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Nanosized palladium supported on diethylenetriamine modified superparamagnetic polymer composite microspheres: Synthesis, characterization and application as catalysts for the Suzuki reactions

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ABSTRACT

Superparamagnetic polymer composite microspheres Fe_3O_4/P(GMA-AA-MMA) prepared by an emulsifier free emulsion polymerization using DPE as free radical control agent were used to support palladium nanoparticles. The magnetic catalyst can provide excellent reactivity in the Suzuki coupling reactions of aryl halides with phenylboronic acids under mild condition (at 80 °C) in EtOH/H_2O (1:1) mixture. Furthermore, the novel catalyst can be conveniently recovered by an external magnet field and reused at least five times without significant loss of its catalytic activity.

1. Introduction

Recently magnetic nanoparticles (MNPS) have been widely used as efficient support materials in the field of Pd-catalyzed Suzuki cross-coupling reaction, due to their superparamagnetic property and nano-scale structure [1–23]. So far, many reports have appeared on Suzuki coupling catalyzed by magnetic palladium catalysts, which were loaded on Fe_3O_4 or modified Fe_3O_4 with various small molecules [3–9], modified $NiFe_2O_4$ with dopamine [10], modified $CoFe_2O_4$ with N-[3-(trimethoxysilyl) propyl] ethylenediamine [11,12], Fe_2O_3 [13–15], γ-Fe_2O_3/Polymer [16], modified Fe_3O_4/SiO_2 with various ligands [17–21] and Fe_3O_4/Polymer [22,23]. However, some magnetic catalysts still showed lower reactivity than homogeneous ones, due to the leaching of palladium species from the supports and agglomeration of palladium particles on the surface of the supports. Thus, it is still urgent to develop highly efficient reusable magnetic catalysts for the Suzuki reactions.

Recently, superparamagnetic polymer composite microspheres prepared by radical polymerization technology are now emerging as new promising support materials for palladium immobilization in the field of catalysis [16,22–24], due to the following beneficial features. Firstly, as a result of superparamagnetic character, palladium catalyst supported by superparamagnetic polymer composite microspheres can be separated and recovered from the reaction medium with an external magnet, meanwhile avoiding the conventional filtration step. Secondly, superparamagnetic polymer composite microspheres are usually made up of a magnetic iron oxide core encapsulated by a layer of polymer shell, which can efficiently stabilize iron oxide nanoparticles. Furthermore, polymer shell usually offers various kinds of functional groups such as amino, thiol, hydroxyl and epoxy groups, which can also work perfectly as coordinating sites for palladium metals and prevent the palladium species from leaching and agglomerating. Despite their mentioned advantages, to the best of our knowledge, only a few papers have reported superparamagnetic polymer composite microspheres were employed as palladium catalyst supports for Suzuki coupling reaction. One major reason is that the magnetic content of superparamagnetic polymer composite microspheres prepared by conventional polymerization technology is often low, which would increase the difficulty of separation the magnetic catalyst in an external magnetic field. Moreover, addition of an emulsifier to the polymerization system results in the surface of superparamagnetic polymer composite microspheres is not clean, which may decrease the catalytic activity of the supported catalyst. All these drawbacks to a large extent limited their applications

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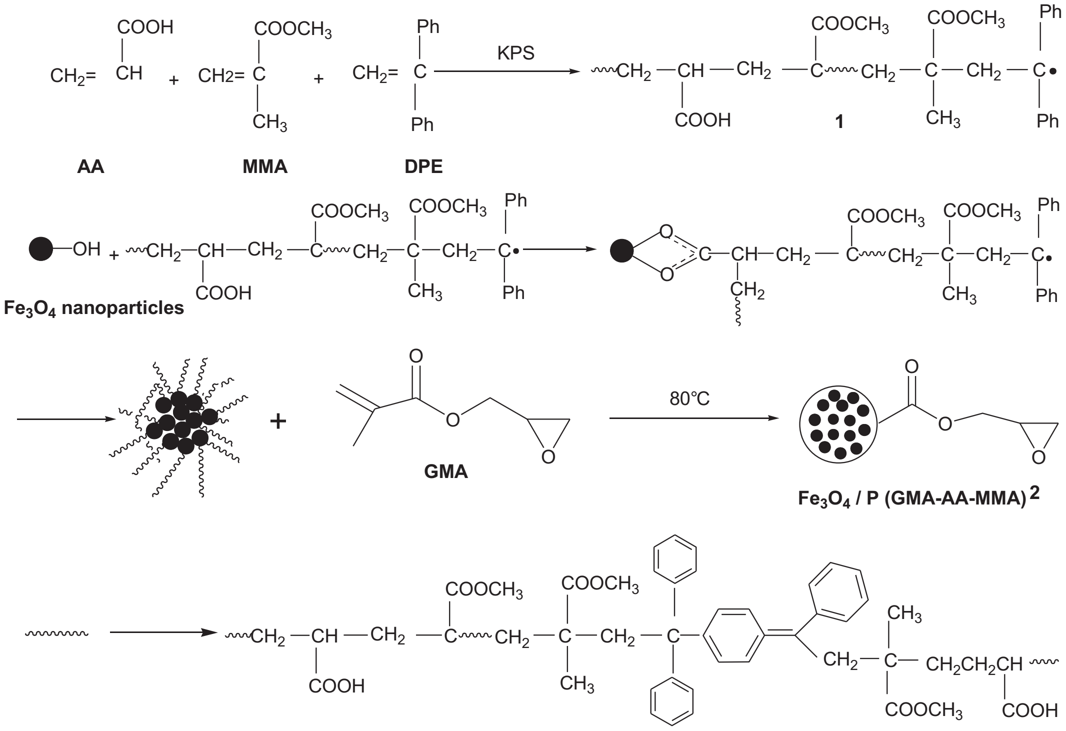


