磁性纳米 Pd/Fe₃O₄ 催化剂的制备及其在 Heck 反应中的应用

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摘要:通过使用聚乙烯吡咯烷酮作为稳定剂,合成了磁性 Pd/Fe₃O₄ 纳米颗粒催化剂。对该催化剂进行粉末 X 射线衍射、透射电子显微镜、感应耦合等离子体和磁性表征。将 Pd/Fe₃O₄ 催化剂用于 Heck 反应,检测其催化性能。测试结果表明 Pd 纳米颗粒负载在 Fe₃O₄ 纳米颗粒上,而且催化剂的尺寸<20 nm,并在 Heck 反应中表现了极好的催化性能。此外,催化剂可以通过磁场回收利用,且催化活性没有显著的降低。

关键词:Pd/Fe₃O₄;磁性纳米颗粒;聚乙烯吡咯烷酮;Heck 反应

Efficient Synthesis and Application in Heck Reaction of Pd/Fe₃O₄ Magnetic Nanoparticles

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Abstract: Pd/Fe₃O₄ NPs have been successfully synthesized using polyvinyl pyrrolidone as a stabilizing agent. The resultant samples were characterized by X-ray diffraction, transmission electron microscopy, inductively coupled plasma, and magnetic studies. The Pd/Fe₃O₄ NPs catalyst was also applied in the Heck reaction to evaluate the catalytic performance. The results show that the cubic phase of Pd coexists with the cubic phase of Fe₃O₄, and the catalysts have size less 20 nm and the excellent catalytic activity of Pd/Fe₃O₄ NPs in the Heck reaction. In addition, the catalyst can be recovered via a magnet and reused several times without significant loss of its catalytic activity.

Keywords: Pd/Fe₃O₄; magnetic nanoparticles; polyvinyl pyrrolidone; Heck reaction

0 Introduction

Palladium-catalyzed C-X (X includes C, N, O, etc.) cross-coupling reaction for forming aryl compounds has become a common bonding strategy and the synthesis methods in organic synthesis. Among them the formation of carbon-carbon bonds is one of the important processes of chemical change[1-3].

Palladium-catalyzed carbon-carbon coupling reactions include Heck-Mizoroki, Suzuki-Miyaura, Sonogashira reaction and so on[4-5]. The Heck reaction, palladium-catalyzed carbon-carbon bond formation between aryl halides and olefins, has become a most powerful synthetic tools[6] and has been proven to be a

rather versatile method in the syntheses of important building blocks in pharmaceuticals and bioactive compounds, natural products, monomers and herbicides[7-8].

Ali et al.[9] employed palladium-phosphine complexes as catalyst and Jhous groups [10] have reported about palladium (Ⅱ) complexes of N-heterocyclic carbine as catalyst in the Heck reaction. However, the catalysts above suffer from a series of drawbacks, such as intrinsic toxicity, poor thermal, air stability, harsh reaction conditions, and making it economically and environmentally malignant[11-12]. Moreover, most of ligands are expensive and its poor recyclability[13]. In order to overcome the disadvantages above, considerable efforts have been made[14-15], it seems that, the nanotechnology is a good candidate[16-18] which allows the surface area to increase dramatically among them and reactants in solution have easy access to the active sites on the surface of nanoparticles[19]. Palladium nanoparticles (PNPs) supported on agarose as catalytic system has an high activity in Heck reaction[13]. Preparation of PNPs under green conditions, the products were also obtained in highly short reaction times with excellent yields[20]. However, the recyclability of PNPs using a simple filtration is a huge problem due to nanoparticles is dispersible in solution, forming emulsion[21]. Moreover, palladium is an expensive metal that limits industrial applications[22-23]. Thus under both economic and environmental concerns, it is essential that the isolation and recovery of PNPs[24-25]. Methods have been focused on magnetic recyclable supports from solution[26-28]. Catalyst on this supports can be separated from reaction condition using an external magnetic eld easily but also the reactivity could be improved[29]. And magnetic nanoparticles (MNPs) have been applied in various fields such as the field of biotechnology[30-32].

In continuation of our efforts to develop environmentally friendly synthetic methodologies, we now report a protocol for the preparation of Pd/Fe$_3$O$_4$ NPs by using polyvinyl pyrrolidone (PVP) as a stabilizing agent and the application of these MNPs as

novel and stable heterogeneous catalysts in the Heck coupling reactions.

