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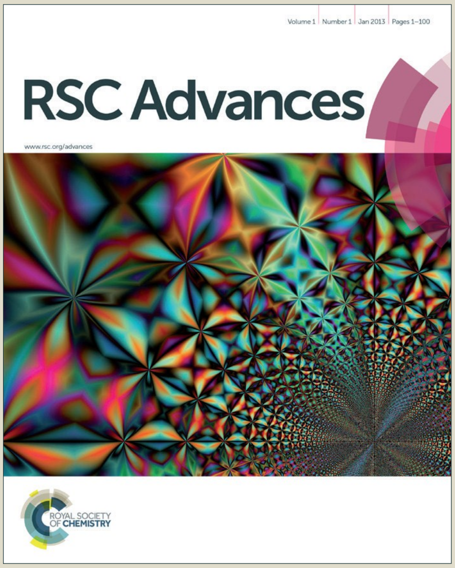

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DOI: 10.1039/C6RA11674D

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

A facile synthesis of solvent-dispersible magnetically recoverable Pd^0 catalyst for C-C coupling reaction

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Solvent-dispersible magnetite particles (Fe_3O_4) functionalized with dopamine (DA) and N,N-dimethylglycine (DMG) were successfully prepared by a one-pot synthesis method with environment-friendly materials. Then Pd^0 nanoparticles were anchored onto the functionalized Fe_3O_4. The prepared materials were thoroughly characterized by TEM, XRD, XPS, FT-IR and VSM. The resultant magnetically recoverable Pd catalyst exhibited excellent catalytic activity for the C-C coupling reaction. In addition, this catalyst revealed high efficiency and stability during recycling stages. This work should be useful for the development and application of magnetically recoverable Pd catalyst on the basis of green chemistry principles.

Introduction

Since the 1970s, a series of methodologies have been well developed to construct C–C bonds through metal-catalyzed cross-coupling, including the Suzuki coupling, Heck coupling, Kumada coupling, Stille coupling, and so on[1]. Metal nanoparticles (MNPs) have attracted scientists due to their unique physical and chemical properties, such as high surface area, high reactivity, and enormous specific surface area. MNPs have been widely applied in many fields, such as drug delivery, photonics, catalysis, energy storage, and conversion devices[1−4]. Over the past few years, MNPs, especially supported magnetic metal nanoparticles (S-MMNPs), have emerged as a new class of nanocatalyst. Recently, the noble metals supported on magnetic nanoparticles have emerged as promising catalysts because of the combined advantages of high surface area-to-volume ratio and better magnetic recovery. For example, Zhu et al. reported[5] Pd immobilized onto magnetic nanoparticles that showed good yields and reusability for Suzuki and Heck reaction. S. Jafar Hoseini et al used the Pd/Fe_3O_4/r-GO nanohybrid as non-phosphine catalyst for Suzuki-Miyaura reaction in water[6]. Some palladium magnetic -nanoparticles (NPs) as catalysts for carbon-carbon coupling reactions such as the Suzuki reaction have been reported [7-9] . Previous studies[10-12] of our group have done a lot in this regard in those years. Importantly, these catalysts can be easily separated from the reaction system using an external magnet without filtration. Furthermore, S-MMNPs catalysts showed high catalytic activities and chemical stabilities in environment friendly solvents.

Homogeneous catalysis for C-C bond coupling in organic synthesis has evolved over the years, which has many advantages, but also has several disadvantages: difficult separation and recovery, high cost etc. Palladium-catalyzed[13-17] Suzuki and Heck cross-coupling reactions constitute important methods for C-C bond formation in organic synthesis. Currently, these C-C coupling reactions are performed mainly in organic solvents with homogeneous palladium salts and complexes, which cause concerns of high costs and environmental issues extensively. Although these homogeneous palladium catalyst nanoparticles have shown outstanding catalytic properties, it remains a major challenge to solve several disadvantages such as cost-effectiveness and environment-friendly . Therefore, it is highly desirable to develop reusable heterogeneous palladium catalysts which can be easily used from the reaction systems Immobilization of Pd NPs on inorganic supports such as silica, alumina, or mesoporous materials, as well as carbon, has been known to produce active catalysts for C-C coupling reactions[18-20]. Furthermore, taking into account the perspective of green chemistry, it is preferable to use water to replace toxic organic solvents as the reaction medium. But many developed heterogeneous catalytic systems get the drawbacks of low catalytic activity and poor dispersibility in water. How to address these issues is now a major problem to chemists studying in this region.