Scheme 1. Synthesis of Fe_3O_4/P(GMA-AA-MMA).

in the Pd-catalyzed Suzuki cross-coupling reaction. Therefore, it is still very emergent to develop a concise and efficient synthetic route to prepare superparamagnetic polymer composite microspheres.

In our previous work, a novel living radical polymerization technology named DPE method based on 1,1-diphenylethylene (DPE) as radical controlling agent has been applied to prepare superparamagnetic polymer composite microspheres with high magnetic content [25–27]. Generally, the DPE method includes a two-step procedure. Firstly, in the presence of DPE, a DPE-containing amphiphilic precursor polymer could be prepared, which would modify magnetic nanoparticles (Fe_3O_4). Secondly, the residual and fresh monomers would be initiated by the activated precursor polymer on the surface of magnetic nanoparticles, yielding superparamagnetic polymer composite microspheres with high magnetic content. Meanwhile, the surface of superparamagnetic polymer composite microspheres is usually clean, due to no addition of an emulsifier to the polymerization system. Thus, superparamagnetic polymer composite microspheres with high magnetic content and clean surface prepared by DPE method may be ideal supports for palladium catalyst for Suzuki reactions.

Herein, we would like to report on the application of superparamagnetic polymer composite microspheres, prepared by DPE method, as the magnetic catalyst body. Before the preparation of the magnetic catalyst, superparamagnetic polymer composite microspheres were firstly treated with diethylenetriamine. And then palladium species were bound to the surface of superparamagnetic polymer composite microspheres by means of the coordination of $-NH_2$ ligand with Pd. The magnetic catalyst can provide excellent reactivity in the coupling reactions of aryl halides with phenylboronic acids in aqueous media under mild condition (at 80 °C). Furthermore, the novel magnetic catalyst can be conveniently recovered by an external magnet field and reused at least five times without significant loss of its catalytic activity.

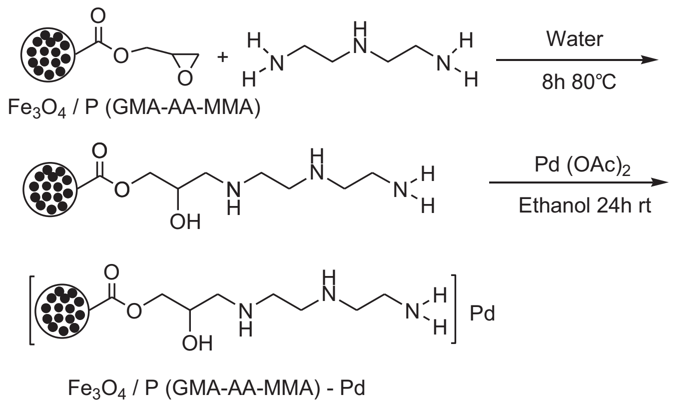
2. Experiments

2.1. Reagents and materials

$Pd(acac)_2$ (acac = acetylacetonate) was obtained from Kaida Metal Catalysis & Compounds Co. Ltd (China). $FeSO_4{\cdot}7H_2O$, $FeCl_3{\cdot}6H_2O$, MMA, GMA, AA and KBH_4 were purchased from Sinopharm Chemical Reagent Co., Ltd. Various arylboronic acids and aryl halides were obtained from J&K Chemical Company. All solvents were of analytical quality. Deionized water was used throughout the experiments.

