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Programmed Synthesis Palladium Supported on Fe_3O_4@C: An Efficient and Heterogeneous Recyclable Catalyst for One-Pot Reductive Amination of Aldehydes with Nitroarenes in Aqueous Reaction Medium

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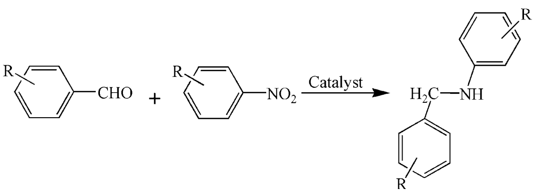
Abstract A highly efficient Pd/Fe_3O_4@C catalytic system has been developed for direct reductive amination of carbonyl compounds with nitroarenes in aqueous reaction medium. The catalyst was characterized by TEM, XRD, XPS and VSM. It was found that the catalyst showed a high activity for the one-pot direct reductive amination of aldehydes with nitroarenes in the presence of molecular hydrogen at mild temperature. Besides, the catalyst could be recovered in a facile manner from the reaction mixture and recycled six times without obvious loss in activity.

Graphical Abstract



Keywords Core–shell · Pd (0) · One-pot direct reductive amination · Aldehydes · Nitroarenes

1 Introduction

Amines and their derivatives are important building blocks possessing wide application in chemical and life science [1, 2]. Due to their importance, several methods have been developed for the preparation of amines, such as direct base-promoted *N*-alkylation and direct reductive amination [3, 4]. However, it's still a challenge to control the monoalkylation of primary amines [5], the synthesis of a wide variety of substituted amines relies heavily on the reductive amination of the carbonyl compounds [6, 7], but the method is usually carried out with hydride-based reagents such as $NaBH_4$ [8], pyridine–BH_3 [9], Zn–AcOH [10], Et_3SiH–CF_3CO_2H [11], $Bu_3SnHDMF$ [12], $InCl_3$–Et_3SiH [13], and various modified borohydride derivatives [14]. These reagents have certain limitations such as the dependence of a stoichiometric amount of reductant, poor functional group tolerance, side reactions, overalkylation, toxic waste, thermal instability, handling risks, and rigorous reaction conditions [15]. Therefore, it is desirable to develop an effective, facile and more economical method for the synthesis of amides.

It has been found that Palladium nanoparticles, particularly with dimension less than 10 nm, exhibit unexpectedly high catalytic activities toward different types of reactions, a property not revealed in bulk palladium. In recent years, many attempts have been made to disperse palladium nanoparticles on support materials which showed high catalytic activities toward the reductive amination reaction [16, 17]. One-pot transformations are economically, ecologically and highly intriguing for developing efficient new synthetic processes. Additionally, one-pot reductive amination using nitroarenes is conceived to be especially attractive as it does not require prior reduction of the nitroarenes [16, 18, 19]. Water is a desirable solvent comparing with common organic solvents for chemical reactions considering the cost, safety, and environmental concerns [20]. Hence, the development of catalytic protocols employing water as a reaction medium could be the answer for the future of green chemistry.

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Based on the above considerations, in this paper, we report our results about Pd well-dispersed on core–shell Fe_3O_4@C (Pd/Fe_3O_4@C) and it shows excellent catalytic activity for one-pot reductive amination reaction in aqueous medium under a hydrogen atmosphere. The catalyst can be easily recovered by using a permanent magnet and recycled six times without obvious loss in activity.

2 Experimental

2.1 Catalyst Preparation

The Fe_3O_4@C was prepared using a published method [21]. In a typical synthesis, ferrocene (0.30 g) was dissolved in acetone (30 mL). After intense sonication for 30 min, 1 mL of hydrogen peroxide was slowly added into the above mixture solution. Then, it was vigorously stirred for 30 min with magnetic stirring. After that, the precursor solution was transferred to the teflon-lined stainless autoclave with a total volume of 50.0 mL, and then heated to and maintained at 210 °C. After 48 h, the precipitates were washed with acetone three times to remove excess ferrocene and dried at room temperature in a vacuum oven.

