room temperature and are presented in Fig. 2. From the hysteresis loop of the samples, it is found that the magnetite spheres exhibit ferromagnetic behavior. From the curves a and b in the Fig. 2, the saturated magnetization values of the hollow Fe_3O_4 and hollow Fe_3O_4-NH_2-Pd are 81.58 emu g^{-1} and 75.57 emu g^{-1}, respectively. This feature will provide an easy and efficient avenue for separating hollow Fe_3O_4-NH_2-Pd nanoparticles from a suspension system under an external magnetic field.

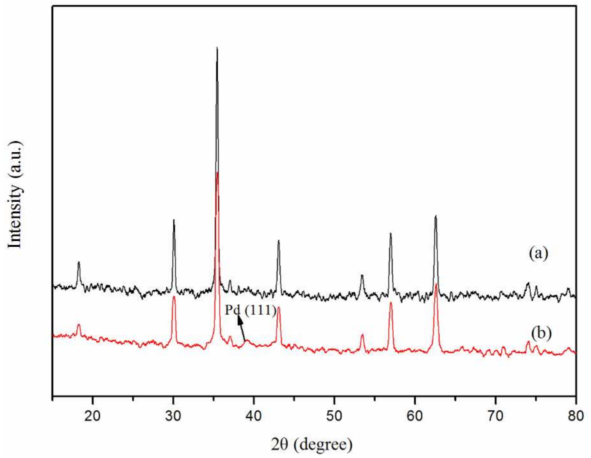


Fig. 3 XRD patterns of (a) hollow Fe_3O_4 and (b) hollow Fe_3O_4-NH_2-Pd

In Fig. 3, the crystallinity and phase composition of the as-prepared samples has been investigated by X-ray powder diffraction (XRD). Fig. 3a shows all the diffraction peaks that can be well indexed to the magnetic cubic structure of Fe_3O_4 (JCPDS NO. 79-0419). In Fig. 3b, we could see the appearance of a diffraction peak at 39.86° due to Pd metallic state.

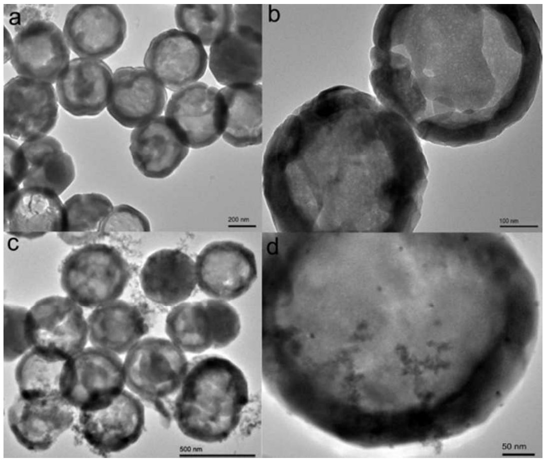


Fig. 4 TEM image of (a, b) hollow Fe_3O_4 and (c, d) hollow Fe_3O_4-NH_2-Pd

Fig. 4 shows the TEM images of hollow Fe_3O_4 and hollow Fe_3O_4-NH_2-Pd catalyst. For hollow Fe_3O_4 (Fig. 4a), the average diameter of the as-synthesized spherical particles was about 400 nm and the particles were nearly uniform in size. Fig, 4b is HRTEM image of hollow Fe_3O_4, from the picture it can be observed that the wall thickness is about 85 nm. The morphology of the hollow Fe_3O_4 does not significantly change after attachment of the palldium onto the surface of the hollow Fe_3O_4. It can also be concluded that the palladium particle size distribution was centered at 9 nm in Fig. 4d.

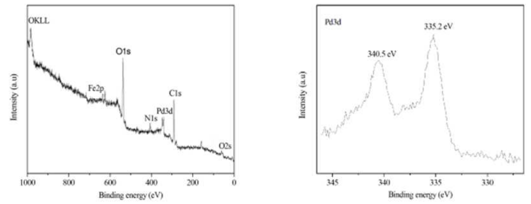
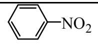
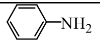
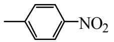
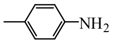
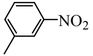
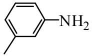
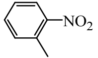
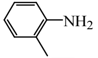
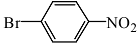
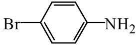
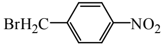
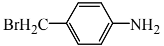
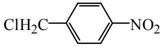
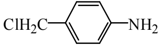