1　Experimental

1.1　Apparatus, materials and measurements

All reagents were purchased from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and Aladdin Industrial Corporation and used without further purification. Products were characterized by comparison of their physical and spectral data with those of authentic samples and reported in the literature.

The analyses by GC were performed on an Agilent 7890B instrument equipped with a capillary (30 m×0.32 mm×0.25 μm film thicknesses). The GC parameters were as follows [33]: initial temperature, 120 ℃; initial time, 1 min; solvent delay, 3.70 min; temperature ramp 1, 10 ℃·min^{-1}; final temperature, 200 ℃; temperature ramp 2, 20 ℃·min^{-1}; final temperature, 240 ℃; final time, 14min; injector port temperature, 260 ℃; detector temperature, 300 ℃, injection volume, 1.0 μL. The thermal properties of samples were examined by thermogravimetric analysis (TGA, model Q50, TA Instruments, USA), with the temperature increasing from RT to 700 ℃ at a rate of 10 ℃·min^{-1} under a flow of high-purity nitrogen at a rate of 60 mL·min^{-1}. X-ray diffraction measurements (XRD) were performed with a Philips powder diffractometer type PW 1373 goniometer (Cu $K\alpha$ radiation, λ =0.154 06 nm, U =40 kV, I =80 mA) at room temperature. The scan rate was 2°·min^{-1} in the 2θ range from 10° to 80°. Pd contents in the catalysts were determined by Inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro) after dissolving each sample in the mixture of HNO$_3$/HCl (1 :3, V/V). Transmission electron microscopy (TEM) analyses were performed on a Philips model CM 10 coupled with an energy dispersive X-ray spectrometer (EDX), with an accelerating voltage of 20 kV. The high resolution TEM (HRTEM) images were collected with Hitachi H9000NAR transmission electron microscope. The magnetic properties of the synthesized samples were measured by using Vibrating Sample Magneto-

meter (VSM, M-155) at a maximum applied eld of 30 kOe.

1.2 Typical procedure for preparations of Fe$_3$O$_4$ NPs, Pd NPs and Pd/Fe$_3$O$_4$ NPs catalyst

Magnetic nanoparticles were prepared via hydrothermal method[34-35] in the presence of urea. In a canonical flask, a mixture of FeCl$_3$·6H$_2$O (0.79 mmol, 0.212 5 g) and PVP (1.50 mmol, 0.166 3 g) with an average molecular weight of 40 000 Da and urea (2.42 mmol, 0.145 3 g) was dissolved in 10 mL of 1,2-propanediol. Then the solution was stirred until dissolved completely. Subsequently, the solution was transferred to the autoclave and the mixture was reacted at 190 ℃ for the appropriate times. The magnetic nanoparticles as a dark solid were isolated from the solution by magnetic separation and washed with deionized water and absolute ethyl alcohol, respectively. Finally, the magnetic nanoparticles are dispersed in 10 mL ethanol.

PVP (0.71 mmol, 0.078 9 g) with an average molecular weight of 40 000 Da was added to Palladium chloride solution (5.5 mL, 0.011 28 mol·L^{-1}) and stirred until the total solubilization of the polymer. Then, a solution of sodium borohydride (0.99 mmol) was added dropwise to the mixture under constant magnetic stirring for 30 min. This solution of Pd (0)-PVP was directly used as the catalyst for the Heck reactions.

The prepared Pd NPs with Fe$_3$O$_4$ NPs were mixed in a round-bottom flask at room temperature under vigorous stirring for 8 h. The value of Pd supported on Fe$_3$O$_4$ was monitored by ICP analyzer.

1.3 Typical procedure for Heck coupling reaction

To a stirred solution of 1.4 mmol of aryl halide in 3 mL of ethanol, 1.7 mmol of alkene, 2.0 mmol of K$_2$CO$_3$ and the Pd/Fe$_3$O$_4$ NPs catalyst was added and the mixture was heated on an water bath at 80 ℃ for 7 h under constant stirring. After completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was separated using a magnetic separator and washed with diethyl ether (2× 10 mL) followed by deionized and oxygen-free water

(2×10 mL). The reused catalyst was dried for the next run. The organic phase was analyzed by GC. All the products are known compounds and the spectral data and melting points were identical to those reported in the literature.