2.2. Preparation of Fe_3O_4/P(GMA-MMA-AA) microspheres

Fe_3O_4/P(GMA-MMA-AA) microspheres were prepared by DPE method (Scheme 1) [25,26]. Typically, 0.125 g of DPE, 0.375 g of AA, 7.5 g of MMA and 75 ml water were placed in a 250 ml three-necked flask equipped with a stirrer, a condenser and a thermometer. When the mixture was heated to 80 °C, 25 g of KPS (1%, w/w in water) was added. After several minutes, 1 g Fe_3O_4 magnetic nanoparticles were dropped into the stirred mixture. Four hours later, the polymerization was ended by cooling the mixture to room temperature. Subsequently, the mixture was heated to 80 °C again and 7.5 g GMA was added to continue polymerization for 4 h. Then the mixture was cooled to room temperature and polymerization stopped. The superparamagnetic polymer composite microspheres were collected by magnetic separation and washed with acetone and deionized water several times. Finally, the separated products were dried in vacuum oven at 40 °C for 24 h to give yellow products (abbreviated as Fe_3O_4/P(GMA-MMA-AA)). The epoxy group content in the magnetic composite microspheres, amounting to 2.0 mmol g^{-1}, was determined by a modification of Jay's method [28].



Scheme 2. Synthesis of Fe_3O_4/P(GMA-AA-MMA)–Pd.

2.3. Amination of Fe_3O_4/P(GMA-MMA-AA) microspheres

To a round bottom flask, Fe_3O_4/P(GMA-MMA-AA) (2.0 g) was added to the solution of diethylenetriamine (10.0 g) in water (100.0 g). The mixture was warmed to 75 °C and stirred in the air for 8 h. Then cooled to room temperature, the amino-functionalized microspheres were separated in an external magnetic field, washed with plenty of ethanol, acetone and water, dried at 45 °C under vacuum for 24 h, got yellow Fe_3O_4/P(GMA-MMA-AA) supported diethylenetriamine (abbreviated as Fe_3O_4/P(GMA-MMA-AA)–NH_2). The amino group content on the surface of Fe_3O_4/P(GMA-MMA-AA) was 2.50 mmol g^{-1} using volumetric method [29].

2.4. Preparation of Fe_3O_4/P(GMA-MMA-AA)–Pd

Fe_3O_4/P(GMA-MMA-AA)–NH_2 (2 g) was added to the solution of $Pd(OAc)_2$ (0.1 g) in ethanol (100 ml). The mixture was stirred at room temperature in the air for 24 h. Then the reaction mixture was separated by an external magnetic field and washed with ethanol (3 × 50 ml) and H_2O (3 × 50 ml), respectively, until no palladium in the filtrate could be detected by atomic absorption spectroscopy (AAS). Then the separated product was dried under vacuum at 45 °C for 24 h to give black magnetic composite microspheres supported palladium complex (abbreviated as Fe_3O_4/P(GMA-AA-MMA)–Pd) (Scheme 2). The palladium content in Fe_3O_4/P(GMA-AA-MMA)–Pd catalyst was determined to be 5.0 wt% by AAS.

2.5. Typical procedure used to separate and purified the corresponding compounds for Suzuki reaction

The novel magnetic supported catalyst (0.2 mol%), aryl halides (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol) and EtOH/H_2O (1:1) (5 ml) were added into a round bottomed flask and stirred at 80 °C under air atmosphere for 2–12 h (Scheme 3). After the reaction mixture was cooled to room temperature, water (10.0 ml) and ether (20.0 ml) were added. The catalyst was magnetically separated and used for the next cycle without further treatment. The organic phase of the filtrate was separated, dried over Na_2SO_4, and evaporated. The crude products obtained were purified by flash chromatography with *n*-hexane/EtOAc as the eluent affording the corresponding products. All products were known compounds and were identified by comparison of their physical and spectra data with those of authentic samples.

The recycling test for the Suzuki coupling was carried out as follows. For each run, a mixture of 4-bromobenzeonitrile (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), Fe_3O_4/P(GMA-AA-MMA)–Pd(0) (0.2 mol% with respect to 4-bromobenzeonitrile) and EtOH/H_2O (1:1) (5 ml) were stirred at 80 °C under air atmosphere. After the reaction mixture was cooled to room temperature, water (10.0 ml) and ether (20.0 ml) were added. The catalyst was magnetically separated and used for the next cycle without further treatment. The fresh solvent and substrates were added, but the molar ratio of substrate to Pd remained the same as that in the first run.