Figure 5 (a) XPS spectrum of the elemental survey scan of hollow Fe_3O_4-NH_2-Pd and (b) XPS spectrum of the hollow Fe_3O_4-NH_2-Pd showing Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies

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. The XPS elemental survey scans of the surface of hollow Fe_3O_4-NH_2-Pd the catalyst are showed in Figure 5. Peaks corresponding to iron, oxygen, sulfur, palladium, silicon and carbon were clearly observed. To ascertain the oxidation state of the Pd, X-ray photoelectron spectroscopy (XPS) studies were carried out. In Figure 3b, the Pd binding energy of hollow Fe_3O_4-NH_2-Pd exhibited two strong peaks centered at 340.5 and 335.2eV, which were assigned to Pd $3d_{3/2}$ and Pd $3d_{5/2}$, respectively. These values agreed with the Pd (0) binding energy of Pd nanoparticles.

Catalyst testing for hydrogenation reactions

Table 1 Hydrogenation of various substrates using Hollow Fe_3O_4-NH_2-Pd [a]

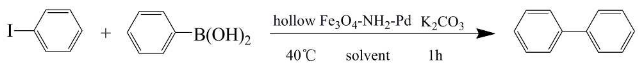
Entry	Substrate	Product	*t* /min	Yield[d] (%)
1			60	>99
			60	>99[b]
			120	>99[c]
2			65	>99
3			65	98
4			65	96
5			70	97
6			70	97
7			70	96

[a] Reaction conditions: catalyst = 1 mol %; H_2 = 1 atm; substrate = 1 mmol; solvent = 5 mL at the room temperature. [b] Yield after 5 runs. [c] Hydrogenation with 10% Pd/C at the same condition.
[d] Determined by GC or GC-MS

Initially, the catalytic activity was tested for the hydrogenation of a variety of aromatic nitro compounds to their corresponding products. The reactions were carried out in ethanol at room temperature and under 1 atm pressure of H_2. Detailed observations of all the reactions are given in Table 1.It has been observed that the catalyst was very active for the hydrogenation reaction under such mild conditions, morever catalytic hydrogenation of aromatic nitro-compounds can be over 95% yields and reused for 5 times with no obvious decrease of conversion and selectivity by a simple magnetic separation. Either hollow Fe_3O_4-NH_2-Pd and the commercial 10% Pd/C has been for the catalytic hydrogenation of nitrobenzene, the commercial product demanded two hours for the completion of the reaction, whereas the hollow Fe_3O_4-NH_2-Pd completed no more than one hour with relatively low Pd loading under similar experimental conditions

. Catalyst testing for Suzuki coupling reactions

Table 2 The cross-coupling of phenylboronic acid and iodobenzene under different solvent in the presence of the hollow Fe_3O_4-NH_2-Pd catalyst[a]



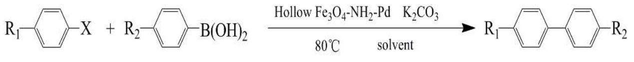
Entry	Solvent	Yiled(%)b
1	Ethanol/water=1:1	100
2	Ethanol	76
3	Toluene	34
4	Acetone	36
5	THF	-

[a] The reaction was carried out with 0.5 mmol of aryl halides, 0.7 mmol of phenylboronic acids, 1mmol of K_2CO_3, 1mol % Pd and 5 ml solvent

[b] Determined by GC or GC-MS.

To test the catalytic activity of hollow Fe_3O_4-NH_2-Pd in the Suzuki reaction, the reaction between iodobenzene and phenylboronic acid was chosen as model reaction using K_2CO_3 as base at the temperature of 40 ℃. Different solvents were examined to obtain the best possible combination. As shown in Table 2, when THF was used as the solvent, poor yield was obtained (Table 2, entry 5). When protic solvent like ethanol was used as solvent, the quantitative product was expected (entry 2); the aprotic solvent such as toluene and acetone gave low yield during the same time (entries 3 and 4). In the comparion with these solvents, the ethanol/water mixture used as the reaction solvent provided much bettter yield (entry 1). The merit of the co-solvent was attributed to the good solubility of the organic reactants and the inorganic base.

