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# Silica-coated nano-$Fe_3O_4$-supported iminopyridine palladium complex as an active, phosphine-free and magnetically separable catalyst for Heck reactions

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A novel magnetic nanoparticle-supported iminopyridine palladium complex was successfully prepared by attaching palladium acetate to iminopyridine ligand-functionalized silica-coated nano-$Fe_3O_4$. The as-prepared catalyst was well characterized and was evaluated in Heck reactions in terms of activity and recyclability. It was found to be highly efficient for the reactions of various aryl iodides and aryl bromides having electron-withdrawing groups with olefins under phosphine-free and inert atmosphere-free conditions. Moreover, the catalyst could be conveniently recovered using an external magnet, and the recyclability was influenced by the base in the Heck reaction. The catalyst could be reused at least six times with no significant loss in activity when triethylamine acted as the base.

KEYWORDS

Heck reaction, heterogeneous catalyst, iminopyridine palladium, magnetic nanoparticle

## 1 | INTRODUCTION

The palladium-catalyzed Heck reaction of aryl halides with olefins is one of the most important and powerful strategies for C─C bond formation in modern organic synthesis.[1–3] And the substituted olefins are versatile and valuable building blocks in the fields of pharmaceuticals, natural products and functional materials.[4,5] Usually, the reaction is catalyzed by palladium salts associated with ligands, such as phosphines,[6,7] which stabilize the palladium species and prevent the appearance of inactive palladium black. However, homogeneous catalytic processes suffer from the tedious separation of the catalyst in order to avoid contamination of residual metals in the final products, especially for pharmaceuticals.[8] Additionally, in view of economic and environmental concerns, the recovery and reuse of the expensive palladium catalyst are highly desirable, particularly in large-scale synthesis. Thus, many efforts have focused on the development of environmentally benign and highly efficient heterogeneous palladium catalysts for this coupling.[9] A series of organic and inorganic materials, such as polymers,[10,11] ionic liquids,[12-,3] silica,[14,15] carbon[16] and metal oxides,[17] have been explored for immobilizing palladium catalysts.

Magnetic nanoparticles (MNPs) have attracted much interest as novel support materials due to high surface area, good stability, facile functionalization and magnetic separation, low cost and low toxicity.[18,19] Because of these attractive features, a variety of MNP-supported catalysts have been designed and widely applied in coupling reactions.[20,21] For example, Du *et al.* prepared an efficient MNP-supported phosphine nano-Pd catalyst for Suzuki and Heck reactions.[22] Zolfigol *et al.* prepared an active magnetically separable Pd catalyst by the immobilization of $PdCl_2$ on silica-coated nano-$Fe_3O_4$ treated with $ClPPh_2$ and used it in coupling reactions.[23] And Li *et al.* designed another phosphine Pd complex for C─C coupling reactions.[24] Lately, Panahi's group developed phosphanamine-functionalized MNPs for the Pd-catalyzed Heck reaction.[25] Shaikh *et al.* used MNP-supported ferrocenylphosphine–Pd as a reusable catalyst for Heck olefination.[26] And Gholinejad *et al.* designed a new phosphinite-functionalized $Fe_3O_4$-supported Pd catalyst for Suzuki coupling.[27] Phosphines are some of the most popular ligands. However, they are air-sensitive, expensive and virulent, which limits wide use in large-scale application. So, it is still desirable to develop phosphine-free MNP-supported Pd catalysts with high activity, excellent stability and low cost.

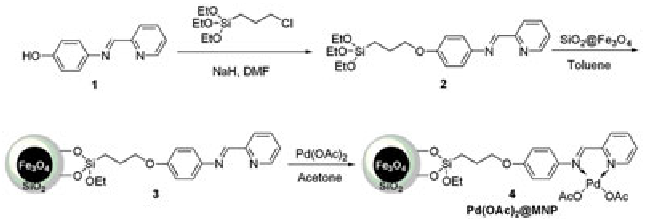
Schiff bases are known as types of powerful organic ligands, which are widely applied in transition metal-catalyzed reactions.[28,29] Iminopyridine bidentate ligands, a new type of Schiff base, have appeared as attractive ligands for Pd-catalyzed polymerization,[30] cyclization[31] or Heck reactions.[32] Previous interesting works on these N,N-chelating ligand-modified silica- or biomaterial-supported Pd catalysts for C─C couplings by Clark's group[33–35] motivate further exploration of better heterogeneous Pd catalysts. More recently, some similar Pd complexes immobilized on polymer,[10] porous silica[36,37] or magnetic supports[38–40] have emerged as active catalysts for Pd-catalyzed C─C coupling reactions.