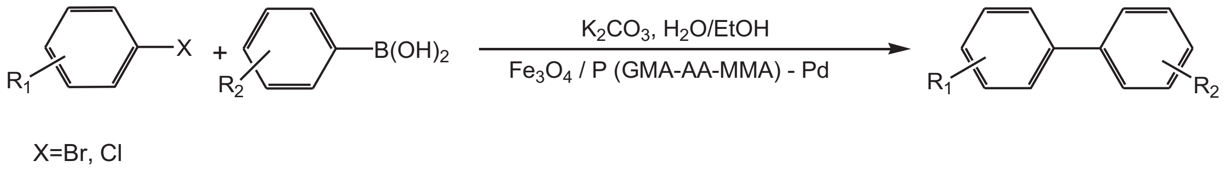
2.6. Characterization

The X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE instrument using Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA. The elemental contents of palladium in the supported catalyst were determined by Z-8000 atomic absorbance spectroscopy (AAS). The microscopic morphologies of Fe_3O_4/P(GMA-MMA-AA) and Fe_3O_4/P(GMA-MMA-A)–Pd were observed in a transmission Electron Microscope (TEM, JEOL JEM-3010). X-ray photoelectron spectra (XPS) were recorded on a kratos Axis Ultra DLD, and the C_{1s} line at 284.8 eV was used as a reference. Magnetic measurements were investigated with a Quantum Design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from −15 to 15 kOe. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 °C/min in air.

3. Results and discussion

3.1. Synthesis and characterization of Fe_3O_4/P(GMA-MMA-AA)–Pd

In the present work, superparamagnetic polymer composite microspheres were synthesized by an emulsifier free emulsion polymerization using 1,1-diphenylethylene (DPE) as free radical control agent (Scheme 1). As shown in Scheme 1, the DPE method used to prepare superparamagnetic polymer composite microspheres included a two-step procedure. Firstly, acrylic acid (AA), methyl methacrylate (MMA) and 1,1-diphenylethylene (DPE) chosen as monomers were added into the reactor to form DPE-containing precursor polymer P(AA-MMA) **1**. Secondly, Due to the amphiphilic property of the DPE-containing precursor, it not only was absorbed on the surface of Fe_3O_4 nanoparticles to stabilize Fe_3O_4 nanoparticles consequently, but also initiated the third monomer to polymerize on the surface of the Fe_3O_4 nanoparticles. Fe_3O_4/P(GMA-AA-MMA)) with high saturation magnetization value then formed, consequently, resulting in the supported catalyst with high saturation magnetization value. In order to confirm whether Fe_3O_4/P(GMA-AA-MMA)) with high saturation magnetization value was obtanied, TEM, XRD and VSM methods



Scheme 3. Suzuki reaction catalyzed by the magnetic catalyst.

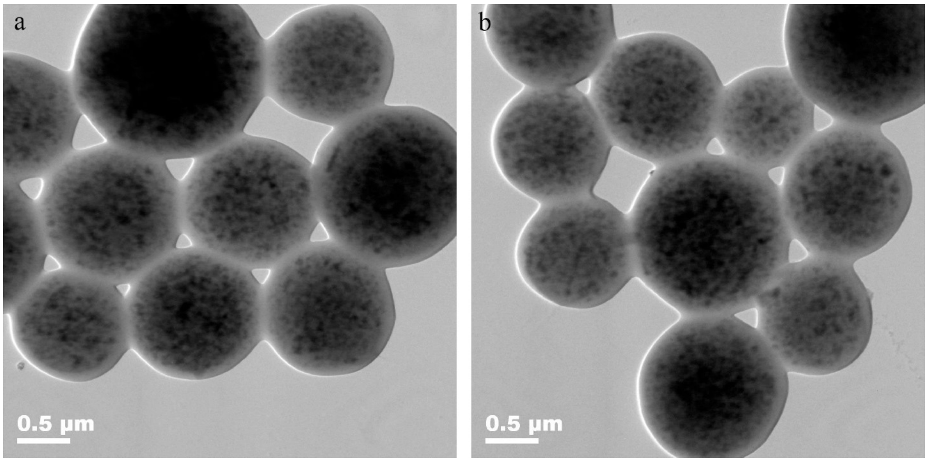


Fig. 1. TEM micrographs of (a) Fe_3O_4/P(GMA-AA-MMA) and (b) Fe_3O_4/P(GMA-AA-MMA)–Pd.

were chosen to characterize the property of superparamagnetic polymer composite microspheres.

Fig. 1a showed the typical TEM image of Fe_3O_4/P(GMA-AA-MMA) prepared by DPE method. As can be seen from the image, many Fe_3O_4 nanoparticles (dark inner) have been successfully encapsulated by polymer shell P(GMA-AA-MMA) (light outer). Furthermore, it also documented that the shape of the microspheres was nearly sphere and its average diameter of the microspheres was around 800 nm. To ascertain whether Fe_3O_4 nanoparticles have been successfully encapsulated by polymer shell P(GMA-AA-MMA) further, X-ray powder diffraction analysis (XRD) of Fe_3O_4/P(GMA-AA-MMA) was carried out. As shown in Fig. 2a, a series of characteristic peaks including (2 2 0), (3 1 1), (4 4 0), (4 0 0), (4 2 2) and (5 1 1) reflected the existence of Fe_3O_4 nanoparticles were clearly identified. Meanwhile, a broad peak at 2θ of about 14.7° could be also clearly observed, which was assigned to the amorphous P(GMA-AA-MMA). Magnetization curve revealed the superparamagnetic behavior of the magnetic nanoparticles. Fig. 3a showed the magnetic curve of Fe_3O_4/P(GMA-AA-MMA) at room temperature. As shown in Fig. 3a, it could be seen that Fe_3O_4/P(GMA-AA-MMA) was superparamagnetic, due to the zero residual magnetism and zero coerctive force. Furthermore, the saturation magnetization value of Fe_3O_4/P(GMA-AA-MMA) was found to be 20.3 emu/g, which also indicated that many Fe_3O_4 nanoparticles had been successfully encapsulated by polymer shell P(GMA-AA-MMA). All these results ascertained that Fe_3O_4/P(GMA-AA-MMA)) microspheres with high saturation magnetization value were obtained.