2 Results and discussion

2.1 XRD, TEM and magnetic analyses

The X-ray diffraction (XRD) results show that all the diffraction peaks in the pattern: Pd/Fe$_3$O$_4$ NPs, as shown in Fig.1. The XRD pattern of the Pd/Fe$_3$O$_4$ NPs catalyst shows that the cubic phase of Pd coexists with the cubic phase of Fe$_3$O$_4$. All the diffraction peaks could be readily indexed to (220), (311), (222), (400), (422), (511), (440) lattice planes of a face-centered cubic (fcc) FeO·Fe$_2$O$_3$ (PDF No. 89-0691) and (111) lattice planes of a face-centered cubic (fcc) Pd crvstal structure (PDF No. 46-1043)[29,36].
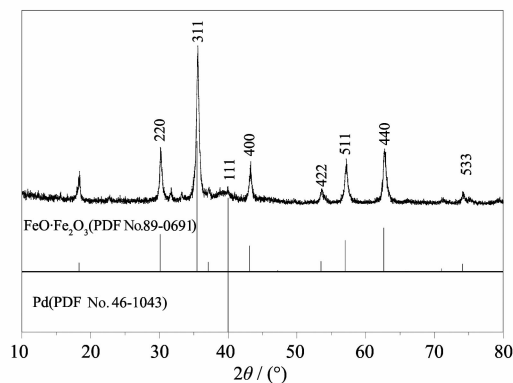

Fig.1　X-ray diffraction patterns of Pd/Fe$_3$O$_4$ NPs

The morphology and microstructure of the as-synthesized Pd/Fe$_3$O$_4$ NPs were characterized by TEM, and the results are shown in Fig.2. Fig.2a~b shows that the functionalized magnetic nanoparticles exhibited relatively good monodispersity. The inset of Fig.2b shows a typical HRTEM image of the Pd/Fe$_3$O$_4$ NPs. This image clearly reveals that the Pd nanoparticles are directly attached onto the Fe$_3$O$_4$ nanocrystals. The lattice fringes of d =0.194 3 and 0.281 6 nm were ascribed to Pd (200) and Fe$_3$O$_4$ (220), respectively [37]. EDS spectrum in Fig. 2c shows the presence of C, Fe, O, Cu and Pd elements, which confirms the co-exists of Pd and Fe$_3$O$_4$. In addition, it
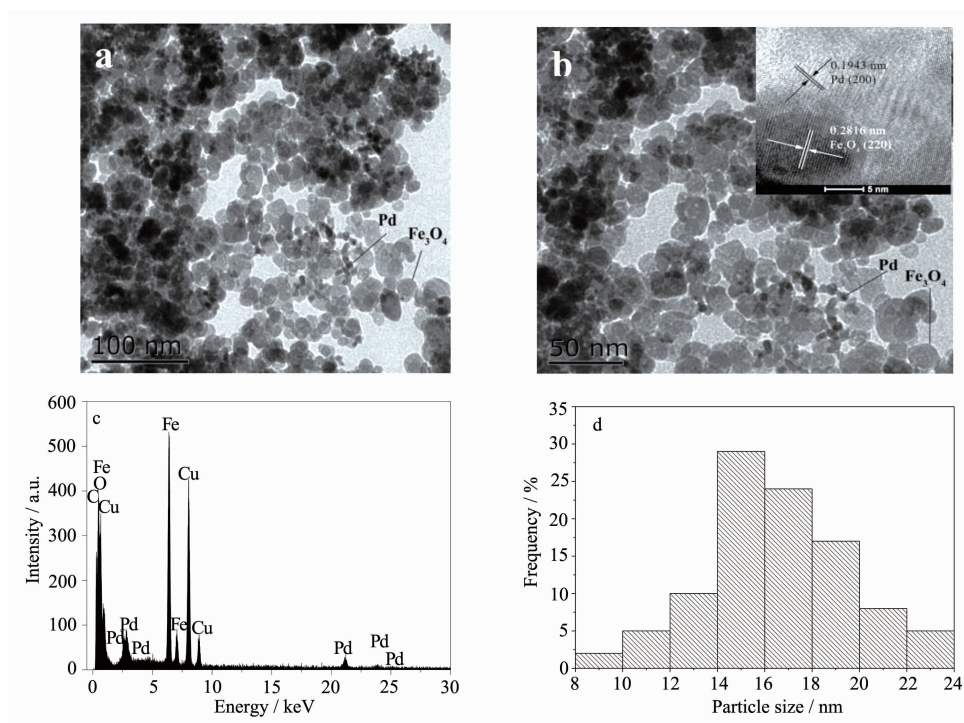
Fig.2   TEM (a~b) and HRTEM (inset of b) image of Pd/Fe₃O₄ NPs, TEM-EDS spectrum of Pd/Fe₃O₄ NPs(c), and the histogram showing the particle size distribution of Pd/Fe₃O₄ NPs(d)

can be seen from the histogram (Fig.2d), the size of Pd/Fe₃O₄ NPs is in the range of 8~24 nm (mean diameter: (16.5±1.5) nm).