It should be mentioned that N, N-dimethylglycine (DMG) is a cheap, efficient and general catalytic ligand for the coupling reaction. DMG has a Chinese name: vitamin B16, which has been applied in many aspects, such as pharmaceutical intermediates, medicine, food and other industries[18]. So it is an environmentally friendly chemical precursor, and it has a useful application for a ligand in some catalytic coupling reaction[21-22]. Dopamine is an important neurotransmitter that plays a number of important roles in the human brain and body，also it is widely used to prepare on various substrates as an eco-friendly surface modification substance[24]. Herein, a magnetically separable heterogeneous Pd^0/Fe_3O_4-DA/DMG catalyst was synthesized by anchoring palladium onto amine-functionalized magnetite particles (Fe_3O_4-DA/DMG), which was prepared by a facile one-pot solvothermal method. This recyclable heterogeneous catalyst was used to catalyze C-C coupling reaction in an aqueous solvent, including Suzuki, Heck and Kumada reaction.

Experimental

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Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, >99%) anhydrous sodium acetate, ethylene glycol, 1, 6-hexanediamine and dopamine hydrochloride，ethanol，N,N-dimethylglycine，Palladium chloride, and Sodium borohydride were purchased from Sinopharm Chemical Reagent Co. Ltd. Various reaction reagents were purchased from Alfa Aesar. All reagents were of analytical grade and used without further purification. Deionized water was used in all of the experiments.

Synthesis of Fe_3O_4-DA/DMG particles

Magnetite particles were prepared by one-pot hydrothermal method. In a typical synthesis, 1.35g $FeCl_3.6H_2O$, 2.96g anhydrous sodium acetate and 0.085 g dopamine hydrochloride were dissolved in 45 mL ethylene glycol. Then 1.0 g DMG was added under continuous stirring. The mixture was stirred vigorously for 30 min at 50℃ and then sealed in a Teflon-lined autoclave (50 mL capacity) .The autoclave was heated to 200℃ and maintained at 200℃ for 10 h, and allowed to cool to room temperature. The black products were thoroughly washed several times with deionized water and ethanol, then dried at 60℃ for 12 h.

Synthesis of Pd^0/Fe_3O_4-DA/DMG catalyst

Fe_3O_4-DA/DMG (0.15 g) was dispersed in a 50 mL ethanol solution under ultrasonication for 1 h. The formed black suspension was ultrasonically mixed with 1.3 mM of a $PdCl_2$ solution for 1 h. Then an excess 0.01M $NaBH_4$ aqueous solution was slowly dropped into the above system with vigorous stirring, and the reaction proceeded at room temperature overnight under stirring. The product was collected, washed with water and ethanol, and finally dried in vacuum. The weight percentage of Pd in Pd^0/Fe_3O_4-DA/DMG, as determined by atomic absorption spectroscopic (AAS) analysis, was 5.6wt%.

Characterization of Pd^0/Fe_3O_4-DA/DMG catalyst

These magnetic micro-materials were characterized by transmission electron microscopy (TEM), inductively coupled plasma (ICP), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform-infrared (FT-IR) spectroscopy and vibrating sample magnetometry (VSM). XRD measurements were performed on a Rigaku D/max-2400 diffractometer using Cu–Kαradiation as the X-ray source in the 2θ range of 10–90°. The size and morphology of the magnetic microparticles 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. Magnetic measurements of Pd^0/Fe_3O_4-DA/DMG were obtained by using a Quantum Design VSM at room temperature in an applied magnetic field sweeping from −8 to 8 kOe. XPS was recorded on a PHI-5702 instrument and the C 1s line at 284.8 eV was used as the binding energy reference. The Pd content of the catalyst was measured by ICP on an IRIS Advantage analyzer to found 5.6 wt% Pd of the catalyst.