These Fe_3O_4@C nanospheres possess functional groups (–COOH) on the surface [22], the Sn(II) can link to the nanospheres' surface through inorganic grafting [23]. 200 mg Fe_3O_4@C was dispersed in 35 mL distilled water and stirred for 20 min as part A. 200 mg $SnCl_2$ was dissolved in 35 mL 0.02 M HCl solution as part B. Parts A and B were mixed together under stirring for 30 min. The suspension was separated from the solution by an external magnet, washed five times with distilled water and dispersed in 80 mL distilled water. Then, 50 mL 12 mg $PdCl_2$ was added to the above mixture. 10 min later, 20 mL of 0.15 M sodium formate solution was added, following stirring for 8 h. The suspension was separated from the solution by an external magnet, washed with distilled water and ethanol for several times and dried at 50 °C for 12 h.

2.2 Characterization

XRD measurement was performed on a Rigaku D/max-2400 diffractometer using Cu-Kα radiation as the X-ray source in the 2θ range of 10–90°. 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 evaporated in air at room temperature. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 instrument and the C_{1s} line at 297.8 eV was used as the binding energy reference. Magnetic measurement of Fe_3O_4@C, Pd/Fe_3O_4@C were investigated with a Quantum Design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from −15 to 15 kOe.

2.3 Typical Procedures for the Catalytic Test

2.3.1 The Catalyst for the Reductive Amination of Different Aldehydes with Nitroarenes

0.5 mmol of the different aldehydes, 0.6 mmol of nitrobenzene and 20 mg of catalyst (2.08 wt%) were added in 3 mL of water by ball milling under a hydrogen atmosphere. After the reaction, the catalyst was separated by a small magnet placed at the bottom of the flask, and the product was extracted with ethyl acetate (5 mL) and the conversion was estimated by GC (P.E. AutoSystem XL) or GC–MS (Agilent 6890 N/5973 N). Thereafter, the catalyst was washed three times with ethanol and dried at room temperature for the next cycle.

2.3.2 The Catalyst for the Reductive Amination of Aldehydes with Different Nitroarenes

20 mg of catalyst (2.08 wt%), 0.6 mmol nitroarene and 0.5 mmol of aldehyde were added in 3 mL of water. The resulting suspension was stirred under a hydrogen atmosphere and at 60 °C for the specified period of time. The reaction process was monitored by thin layer chromatography (TLC). After completion of the reaction, the catalyst was separated from the reaction mixture with the aid of an external magnet. The conversion was estimated by GC or GC–MS 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 for its reuse.

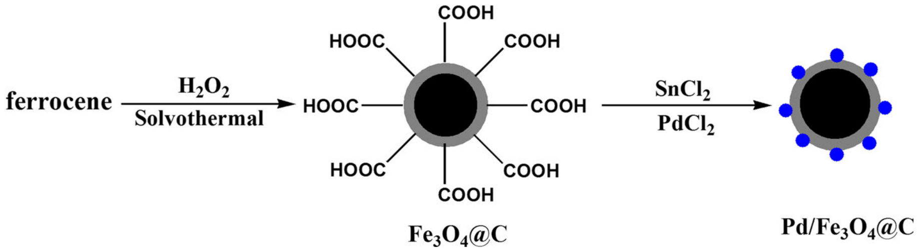
3 Results and Discussions

3.1 Catalyst Preparation and Characterization

The preparation of the Pd/Fe_3O_4@C catalyst followed the steps described in Scheme 1. Firstly, Fe_3O_4@C was prepared. It was proved the existence of carboxyl groups in the outer carbon layer. Next is to link the Sn(II) to the Fe_3O_4@C precursor surface through inorganic grafting [22]. Thirdly, the linked Sn(II) species acted as a reducing reagent to reduce Pd(II) in situ. The amount of Pd in the obtained catalyst was found to be 2.08 wt% based on ICP analysis.