Driven by the unique properties of MNPs and the valuable applications of iminopyridine bidentate ligands and in continuation of our efforts in designing heterogeneous catalysts,[41–44] herein we present a silica-coated nano-$Fe_3O_4$-supported iminopyridine Pd complex ($Pd(OAc)_2$@MNP; Scheme 1) as a new magnetically separable catalyst for the Heck reaction of aryl halides with olefins.

## 2 | EXPERIMENTAL

### 2.1 | General remarks

Silica-coated nano-$Fe_3O_4$ ($SiO_2$@$Fe_3O_4$) was prepared according to our previously reported procedure.[41] All solvents used were strictly dried according to standard operations and stored over 4 Å molecular sieves. Other chemicals (AR grade) were commercially available and used without further purification. Infrared (IR) spectra were obtained with a Nicolet spectrometer (KBr). NMR spectra were recorded with a Bruker DRX500 (500 MHz) spectrometer. Thermogravimetric analysis (TGA) was carried out under nitrogen using a Shimadzu TGA-50 spectrometer. Elemental analysis was performed with an Elementar Vario EL III recorder. Transmission electron microscopy (TEM) images were obtained with a JEM-2100 instrument. Palladium content of the catalyst was measured using inductively coupled plasma (ICP) analysis with an L-PAD analyzer (Prodigy). The magnetization curve was obtained with a vibrating sample magnetometry (VSM) instrument (JDM-13 T). Quantitative analysis of the conversion yield was conducted using GC (Varian CP-3800).



**SCHEME 1** Synthetic route to MNP-supported palladium catalyst Pd(OAc)2@MNP

### 2.2 | Synthesis of $Pd(OAc)_2$@MNP

#### 2.2.1 | Synthesis of silane-functionalized iminopyridine ligand (2)[42]

A mixture of pyridine-2-carbaldehyde (5.35 g, 50.0 mmol), *p*-aminophenol (5.46 g, 50.0 mmol) and methanol (25 ml) was stirred for 3 h under reflux. Then, the mixture was cooled to ambient temperature and the iminopyridine ligand **1** was obtained immediately by filtration (6.44 g, 65%).

Compound **1** (3.97 g, 20.0 mmol) and NaH (0.72 g, 30.0 mmol) were added into 30 ml of anhydrous dimethylformamide (DMF) and the resulting mixture was stirred for 2 h at room temperature. 3-Chloropropyltriethoxysilane (5.06 g, 21 mmol) was then added dropwise and the mixture was stirred at 85°C under nitrogen atmosphere for 24 h, and then cooled and filtered. The filtrate was concentrated under vacuum. The desired product **2** was obtained by purification with silica gel chromatography (hexane–EtOAc, 5:1) as a yellow oil (5.8 g, 72%).

#### 2.2.2 | Synthesis of iminopyridine-functionalized MNPs (3)

A mixture of $SiO_2$@$Fe_3O_4$ (1.0 g) and dry toluene (50 ml) was sonicated for 1 h, and compound **2** (0.5 g, 1.24 mmol) and pyridine (0.25 ml, 3.08 mmol) were then added. After stirring for 24 h under reflux in nitrogen atmosphere, the mixture was cooled to ambient temperature. The product **3** was collected using a permanent magnet, washed several times with toluene and acetone and then dried under vacuum overnight.

#### 2.2.3 | Synthesis of palladium catalyst $Pd(OAc)_2$@MNP (4)

Powder **3** (1.0 g) was added into an acetone (50 ml) solution of palladium acetate (67.2 mg, 0.30 mmol), and the mixture was stirred at room temperature for 24 h under nitrogen atmosphere. Then, the solid was collected using a permanent magnet, washed several times with acetone and then dried under vacuum overnight to afford the $Pd(OAc)_2$@MNP catalyst. The content of Pd was 1.57% as determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

### 2.3 | General procedure for heck reactions

Aryl halide (1.0 mmol), olefin (1.5 mmol), $Pd(OAc)_2$@MNP (35.0 mg, 0.5 mol%), triethylamine (2.0 mmol) and DMF (5 ml) were added to a tube and sealed. The reaction mixture was stirred at 100°C for an appropriate time. After completion of the reaction, the catalyst was separated using a permanent magnet, and washed sequentially with water, ethanol and ether, and dried under vacuum. The obtained DMF solution was diluted with water (15 ml) and extracted with ether (2 × 10 ml). The combined ether fractions were dried over $Na_2SO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether–ethyl acetate, 10:1) to afford the corresponding products.

## 2.4 | Analytical data for products

(*E*)-Methyl cinnamate (**a**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.72 (d, *J* = 16.0 Hz, 1H), 7.61–7.48 (m, 2H), 7.41–7.39 (m, 3H), 6.46 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H).