Catalytic performance

Pd^0/Fe_3O_4-DA/DMG catalyst for Suzuki reaction

A mixture of aryl halide (1 mmol), arylboronic acid (1.5 mmol), Pd^0/Fe_3O_4-DA/DMG (for aryl bromide 1 mol%, for aryl chloride 2 mol%), and K_2CO_3 (2 mmol) was stirred in H_2O at suitable temperature for indicated time in air. After completion of the reaction, the mixture was cooled to room temperature, separated by magnetic decantation, and extracted by Et_2O (10 mL) for three times. And then the organic phase was combined and evaporated under reduced pressure. Finally, the reaction yields were obtained by GC. The yields of the concrete calculation method is Gas chromatography area normalization method.

Pd^0/Fe_3O_4-DA/DMG catalyst for Heck reaction

0.5 mmol of the aryl halides, 0.6 mmol of styrene, and 0.6 mmol of K_2CO_3 were taken into 5 mL of H_2O. and 1 mol% palladium catalyst was stirred in the reaction mixture and refluxed at 90℃. After completion of the reaction, the mixture was cooled to room temperature, separated by magnetic decantation, and extracted by Et_2O (10 mL) for three times. And then the organic phase was combined and evaporated under reduced pressure. Finally, the reaction yields were obtained by GC. The yields of the concrete calculation method is area normalization method.

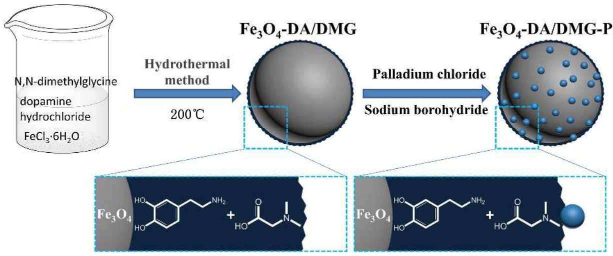
Pd^0/Fe_3O_4-DA/DMG catalyst for Kumada coupling reaction

All manipulations were carried out under an inert N_2 atmosphere，a mixture of iodobenzene (1 mmol) and 1 mol% Pd^0/Fe_3O_4-DA/DMG in freshly distilled anhydrous THF (5 mL) under N_2 atmosphere was prepared. Then a solution of BuMgCl (1 mL, 25 wt% in THF, 1.84 mmol) was added dropwise at room temperature (20 ℃) with gentle magnetic stirring. After completion of the reaction, the mixture was cooled to room temperature, separated by magnetic decantation, and extracted by Et_2O (10 mL) for three times. And then the organic phase was combined and evaporated under reduced pressure. Finally, the reaction yields were obtained by GC. The yields of the concrete calculation method is area normalization method.

Results and Discussion

Catalyst preparation

The process for the preparation of the catalyst Pd^0/Fe_3O_4-DA/DMG is schematically described in Scheme 1. First, the functionalized magnetite particles were synthesized by a facile solvothermal synthetic strategy[11]. The purpose of this operation was to introduce the DA and DMG onto the surface of Fe_3O_4 particles. Second, Pd^0 nanoparticles were immobilized on DA/DMG-functionalized magnetic particles through the reduction of $PdCl_2$ by $NaBH_4$. We were pleased to acquire a simply green efficiently method to prepare magnetically recoverable nanocatalyst.



Scheme 1. Schematic formation of Fe_3O_4-DA-DMG/Pd^0 nanoparticles.

Catalyst characterization

The TEM images of Fe_3O_4, Fe_3O_4-DA/DMG and Pd^0/Fe_3O_4-DA/DMG catalyst are presented in Fig. 1. The

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obtained Fe_3O_4-DA/DMG microparticles have an average diameter of 200±5 nm (Fig. 1b). As shown in Fig. 1b, a continuous layer can be observed on the surface. Meanwhile, the resulting Fe_3O_4-DA/DMG composites have good dispersibility and spherical morphology(Fig. 1a,b). After the loading of Pd^0 (Fig. 1c), Pd nanoparticles supported on Pd^0/Fe_3O_4-DA/DMG disperse well and have a uniform particle size. In order to give a powerful evidence for the existence of Pd^0, EDX spectra of Pd^0/Fe_3O_4-DA/DMG is presented in Fig. 2. The peaks corresponding to Pd are clearly found in EDX spectra of Pd^0/Fe_3O_4-DA/DMG.