Room temperature magnetic characteristics of the Fe₃O₄ NPs, the Pd/Fe₃O₄ NPs and Recycled Pd/Fe₃O₄ NPs were investigated by recording the magnetization versus applied field curves (Fig.3)[38]. At 298.15 K and 30 kOe, the hysteresis loops of the Fe₃O₄ NPs and the Pd/Fe₃O₄ NPs show that the magnetization decreases on palladium, which indicate the Pd NPs load on Fe₃O₄ NPs. Furthermore, the magnetization of recycled

Pd/Fe₃O₄ NPs is higher than Pd/Fe₃O₄ NPs, showing a loss of the Pd NPs during Heck reaction.

2.2 Pd content

The content of Pd loaded on Fe₃O₄ was investigated via ICP, the results were shown in Fig.4. The initial content of Pd was 2.25% (n/n, the same below), whereas the Pd content decreased after the first run, the one recovered via magnetic separation, suggesting the Pd NPs may be leached out during reaction and recovery. Although palladium nanoparticles were lost, the loss is small after five
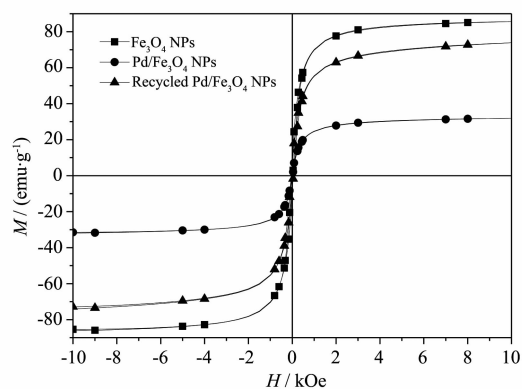

Fig.3   Hysteresis loops of Fe₃O₄ NPs, Pd/Fe₃O₄ NPs and recycled Pd/Fe₃O₄ NPs
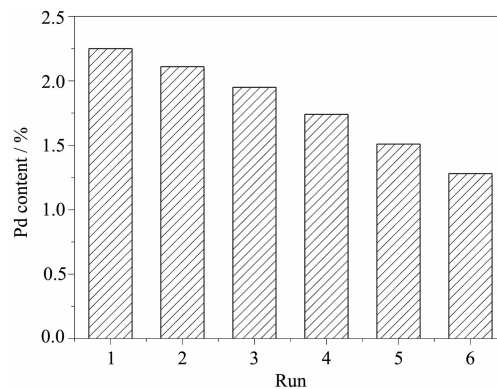

Fig.4   ICP results for the content of Pd loaded on Fe₃O₄ for each run

recycling runs (from 2.25% to 1.28%). This finding revealed that the as-synthesized catalyst was Pd/Fe$_3$O$_4$ and the catalyst can be used as a stable catalyst for Heck reactions.

2.3 TGA Analyses

TGA was used to determine the thermal stability. Fig.5 depicts the TGA result of Pd/Fe$_3$O$_4$ NPs under a nitrogen atmosphere. The first weight loss at 162 ℃ that is less weight loss is completely attributed to the removal of physically adsorbed solvent molecules and moisture. The other weight loss at 417 ℃ corresponds to the degradation of PVP-Pd (0) complex. Thus, the catalyst was stable up to 162 ℃. In addition, the coated Fe$_3$O$_4$ nanoparticles show an excellent thermal stability up to 800 ℃.
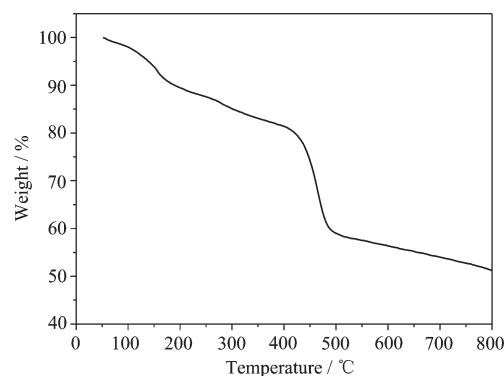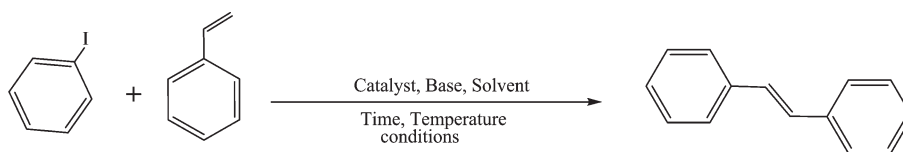