(*E*)-Ethyl cinnamate (**b**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.71 (d, *J* = 16.0 Hz, 1H), 7.55–7.53 (m, 2H), 7.41–7.38 (m, 3H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

(*E*)-Butyl cinnamate (**c**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.71 (d, *J* = 16.0 Hz, 1H), 7.56–7.53 (m, 2H), 7.41–7.38 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 1.71–1.66 (m, 2H), 1.48–1.44 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

(*E*)-Stilbene (**d**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.54 (d, *J* = 7.4 Hz, 4H), 7.38 (t, *J* = 7.7 Hz, 4H), 7.28 (m, 2H), 7.14 (s, 2H).

(*E*)-Butyl 3-(4-bromophenyl)acrylate (**e**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.61 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.71–1.65 (m, 2H), 1.44–1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

(*E*)-Butyl 3-(4-nitrophenyl)acrylate (**f**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 8.26–8.24 (m, 2H), 7.69–7.67 (m, 3H), 6.57 (d, *J* = 16.0 Hz, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 1.74–1.68 (m, 2H), 1.47–1.43 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

(*E*)-Butyl 3-(4-hydroxyphenyl)acrylate (**g**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.63 (d, *J* = 16.0 Hz, 1H), 7.45–7.42 (m, 2H), 6.86–6.83 (m, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 5.69 (s, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.71–1.67 (m, 2H), 1.48–1.43 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

(*E*)-Butyl 3-(4-aminophenyl)acrylate (**h**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.59 (d, *J* = 15.9 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.66–6.63 (m, 2H), 6.24 (d, *J* = 15.9 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.94 (s, 2H), 1.70–1.64 (m, 2H), 1.43–1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

(*E*)-Butyl 3-(4-methoxyphenyl)acrylate (**i**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.63 (d, *J* = 16.0 Hz, 1H), 7.46–7.44 (m, 2H), 6.89–6.87 (m, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.80 (s, 3H), 1.68–1.64 (m, 2H), 1.44–1.39 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

(*E*)-Ethyl 3-(2-methoxyphenyl)acrylate (**j**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 8.00 (d, *J* = 16.2 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.36–7.32 (m, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.53 (d, *J* = 16.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

(*E*)-Ethyl 3-*p*-tolylacrylate (**k**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.68 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).

(*E*)-Ethyl 3-(4-acetylphenyl)acrylate (**l**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.97–7.95 (m, 2H), 7.69 (d, *J* = 16.0 Hz, 1H), 7.61–7.59 (m, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.61 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

(*E*)-Ethyl 3-(4-formylphenyl)acrylate (**m**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 9.99 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.68–7.63 (m, 3H), 6.51 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

(*E*)-Ethyl 3-(3-formylphenyl)acrylate (**n**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 10.01 (s, 1H), 7.99 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 16.1 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

(*E*)-Ethyl 3-(4-(trifluoromethyl)phenyl)acrylate (**o**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.68 (d, *J* = 16.0 Hz, 1H), 7.64–7.60 (m, 4H), 6.50 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

(*E*)-Ethyl 3-(4-nitrophenyl)acrylate (**p**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 8.25 (d, *J* = 8.6 Hz, 2H), 7.73–7.67 (m, 3H), 6.56 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

(*E*)-Ethyl 3-(4-cyanophenyl)acrylate (**q**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$, ppm): 7.69–7.65 (m, 3H), 7.61 (d, *J* = 8.3 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).

## 3 | RESULTS AND DISCUSSION

The $Pd(OAc)_2$@MNP catalyst was prepared via the procedure shown in Scheme 1. Firstly, the precursor silane-functionalized iminopyridine ligand **2** was synthesized by nucleophilic substitution of iminopyridine ligand **1** and (3-chloropropyl)triethoxysilane under basic conditions. Secondly, a condensation reaction of $SiO_2$@$Fe_3O_4$ with precursor **2** afforded iminopyridine ligand-functionalized MNPs (**3**). Ultimately, the obtained **3** was reacted with palladium acetate in acetone at room temperature for 24 h to afford the target catalyst, $Pd(OAc)_2$@MNP.

In order to confirm the successful functionalization of MNPs, IR spectroscopy was employed to allow a detailed investigation of $SiO_2$@$Fe_3O_4$, precursor **2** and functionalized MNPs **3** (Figure 1). The Si─O─Si and Fe─O vibrations of $SiO_2$@$Fe_3O_4$ can be obviously observed at 1090.8 and 578.6 cm$^{-1}$, respectively. The IR spectrum of precursor **2** shows typical bands at around 1589 cm$^{-1}$ (C═N vibration), 1497 cm$^{-1}$ (C═C vibration of aryl ring), 2926 and 2879 cm$^{-1}$ (alkyl chain stretching vibrations). While in the spectrum of functionalized MNPs **3**, these characteristic peaks are at similar wavenumbers, with a slight offset due to the interaction with the support. Nevertheless, none of these significant