The morphologies and structures of the products at different synthetic steps were observed by TEM. Figure 1a is the TEM image of a single Fe_3O_4@C nanoparticle.

Scheme 1 Preparation of the catalysts



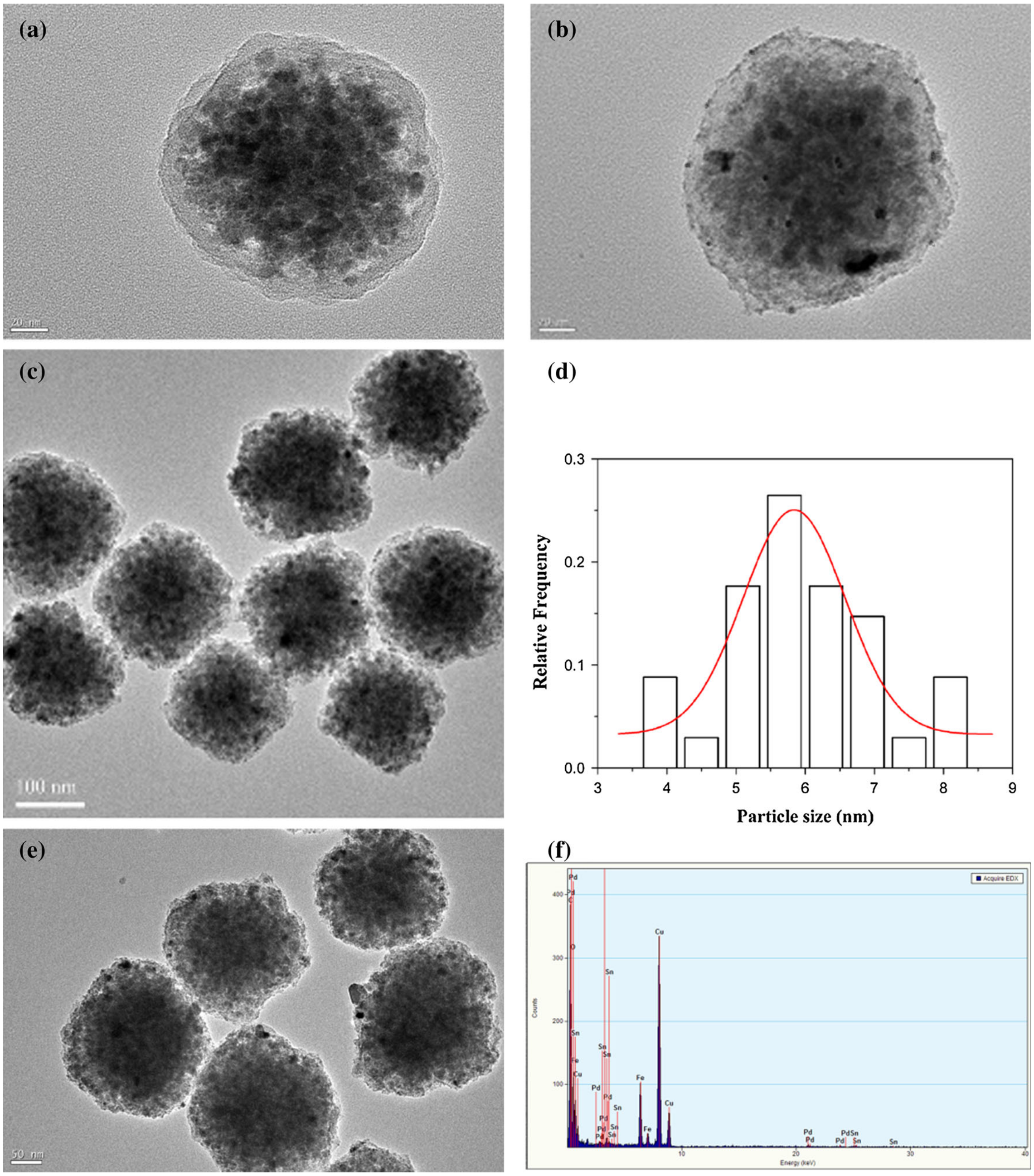


Fig. 1 TEM images of **a** Fe_3O_4@C, **b**, **c** Pd/Fe_3O_4@C, **d** size distribution histograms image of the Pd