Fig.5　TGA curve for Pd/Fe$_3$O$_4$ catalyst

2.4 Catalytic activity for Heck coupling reaction

The Pd/Fe$_3$O$_4$ NPs catalyst was applied in the Heck reaction to evaluate the catalytic performance (Scheme 1). Initially, the reaction was carried out
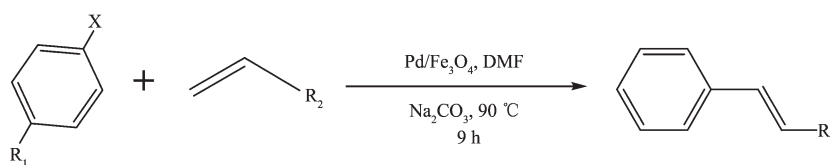

Scheme 1

Table 1　Various conditions for Heck reaction between iodobenzene and styrene using Pd/Fe₃O₄ NPs catalyst[a]

Entry	Catalyst(Pd content / %)	Base	Solvent	Time / h	T / ℃	Yield [b] / %
1	Pd/Fe$_3$O$_4$ (1.84)	K$_2$CO$_3$	EtOH	7	80	40
2	Pd/Fe$_3$O$_4$ (2.04)	K$_2$CO$_3$	EtOH	7	80	46
3	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	EtOH	7	80	70
4	Pd/Fe$_3$O$_4$ (2.45)	K$_2$CO$_3$	EtOH	7	80	57
5	Pd/Fe$_3$O$_4$ (2.65)	K$_2$CO$_3$	EtOH	7	80	54
6	Pd (2.25)	K$_2$CO$_3$	EtOH	7	80	43
7	Fe$_3$O$_4$ (0)	K$_2$CO$_3$	EtOH	7	80	0
8	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	EtOH	8	80	61
9	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	EtOH	9	80	83
10	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	EtOH	10	80	72
11	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	EtOH	11	80	81
12	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	EtOH	9	70	53
13	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	EtOH	9	90	90
14	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	EtOH	9	100	66
15	Pd/Fe$_3$O$_4$ (2.25)	NaOH	EtOH	9	90	84
16	Pd/Fe$_3$O$_4$ (2.25)	Pyridine	EtOH	9	90	50
17	Pd/Fe$_3$O$_4$ (2.25)	NaHCO$_3$	EtOH	9	90	79
18	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	H$_2$O	9	90	89
19	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	DMSO	9	90	91
20	Pd/Fe$_3$O$_4$ (2.25)	K$_2$CO$_3$	DMF	9	90	93

[a]Reaction condition: iodobenzene (1.4 mmol), styrene (1.7 mmol), Pd/Fe$_3$O$_4$ (0.075 g), base (2.0 mmol), solvent (3 mL).

[b]GC yield to the *E*-alkene related to iodobenzene, normalized areas.

Scheme 2

Table 2 Heck reaction using different aryl halides with terminal alkenes catalyzed by Pd/Fe$_3$O$_4$ NPs[a]

Entry	Aryl halide	Alkene	Yield[b] / %
1			93
2			91
3			85
4			89
5			82
6			74
7			90
8			82
9			83
10			86
11			79
12			75

[a]Reaction condition: aryl halide (1.4 mmol), alkene (1.7 mmol), Pd/Fe$_3$O$_4$ (0.075 g, 2.25%), Na$_2$CO$_3$ (2.0 mmol), DMF (3 mL), 90 ℃, 9 h;

[b]GC yield to the *E*-alkene related to iodobenzene, normalized areas.

between iodobenzene and styrene as model substrates for the development of optimized conditions (Table 1).