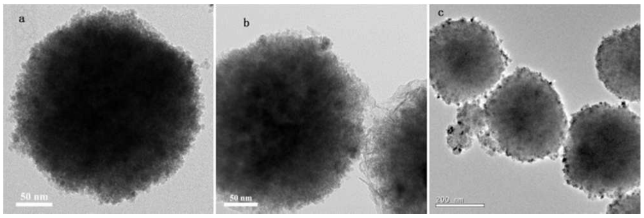

Figure 1. TEM images of (a) Fe_3O_4, (b) Fe_3O_4-DA–DMG, and (c) Pd^0/Fe_3O_4-DA/DMG catalyst.

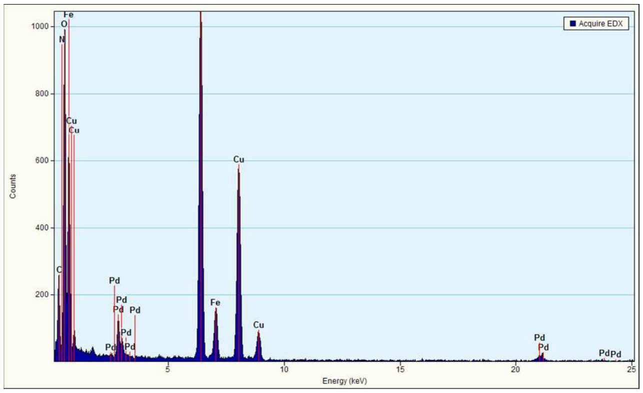

Figure 2. EDX spectra of Pd^0/Fe_3O_4-DA/DMG.

The FT-IR spectra of (a) Fe_3O_4 , (b) Fe_3O_4-DA -DMG and (c) Pd^0 Fe_3O_4-DA –DMG are shown in Figure 3. In Figure 3, the band at 585 cm^{-1} can be attributed to Fe-O stretching vibration. In curve b and c, the absorption bands at 1617, 1469, and 878 cm^{-1} associated with amine and 1635, 1416 cm^{-1} associated with carboxylate, indicating that plenty of L-dopa molecules are immobilized on the surface of the nanoparticles. The bands at 1625 cm^{-1}, 1570cm^{-1}， 1436 cm^{-1} can be attributed to the C=O stretching vibration. The band at 1089 cm^{-1} and 1092 cm^{-1} in the curve b and c can be attributed to C-N stretching vibration. All the characteristic bands in the FT-IR spectrum (Fig. 3b) demonstrate that the Fe_3O_4-DA -DMG magnetic microgel has been successfully prepared.

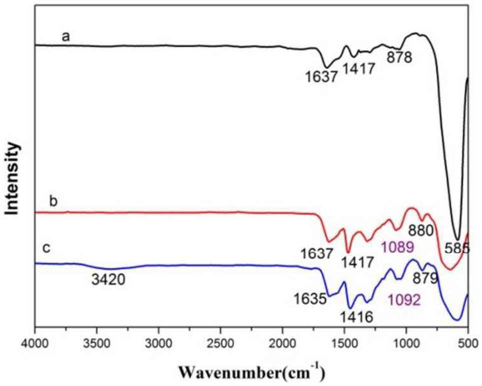

Figure 3. FT-IR spectra of (a) Fe_3O_4 (b) Fe_3O_4-DA –DMG (c) Pd^0 Fe_3O_4-DA –DMG

The XRD patterns of the Fe_3O_4-DA/DMG and Pd^0/Fe_3O_4-DA/DMG are presented in Fig 4. The characteristic diffraction peaks in the samples at 2θ of 30.2º, 35.5º, 43.3º, 53.8º, 57.2º, and 62.8º are corresponded to the diffraction of (220), (311), (400), (422), (511), and (440) of the Fe_3O_4. All the diffraction peaks match with the magnetic cubic structure of Fe_3O_4 (JCPDS 65-3107) [19]. Figure 4b 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 (111), (200), (220) species. The results from XRD imply that the Pd nanoparticles have been successfully immobilized onto the surface of the magnetic particles.