nanoparticles crystal structure in detail on Pd/Fe_3O_4@C, **e** Pd/Fe_3O_4@C catalyst after six runs, **f** EDX analysis

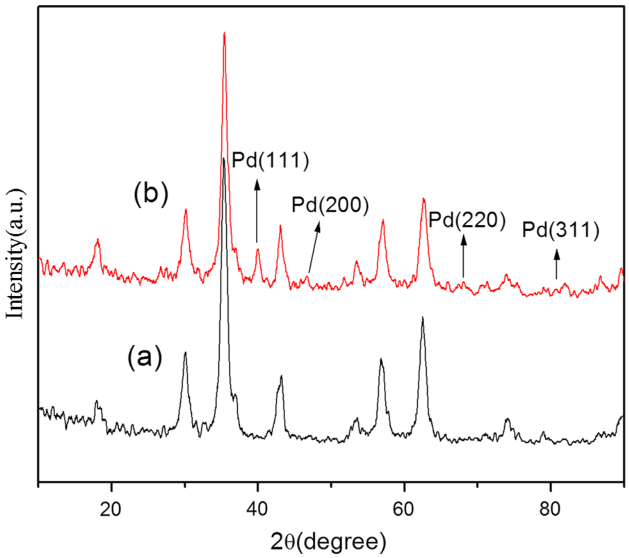


Fig. 2 XRD patterns of **a** Fe$_3$O$_4$@C, **b** Pd/Fe$_3$O$_4$@C

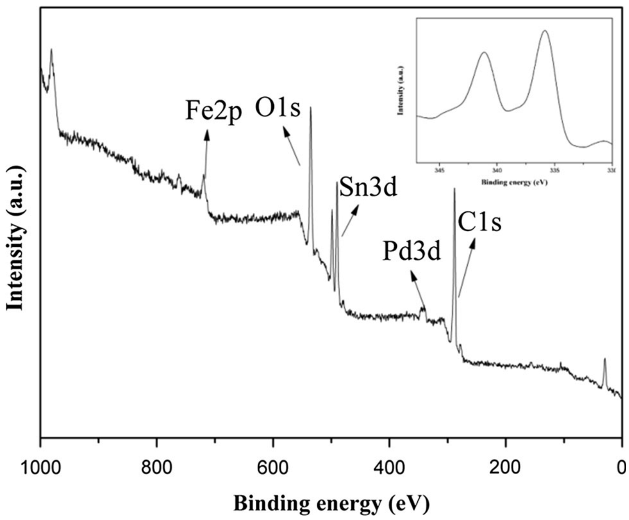


Fig. 3 XPS wide-scan spectrum of the Pd/Fe$_3$O$_4$@C (*inset* high-resolution spectrum of Pd 3d)

