



## Supported nanosized palladium on superparamagnetic composite microspheres as an efficient catalyst for Heck reaction

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### ABSTRACT

A magnetically separable palladium catalyst has been easily synthesized by immobilizing palladium nanoparticles on the surface of superparamagnetic composite microspheres. It can promote Heck cross-coupling reactions efficiently without an inert atmosphere. The novel catalyst can be conveniently recovered by applying a permanent magnet externally and reused at least six times without significant loss of its catalytic activity.

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### 1. Introduction

Immobilization of homogeneous catalyst on various support materials has been extensively employed in various fields since immobilized catalysts have fewer of the drawbacks of homogeneous catalyst, such as the difficulties in recovery and regenerations [1–3]. However, a substantial decrease in activity and selectivity of the immobilized catalysts is frequently observed, due to the problem of slow diffusion rate of reactants to the surface anchored catalyst. Thus, in order to increase the diffusion rate, a method of utilizing nanoparticles as support materials is frequently used in this field [4,5]. This is because when the size of support materials is decreased to the nanometer scale, the surface area will increase dramatically and nanometer sized supports will even be dispersible in solution to form an emulsion. Therefore, reactants in solution have easy access to the active sites on the surface of nanoparticles, accordingly avoiding the problems encountered in many heterogeneous support matrixes, where a great portion of catalysts are present deep inside the matrix backbone and reactants have the limited access to the catalytic sites [6,7]. And until now, many nanomaterials such as nanotubes [8] and monolayer protected Au nanocluster (Au MPCs) [9] have been selected for supporting homogeneous catalyst because of their excellent properties. However, in this extreme case of immobilized systems, the same problems of isolation and recycling of nanocatalysts will also be encountered, due to the fact that nanoparticles, which include

nanoscaled metal catalyst and support, are difficult to be separated from the reaction mixture [10,11].

Currently, a method used to address this problem is through the use of magnetic nanoparticles, due to that they can be easily recovered and separated by using an external magnetic field. So far, the reports on the magnetic nanoparticles as catalyst supports are mainly focused on  $\text{Fe}_3\text{O}_4$  nanoparticles because they can be prepared by co-deposition method conveniently and have strong magnetic responsiveness [10–18]. Unfortunately, due to the high ratio of surface to volume and magnetization, magnetic nanoparticles are prone to aggregate, which will limit their applications. Thus, it is still important to develop a reliable synthetic route to highly efficient reusable catalysts [19]. Recently, superparamagnetic composite microspheres have received much attention in the fields of potential applications, such as magnetic bioseparation, enzyme immobilization, cell isolation, nuclei acid, protein purification and immunoassay because of their non-toxicity, good stability, high concentration of magnetite and functional groups [20–26]. These magnetic composite microspheres are usually composed of magnetic cores and polymer shells. Magnetic cores can respond to a magnetic field and retain no magnetization properties when the field is removed. While polymer shells can not only stabilize nanoparticles by preventing aggregation of inorganic cores, but provide favorable functional groups for immobilizing catalyst.

Herein, we would like to report the feasibility of using the new materials, which have been prepared by soap free emulsion polymerization, for supporting homogeneous catalyst. The Pd catalysts immobilized on superparamagnetic composite microspheres could be easily separated by using an external magnetic field. In addition,

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the magnetic supported catalyst could be reused at least six times without significant loss of its catalytic activity.

## 2. Experiments

### 2.1. Preparation of $Fe_3O_4$ nanoparticles

$Fe_3O_4$  nanoparticles were prepared via co-precipitation of  $Fe^{3+}$  and  $Fe^{2+}$  ions in the presence of NaOH. About 11.2 g  $FeSO_4 \cdot 7H_2O$  and 16.3 g  $FeCl_3 \cdot 6H_2O$  were dissolved in 200 ml of deionized water in a flask. This solution was stirred followed by adding 3 M NaOH solution quickly at 30 °C until the mixture reached a pH around 11. Then the mixture was heated to 80 °C for 30 min. The  $Fe_3O_4$  nanoparticles were isolated from the solution by magnetic separation and washed with deionized water until pH 7 reached. Finally, the  $Fe_3O_4$  nanoparticles were kept at room temperature.