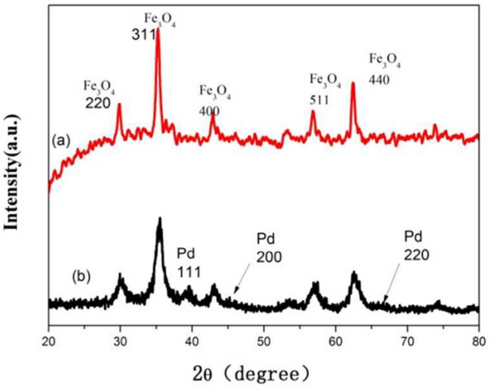

Figure 4 XRD patterns of (a) Fe_3O_4-DA/DMG and (b) Pd^0/Fe_3O_4-DA/DMG

XPS is performed to investigate the chemical state of the surface of the obtained Pd^0/Fe_3O_4-DA/DMG catalyst (Fig. 5). The XPS elemental survey scan of the surface of the Pd^0/Fe_3O_4-DA/DMG catalyst reveals the presence of the O, Fe, Pd, N, and C elements in the samples. As shown in Fig. 5b, the spectra of the Pd 3d region of the two catalysts confirm the presence of Pd^0 with the peak binding energy of 338.65 and 333.45 ev, which are assigned to Pd $3d_{3/2}$ and Pd $3d_{5/2}$, respectively. It is powerful and direct evidence confirming the existence of Pd (0) in Pd^0/Fe_3O_4-DA/DMG catalyst.

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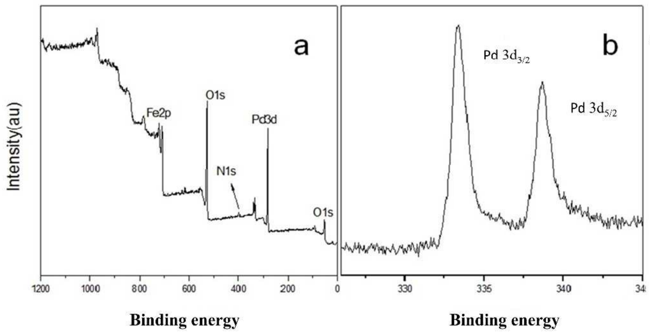


Figure 5. XPS spectra of (a) Pd^0/Fe_3O_4-DA/DMG; and (b) show Pd $3d_{3/2}$, Pd $3d_{5/2}$ binding energies of Pd^0/Fe_3O_4-DA/DMG.

The magnetic measurements were carried out by VSM at room temperature. The magnetization curves measured for Fe_3O_4-DA/DMG and Pd^0/Fe_3O_4-DA/DMG are presented in Fig 6. The magnetic saturation values of Fe_3O_4-DA/DMG and Pd^0/Fe_3O_4-DA/DMG are 31.8 and 19.6 emu/g, respectively. The decrease in the saturation magnetization is due to the presence of the DA-DMG and Pd nanoparticles on the Fe_3O_4 surface. Moreover, the inset image shows the separation–redispersion process of the Pd^0/Fe_3O_4-DA/DMG catalyst. Therefore, the above mentioned results indicated an easy and efficient way to separate and recycle the Pd^0/Fe_3O_4-DA/DMG catalyst from the solution by an external magnetic force.