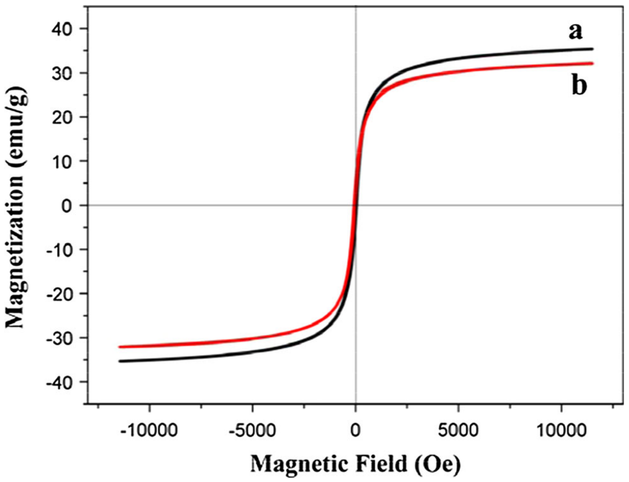


Fig. 4 Room temperature magnetization curves of **a** Fe$_3$O$_4$@C, **b** Pd/Fe$_3$O$_4$@C

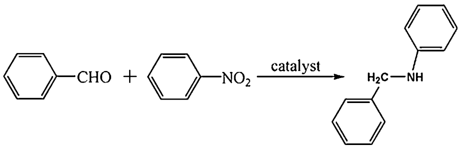
Fe$_3$O$_4$@C nanoparticle could be observed from the picture and the carbon thickness was about 10 nm and the diameter of the as-synthesized spherical particles was about 160 nm. Figure 1b, c are the TEM images of Pd/Fe$_3$O$_4$@C catalysts. From the picture of Fig. 1d, it could be seen that the size distribution histograms indicated that the most Pd particles fall in the size range 3–8 nm and the mean particle diameter was about 5.9 nm. In Fig. 1e, we can see that the catalysts recycled six times without obvious change in morphology and dispersity. The elemental composition of the Pd/Fe$_3$O$_4$@C samples was determined by EDX analysis. The result shown in Fig. 1f revealed that the as-prepared products contain Fe, Pd, Sn, Cu, C and O. Among these elements, Cu was generally influenced by the copper network support films, Sn, O, C, Fe and Pd signals resulted from the Pd/Fe$_3$O$_4$@C particles which formed the products.

Figure 2 shows the XRD patterns between 10° and 90° of the samples. Figure 2b shows that apart from the original peaks, the appearance of the new peaks at $2\theta = 40.1°$, 46.5°, 68.0° and 82.1° corresponding to the reflections of (111), (200), (220) and (311) crystal planes of palladium, respectively. The results from XRD implied that the Pd nanoparticles had been successfully immobilized on the surface of magnetic nanoparticles.

Figure 3 shows the XPS spectrum of the synthesized Pd/Fe$_3$O$_4$@C catalyst. Peaks corresponding to oxygen, carbon, palladium, tin and iron were observed. To ascertain the oxidation state of the Pd, XPS studies were carried out. The Pd binding energy of Pd/Fe$_3$O$_4$@C exhibited two strong peaks centered at 341.5 and 335.5 eV, which were assigned to Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$, respectively.

Magnetic measurements were carried out by employing VSM at room temperature. The magnetization curves measured for Fe$_3$O$_4$@C, Pd/Fe$_3$O$_4$@C are compared in Fig. 4. There was no hysteresis in the magnetization for the three tested nanoparticles. It could be seen that the values of the saturation magnetization were 35.1 emu/g for Fe$_3$O$_4$@C, 32.3 emu/g for Pd/Fe$_3$O$_4$@C respectively. The decrease of the saturation magnetization suggested the presence of some palladium particles on the surface of magnetic supports. The catalyst exhibited similar catalytic performance without visible reduction in the conversion for the same reaction conditions even after running for more than 6 cycles (Fig. 5).