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

$Fe_3O_4$  nanoparticles (2 g), KPS (0.1 g) and water (50 ml) constituted the aqueous phase, glycidyl methacrylate (GMA) (3.5 g), methyl methacrylate (MMA) (3 g) and acrylic acid (AA) (0.25 g) constituted the oil phase. The aqueous phase was homogenized at room temperature with an ultrasound mixer for 3 min, and then the oil phase was continuously added in an aqueous phase to disperse for 5 min. The mixture was then charged in a four necked flask equipped with a stirrer, a condenser, at 80 °C in a water bath under  $N_2$  atmosphere for 10 h. The magnetic composite microspheres were collected by magnetic separation and washed with acetone and deionized water several times. Finally, the separated product was dried in a vacuum oven at 40 °C for 24 h to give yellow magnetic composite microspheres (abbreviated as  $Fe_3O_4/P$  (GMA-AA-MMA)). The epoxy group content in the magnetic composite microspheres, amounting to 1.8 mmol  $g^{-1}$ , was determined by a modification of Jay's method [27].

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

To a solution of triethylene tetramine (10 ml) in DMF (100 ml),  $Fe_3O_4/P$  (GMA-AA-MMA) microspheres (5 g) were added. Then the mixture was stirred at 80 °C in the air for 8 h. The amino-functionalized microspheres were washed with plenty of ethanol, acetone and  $H_2O$ , and then dried at 45 °C under vacuum for 24 h to give yellow  $Fe_3O_4/P$  (GMA-AA-MMA) microspheres supported triethylene tetramine (abbreviated as  $Fe_3O_4/P$  (GMA-AA-MMA)- $NH_2$ ). The amino group content on the surface of  $Fe_3O_4/P$  (GMA-AA-MMA) microspheres was determined to be 2.3 mmol  $g^{-1}$  using volumetric method [28]. The nitrogen content was also confirmed by element analysis: N: 3.58; C: 42.43; H: 7.11%.

### 2.4. Preparation of $Fe_3O_4/P$ (GMA-AA-MMA) supported palladium complex catalyst

To a solution of  $Fe_3O_4/P$  (GMA-AA-MMA)- $NH_2$  (2 g) in ethanol (50 ml),  $Pd(OAc)_2$  (0.1 g) was added. And the mixture was stirred at 45 °C in the air for 24 h. Then the mixture was separated by using an external magnetic field and washed with ethanol (3 × 30 ml) and  $H_2O$  (3 × 30 ml), until no palladium in the filtrate can be detected by atomic absorption spectroscopy (AAS). Then the separated product was dried under vacuum at 60 °C for 24 h to give yellow magnetic composite microspheres supported palladium complex (abbreviated as  $Fe_3O_4/P$  (GMA-AA-MMA)- $Pd(II)$ ).  $Fe_3O_4/P$  (GMA-AA-MMA)- $Pd(II)$  (2 g) was put into a solution of  $KBH_4$  (0.05 g) in ethanol (50 ml) at 45 °C for 24 h, then washed with ethanol (3 × 30 ml) and  $Et_2O$  (3 × 30 ml) and dried under vacuum at

60 °C for 24 h to give yellow magnetic composite microspheres supported palladium complex catalyst (abbreviated as  $Fe_3O_4/P$  (GMA-AA-MMA)- $Pd(0)$ ) (Scheme 1). The palladium content in  $Fe_3O_4/P$  (GMA-AA-MMA)- $Pd(0)$  catalyst was determined to be 4.57 wt% by AAS.