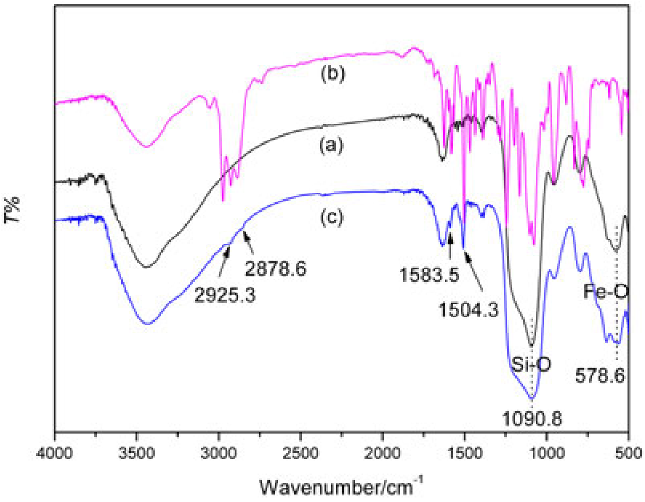


**FIGURE 1** IR spectra of (a) SiO2@Fe3O4, (b) precursor 2 and (c) functionalized MNPs 3

features can be observed in the spectrum of the $SiO_2@Fe_3O_4$ support. Moreover, the nitrogen content of the functionalized MNPs **3** determined by elemental analysis is 0.56%, which shows that the loading amount of the iminopyridine ligand is 0.20 mmol $g^{-1}$. These results indicate that the iminopyridine ligand was successfully grafted onto $SiO_2@Fe_3O_4$.

The resulting functionalized MNPs **3** were treated with an acetone solution of palladium acetate at ambient temperature to provide the desired catalyst $Pd(OAc)_2@MNP$ (**4**). The Pd content measured using ICP-AES is 1.57%, which indicates the loading amount of Pd is 0.15 mmol $g^{-1}$. The morphology of $Pd(OAc)_2@MNP$ was investigated using TEM. The dark nano-$Fe_3O_4$ cores are surrounded by grey silica shell and the mean grain size is 20–25 nm (Figure 2a).

The stability of the $Pd(OAc)_2@MNP$ catalyst was also investigated using TGA (Figure 3). The TGA curve indicates an initial weight loss of 1.1% up to 120°C, owing to the adsorbed water catalyst on the support. The organic fractions are decomposed in the range 150–500°C. The obvious thermal degradation of the catalyst occurs after 200°C, which reveals good stability. The main weight loss of the organic moieties is about 8.0%, which is well consistent with the elemental analysis.

The magnetic property of $Pd(OAc)_2@MNP$ was evaluated using VSM at room temperature. The VSM magnetization curve goes through the zero point (Figure 4). The phenomenon of no magnetic hysteresis indicates that the as-prepared catalyst is superparamagnetic. As a result, the catalyst can be simply separated from the reaction system using an external magnet.

The activity of $Pd(OAc)_2@MNP$ was initially investigated in the Heck reaction of iodobenzene and butyl acrylate. The effects of base, solvent, temperature and Pd loading were screened to optimize reaction conditions (Table 1). Initially, $K_2CO_3$, $K_3PO_4$, NaOAc, KF, $NEt_3$, $NBu_3$ and pyridine were investigated as bases. As a result, $NEt_3$ is found to be the best

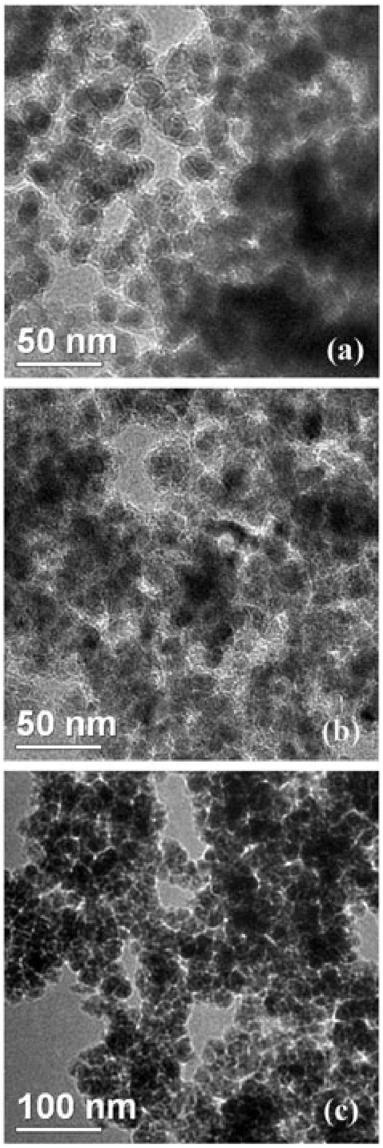


**FIGURE 2** TEM images of (a) fresh catalyst, (b) catalyst reused six times with triethylamine as the base and (c) catalyst reused three times with potassium carbonate as the base