Table 1 Optimization of reaction conditions



Entry	Solvent	Temperature (°C)	Time (h)	Conversion (%)	Yield (%)[a]
1	Ethanol	60	8	90	82
2	DMF	60	8	96	81
3	Water	60	8	99	92
4	Methanol	60	8	71	38
5	Toluene	60	8	30	28
6	Water	30	8	79	72
7	Water	40	8	78	71
8	Water	50	8	92	87
9	Water	60	8	99	92
10	Water	80	8	98	89
11	Water	60	4	86	44
12	Water	60	6	92	83
13	Water	60	8	99	92

Reaction conditions: benzaldehyde (0.5 mmol), nitrobenzene (0.6 mmol), 20 mg Pd/Fe_3O_4@C catalyst, and water (3 mL) at room temperature under a H_2 atmosphere

[a] Yield was determined by GC analysis and *n*-tridecane was used as the internal standard

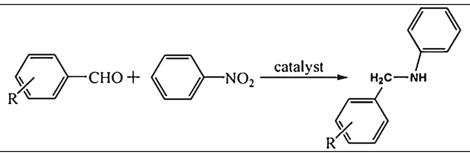
3.1.1 Catalytic Performance

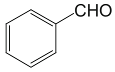
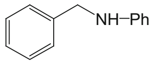
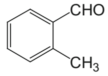
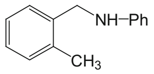
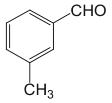
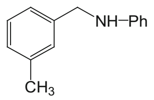
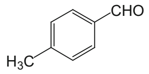
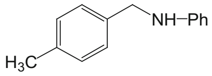
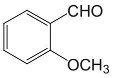
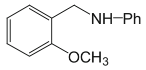
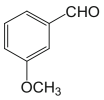
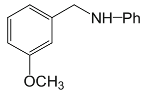
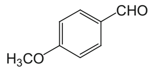
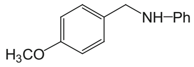
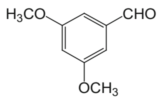
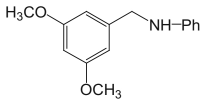
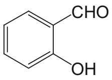
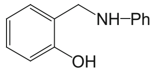
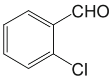
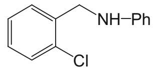
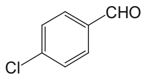
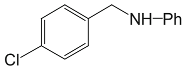
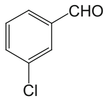
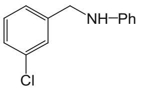
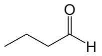
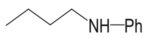
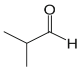
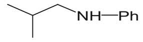
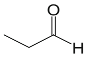
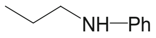
In the first step of experiments, various reaction parameters such as effect of solvent, reaction temperature and time were studied and the results obtained are summarized in Table 1. Initially, we studied the effect of the solvent on direct reductive amination. Some polar solvents such as ethanol (82 %), methanol (38 %), DMF (81 %) and water (92 %) were good to yield the desired product (entries 1–4). However, a non-polar solvent, namely toluene (28 %), was screened. Little yield of the desired product was obtained (entry 5). It was worth mentioning that the conversion of the desired product was considerably improved by changing solvent from organic solvent to water in the presence of Pd/Fe_3O_4@C as the catalyst. These results clearly showed that the efficiency of the reaction was affected by different solvents. In order to examine the effect of temperature on the reaction outcome, reactions were carried out at different temperatures ranging from 30–80 °C (entries 6–10). It was observed that at 30 °C the yield of the desired product was low whereas with the increase in temperature up to 60 °C, 92 % yield of the desired product was obtained within 8 h. The increase of reaction temperature up to 80 °C led to low yields (89 %) due to the generation of by-products. Based on the reaction yields and environmental consideration, water was proved to be superior to the other solvent. The reaction yields were susceptible to temperature changes (entries 6–8). Hence, the final optimized reaction parameters for direct reductive amination were benzaldehyde (0.5 mmol), nitroarene (0.6 mmol), catalyst 20 mg, water as solvent (3 mL), temperature (60 °C), and reaction time (8 h).