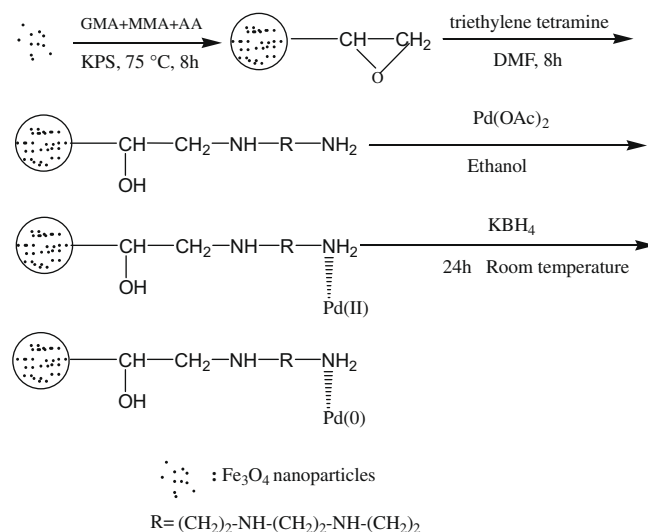
### 2.5. General procedures for Heck reactions and recovery of the supported magnetic catalyst

The novel magnetic supported catalyst (0.5 mol%), acrylic acid (7.5 mmol), aryl halides (5 mmol), base (10 mmol) and solvent (5 ml) were added into a round bottomed flask and stirred at 90–140 °C in atmosphere for 3–12 h. After the reaction mixture was cooled to room temperature, the catalyst was magnetically separated. The product was analyzed by HPLC to give corresponding yield. All the products have been identified by comparison of their IR,  $^1H$  NMR and melting points with those reported previously (see Supporting information).