To immobilize Pd catalyst, diethylenetriamine was loaded onto the surface of superparamagnetic polymer composite microspheres by mixing diethylenetriamine with them in water, due to its strong affinity with Pd nanoclusters [30–32]. Pd catalyst was then readily prepared by exposing diethylenetriamine modified superparamagnetic polymer composite microspheres to $Pd(OAc)_2$ in ethanol, washing with ethanol to remove the surface Pd(II) ions. Then the resulting black products were collected by a magnet, washed with ethanol for three times and dried under vacuum at 45 °C for 24 h to obtain the magnetic catalyst (abbreviated as Fe_3O_4/P(GMA-AA-MMA)–Pd). Fig. 1b revealed that the morphology Fe_3O_4/P(GMA-AA-MMA)–Pd did not change considerably after amination with diethylenetriamine and coordination with palladium onto the surface of the support. HRTEM micrograph (Fig. 4a) revealed Pd nanoparticles (5–10 nm) could be obviously found on the surface of the support materials, indicating that Pd nanoparticles might be highly dispersed around the surface of support materials. Furthermore, the metallic nature of these Pd(0) nanoparticles could be also confirmed by XRD (Fig. 2b). The sharp peaks at 2θ of about 40.1° (1 1 1), 46.7° (2 0 0) and 67.5° (2 2 0) assigned to

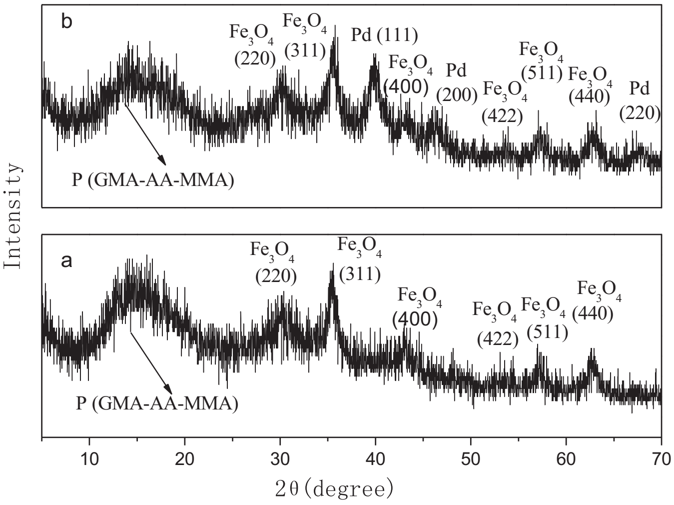


Fig. 2. XRD pattern of (a) Fe_3O_4/P(GMA-AA-MMA) and (b) Fe_3O_4/P(GMA-AA-MMA)–Pd.

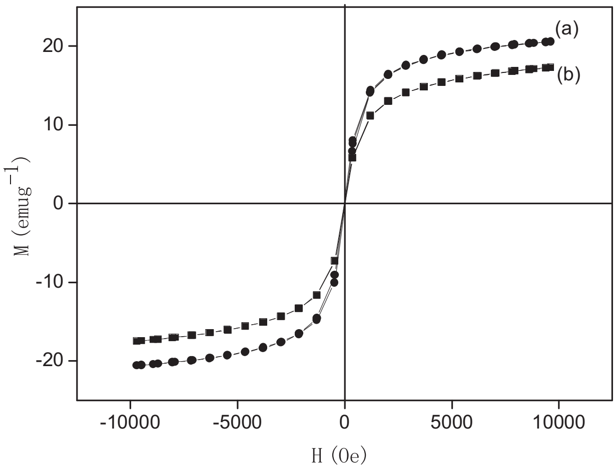


Fig. 3. The magnetization curve measured at room temperature for (a) Fe_3O_4/P(GMA-AA-MMA) and (b) Fe_3O_4/P(GMA-AA-MMA)–Pd.