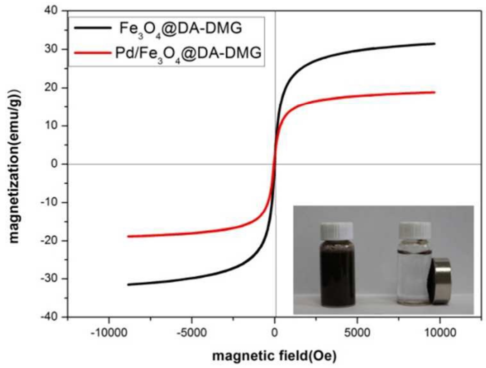


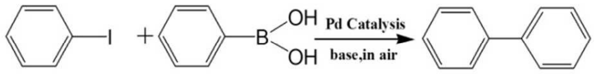
Figure 6 .VSM spectra of (a) Fe_3O_4-DA/DMG and (b) Pd^0/Fe_3O_4-DA/DMG

Catalytic Activity

Catalyst testing for the Suzuki coupling reaction

C-C coupling reactions such as the Suzuki and Heck coupling reactions play an important role in many types of organic syntheses, as well as in the chemical, pharmaceutical, and agricultural industries[26-27]. Initially, the catalytic activity of Pd^0/Fe_3O_4-DA/DMG was tested for the Suzuki cross coupling reaction of a variety of iodobenzene with phenylboronic acid to their corresponding products. Firstly, the reaction of iodoanisole with phenylboronic acid was used as a model reaction for the screening of optimum reaction conditions, and the results were summarized in Table 1. It was known that the Suzuki reaction was largely affected by the type of alkaline and the amount of catalyst used[28-34]. To explore the optimal reaction conditions, a series of reactions was performed using several time durations, solvents, bases, and temperatures to obtain the best possible combination. According to the evaluated results: K_2CO_3 is found to be the most effective base[29], the best reaction temperature is 80 ℃, H_2O is the best solvent.

Table 1. Optimization of conditions for the Suzuki reaction of iodobenzene with phenylboronic acid[a]



Entry	Solvent	base	temp	time	Yield(%)[b]
1	DMF	K_2CO_3	80℃	30min	69.1
2	Toluene	K_2CO_3	80℃	30min	54.3
3	EtOH	K_2CO_3	80℃	30min	66.9
4	H_2O	K_2CO_3	80℃	30min	99.9
5	H_2O	K_2CO_3	70℃	30min	95.3
6	H_2O	K_2CO_3	60℃	30min	61.2
7	H_2O	$NaHCO_3$	80℃	30min	80.3
8	H_2O	NaOAc	80℃	30min	17.4
9	H_2O	KOH	80℃	30min	55.7
10	H_2O	No base	80℃	30min	Trace

a Reaction conditions: iodobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), H2O (5.0 mL), in air. Pd catalyst (1 mol%) b Determined by using GC.

With the optimized reaction conditions in hand, the scope of the Pd^0/Fe_3O_4-DA/DMG-catalyzed Suzuki reactions was investigated employing various substituted aryl halides to react with various substituted arylboronic acid. The results are summarized in Table 2. The most relevant results in terms of conversion were obtained by using 4-substituted bromoarenes bearing electron-withdrawing groups (entries 4, 7, Table 2), but for the substrates bearing electron-donating groups the yield dropped significantly, as expected[28]. The scope of the reaction was expanded to other challenging chloride derivatives (entries 19 and 20, Table 1). Unfortunately, they showed much less reactivity than the bromide counterparts in good accord with the literature[35].The catalyst kept similar conversion after 6 successive runs. The above mentioned results revealed that the Pd^0/Fe_3O_4-DA/DMG catalyst exhibited excellent properties for the Suzuki cross coupling reactions.

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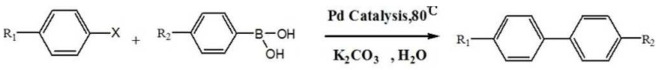
Table 2. Suzuki cross coupling of aryl halides with aryl boronic acids using the Fe_3O_4-DA-DMG/Pd^0 nanocatalyst in water[a]