Under the optimized reaction conditions, the scope of the reaction was explored with structurally different aldehydes and nitroarenes. As shown in Table 2, various aldehydes were reductively aminated with nitrobenzene in water at 60 °C and under a hydrogen atmosphere. It could be seen that there was no remarkable electron withdrawing and steric effects for the aromatic aldehydes during this reaction, although benzaldehydes are with o-, m-, and p-substituents (entries 1–7). We also found that salicylaldehyde, o-chlorobenzaldehyde and 2-chlorobenzaldehyde had low yields (entries 9, 10, 12), those probably due to the intramolecular hydrogen bond, electron withdrawing and steric effects for the aromatic aldehydes during this reaction. Besides, aliphatic aldehydes, regardless of whether they were linear or R-branched, underwent the reductive amination rapidly and gave the products in excellent yields nearly without the formation of any side products (entries 13–15).

Table 3 shows the results obtained for reactions carried using benzaldehyde with different nitrobenzenes. Unsubstituted (Table 3, entry 1) as well as substituted 4-methyl, 4-chlorine, 4-bromine, 4-methoxy nitrobenzenes obtained the desired product in high yields. It was observed that all of these reactions have nearly no formation of side products.

Table 2 Pd/Fe_3O_4@C catalyst for the reductive amination of different aldehydes with nitrobenzene



Entry	Aldehyde	Product	Conversion(%)	Yield[%][a]
1			99	92
2			98	89
3			99	90
4			100	94
5			100	94
6			96	94
7			90	86
8			95	80
9			75	65
10			85	78
11			91	84
12			83	75
13			87	86
14			84	82
15			88	86

Reaction conditions: benzaldehydes (0.5 mmol), nitrobenzene (0.6 mmol), 20 mg Pd/Fe3O4@C catalyst, and water (3 mL) at 60 °C under a H_2 atmosphere

[a] Yield was determined by GC analysis and n-tridecane was used as the internal standard

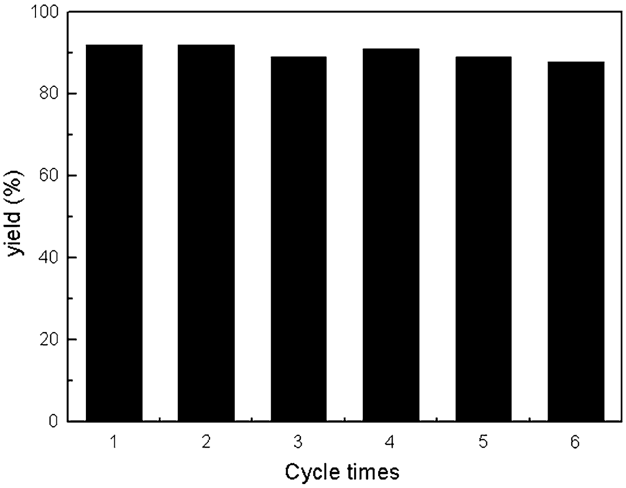


Fig. 5 Catalyst recyclability study

The hot-filtration have been performed. After 4 h of the reaction, we filtered the whole reaction system. We take part of the filtrate sent for GC–MS and elemental analysis,the conversion is 56 % and the elemental analysis results indicated that there was no palladium in the filtrate. In addition, the other part of the filtrate was continued to be heated under the original reaction condition without catalysts. After 8 h, the solution was sent for GC–MS and elemental analysis, the conversion is 57 % and there was no significant change compared with the former.

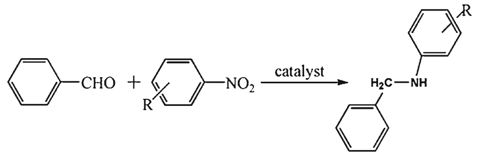
Compared with our previous work [24], this work have several advantages as follows: Firstly, the methods of synthesis Catalyst are simple and convenient, these advantages make this methodology attractive for the development of large-scale industrial synthesis. Secondly, we chose water as our reaction solvent, because it was much cheaper, safer and more environmentally friendly than organic solvent. Finally, the synthetic methodology can be extended to the fabrication of other noble metal catalysts (such as Au- and Pt-based catalysts) with integrated and enhanced properties for various advanced applications, multicomponent nanosystems.

