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One-pot synthesis of L-dopa-functionalized waterdispersible magnetite nano-palladium catalyst and its application in the Suzuki and Heck reactions in water: a novel and highly active catalyst⁺

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A palladium catalyst supported on water-dispersible magnetite nanoparticles end-functionalized with amino and carboxyl groups was successfully prepared by a facile one-pot template-free method combined with a metal adsorption-reduction procedure. It was characterized by TEM, XRD, XPS, FT-IR and VSM. This catalyst exhibits excellent catalytic activity for Suzuki and Heck reactions in water. Furthermore, the newly developed catalyst is easy to be recovered and recycled by magnetic separation from aqueous phase reactions. More importantly, the catalyst revealed high efficiency and high stability under the reaction conditions and during recycling stages. This catalyst can be used consecutively six times without significant loss in catalytic activity.

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1 Introduction

It is well known that Pd-catalyzed Suzuki and Heck reactions are significantly important methods for C-C formation in modern chemical transformations and industrial processes.1-3 One of the most challenging tasks in inorganic chemistry today is to design efficient and eco-friendly catalysts for C-C bond formation reactions.⁴ Homogeneous palladium catalysis possesses many merits, such as high reaction rate, high turnover number, and efficient selectivity.5,6 However, one of the great drawbacks of such catalysis is that the products might be contaminated by metal leaching.7 Moreover, homogenous Pd catalysts used in these reactions need tedious and time-consuming work-up procedures associated within efficient recycling. A heterogeneous Pd-catalyst can solve these problems very efficiently because these heterogeneous systems are easy to handle, recover and are "green" processes, and thus supported Pdcatalysts can offer high activity and selectivity in the C-C coupling reactions.8-11 Very recently, magnetic nanoparticles have emerged as viable alternatives to conventional materials as robust, readily available, high surface area heterogeneous catalyst supports.12 On the other hand, the Heck and Suzuki reactions are performed mostly in organic solvents. In order to

comply with the idea of green chemistry, many teams prefer to carry out these two reactions in water to replace toxic organic solvents as the reaction medium since water is the safest solvent.

As it was difficult to use magnetic nanoparticles directly, surface modification with active groups was usually required for further applications.¹³ Carboxyl and primary amino groups are the most attractive functional groups, which were especially suitable for the immobilization of Pd nanoparticles. In particular, much attention has been focused on functionalized magnetic nanoparticles since after the functionalization the magnetic nanoparticles can be against aggregation without disturbing their desirable properties and also recognized to increase their catalytic activity.¹⁴⁻²⁰ Unfortunately, most of the conventional functionalized methods require long reaction times, toxic solvents and tedious synthetic steps. Therefore, developing a simple and facile approach to obtain functionalized magnetic nanoparticles with a good dispersibility is highly desirable.

To address this problem, we introduce a simple and facile one-pot solvothermal synthesis of highly water-dispersible magnetic nanoparticles, end-functionalized with amino and carboxyl groups. L-dopa was used both as a surfactant and an interparticle linker, due to it being both economical and environment-friendly.¹³ L-dopa is widely used in therapeutics; therefore, they might be non-toxic and considered as excellent candidates for synthesizing functionalization of magnetic supporters. Herein, we report a one-pot, template-free synthesis of an end-functionalized with amino and carboxyl groups, magnetically recyclable and highly active Pd catalyst, and its application in Suzuki and Heck reactions in water.

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2 Experimental

2.1 Characterization

XRD measurement was performed on a Rigaku D/max-2400 diffractometer using Cu-K α radiation as the X-ray source in the 2θ range of 20° – 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. Magnetic measurement of Fe₃O₄, Fe₃O₄-L-dopa and Fe₃O₄-L-dopa-Pd⁰ was investigated with a Quantum Design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from 15 to 15 kOe.

2.2 Synthesis of the L-dopa modified magnetic nanoparticles

Typically, FeCl₃ (0.973 g) was dissolved in ethylene glycol (30 mL) to form a clear solution, followed by the addition of NaOAc (3.260 g) and L-dopa (0.2 g). The mixture was stirred vigorously for 30 min, and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). Then, the autoclave was heated to and maintained at 200 °C for 12 h, and allowed to cool to room temperature. The black products were washed several times with ethanol and dried at 50 °C for 24 h.