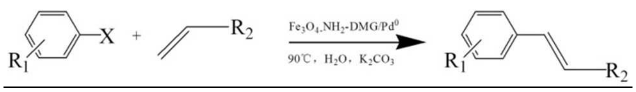
entry	R_1	X	R_2	T	Yield(%)[b]
1	H	I	H	30min	99.9
2	H	I	CH_3	60min	91.2
3	4-CH_3	I	CH_3	2h	90.1
4	4-$COCH_3$	I	H	2h	97.5
5	4-CH_3	I	H	2h	96.3
6	4-OH	I	H	2h	95.1
7	4-NO_2	I	H	2h	93.9
8	4-NO_2	I	CH_3	2h	94.0
9	4-CN	I	H	2h	92.8
10	4-$NHCOCH_3$	I	H	2h	96.2
11	4-NO_2	Br	H	9h	80.8
12	H	Br	H	12h	97.4
13	4-$COCH_3$	Br	H	60min	99.2
14	4-CH_3	Br	CH_3	90min	91.7
15	4-OCH_3	Br	Cl	60min	91.1
16	4- NO_2	Br	CH_3	90min	94.2
17	H	Br	Cl	90min	80.1
18	H	Cl	H	24h	73.6
19	H	Cl	OCH_3	24h	51.1

a Reaction condition: aryl halide (0.5 mmol), aryl boronic acid (0.75 mmol), K_2CO_3 (1.0 mmol), Fe_3O_4-DA-DMG/Pd^0 nanocatalyst (1mol%), and 80 C, in air. b. Yield was determined by GC analysis.

Catalyst testing for the Heck coupling reaction

Encouraged by the exciting results with the **S**uzuki reactions, the newly environment-friendly catalyst was applied to the Heck reaction subsequently. With the intention of catalytic properties, 1.5 mol% of Pd^0/Fe_3O_4-DA/DMG was used to the reaction of aryl halides and styrene in water. Table 3 displays the results of the Heck reaction. As shown in Table 3, the Heck reaction of various aryl iodides with styrene proceeded well in water at 90 °C, resulting in the corresponding coupling Heck products in yields of 91%-99%. The reaction consequence shows that electron-withdrawing substituents enhance the coupling product formation, while electron-donating groups have a negative influence on the reaction process.

Table 3. Heck reactions using the Fe_3O_4-DA-DMG/Pd^0 nanocatalyst[a]



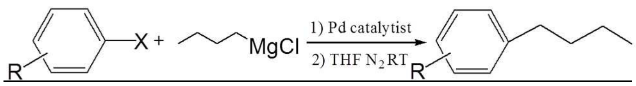
Entry	R_1	X	R_2	T	Yield (%) [b]
1	H	I	Ph	14h	99.9
2	4-CH_3	I	Ph	14h	95.8
3	4- OCH_3	I	Ph	14h	98.9
4	4-$COCH_3$	I	Ph	14h	99.9
5	H	Br	Ph	14h	94.2
6	4-CH_3	Br	Ph	14h	91.0
7	4-OCH_3	Br	Ph	14h	98.0
8	4- $COCH_3$	Br	Ph	14h	97.2

a. The reaction was carried out with 0.50 mmol of aryl halides, 0.6 mmol of styrene, 0.6 mmol of K_2CO_3, 1 mol% palladium catalysts with respect to the aryl halides and 5 mL of H_2O under an N_2 atmosphere. b. Yield was determined by GC analysis.

Catalyst testing for the Kumada coupling reaction

Following the preferably catalytic properties, we carried out similar Kumada cross-coupling reactions on iodobenzene and butylmagnesium. In organic chemistry, the Kumada coupling is a useful cross coupling reaction for generating C-C bonds by the reaction of a Grignard reagent and an organic halide. As shown in Table 4, the reaction performed very well and the coupled product was obtained in an excellent yield. The catalyst was further recycled and reused again.

Table 4. Schematic representation of Kumada cross-coupling reaction between aryl halides and butylmagnesium chloride at room temperature (20 ℃) in presence of Pd^0/ Fe_3O_4@DA-DMG as catalyst.



Entry	R	X	t	Yield (%)[b]
1	H	I	30min	92.3
2	4-CH_3	I	2h	90.1
3	4-$COCH_3$	I	2h	93.5
4	H	Br	12h	94.1
5	4-CN	Br	2h	85.1
6	4-CH_3	Br	2h	89.7

a. ArX (1 mmol), BuMgCl (1 mL, 1.84 mmol), Pd^0/Fe_3O_4-DA/DMG (1 mol%，), THF (5 mL) stirring at room temperature (20℃) under N_2.b. Yield was determined by GC analysis.