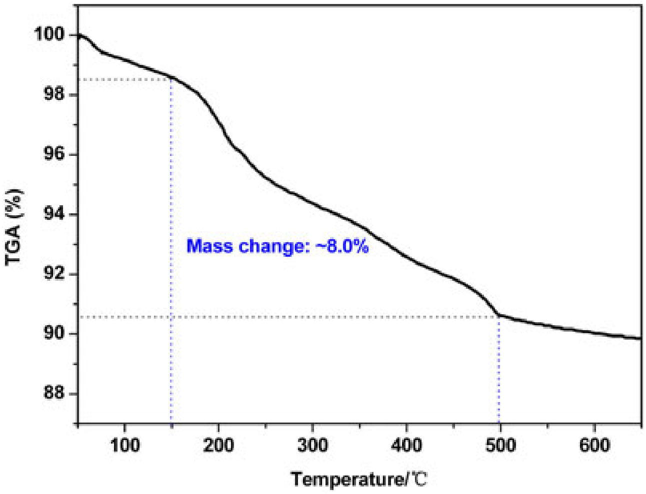


**FIGURE 3** TGA of Pd(OAc)2@MNP

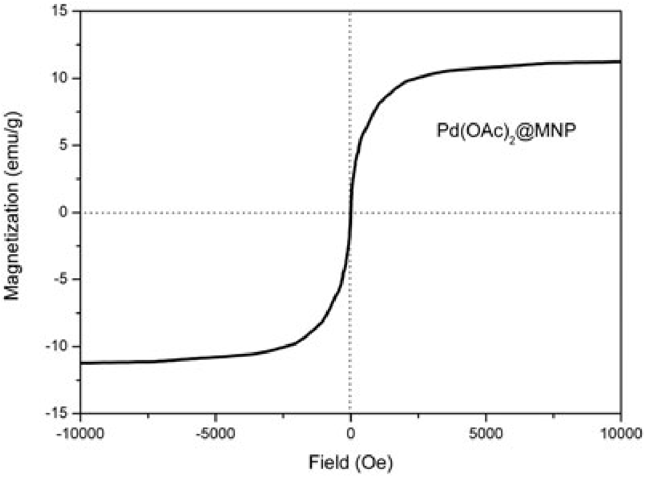
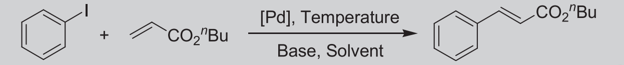


**FIGURE 4** Magnetization curve of Pd(OAc)2@MNP

**TABLE 1** Optimization of reaction conditions[a]



| Entry | Base | Solvent | Time (h) | Temp. (°C) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $K_2CO_3$ | DMF | 1.5 | 100 | 95 |
| 2 | $K_3PO_4$ | DMF | 1.5 | 100 | 90 |
| 3 | NaOAc | DMF | 1.5 | 100 | 56 |
| 4 | KF | DMF | 1.5 | 100 | 18 |
| 5 | $NEt_3$ | DMF | 1.5 | 100 | 96 |
| 6 | $NBu_3$ | DMF | 1.5 | 100 | 92 |
| 7 | Pyridine | DMF | 1.5 | 100 | <5 |
| 8 | $NEt_3$ | NMP | 1.5 | 100 | 90 |
| 9 | $NEt_3$ | PhMe | 3 | 100 | 56 |
| 10 | $NEt_3$ | EtOH | 3 | 80 | 22 |
| 11 | $NEt_3$ | $CH_3CN$ | 3 | 80 | 28 |
| 12[c] | $NEt_3$ | DMF–$H_2O$ | 3 | 100 | 62 |
| 13 | $NEt_3$ | None | 1.5 | 100 | 76 |
| 14 | $NEt_3$ | DMF | 1.5 | 80 | 72 |
| 15[d] | $NEt_3$ | DMF | 1 | 100 | 98 |
| 16[e] | $NEt_3$ | DMF | 6 | 100 | 67 |
| 17[f] | $NEt_3$ | DMF | 1.5 | 100 | 82 |

[a] Reaction conditions: iodobenzene (1.0 mmol), butyl acrylate (1.5 mmol), base (2.0 mmol), Pd(OAc)$_2$@MNP (0.5 mmol% Pd), solvent (5 ml).

[b] Isolated yield.

[c] 1:1, *v*/v.

[d] Pd(OAc)$_2$@MNP (1.0 mmol% Pd).

[e] Pd(OAc)$_2$@MNP (0.1 mmol% Pd).