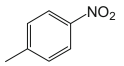
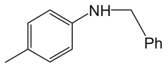
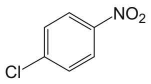
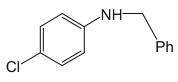
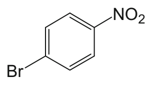
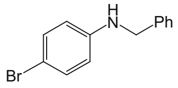
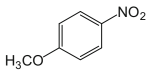
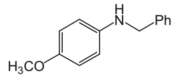
Although these catalysts give a good yields in a short time and mild room temperature. And we chosen water as our reaction solvent, because it was much cheaper, safer and environmentally friendly than organic solvent. To make the synthetic protocol more economical, recyclability study of the catalyst was examined for direct reductive amination of aldehydes with nitroarenes (Fig. 4).We observed that the catalyst was highly active under the present reaction conditions and could be effectively reused for six consecutive recycles.

3.1.2 ^{1}H NMR Data of Some Selected Compounds

3.1.2.1 N-Benzylaniline (Table 2, Entry 1) ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.38–7.30 (m, 5H), 7.20 (t, 2H), 6.76 (t, 1H), 6.68 (d, 2H), 4.37 (s, 2H), 4.01 (br, 1H);

Table 3 Pd/Fe_3O_4@C catalyst for the reductive amination of aldehydes with different nitroarenes



Entry	Nitroarenes	Product	Conversion(%)	Yield[%][a]
1			98	91
2			97	83
3			94	78
4			93	86

Reaction conditions: benzaldehyde (0.5 mmol), nitroarenes (0.6 mmol), 20 mg Pd/Fe_3O_4@C catalyst, and water (3 mL) at 60 °C under a H_2 atmosphere

[a] Yield was determined by GC analysis and *n*-tridecane was used as the internal standard

3.1.2.2 N-(4-Methoxybenzyl)aniline (Table 2, Entry 7) ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 7.33$ (d, 2H), 7.21 (t, 2H), 7.01–6.98 (m, 2H), 6.92 (d, 2H), 6.76 (t, 1H), 6.68 (d, 2 H), 4.28 (s, 2H), 3.98 (br, 1H), 3.82 (s, 3H);

3.1.2.3 N-(4-Chlorobenzyl)aniline (Table 2, Entry 11) ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 7.32$ (s, 4H), 7.19 (t, 2H), 6.73 (t, 1H), 6.61 (d, 2H), 4.32 (s, 2H), 4.02 (br, 1H);

3.1.2.4 N-Benzyl-4-methylaniline (Table 3, Entry 1) ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 7.4$–7.21 (m, 5H), 7.04 (d, 2H), 6.60 (d, 2H), 4.36 (s, 2H), 3.9 (br, 1H), 2.2 (s, 3H);

3.1.2.5 N-Benzyl-4-chloroaniline (Table 3, Entry 2) ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 7.37$–7.31 (m, 5H), 6.13 (d, 2H), 6.57 (d, 2H), 4.32 (s, 2H), 4.1 (brna, 1H);

4 Conclusions

In conclusion, we demonstrated a successful synthesis of multicomponent Pd/Fe_3O_4@C magnetic catalysts with well-defined core–shell nanostructures. Tiny palladium nanoparticles were successfully supported on the surface of core–shell Fe_3O_4@C spheres. The obtained multicomponent Pd/Fe_3O_4@C magnetic catalysts showed excellent catalytic performance for one-pot reductive amination under mild conditions and could be recovered in a facile manner from the reaction mixture. What's more, our catalyst had both convenient separability and excellent reusability. Therefore, this functional nanostructure held great promise as a novel Pd-based catalyst system for various catalytic reactions. Additionally, the design concept for the multifunctional nanomaterials can be extended to the fabrication of other multicomponent nanosystems with integrated and enhanced properties for various advanced applications.

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