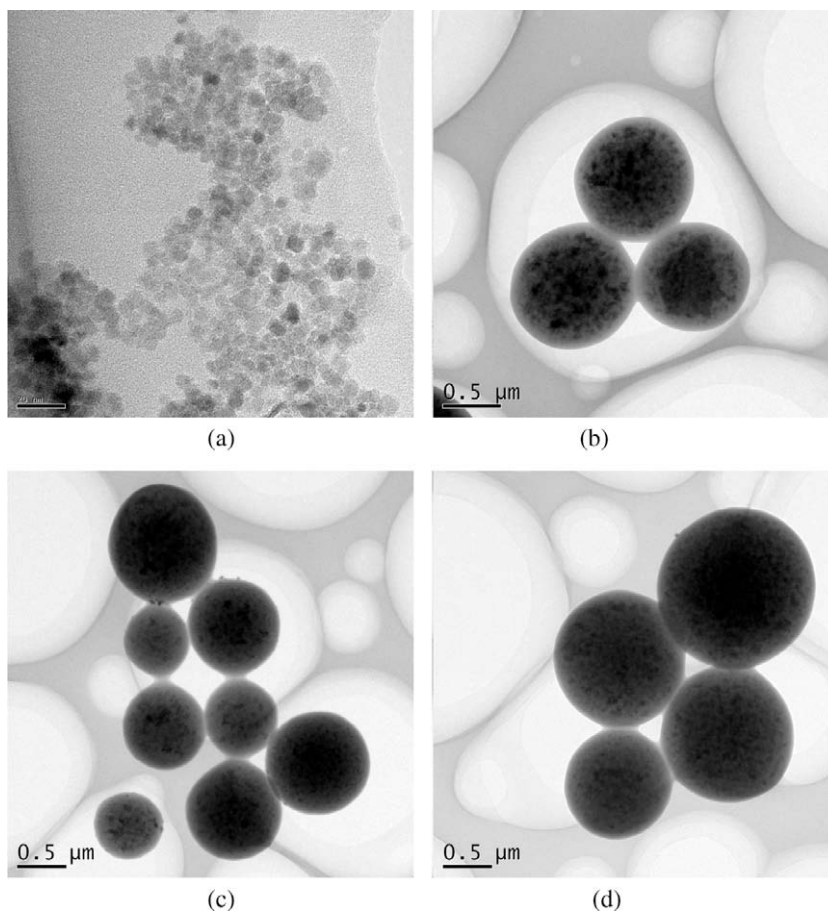
## 3. Results and discussion

### 3.1. Characterization of magnetic composite microsphere $Fe_3O_4/P$ (GMA-AA-MMA) supported palladium complex

Fig. 1 shows the TEM images of the different samples. As shown in Fig. 1a, the  $Fe_3O_4$  nanoparticles prepared by the chemical co-precipitation are quasi spherical with an average of 10 nm. Fig. 1b clearly displays that  $Fe_3O_4$  nanoparticles have been successfully encapsulated into the polymer shell, and the dispersion of particles has been improved greatly, which can be explained by the steric hindrance between the polymer chains on the surface of the  $Fe_3O_4$  nanoparticles. The dispersed  $Fe_3O_4/P$  (GMA-MMA-AA) microspheres with perfect sphere shaped morphologies consist of a dark core and a light shell. The dark inner corresponds to magnetic nanoparticles, while the light outer attributes to P (GMA-MMA-AA). Additionally, as shown in Fig. 1c and d, it can be seen that magnetic microspheres were not broken in the coordination process. Furthermore, as presented in Fig. 1d, it can be seen that the surface of the magnetic composite microsphere is very smooth and no other particles are found on the surface of polymer nanobead. This is a significant indication that the prepared Pd nanoparticles are highly dispersed around the surface of



**Scheme 1.** Preparation of  $Fe_3O_4/P$  (GMA-AA-MMA) composite microspheres and  $Fe_3O_4/P$  (GMA-AA-MMA)- $Pd(0)$ .



**Fig. 1.** TEM Images of the samples (a)  $\text{Fe}_3\text{O}_4$  nanoparticles, (b)  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA), (c)  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA)- $\text{NH}_2$ , (d)  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA)-Pd(0).

the magnetic composite microspheres, resulting in that they may be less than 1 nm in diameter and thus cannot be detected by the TEM [10].

The FTIR spectra of different samples are displayed in Fig. S-1 in the Supporting information. As shown in Fig. S-1a, the characteristic absorption band of  $\text{Fe}_3\text{O}_4$  appears at  $558\text{ cm}^{-1}$ . While in Fig. S-1b, the absorption band mentioned above almost disappeared, and many characteristic absorption bands of P (GMA-MMA-AA) occur. For example, the peak at  $1726\text{ cm}^{-1}$  corresponds to carbonyl stretch. The peaks at  $908$  and  $843\text{ cm}^{-1}$  ascribe to epoxy ring vibration. The peaks at  $2944$  and  $1499\text{ cm}^{-1}$  are the absorption bands of methyl and methylene. The peaks at  $1263$  and  $1170\text{ cm}^{-1}$  ascribe to C-O-C vibration. All these results suggest that the surface of magnetic nanoparticles has been successfully functionalized with the polymer. Fig. S-1c displays the IR spectra of  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA)- $\text{NH}_2$ . It can be found that after modification of triethylene tetramine, the new peaks at  $1591\text{ cm}^{-1}$  ( $-\text{NH}_2$ ) and  $1383\text{ cm}^{-1}$  (C-N) occur in the spectra. The result indicates that the modification of the magnetic microspheres with triethylene tetramine is successful.

X-ray powder diffraction (XRD) patterns of  $\text{Fe}_3\text{O}_4$  nanoparticles,  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA),  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA)- $\text{NH}_2$  and  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA)-Pd(0) are displayed in Fig. 2. As presented in Fig. 2a, the XRD pattern of nanosized magnetic particles shows the characteristic peaks of  $\text{Fe}_3\text{O}_4$ . Meanwhile, as shown in Fig. 2, it can be found that the XRD results of  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA),  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA)- $\text{NH}_2$  and  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA)-Pd(0) and pure  $\text{Fe}_3\text{O}_4$  are mostly coincident except a broader peak at  $2\theta$  of about  $17.4^\circ$  originating from amorphous P (GMA-MMA-AA) copolymers. Furthermore, it can also be seen that