2.3 Loading of Pd on L-dopa functionalized magnetic nanoparticles (Fe₃O₄-L-dopa-Pd⁰)

500 mg of as-synthesised Fe₃O₄ samples were first dispersed in a 50 mL ethanol solution with ultrasonication for 0.5 h. The formed black suspension was ultrasonically mixed with 3.0 mM of a PdCl₂ solution for 1 h, and then an excess of 0.01 M NaBH₄ solution was slowly dropped into the above mixture with vigorous stirring. After 6 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 loading level of Pd in Fe₃O₄-L-dopa-Pd⁰ catalyst was measured to be 5.31% by AAS.

2.4 General procedure for Suzuki reaction in water

In air, aryl halide (0.5 mmol), arylboronic acid (0.75 mmol), K_2CO_3 (1.0 mmol), 5 mL of distilled water, the Fe₃O₄-L-dopa-Pd⁰ catalyst (Pd 1 mol% based on Aryl halide) were combined in a 10 mL round-bottomed flask. The reaction mixture was magnetically stirred and the temperature was maintained at 80 °C in an oil bath. The reaction process was monitored by thin layer chromatography (TLC). After completion of the reaction, the mixture was cooled to room temperature and separated by magnetic decantation, the resultant residual mixture diluted with 10 mL ethyl acetate. The organic fraction was dried over MgSO₄, and an aliquot was taken with a syringe and subjected to GC or GC-MS analysis. Yields were calculated against the consumption of aryl halides. After the first cycle of the reaction, the catalyst was recovered with the help of a magnet, successively rinsed with ethanol and distilled water (to remove excess of base) and dried at room temperature ready for the next cycle.

For the ¹H NMR spectra, after the organic fraction was dried over MgSO₄, the solvent was evaporated under reduced pressure. The resultant residual was chromatographed on silica gel (hexane/ethyl acetate) to give a pure product.²¹

2.5 General procedure for Heck reaction in water

For the Heck coupling reactions, 0.5 mmol of the aryl halides, 0.75 mmol of styrene or acrylic acid, and 1.5 mmol of K_2CO_3 were taken into 5 mL of water. The amount of catalyst used in each reaction was 1.5 mmol% (based on Aryl halide), and the reaction mixture was at 90 °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 water, followed by extraction twice (2 × 15 mL) with ethyl acetate (for the substrates containing –COOH, the solution was diluted with water, acidified with 1 mol L⁻¹ HCl and then extraction with ethyl acetate). The organic fraction was dried over MgSO₄, and an aliquot was taken with a syringe and subjected to GC or GC-MS analysis. Yields were calculated against the consumption of aryl halides.

For the ¹H NMR spectra, after the organic fraction was dried over MgSO₄, the solvent was evaporated under reduced pressure. Crude product was isolated and repeatedly re-crystallized from ethyl acetate–hexane mixture to obtain compounds having sufficient purity for further characterization purposes.²²

3 Result and discussions

Catalyst preparation and characterization

The process for the preparation of the catalyst Fe_3O_4 -L-dopa-Pd⁰ is schematically described in Scheme 1. First, L-dopa-functionalized magnetite nanoparticles were synthesized by a facile one-pot solvothermal synthetic strategy. Second, Pd⁰ nanoparticles were immobilized on L-dopa-functionalized magnetic nanoparticles through the reduction of PdCl₂ by NaBH₄ with the assistance of intense agitation. Briefly, magnetite particles were first prepared by a one-pot method and then immobilized Pd⁰ on the surface of the magnetic nanoparticles act as a robust anchor and avoid Pd leaching).

Fig. 1a shows the typical TEM image of Fe_3O_4 -L-dopa nanoparticles prepared by the versatile solvothermal reaction. As can be seen from the TEM (Fig. 1a and b) images indicated that the Fe_3O_4 modified with L-dopa were highly dispersed with a spherical shape and a nearly uniform size of approximately 350 nm in diameter. The TEM image in Fig. 1c shows that the Fe_3O_4 -L-dopa-Pd⁰ catalyst did not change considerably after attachment of the palladium onto the surface of the magnetic nanoparticles. From Fig. 1d it can also be concluded that the palladium particle sized is centered at 10 nm.

Unambiguous evidence of palladium particles on Fe₃O₄-Ldopa is provided *via* X-ray powder diffraction analysis (XRD). In Fig. 2b, the characteristic diffraction peaks in the samples at 2θ of 30.2°, 35.5°, 43.3°, 53.8°, 57.2°, and 62.8° correspond to the diffraction of (220), (311), (400), (422), (511), and (440) of the



Scheme 1 Preparation of Fe $_3O_4$ -L-dopa functionalized magnetic nanoparticles and Fe $_3O_4$ -L-dopa-Pd⁰ catalyst.