[f] Pd(OAc)$_2$@MCM-41 (0.5 mmol% Pd).

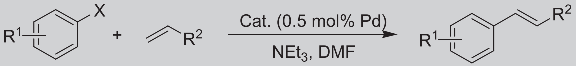
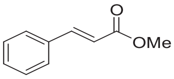
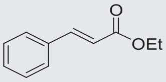
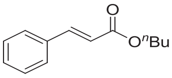
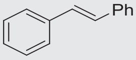
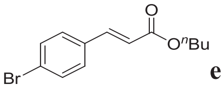
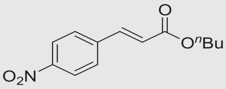
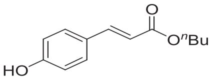
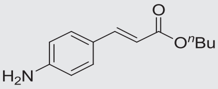
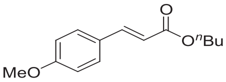
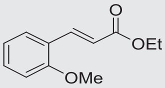
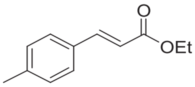
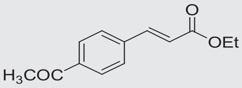
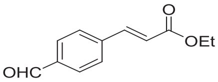
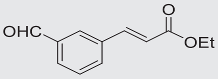
base (Table 1, entry 5). Slightly lower yields are obtained when $K_2CO_3$, $K_3PO_4$ or $NBu_3$ is used as the base (Table 1, entries 1, 2 and 6). However, when NaOAc acts as the base, a moderate yield is obtained and only trace product is detected with pyridine as the base (Table 1, entries 3 and 7). Subsequently, various solvents were screened, DMF giving the best result (Table 1, entry 5). But, the reaction is less efficient when hydrous DMF is used as the solvent (Table 1, entry 12). It is worth noting that the reaction can be carried out under solvent-free conditions, which afford the product with 76% yield (Table 1, entry 13). Finally, the temperature and Pd loading were evaluated. Reducing the reaction temperature or Pd loading leads to a decrease in yield (Table 1, entries 14 and 16). Interestingly, Pd(OAc)$_2$@MNP can promote the Heck reaction more efficiently than Pd(OAc)$_2$@MCM-41[42] (Table 1, entry 17), which indicates that the smaller particles allow more diffusion effects and then accelerate the reaction.

Under the optimized reaction conditions, the Heck reactions of a variety of aryl halides with olefins were investigated, and the results are summarized in Table 2. Aryl iodides with electron-withdrawing or electron-donating groups undergo efficient couplings with olefins at 100°C for 1–4 h, which afford the corresponding products in good to excellent yields ranging from 80 to 98% (Table 2, entries 1–11). As for aryl bromides with electron-withdrawing groups, satisfactory yields (84–93%) are also obtained when the coupling reactions are carried out at 120°C for 4 h (Table 2, entries 12–17). However, for other aryl bromides and aryl chlorides as substrates, the catalytic system is less effective even for a prolonged time or at higher temperature (Table 2, entries 18–20). Since the Heck reaction with unsubstituted olefins is rarely investigated,[45] a preliminary study of the coupling reactions with simple olefins was also undertaken. Unfortunately, there is no substantial improvement in the Heck reaction of iodobenzene with 1-octene or cyclohexene for our catalytic system (Table 2, entries 21 and 22).

To further evaluate the catalytic performance of Pd(OAc)$_2$@MNP, a comparison was made of the activity of various supported Pd catalysts in the Heck reaction of iodobenzene with ethyl acrylate (Table 3). The as-prepared catalyst Pd(OAc)$_2$@MNP is an equally or more efficient catalyst with respect to yield and turnover frequency (TOF) value than previously reported ones.

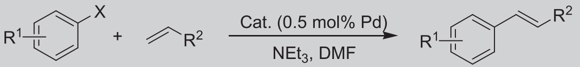
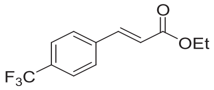
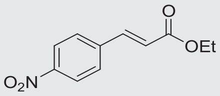
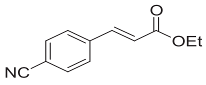
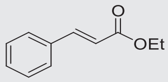
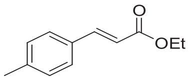
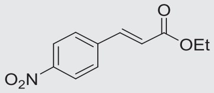
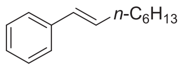
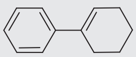
The recyclability of the MNP-supported Pd catalyst was then investigated using the Heck reaction of iodobenzene with butyl acrylate under the optimal conditions. After completion of the reaction, the catalyst was conveniently recovered using an external magnet (Figure 5), washed sequentially with water, ethanol and ether, and dried under vacuum for the next run. As can be seen from Figure 6, the catalyst can be reused six times with no significant loss in activity. As we know, an excellent yield can also be obtained when $K_2CO_3$ acts as the base (Table 1, entry 1); thus another recycling experiment using potassium carbonate as the base was conducted. The catalyst loses its activity gradually (Figure 6). After long-term heat stress, some corrosion occurs slowly due to the weak interactions between the silica layer of the catalyst and the strong alkali $K_2CO_3$ in strongly polar system, then the appearance of Pd leaching or aggregation leads to catalyst deactivation, which might be the main reason for loss of activity. In contrast, with triethylamine as an organic weak base, the corrosion of the silica layer could be