Reusability of the catalyst Pd^0/Fe_3O_4-DA/DMG

Finally, the durability is another important factor for catalysts when involved in practical applications. Herein, as-synthesized Pd^0/Fe_3O_4-DA/DMG catalyst has been tested for the reaction of iodobenzene with phenylboronic acid employing mg of the catalyst in the presence of K_2CO_3/H_2O at 80℃. The catalyst was separated by an external magnet, washed with ethanol, water and dried under vacuum. The resulting solid catalyst was used directly for the next run. The yield of the desired product dropped from 93% to 86% after six runs, which shows a negligible loss in activity of the catalyst (Table 5). Inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements

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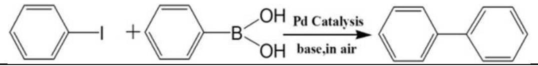
indicate that the Pd content in the recycled catalysts after six reaction cycles is about 2.30wt%, close to that 2.61 wt % of the as-made Fe_3O_4-DA-DMG/Pd^0sample.

Table 5. Recycling of Fe_3O_4-DA-DMG/Pd^0 for the reaction of iodotoluene with phenylboronic acid [a]



No. of runs	1	2	3	4	5	6
Yield (%)[b]	93	93	92	90	89	87

a Reaction conditions: iodobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), H_2O (5.0 mL), K_2CO_3 (1.0 mmol) in air.

b Determined by using GC.

Conclusion

In this study, we have developed an efficient method to generate highly active Pd^0/Fe_3O_4-DA/DMG composite by a simple method with environment-friendly materials. This new compound was characterized by TEM, EDX, FT-IR, VSM, and XRD analysis. Pd_0/Fe_3O_4-DA/DMG shows good magnetic properties and solvent-dispersiblity, and has been successfully applied as a catalyst for Suzuki, Heck and Kumada crossing reactions of structurally different substrates in water and THF. The Pd^0/Fe_3O_4-DA/DMG catalyst exhibited excellent catalytic activity toward the Suzuki, Heck and Kumada cross coupling reaction with a high yield in water. This catalyst offers a number of advantages including high reactivity, mild reaction conditions, and short reaction times in an environmentally benign solvent system. Furthermore, the magnetic properties imparted by the Fe_3O_4 component of the catalyst enables the catalyst to be easily isolated and recycled, thus increases the economic value of the catalyst.

Acknowledgements

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

Notes and references

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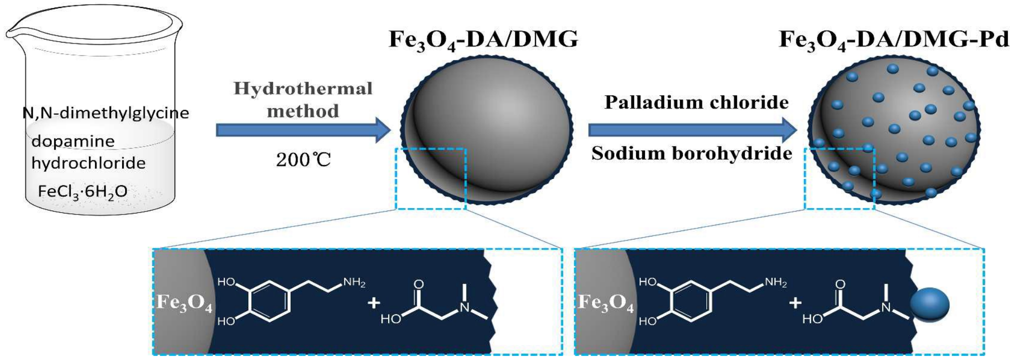

The Pd^0/Fe_3O_4-DA/DMG catalyst exhibited excellent catalytic activity toward the Suzuki, Heck and Kumada cross coupling reaction with a high yield . Especially its efficient catalyst for Suzuki and Heck coupling in water.