Table 3 Suzuki coupling reaction of various aryl halides with phenylboronic acids in the presence of the hollow Fe_3O_4-NH_2-Pd catalyst



Entry	R_1	X	R_2	T	Yield [b] (%)
1	-H	I	H	5min	82
2	-H	I	H	15min	>99
3	$-CH_3$	I	H	25min	96
4	$-OCH_3$	I	H	30min	96
5	-OH	I	H	30min	95
6	$-COCH_3$	I	H	15min	96
7	-H	Br	H	5h	52
8	-H	Br	H	3.5h	93[c]
9	$-CH_3$	Br	H	4.5h	72[c]
10	$-NH_2$	Br	H	6h	74[c]
11	$-COCH_3$	Br	H	50min	98
12	$-NO_2$	Br	H	50min	97
13	-H	Cl	H	10h	74[c]
14	-H	I	Cl	20min	99
15	$-CH_3$	I	Cl	30min	94
16	$-OCH_3$	I	Cl	25min	93
17	$-COCH_3$	I	Cl	15min	97
18	-OH	I	Cl	30min	94
19	-H	Br	Cl	4h	92[c]
20	$-CH_3$	Br	Cl	6h	88[c]
21	-H	Cl	Cl	13h	77
22	-H	I	CH_3	45min	96
23	-H	Br	CH_3	7h	92[c]
24	-H	Cl	CH_3	13h	73[c]

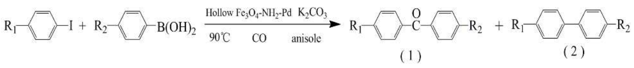
[a] The reaction was carried out with 0.5 mmol of aryl halides, 0.7 mmol of phenylboronic acids or 4 - methylphenylboronic acid, 1 mmol of K_2CO_3, 1.0 mol % of Pd and 5 ml ethanol.

[b] Determined by GC or GC-MS.

[c] the reaction solvent: ethanol/water=1:1

In order to verify the higher activity of hollow Fe_3O_4-NH_2-Pd, its activity towards other substrances with variation of different substituents were examined. These results were smmarized in Table 3. A wide range of functional groups has also been tolerated in the reaction. The cross-coupling reaction of phenylboronic acid with a variety of aryliodides proceeded smoothly, affording high yield at 95-99% (Table 3, entries 2-6). Various electron-donating and electron-with drawing groups, such as $-OCH_3$, $-CH_3$ and $-COCH_3$, on the aryl iodide were well tolerated. Electron-donating groups, such as $-OCH_3$ and $–CH_3$, on the iodoaryl partner gave excellent results. The presence of a strong electron-withdrawing group, such as $–COCH_3$, is known to promote the direct coupling, producing the biaryl. The optimized reaction conditions were also applied to the cross-coupling of substituted phenylboronic acid such as 4-methylphenylboronic acid and 4-chlorophenylboronic acid with variety of aryl iodides (Table 3, entries 14-18 and 22). Since the reaction using ethanol as a solvent obtained in short time a relatively good result, the mixture of ethanol and water as the reaction solvent has not been used. Vartious electron-donating and electron-withdrawing groups, on both aryl iodides and arylboronic acids were tolerated to give the desired biaryl in good yields. The results above prompted the authors to investigate the reaction of aryl bromides. Hollow Fe_3O_4-NH_2-Pd also afforded a satisfactory yield for bromides containing $–CH_3$ and $–NH_2$ groups (Table 3, entries 7-12, 19-20, 23). Bromoarenes with either electron-with drawing substituents, such as $–NO_2$ and $–CH_3$, or electron-donating substituents, such as $–CH_3$ and $–NH_2$ coupled readily with arylboronic acids in excellent yields. Aryl bromides containing electron-withdrawing substituents reacted faster than those with electron-donating substituents. Besides, with regard to aryl iodides, aryl bromides took a slightly longer time to complete the reaction. Additionally, hollow Fe_3O_4-NH_2-Pd showed high activity towards aryl chlorides (Table 3, entries 13, 21, 24).

Table 4 Carbonylative Suzuki coupling reaction of various aryl iodides with arylboronic acids in the presence of the hollow Fe_3O_4-NH_2-Pd catalyst [a]



Entry	R_1	R_2	Time (h)	Yield (%)[b]	
				(1)	(2)
1	-H	-H	12	90.4	6.2

2	$-CH_3$	-H	12	92.4	7.3
3	$-OCH_3$	-H	12	78.1	11.2
4	-H	$-CH_3$	12	85.3	13.6
5	$-CH_3$	$-CH_3$	12	74.2	17.7
6	$-OCH_3$	$-CH_3$	12	65.7	15.2
7	-H	-Cl	12	84.3	14.7

[a] The reactions were carried out with aryl iodide (0.5 mmol), arylboronic acid (0.75 mmol), CO (1 atm), K_2CO_3 (1.0 mmol) and 1 mol % palladium in anisole (5 mL) at 90 ºC.

b Determined by GC.