Control experiments show that there are different yields for the prepared catalysts with different contents of Pd (Entries 1~5). A decrease in the catalyst loading from 2.25% to 1.84% afford the product in lower yield (Entries 1~3). No significant improvement on the yield was observed using the catalyst with higher amounts of Pd (Entries 3~5) and single Pd (Entry 6). And Fe₃O₄ (Entry 7) have a lower yield. The catalyst with 2.25% of Pd was found to be optimum (Entry 3). The better yields were obtained when the time of the reaction was 9 h (Entry 9) and the temperature of the reaction was 90 ℃ (Entry13). The reactivity of the catalyst in various solvents using both organic and inorganic bases was investigated to check the influence of nature solvent on the yield of the product (Entries 13, 15~20). The results indicated that the nature of the base is of great importance in the Heck coupling. Among the tested bases, K_2CO_3 was found to be superior (Entry 13). From cost, availability, and environmental impact, water (Entry 18) is the best solvent for reaction especially for potential industry application, even if a slightly higher yield (93% vs 90%) was achieved as DMF (Entry 20) was employed. But the cycle performance of the catalyst is poor, when water acts as a solvent for reaction. In addition, the use of polar solvents such as ethanol, DMSO (Entries 13, 19) is not beneficial to the reaction as the yield of the product was same or very less than.

According to the data which were obtained from optimizing study, the Heck reaction can be properly carried out at 90 ℃ in the presence of Pd/Fe₃O₄ NPs (2.25%), using K_2CO_3 as base, in DMF solvent for 9 h.

Next, using the optimized procedure, a variety of aryl halide and alkene possessing were employed (Scheme 2). As shown in Table2, a reaction of iodobenzene and styrene has a higher yield under the optimized conditions (Entry 1).

To show the advantages of Pd/Fe₃O₄ NPs catalyst in comparison with other catalysts, we summarized some other reported homogeneous and heterogeneous palladium catalysts for Heck reaction between aryl halide and alkene. As shown in Table 3, the title catalyst is superior to some of the previously reported catalysts[33-37] with respect to reaction time, reaction temperature and yield. The notable features of this method are: the reaction system is simple; toxic reagents and homogeneous catalysts are eliminated; the Pd/Fe₃O₄ NPs catalyst can be easily recovered.

2.5 Catalyst recyclability

The reusability of the catalysts is one of their most important advantages, which makes them useful for commercial applications. The reusability of the heterogeneous Pd/Fe₃O₄ NPs catalyst was also evaluated in Heck coupling reaction under the optimized conditions. The recycled catalyst could be reused for five times without any treatment (Fig.6).

The reaction was found to yield products from 93% to 52%, and Pd leaching is the main cause for the activity drop (Fig.4). Thus, the magnetic catalyst is stable during the Heck coupling reaction.

Table 3　Comparison of present methodology with other reported methods for Heck reaction between iodobenzene with styrene

Entry	Catalyst	Time / h	Temperature / ℃	Yield* / %
1[39]	Pd₄Cl₈(PzTB)₂	3.5	120	90
2[40]	Pd(0)-PVP	4	80	93
3[41]	[Gmim]CL-Pd(Ⅱ)	8	25	83
4[42]	Oxamate-containin palladium(Ⅱ)	0.5	120	69
5[43]	Pd-PEG	8	100	4
6(This work)	Pd/Fe₃O₄ NPs	9	90	93

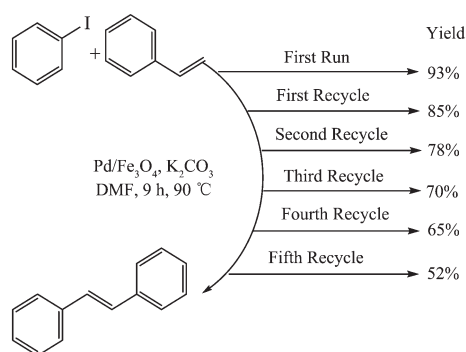*Isolated yields determined by GC, based on iodobenzene.

Fig.6　Reusability of Pd/Fe$_3$O$_4$ NPs for Heck coupling reaction

3　Conclusions

Palladium modied Fe$_3$O$_4$ nanoparticles prepared by PVP as stabilizer is a highly efficient, magnetically recoverable and recyclable catalyst for the Heck coupling reaction under optimal conditions. Easy workup (using external magnetic attraction) and environment are two other advantages of this catalyst system. Thus, the superior performance of Pd/Fe$_3$O$_4$ NPs makes it a promising catalyst in organic synthesis.

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