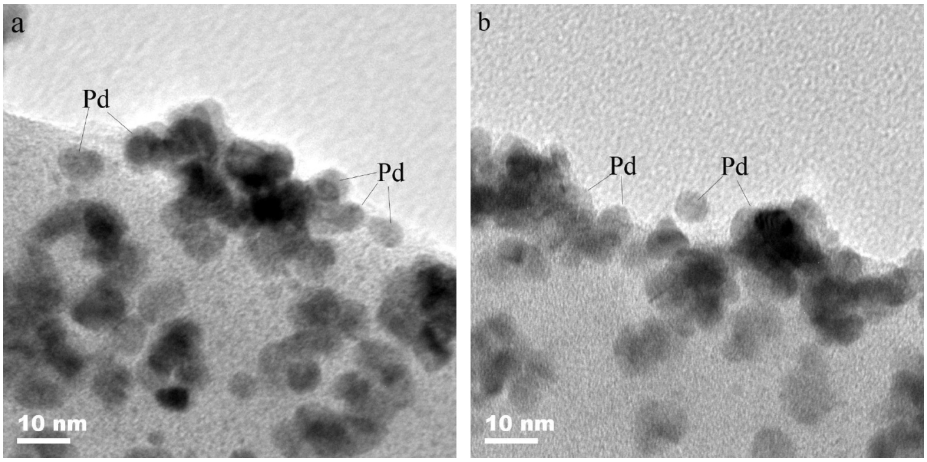


Fig. 4. HRTEM micrographs of Fe_3O_4/P(GMA-AA-MMA)–Pd before (a) and after (b) Suzuki reaction.

the characteristic peaks of Pd(0) could be observed clearly, except for the characteristic sharp peaks of Fe_3O_4 and a broad peaker of amorphous P(GMA-AA-MMA). Unfortunately, owing to that the nearby broader peak at the $2\theta = 35.6^\circ$ ((3 1 1) crystal plane for MP) also contributed to the Fe_3O_4 d-spacings for their overlapping, the average size of the Pd nanoparticles could not be calculated by the Debye-Scherrer equation [33].

Vibrating sample magnetometer (VSM) study confirmed that the supported magnetic catalyst was still superparamagnetic and its saturation magnetization value of the magnetic catalyst was 17.4 emu/g (Fig. 3b), which was higher than those of similar works reported in the literatures [24,30]. With such high saturation magnetization value, Fe_3O_4/P(GMA-AA-MMA)–Pd could be recovered quickly from the solutions using an external magnet.

In order to ascertain whether the coordination between N and Pd was formed, X-ray photoelectron spectroscopy (XPS) study was carried out. The XPS data for all samples were listed in Table 1. As shown in Table 1, the binding energy of Pd $_{3d5/2}$ of the supported catalyst was 335.2 eV, which indicated there was only one chemical state of palladium, Pd(0). Furthermore, the Pd(0) $_{3d5/2}$ of the supported catalyst was lower than that of $Pd_{3d5/2}$. Meanwhile, the binding energy of N_{1S} of Fe_3O_4/P(GMA-AA-MMA)–Pd was 400.2 eV, which was higher than that of N1s of Fe_3O_4/P(GMA-MMA-AA)–NH_2. All these results were probably due to the coordination of N with Pd.

Finally, thermal stability of the magnetic catalyst was also determined, since Suzuki reactions were usually carried out at high temperature. Fig. 5 showed the TG curve of Fe_3O_4/P(GMA-AA-MMA)–Pd in the air. As shown in Fig. 5, Fe_3O_4/P(GMA-AA-MMA)–Pd was stable even at 250 °C. Then the magnetic catalyst began to lose weight due to the oxidative decomposition of the P(GMA-AA-MMA) copolymers. Thermal analysis indicated that the novel magnetic catalyst could meet with the basic thermal qualifications as an efficiently supported catalyst for the Suzuki reactions.

Table 1
XPS data for Pd, $Pd(OAc)_2$, Fe_3O_4/P(GMA-MMA-AA)–NH_2 and Fe_3O_4/P(GMA-AA-MMA)–Pd (in eV)[a].

Samples	N_{1s}	Pd $3d_{5/2}$
Pd	–	335.4
$Pd(OAc)_2$	–	338.7
Fe_3O_4/P(GMA-MMA-AA)–NH_2	399.8	–
Fe_3O_4/P(GMA-AA-MMA)–Pd	400.2	335.2

[a] All relative to C_{1S} = 284.8 eV.