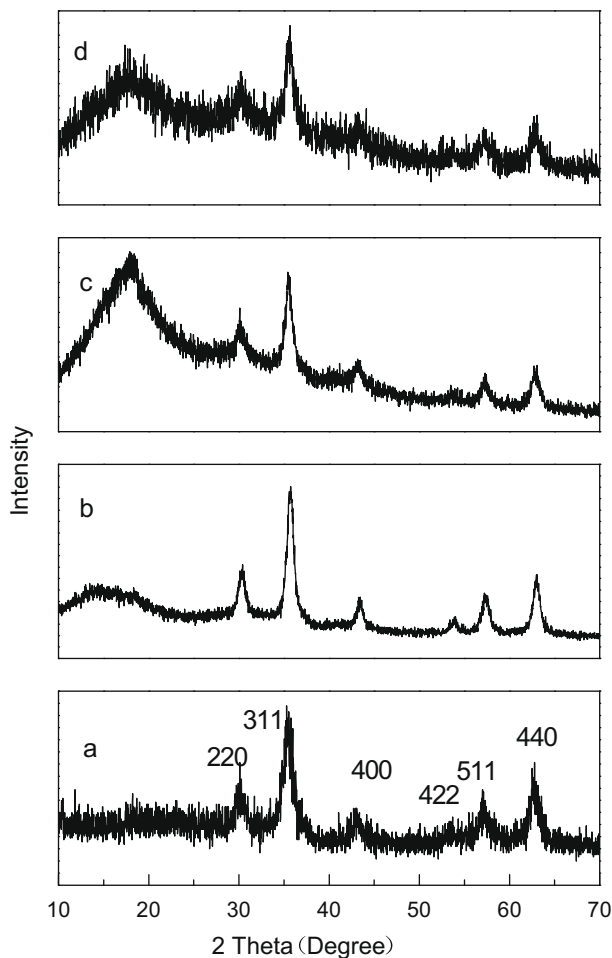
a sharp peak at  $2\theta$  of about  $44.75^\circ$ , which is attributed to the diffraction of scattering of Fe nanoparticles, is not observed (Fig. 2d). All the results demonstrate that  $\text{Fe}_3\text{O}_4$  nanoparticles encapsulated into the polymer shell are not reduced during the preparation of the catalyst, especially after treatment with  $\text{KBH}_4$ .

The supported catalyst was analyzed using XPS to investigate the chemical oxidation state of the supported palladium species. The XPS spectrum (Fig. 3) shows typical Pd(0) absorption at 335.2 and 340.4 eV. These two peaks are assigned to electron transitions of  $3d_{5/2}$  and  $3d_{3/2}$  of Pd(0) respectively, which indicates that the Pd(II) can be reduced to metallic Pd(0). Besides, as shown in Fig. 3, it can also be seen that the Pd  $3d_{5/2}$  and  $3d_{3/2}$  peaks corresponding to the Pd(II) ions with photoelectron energies of 337.2 and 342.5 eV are still detected, which indicates that a little amount of Pd(II) ions have not been reduced with  $\text{KBH}_4$ .

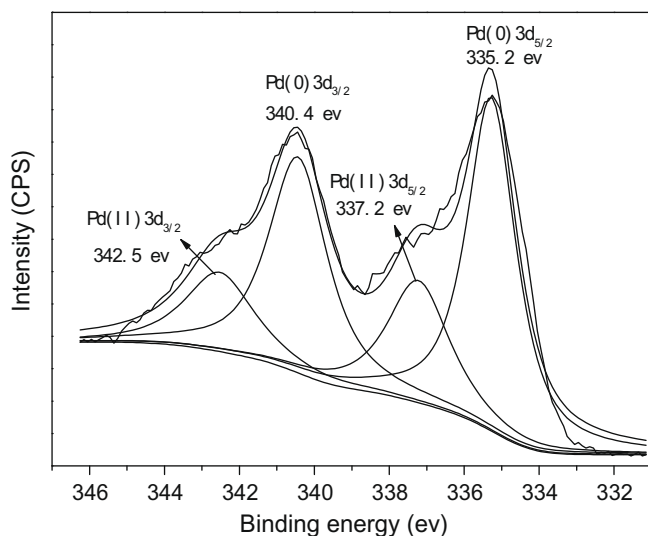
Fig. 4 shows the magnetic curve of  $\text{Fe}_3\text{O}_4/\text{P}$  (GMA-MMA-AA) supported palladium complex catalyst at room temperature. As shown in Fig. 4, it can be seen that no hysteresis loop is observed, with both remanence and coercivity being zero, suggesting that the magnetic supported catalyst is superparamagnetic. The saturation magnetization is found to be 8.26 emu/g at an external field of 10 K Oe. With such high magnetization value, the magnetic supported catalyst can be easily separated from the solutions by using a relatively low external magnetic field.