**TABLE 2** Heck reactions of aryl halides with olefins catalyzed by $Pd(OAc)_2$@MNP[a]

| Entry | $R^1$ | X | $R^2$ | Product | Time (h) | Temp. (°C) | Yield (%)[b] |
|---|---|---|---|---|---|---|---|
| | | | |  | | | |
| 1 | H | I | $CO_2Me$ |  **a** | 1 | 100 | 97 |
| 2 | H | I | $CO_2Et$ |  **b** | 1.5 | 100 | 98 |
| 3 | H | I | $CO_2{}^nBu$ |  **c** | 1.5 | 100 | 96 |
| 4 | H | I | Ph |  **d** | 2 | 120 | 90 |
| 5 | 4-Br | I | $CO_2{}^nBu$ |  **e** | 2 | 100 | 92 |
| 6 | 4-$NO_2$ | I | $CO_2{}^nBu$ |  **f** | 2 | 100 | 94 |
| 7 | 4-OH | I | $CO_2{}^nBu$ |  **g** | 3.5 | 100 | 86 |
| 8 | 4-$NH_2$ | I | $CO_2{}^nBu$ |  **h** | 4 | 100 | 80 |
| 9 | 4-OMe | I | $CO_2{}^nBu$ |  **i** | 3 | 100 | 91 |
| 10 | 2-OMe | I | $CO_2Et$ |  **j** | 4 | 100 | 84 |
| 11 | 4-Me | I | $CO_2Et$ |  **k** | 2 | 100 | 93 |
| 12 | 4-$COCH_3$ | Br | $CO_2Et$ |  **l** | 4 | 120 | 88 |
| 13 | 4-CHO | Br | $CO_2Et$ |  **m** | 4 | 120 | 92 |
| 14 | 3-CHO | Br | $CO_2Et$ |  **n** | 4 | 120 | 84 |

(*Continues*)

**TABLE 2** (Continued)

| Entry | $R^1$ | X | $R^2$ |  Product | Time (h) | Temp. (°C) | Yield (%)[b] |
|---|---|---|---|---|---|---|---|
| 15 | 4-$CF_3$ | Br | $CO_2Et$ |  **o** | 4 | 120 | 87 |
| 16 | 4-$NO_2$ | Br | $CO_2Et$ |  **p** | 4 | 120 | 93 |
| 17 | 4-CN | Br | $CO_2Et$ |  **q** | 4 | 120 | 91 |
| 18 | H | Br | $CO_2Et$ |  **b** | 8 | 120 | 56 |
| 19 | 4-Me | Br | $CO_2Et$ |  **k** | 12 | 120 | 37 |
| 20 | 4-$NO_2$ | Cl | $CO_2Et$ |  **p** | 12 | 130 | <5 |
| 21 | H | I | $n$-$C_6H_{13}$ |  **r** | 4 | 120 | 11[c] |
| 22 | H | I | –$C_4H_8$– |  **s** | 4 | 100 | 6[c] |

[a] Reaction conditions: aryl halide (1.0 mmol), olefin (1.5 mmol), NEt3 (2.0 mmol), Pd(OAc)2@MNP (0.5 mmol% Pd), DMF (5 ml).

[b] Isolated yield.

[c] Conversion yield of iodobenzene based on GC analysis.