3.2. *Suzuki coupling reactions catalyzed by Fe_3O_4/P(GMA-AA-MMA)–Pd(0) in aqueous media*

The Suzuki coupling reactions of various substituted aryl halides with phenylboronic acids were investigated using 0.2 mol% of the magnetic catalyst. We used aqueous ethanol as the reaction media for environmental protection and economic benefit. To our delight, the aryl bromides with electron-withdrawing or electron-donating groups could efficiently couple with phenylboronic acid and give the corresponding products in 90–99% yields at 80 °C for 2–6 h. (Table 2, entries 1–9). A catalyst loading as low as 0.05 mol% was also shown to be effective, although a comparatively long reaction time was needed (entry 10). Then, the magnetic catalyst was further extended to the coupling reaction of aryl bromides with different arylboronic acids. As expected, outstanding catalytic activities were also observed for the coupling reactions of aryl bromides with different phenylboronic acids (entries 11–13). Encouraged by the efficiency of the reaction protocol described above, we believed that the magnetic catalyst could be applicable to a wide range of phenylboronic acids in all cases. Meanwhile, a range of activated and deactivated aryl chlorides have also been studied for the study of the catalytic activity of the magnetic catalyst. The results showed that the poor yields were obtained at given reaction conditon (entries 14–17), due to that the bond energy of C–Cl of aryl chlorides was higher than that of C–Br of aryl bromides. However, addition of tetrabutylammonium bromide (TBAB) to the reaction of 4-nitrochlorobenzene with phenylboronic acid could enhance

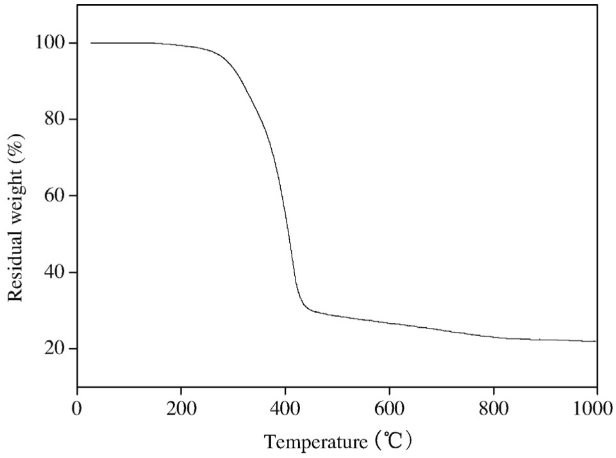


Fig. 5. TG curve of Fe_3O_4/P(GMA-AA-MMA)–Pd.

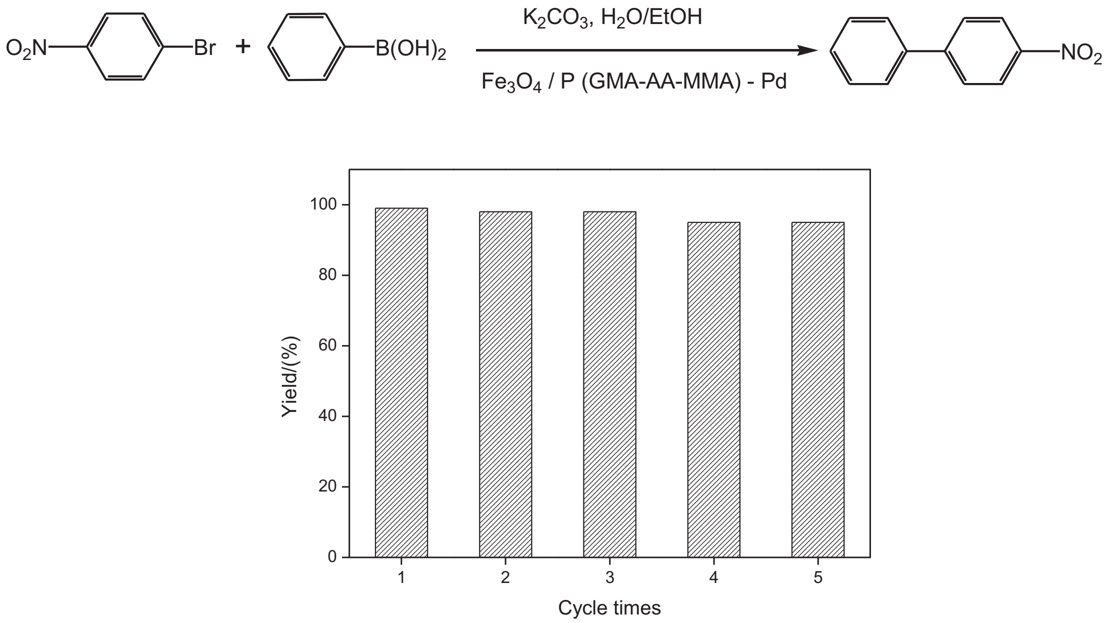


Fig. 6. Recycling yields of the Suzuki reaction in aqueous media catalyzed by Fe_3O_4/P(GMA-AA-MMA)–Pd.

the reactivity of the reaction (entry 18). Additionally, the magnetic catalyst exhibited high stability in the air. It was found that the magnetic catalyst was fairly active even if it was stored in the air for two weeks (entry 19), which was superior to the immobilized phosphine catalysts. In general, the catalyst showed better catalytic activity than commercial Pd/C (10.0 wt%) catalyst. For example, 0.5 mol% of the catalyst was used to catalyze the reaction between p-bromoanisoles with phenylboronic for an average of 94% isolated yield at room temperature for 8 h, while more Pd catalyst (3.5 mol%) was needed to achieve a similar reaction efficacy using Pd/C catalyst at room temperature for 24 h.