### 3.2. Heck reaction catalyzed by the magnetic supported catalyst

To investigate the catalytic activity of the novel magnetic catalyst, Heck reaction of cross-coupling of aryl halide with acrylic acid using DMF as a solvent and tributylamine as a base under

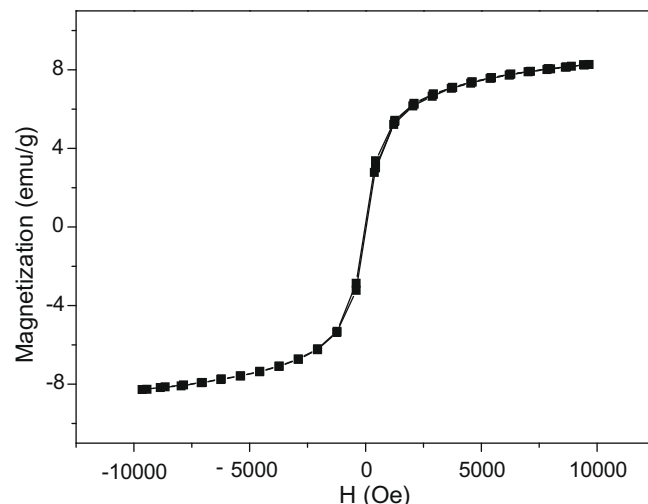


**Fig. 2.** XRD pattern of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-MMA-AA})$ , (c)  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-MMA-AA})-\text{NH}_2$  and (d)  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-MMA-AA})-\text{Pd}(0)$ .

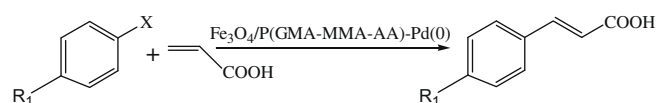


**Fig. 3.** XPS spectrum of  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-MMA-AA})-\text{Pd}(0)$ .

atmosphere conditions were examined (Scheme 2). As shown in Table 1, Heck reaction of acrylic acid with aryl iodides were catalyzed at 90 °C in the presence of the novel magnetic catalyst to afford the *trans*-product in high yields and no *cis*-product was



**Fig. 4.** The magnetization curves measured at room temperature for  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-MMA-AA})-\text{Pd}(0)$ .



**Scheme 2.** Heck reaction of aryl halide with acrylic acid catalyzed by the novel catalyst.

observed. Furthermore, due to the high reactivity of the aryl iodides, neither electron-donating group (entries 2–3) nor electron-withdrawing group (entries 4–6) has much influence on the yield of product. As for bromobenzene, only corresponding product in 8.2% yield (entry 7) was detected under the same reaction condition as iodobenzene, but the moderate yield (entry 8) was obtained when the reaction time extended to 12 h and the reaction temperature increased to 140 °C. It can be also seen that the reactivity of aryl bromides with electron-withdrawing substituents (entry 11) was higher than that of aryl bromides with electron-donating substituents (entries 9–10).

Finally, in order to check the recycling efficiency of the novel magnetic supported catalyst, Heck reaction of the cross-coupling of acrylic acid with iodobenzene was investigated. In each cycle, the magnetic supported catalyst can be easily recovered and separated using a permanent magnet, washed with ethanol and used directly for a subsequent round of a reaction without further

**Table 1**

Heck reactions of various aryl halides and acrylic acid catalyzed by the magnetic catalyst.<sup>a</sup>