**TABLE 3** Comparison of $Pd(OAc)_2$@MNP with other catalysts for the Heck reaction of iodobenzene with ethyl acrylate

| Entry | Catalyst (mol%) | Conditions | Yield (%) | TOF ($h^{-1}$) |
|---|---|---|---|---|
| 1 | SBA-15/$PrSO_3Pd$ (0.5) | $Et_3N$, toluene, 80°C, 4 h | 95[14] | 48 |
| 2 | $TiO_2$@Pd NPs (1) | $Et_3N$, DMF, 140°C, 10 h | 93[17] | 9 |
| 3 | $Pd(OAc)_2$/[HQ-PEG-DIL][$BF_4$] (1) | $Et_3N$, 100°C, 2 h | 94[12] | 47 |
| 4 | Pd–Schiff base complex/PS (0.5) | $K_2CO_3$, DMF, 100°C, 2 h | 99[11] | 99 |
| 5 | Pd-DABCO-γ-$Fe_2O_3$ (1) | $Et_3N$, DMF, 100°C, 0.5 h | 88[46] | 176 |
| 6 | $PdCl_2$/[DEA][HAc] (1.5) | 100°C, 12 h | 95[13] | 5 |
| 7 | Pd(0)-PVP (1) | $K_2CO_3$, EtOH, 80°C, 4 h | 78[47] | 20 |
| 8 | Pd/ZnO NPs (0.8) | $K_2CO_3$, DMF, 100°, 3.1 h | 98[48] | 38 |
| 9 | Pd/MNP@IL-$SiO_2$ (1) | $Et_3N$, DMAc, 110°C, 24 h | 100[49] | 4 |
| 10 | Pd@MOF-3 (1.25) | $Et_3N$, $^{n}$BuOH, 80°C, 24 h | 99[50] | 3 |
| 11 | Pd/Nf-G (0.3) | $Et_3N$, DMF, 120°C, 2 h | 90[51] | 150 |
| 12 | $Pd(OAc)_2$@MNP (0.5) | $Et_3N$, DMF, 100°C, 1.5 h | 98 | 131 |

negligible. Excitingly, TEM analysis of these two reused catalysts confirms the hypotheses. Apparently, the morphology of the catalyst reused six times with triethylamine as the base is similar to that of the fresh catalyst (Figure 2b). However, as can be seen from the morphology of the catalyst reused three times with potassium carbonate as the base, parts of grey

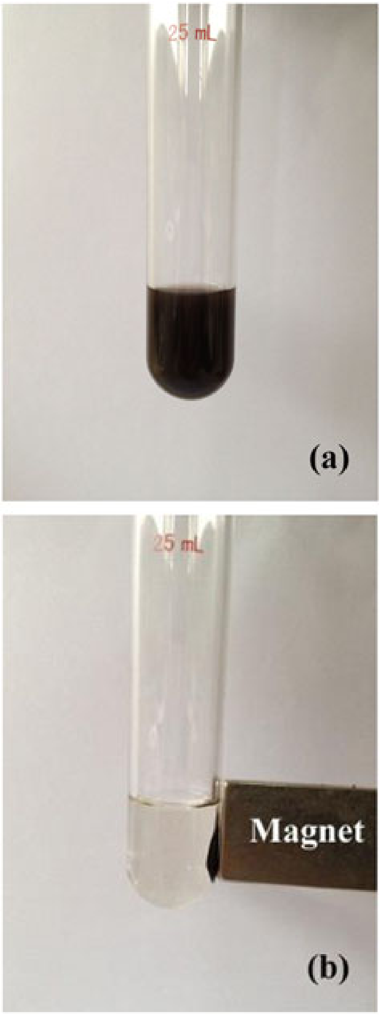


**FIGURE 5** Pd(OAc)2@MNP was (a) dispersed well in the reaction system and (b) was separated simply from the reaction system using an external magnet

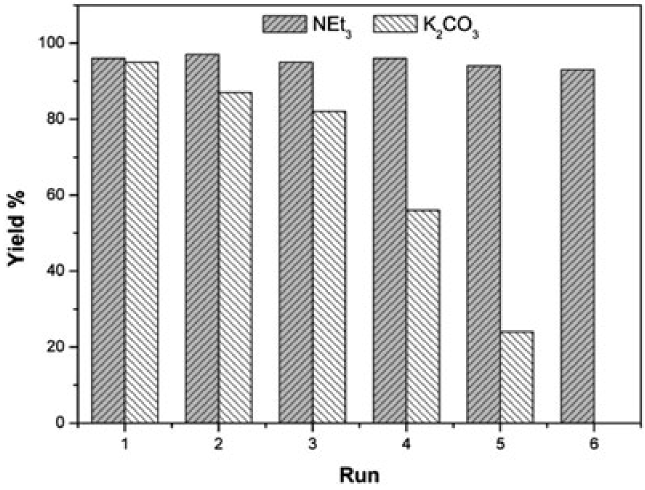


**FIGURE 6** Recycling experiment of Pd(OAc)2@MNP

silica shell-coated nano-$Fe_3O_4$ cores disappear (Figure 2c). Therefore, the reusability of the catalyst is obviously influenced by the base in the reaction system.

## 4 | CONCLUSIONS

In summary, we have developed a novel MNP-supported iminopyridine Pd complex as a new magnetically separable catalyst for the Heck reaction of aryl halides with olefins. High activity was observed and the catalyst could be conveniently recovered using an external magnet. Interestingly, the recyclability of $Pd(OAc)_2$@MNP was obviously influenced by the base in the Heck reaction. The catalyst could be reused at least six times with no significant loss in activity when triethylamine acted as the base.

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