Due to the superparamagnetic property, the catalyst could be easily collected by an external magnet for reuse. The reusability of the catalyst was investigated using 4-bromobenzeonitrile with phenylboronic acid as model substrates. The reactivity of the catalyst was significantly unchanged after five cycles (Fig. 6). HRTEM micrograph revealed there was no obvious change of Pd size and morophölgy after five cycles (Fig. 3b). Meanwhile, the AAS analysis showed palladium content of the catalyst did not change at all consequently, no significant leaching of palladium to the solution occurred during the catalytic process. The excellent reusability and high stability of the magnetic catalyst might be attributed to the strong bonding between Pd and amino groups of the surface of Fe_3O_4/P(GMA-AA-MMA), which could prevent Pd nanoparticles from aggregating into less active Pd black and from leaching as well. On the basis of these data, the magnetic catalyst might be an excellent potential candidate for reusable and recoverable catalyst.

Table 2
Suzuki coupling reactions of aryl halides and $ArB(OH)_2$ in the presence of Fe_3O_4/P(GMA-AA-MMA)–Pd.[a]

Entry	X	R_1	R_2	Time (h)	Yield (%)[b]
1	Br	H	H	3	96
2	Br	*p*-CH_3	H	3	95
3	Br	*p*-CH_3O	H	3	94
4	Br	*p*-Cl	H	3	95
5	Br	*o*-CH_3O	H	6	91
6	Br	*m*-CH_3O	H	6	92
7	Br	*p*-NO_2	H	2	99
8	Br	*p*-CH_3CO	H	2	99
9	Br	*p*-CHO	H	2	99
10[c]	Br	H	H	12	80
11	Br	H	*p*-CH_3	3	95
12	Br	H	*p*-Cl	3	95
13	Br	H	*p*-CH_3O	3	94
14	Cl	H	H	3	9
15	Cl	*p*-OCH_3	H	3	8
16	Cl	*p*-CH_3	H	3	8
17	Cl	*p*-NO_2	H	3	15
18[d]	Cl	*p*-NO_2	H	3	89
19[e]	Br	H	H	3	95

[a] *Reaction conditions*: aryl halides (1.0 mmol), arylboronic acids (1.5 mmol), K_2CO_3 (2.0 mmol), catalyst (0.2 mol%) in 5 ml EtOH/H_2O (1:1) at 80 °C in air,

[b] Isolated yield.

[c] In the presence of 0.05 mol% of the magnetic catalyst.

[d] 4-Nitrochlorobenzene (1.0 mmol), arylboronic acids (1.5 mmol), K_2CO_3 (2.0 mmol), TBAB (0.5 mmol), catalyst (0.2 mol%) in 5 ml H_2O at 100 °C in air.

[e] After being stored for two weeks.

Finally, the catalytic mechanism of the magnetic catalyst Fe_3O_4/P(GMA-AA-MMA)–Pd was also explored. Generally, the catalytic mechanism of the supported catalyst for Suzuki reactions can be divided into heterogeneous and homogeneous fashion. In order to determine whether the reaction proceeded in a heterogeneous or homogeneous fashion, a hot-filtration test using the Suzuki reaction of aryl bromide (1.0 mmol) with arylboronic acid (1.5 mmol) was performed. The supported catalyst was separated with an external magnetic field after reacting at 80 °C for 30 min. Then the filtrate was treated with fresh K_2CO_3 under the same reaction condition and heated for an additional 3 h. It was found that, after the hot filtration, no considerable progress was observed. The result proved that the catalytic activity came from the heterogeneous catalyst.

4. Conclusions

In summary, superparamagnetic polymer composite microspheres Fe_3O_4/P(GMA-AA-MMA) were successfully prepared by DPE method for immobilization of Pd catalyst. The magnetic catalyst could be easily recovered using an external magnet. It was noteworthy that the magnetic catalyst provided excellent reactivity and reusability in the Suzuki reaction of aryl halides with phenylboronic acids. As a consequence, Fe_3O_4/P(GMA-AA-MMA) could be ideal supports for immobilization of homogeneous catalyst. Further study regarding the effects of magnetic composite microspheres properties on the catalyst's reactivity are in progress and will be reported in due course.

Acknowledgments

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