Fig. 1 TEM images of (a) Fe₃O₄-L-dopa (b) The HRTEM image of Fe₃O₄-L-dopa (c) Fe₃O₄-L-dopa-Pd⁰ (d) The HRTEM image of Fe₃O₄-L-dopa-Pd⁰.



Fig. 2 XRD patterns of (a) Fe_3O_4 -L-dopa-Pd⁰ and (b) Fe_3O_4 -L-dopa.

Fe₃O₄. All the diffraction peaks match with the magnetic cubic structure of Fe₃O₄ (JCPDS 65-3107),²³ and the sharp and strong peaks confirm the products are well crystallized. Fig. 2a shows that apart from the original peaks, the appearance of the new peaks at $2\theta = 40.1^{\circ}$, 46.5° and 68.0° are attributed to the Pd species. The results from XRD indicate that the Pd nanoparticles have been successfully immobilized onto the surface of the magnetic nanoparticles. According to the Debye–Scherrer formula, the nanocrystal size of magnetite particles was calculated to be 10.1 nm, in good agreement with the TEM observations.

Fig. 3 presents XPS elemental survey scans of the surface of the Fe₃O₄-L-dopa-Pd⁰ catalyst. Peaks corresponding to oxygen, carbon, nitrogen, palladium and iron are clearly observed. To establish the oxidation state of Pd in Fe₃O₄-L-dopa-Pd, XPS analysis was conducted, and the result is shown in Fig. 2b. The binding energy of Pd 3d5/2 and 3d3/2 for the fresh Fe₃O₄-L-dopa-Pd is found to be 336 and 341 eV (Fig. 2b), indicating that the loaded palladium is in its 0 state.

The FT-IR spectra of (a) Fe_3O_4 (b) Fe_3O_4 -L-dopa and (c) Fe_3O_4 -L-dopa-Pd⁰ are shown in Fig. 4. In Fig. 4, the band at 585 cm⁻¹ can be attributed to Fe–O stretching vibration. In Fig. 4b, the absorption bands at 1617, 1469, and 878 cm⁻¹ associated with amine and 1638, 1415 cm⁻¹ associated with carboxylate,



Fig. 3 XPS spectrum of the Fe_3O_4-L-dopa-Pd showing Pd 3d5/2 and Pd 3d3/2 binding energies.



Fig. 4 $\,$ FT-IR spectra of (a) Fe_3O_4 (b) Fe_3O_4-L-dopa and (c) Fe_3O_4-L-dopa-Pd^0.

indicating that plenty of L-dopa molecules are immobilized on the surface of the nanoparticles. The IR spectrum of the Fe₃O₄-L-dopa-Pd⁰ catalyst (in Fig. 4c) demonstrates that almost no change occurs after immobilization of palladium on the magnetite nanoparticle surface.

The magnetic property of magnetic nanoparticles were investigated with a vibrating sample magnetometer (VSM) at room temperature. The hysteresis loops of Fe_3O_4 -L-dopa and Fe_3O_4 -L-dopa-Pd⁰. As shown in Fig. 5, magnetization curves revealed the superparamagnetic behaviour of the magnetic nanoparticles and the magnetic saturation values of these are 76 and 66 emu g⁻¹, respectively. The decrease of the saturation magnetization suggests the presence of some palladium particles on the surface of the magnetic supports. Even with this reduction in the saturation magnetization, the nanomaterials still could be efficiently separated from the solution by placing a magnet near the vessels (shown in the inset of Fig. 5).

After the successful preparation of Fe_3O_4 -L-dopa/Pd⁰, its effectiveness for the Suzuki coupling reaction was examined next. As is well known, the Suzuki reaction is largely effected by the type of alkaline and the temperature. Therefore, firstly, the reaction of iodobenzene with phenylboronic acid was used as a model reaction for the screening of bases, and the results were summarized in Table 1 (entry 2, 4-7). With the temperature fixed as 70 °C, the reaction proceeded very well (yield is 99%) when the inorganic base K₂CO₃ was used. By comparison, NaOH, a stronger inorganic base, was less effective for the reaction (entry 5). As K₂CO₃ was the most efficient base for the present catalytic system, it was chosen for subsequent investigations. Further experiments showed that when the temperature increased from 60 to 70 °C, the yield of product increased from 70 to 99% (entry 1-2). On the other hand, when the temperature was 80 °C, the yield of product did not increase (entry 3). Therefore, the optimized reaction conditions are: 70 °C, water, and K₂CO₃.