Encouraged by the impressive results for the Suzuki coupling of aryl halides and phenylboronic acids, it was decided to test the catalytic activity the Suzuki carbonylative reaction. The Suzuki carbonglative coupling reaction is one of the most promising methods for the direct synthesis of biaryl hetones from carbon monoxide, aryl hadides and arylboronic acids. The Suzuki carbonglative coupling reaction Pd (Ⅱ) is normally used as a catalyst[14], but Pd (0) still achieved the desired results in this experiment. In Table 4, various aryl iodides as well as arylboronic acids were examined and good functional group tolerance of the hollow Fe_3O_4-NH_2-Pd catalytic system was observed. In addition, both 4-methylbenzeneboronic acid and 4-chlorophenylboronic acid reacted smoothly with aryl iodides to give unsymmetrical biaryl ketones in high yields.

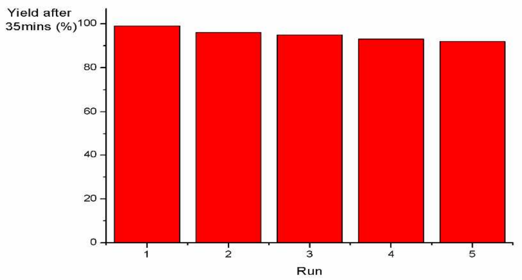


Fig.6 reusability of the hollow Fe_3O_4-NH_2-Pd catalyst for the Suzuki reaction.(The reaction condition: iodobenzene (0.5 mmol), phenylboronic acid (0.7 mmol), Ethanol (5 ml), 1mol % catalyst K2CO3 (1 mmol) and 80 ℃.)

The recyclability of hollow Fe_3O_4-NH_2-Pd was further studied because the recycling of the heterogeneous catalyst was an important issue for practical applications. The coupling reaction of iodobenzene with phenylboronic acid was chosen as the model reaction. As shown in Fig.6, recovered catalyst was added to reaction mixture under the same condition for five cycles without a significant loss of yield and catalyst activity. The good reusability may be attributed to the amino groups present on the surface of the Fe_3O_4, which could efficiently prevent the aggregation of Pd particles formed during the catalytic reaction.

Conclusions

In the study, a new hollow Fe_3O_4 supported palladium catalyst had been successfully prepared. The catalyst has shown high activity towards hydrogenation and Suzuki coupling reaction. The novel catalyst could be recovered in a facile manner from the reaction mixture and a good yield was obtained even after the catalyst was reused five times.

Acknowledgement

This work was supported financially by the Key Laboratory of Noferrous Metals Chemistry and Resources Utilization, Gansu Province and Gansu provincial Engineering Laboratory for chemical catalysis,

Notes and references

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China, Fax: +86 931 8912311, Tel.: +86 931 8912311,E-mail: majiantai@lzu.edu.cn