Entry	R1	X	Time (h)	Temperature(°C)	Conversion (%) <sup>b</sup>	Yield (%) <sup>c</sup>
1	H	I	3	95	98.0	97.2
2	OCH <sub>3</sub>	I	3	95	98.5	92.0
3	CH <sub>3</sub>	I	3	95	97.8	92.5
4	Cl	I	3	95	98.5	96.5
5	CHO	I	3	95	99.5	97.8
6	NO <sub>2</sub>	I	3	95	100.0	97.5
7	H	Br	3	95	25.0	8.2
8	H	Br	12	140	52.0	47.8
9	OCH <sub>3</sub>	Br	12	140	47.0	44.5
10	CH <sub>3</sub>	Br	12	140	45.6	45.6
11	NO <sub>2</sub>	Br	12	140	91.5	87.5

<sup>a</sup> Reaction conditions: aryl halide (5 mmol), acrylic acid (7.5 mmol),  $\text{Bu}_3\text{N}$  (10 mmol), DMF (5 ml). The supported magnetic catalyst (0.5 mol%).

<sup>b</sup> Determined by GC.

<sup>c</sup> HPLC yield based aryl halide.

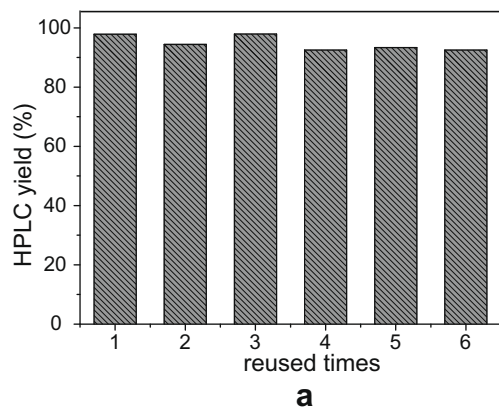


Fig. 5. Recycle of the  $\text{Fe}_3\text{O}_4/\text{P}(\text{GMA-MMA-AA})-\text{Pd}(0)^1$ .

purification. As shown in Fig. 5a, the novel catalyst can be reused at least six times only with a slight loss of activity for the Heck reaction of iodobenzene and acrylic acid.

Furthermore, in order to check the stability of the catalyst, the supported catalyst after sixth run for Heck reaction has been characterized by AAS, TEM and XPS (see Supporting information). The AAS result shows that only the leaching of 0.5 wt% palladium occurs during the reaction, which indicates the coordination link of Pd(0) with  $-\text{NH}_2$  ligand is strong, resulting that Pd(0) is strongly bound to the surface of magnetic microspheres. Meanwhile, from the TEM micrograph of the supported catalyst after sixth run, we did not observe much change compared to the TEM image of the fresh catalyst. And only few Pd nanoparticles have grown into bigger nanoparticles, which also indicate that the magnetic catalyst is very stable during the reaction process. Additionally, as shown in the XPS spectra of the catalyst reused after sixth run, only Pd(0) particles is present in the re-catalyst, which indicates that the Pd(II) in the fresh catalyst has been reduced to Pd(0) during the Heck reaction, and the Pd(0) is the center of catalytic activity [29].

Overall, all these results show that the novel catalyst is an excellent potential candidate for reusable and recoverable catalyst.

#### 4. Conclusions

In conclusion, magnetic composite microspheres supported palladium complex catalyst has been prepared by immobilizing Pd nanoparticles on the surface of magnetic composite microspheres.

The novel magnetic catalyst is stable and shows high catalytic activity in promoting Heck cross-coupling reaction. In addition, the novel catalyst can be easily recovered by using a permanent magnet and reused at least six times without significant loss of its catalytic activity and selectivity. As a consequence, magnetic composite microspheres prepared by soap free emulsion can be ideal supports for immobilization of industrial homogeneous catalyst. Further studies on the effects of magnetic composite microspheres properties on the catalytic activity of the immobilized catalyst as well as the application of the novel catalyst to other palladium catalyst reactions are now in progress.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.catcom.2010.01.005.

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<sup>1</sup> Reactions were carried out with the magnetic catalyst (0.5 mol% Pd), iodobenzene (5 mmol), acrylic acid (7.5 mmol), Bu<sub>3</sub>N (10 mmol), DMF (5 ml) at 95 °C in the air, reaction time (3 h).