With the optimized reaction conditions in hand, the scope of the Fe_3O_4 -L-dopa-Pd⁰ catalyzed Suzuki reactions was investigated by employing various substituted aryl halides to react with



Fig. 5 Room temperature magnetization curves of (a) Fe_3O_4-L -dopa and (b) Fe_3O_4-L -dopa-Pd⁰.

Table 1 Optimization of the reaction conditions^a

) +	B(OH)2	Fe ₃ O ₄ /L-Dopa/Pd ⁰ base, T/ [°] C, Water	•	\rightarrow
Entry	Base	Solvent	Time	$T/^{\circ}\mathrm{C}$	$\operatorname{Yield}^{b}(\%)$
1	K ₂ CO ₃	Water	50 min	60	70
2	K_2CO_3	Water	50 min	70	99
3	K_2CO_3	Water	50 min	80	98
4	NaOAc	Water	50 min	70	20
5	NaOH	Water	50 min	70	87
6	КОН	Water	50 min	70	60
7	K_3PO_4	Water	50 min	70	76

^{*a*} The reaction was carried out with 0.5 mmol of iodobenzene, 0.7 mmol of phenylboronic acids, 1 mmol of K_2CO_3 , 1 mol% of catalyst and water (5 mL). ^{*b*} Determined by GC or GC-MS.

arylboronic acid, and the results are shown in Table 1. With iodobenzene and 4-iodoacetophenone as the reactants, the reaction finished within fifty minutes, the yields of the corresponding coupling products were 99% and 97% (Table 2 entry 1 and 3). However, when the 2-iodoaniline reacted with phenylboronic acids, the reaction time must be extended to 2 h, and the yield was 96%. The substituted bromobenzenes, such as 4-NO₂, 4-COCH₃ also afforded satisfactory yields (90–99%) react with phenylboronic acids or 4-methylphenylboronic acid (Table 2 entry 10–13) within a little time. Comparing the reactions of bromobenzenes with strong electron-withdrawing, aryl

Table 2Suzuki coupling reaction of various aryl halide with arylbor-
onic acids in the presence of the Fe_3O_4/L -Dopa/Pd⁰ catalyst^a

$ \begin{array}{c} & & \\ & & $							
Entry	R ₁	Х	R_2	Т	$\operatorname{Yield}^{b}(\%)$		
1	Н	Ι	Н	50 min	99		
2	o-NH ₂	Ι	Н	2 h	96		
3	4-COCH ₃	Ι	Н	15 min	97		
4	Н	Br	Н	9 h	97		
5	$2-NH_2$	Br	Н	9 h	60		
6	$4-CH_3$	Br	Н	9 h	90		
7	m-CH ₃	Br	Н	9 h	85		
8	$4-OCH_3$	Br	Н	9 h	88		
9	o-NO ₂	Br	Н	9 h	51		
9 ^c	$o-NO_2$	Br	Н	9 h	98		
10	4-COCH ₃	Br	Н	60 min	99		
11	4-COCH ₃	Br	CH_3	75 min	98		
12	$4-NO_2$	Br	Н	60 min	94		
13	$4-NO_2$	Br	CH_3	75 min	90		
14	-H	Cl	Н	20 h	77		

^{*a*} The reaction was carried out with 0.5 mmol of arylhalides, 0.7 mmol of phenylboronic acids or 4-methylphenylboronic acid, 1 mmol of K₂CO₃, 1 mol% of catalyst and water (5 mL). ^{*b*} Determined by GC or GC-MS and ¹H NMR. ^{*c*} TBAB (1 mmol).

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bromides bearing strong electron donating groups, such as 4-CH₃, 4-OCH₃, needed a relatively longer time to obtain a moderate yield (Table 2 entry 4, 6 and 8). The yield was a little lower (60%) when 4-bromoaniline was used as the substrate (entry 5). On the other hand, in the same time, 4-bromotoluene (90%) afforded a higher yield than 3-bromotoluene (85%). Interestingly, the Suzuki reaction of 1-bromo-2-nitrobenzene with phenylboronic acid proceeded poorly under the same conditions, and only 51% yield was obtained (entry 9). However, when TBAB was added to the reaction mixture, a satisfactory yield of 98% was achieved (entry 9^c). It is noteworthy that chlorobenzene could also react with phenylboronic acid by the action of 1 mol% Fe₃O₄-L-dopa-Pd⁰ to afford the coupling product in 77% yield (entry 14), although a longer time (20 h) was required.