1. J. Deng, L. P. Mo, F. Y. Zhao, L. L. Hou, L. Yang and Z. H. Zhang, *Green Chem.*, 2011, **13**, 2576
2. (*a*) K. Kaneda and T. Mizugaki, *Energy Environ. Sci.*, 2009, **2**, 655–673; (*b*) K. Shimizu, K. Satwabe and A. Satsuma, *Catal. Sci. Technol.*, 2011, **1**, 331
3. (*a*) S. Jansat, M. Gomez, K. Philippot, G. Muller, E. Guiu, C. Claver, S. Castillon and B. Chaudret, *J. Am. Chem. Soc.*, 2004, **126**, 1592; (*b*) S. Kidambi, J. Dai, J. Li and M. L. Bruening, *J. Am. Chem. Soc.*, 2004, **126**, 2658; (*c*) H. Kobayashi, M. Yamauchi, H. Kitagawa, Y. Kubota, K. Kato and M. Takata, *J. Am. Chem. Soc.,* 2008, **130**, 1828
4. S. Ogasawara and S. Kato, *J. Am. Chem. Soc*., 2010, **132**, 4608.
5. (*a*) B. Karimi, S. Abedi, J. H. Clark and V. Budarin, *Angew. Chem. Int. Ed.,* 2006, **45**, 4776; (*b*) B. Karimi, A. Zamani, S. Abedia and J. H. Clark, *Green Chem.,* 2009, **11**, 109. (d) M. Y. Zhu, Y. Wang, C. J. Wang, W. Li and G. W. Diao, *Catal. Sci. Technol.*, 2013, **3**, 952
6. (*a*) K. I. Shimizu, K. Shimura, K. Ohshima, M. Tamura and A. Satsuma, *Green Chem.,* 2011, **13**, 3096; (*b*) Y. Zhang, X. J. Qi, X. J. Cui, F. Shi and Y. Q. Deng, *Tetrahedron Lett.,* 2011, **52**, 1334; (c) S. Paul and J. H. Clark, *Green Chem.*, 2003, **5**, 635; (d) C. M. Crudden, M. Sateesh and R. Lewis, *J. Am. Chem. Soc.*, 2005, **127**, 10045; (e) D. H. Lee, J. Y. Jung and M.J. Jin, *Green Chem.*, 2010, **12**, 2024; (f) S. Y. Gao, Z. L. Zheng, J. Lü and R. Cao, *Chem. Commun.*, 2010, **46**, 7584; (g) Z. Chen, Z. M. Cui, F. Niu, L. Jiang and W. G. Song, *Chem. Commun.*, 2010, **46**, 6524
7. (a) Z. Chen, Z. M. Cui, F. Niu, L. Jiang and W. G. Song, *Chem. Commun.,* 2010, **46**, 6524; (b) P. Wang, F. W. Zhang, Y. Long, M. Xie, R. Li and J. T. Ma, *Catal. Sci. Technol.*, 2013,**3**, 1618.
8. (*a*) S. Shylesh, V. Schunemann and W. R. Thiel, *Angew. Chem., Int. Ed.,* 2010, **49**, 3428; (*b*) Y. H. Zhu, L. P. Stubbs, F. Ho, R. Z. Liu, C. P. Ship, J. A. Maguire and N. S. Hosmane, *ChemCatChem*, 2010, **2**, 365; (*c*) K. Mori, N. Yoshioka, Y. Kondo, T. Takeuchi and H. Yamashita, *Green Chem.,* 2009, **11**, 1337; (d) V. Polshettiwar, R. Luque, A. Fihri, H. Zhou, M. bouhara, J. M. Basset, *Chem. Rev.*, 2011, **111**, 3036;(e) R. Linhardt, Q. M. Kainz, R. N. Grass, W. J. Stark and O. Reiser, *Rsc. Adv.* 2014, **4**, 8541, (f) Q. M. Kainz, R. Linhardt, R. N, Grass, G, Vilé, J. Pérez-Ramírez, W. J. Stork and O. Rever. *Adv. Funct.Mater.* 20414,**24**, 2020,(g)A. schätz, T. R. Long, R. N. Grass, W. J. stork, P. R. Hanson and O. Reiser. *Adv. Funct. Mater.* 2010, **20**, 4323,;(h) M. Keller, V. Collière, O. Reiser, A. M. Caminade, J. P. Majoral and A. Ouali. *Angew. Chem. Int. Ed.* 2013, **52**. 3626
9. (a) J. Hu, M. Chen, X. S. Fang and L. M. Wu, *Chem. Soc. Rev.*, 2011, **40**, 5472; (b) R. V. Islam, M. J. Witcomb, M. S. Scurrell, E. Lingen, W. V. Otterlo and K. Mallick, *Catal. Sci. Technol*, 2011, **1**, 308; (c) N. T. S. Phan and P. Styring, *Green Chem.*, 2008, **10**, 1055;
10. (a) L. Wang, J. Zhang, S. Yang, Q. Sun, L. F. Zhu, Q. M. Wu, H. Y. Zhang, X. J. Meng and F. S. Xiao., *J. Mater. Chem. A.*, 2013, **1**, 9422; (b) C. A. Wang, S. Li and L. N. An, *Chem. Commun.*, 2013, **49**, 7427. (c) M. Y. Zhu, C. J. Wang, D. H. Meng and G. W. Diao, *J. Mater. Chem. A*, 2013, **1**, 2118
11. (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; (c) A. J. Amali and R. K. Rana, *Green. Chem.*, 2009, **11**, 1781.
12. A. Fihri, M. bouhrara, B. Nekoueisharki, J. M. Basset and V. Polshettiwar, *Chem. Soc. Rev.*, 2011, **40**, 5181

13. X. H. Lin, G. B. Ji, Y. S. Liu, Q. H. Huang, Z. H. Yang and Y. W. Du, *CrystEngComn.*, 2012, **14**, 8658
14. (a) T. Ishiyama, H. Kizaki, T. Hayashi, A. Suzuki and N. Miyaura, J. Org. Chem. 1998, 63, 4726; (b) S. Bonnaire, J. F. Carpentier, A.Mortreux and Y. Castanet, Tetrahedron. Lett. 2001, 42, 3689; (c) S. Bonnaire, J. F. Carpentier, A. Mortreux and Y. Castanet, Tetrahedron. 2003, 59, 2793.