Encouraged by the exciting results with the Suzuki reactions, the newly prepared catalyst was applied to the Heck reaction next. For this purpose, 1.5 mol% of Fe₃O₄/L-Dopa/Pd⁰ was used for the reaction of aryl halides and styrene or acrylic acid in water. Table 3 lists the results of the Heck reaction. As shown in Table 3, the Heck reaction of various aryl iodides with hydrophilic acrylic acid or styrene proceeded well in water at 90 °C, resulting in the corresponding coupling Heck products in yields of 83-99% (entry 1-8). The results show that electronwithdrawing substituents enhance the coupling product formation, while electron-donating groups have a negative influence on the reaction process. Bromobenzene did not react with hydrophobic styrene in H₂O, but when a solvent of NMP was used, the reaction took place, and a satisfactory yield of 93% was achieved in 8 h (entry 9 and 9^c). This protocol is also applicable to substituted bromobenzenes, such as 4-CH₃OC, 4-CH₃ and 4-CH₃O, react with acrylic acid (entry 10-12). The

Table 3 Heck coupling reaction of various aryl halide with styrene or acrylic acid in the presence of the Fe_3O_4/L - $Dopa/Pd^0$ catalyst^a



Entry	R ₁	Х	R_2	Time (h)	Yield ^b (%
4			nh	10	07
1	н	1	Pn	12	97
2	$4-CH_3CO$	Ι	Ph	10	>99
3	$4-CH_3$	Ι	Ph	12	85
4	$4-CH_3O$	Ι	Ph	12	83
5	Н	Ι	COOH	12	98
6	4-CH ₃ CO	Ι	COOH	12	99
7	$4-CH_3$	Ι	COOH	12	92
8	$4-CH_3O$	Ι	COOH	12	89
9	4-CH ₃ CO	Br	Ph	12	Trace
9 ^c	4-CH ₃ CO	Br	Ph	8	93
10	4-CH ₃ CO	Br	COOH	12	95
11	$4-CH_3$	Br	COOH	12	85
12	4-CH ₃ O	Br	COOH	12	82

 a Reaction conditions: aryl halide (0.5 mmol), vinyl substrates (1 mmol), Fe₃O₄/L-Dopa/Pd⁰ (1.5 mol%), K₂CO₃ (3 mmol), Water (5 mL) and argon atmosphere. b Determined by GC or GC-MS and ¹H NMR. c Reaction in NMP.



Fig. 6 Recycle efficiency of Fe_3O_4/L -Dopa/Pd⁰ in Suzuki coupling reaction between iodobenzene and phenylboronic acid.

results show that substituted aryl bromides can be easily converted to the corresponding coupling products in high yields and it also conforms to the law of electron-withdrawing substituents enhance the coupling product formation, while electron-donating groups have a negative influence on the reaction process.

The reaction was carried out with 0.5 mmol of iodobenzene, 0.7 mmol of phenylboronic acids, 1 mmol of K₂CO₃, 1 mol% of catalyst and water (5 mL). The recyclability of Fe₃O₄-L-dopa/Pd⁰ 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 Fig. 6, the catalyst was recycled in the Suzuki coupling of iodobenzene with phenylboronic acids. It is worth noting that the catalyst gave a complete conversion of iodobenzene, and over 93% yield was achieved within 50 min 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 Fe₃O₄-L-dopa/Pd⁰. The weight percentage of Pd in the HMMS-SH-Pd, as determined by atomic absorption spectroscopic (AAS) analysis, was 5.31 wt% before and 4.73% after five cycles.

4 Conclusion

In summary, a nanosized water-dispersible heterogeneous Pd catalyst has been developed by immobilizing Pd^0 onto the Fe_3O_4 -L-dopo magnetic nanoparticles. In this system, the magnetite nanomaterials play two important roles: one is in increasing the stability and water-dispersible of the nanoparticles because of their surface amino and carboxyl groups, and the other in supporting Pd by means of coordination. On the basis of the above-mentioned reasons, the catalyst revealed high efficiency and high stability under the reaction conditions and during recycling stages. The newly prepared catalyst was successfully applied to Suzuki and Heck reactions in water with the fascinating nature of both a high activity and durability.

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