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Magnetic polymer nanocomposite-supported Pd: an efficient and reusable catalyst for the Heck and Suzuki reactions in water†

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A novel type of magnetically responsive polymer nanocomposite Fe$_3$O$_4$@poly(undecylenic acid-*co*-4-vinyl pyridine-*co*-sodium acrylate) (Fe$_3$O$_4$@PUVS) was synthesized by the free radical polymerization of 4-vinyl pyridine (4-VP) with sodium acrylate (SAA) and Fe$_3$O$_4$@undecylenic acid. Pd^{2+} was then immobilized on this magnetic nanocomposite to form the magnetic Fe$_3$O$_4$@PUVS-Pd catalyst. This catalyst exhibited excellent catalytic activity for the Heck and Suzuki coupling reactions in water, and could be simply separated by using a permanent magnet. The supported catalyst could be used consecutively for six runs without significant loss of catalytic activity.

1 Introduction

Palladium-catalyzed Heck and Suzuki cross-coupling reactions constitute powerful synthetic methods for the carbon–carbon bond formation in pharmaceuticals and fine chemical technology.[1,2] Because of the high cost as well as the increasing shortage of palladium, its recycling and recovery in practical applications are becoming more and more necessary. Therefore, a variety of inorganic and organic solid-supported catalytic systems have been developed to solve these problems.[3–5] However, compared with their homogeneous counterparts, the solid-supported catalysts often suffer from lower activity and selectivity,[6,7] and it is highly desirable to develop new ones comparable to homogeneous catalysts in catalytic performance.

Polymer modified nanoparticle-supported catalysts have generated a lot of interest due to their unique properties. Polymer supports can be chemically modified easily with functional groups to coordinate with transition metals, and thus the stability of the catalyst could be improved.[8] Moreover, the nanoscale particles can enhance the catalytic performance due to their large surface-to-volume ratios and high densities of active sites relative to the bulk materials.[9–11] Therefore, polymer-modified nanoparticle-supported catalysts are expected to combine the advantages of both the homogeneous and heterogeneous catalysts.

In this regard, Isfahani and colleagues[12] recently prepared a new catalyst by immobilizing palladium nanoparticles on the nano-silica triazine dendritic polymer. This catalyst exhibits high activity for the Suzuki and Heck reactions at low concentrations (0.006 mol% and 0.01 mol% palladium respectively for these two reactions). In addition, it can be reused six times with no obvious decrease in yield. Despite this merit, however, this catalyst suffers from the drawback of a tedious centrifugation procedure to recover it because of its nanoscale size.

Fe$_3$O$_4$ nanoparticle-supported catalysts have attracted extensive attention because they can be simply separated from the reaction mixture using an external magnet.[13–15] The polymer-modified magnetic nanoparticle-supported palladium catalysts have been prepared to simplify the separation steps while maintaining high activity and selectivity of palladium.[16] Amali *et al.*[17] developed a magnetic catalyst by using highly branched polyethylenimine to entrap Pd nanoparticles onto the surface of Fe$_3$O$_4$. Du and co-workers[18] prepared a nanosized catalyst (Fe$_3$O$_4$/SiO$_2$/HPG-OPPh$_2$-PNP) by modifying Fe$_3$O$_4$/SiO$_2$ nanoparticles with glycerol and chlorodiphenyl phosphine. These catalysts are magnetically separable and highly active for the Suzuki and Heck reactions.[16–19]

So far, in most of the studies concerning the applications of Fe$_3$O$_4$ nanoparticle-supported catalysts, organic solvents, or mixed solvents containing DMF and NMP, are used as the reaction media. These organic solvents are inflammable, hazardous and have high boiling points, and cause concerns for human health and environment when used on a large scale. Water is an attractive green reaction medium because it is nontoxic, safe and cheap.[20,21] Therefore, it is highly desirable to develop efficient catalytic systems which can work in aqueous media. On the basis of our previous studies on solid-supported catalysts,[22] we recently

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prepared a novel catalyst Fe$_3$O$_4$@PUVS-Pd from readily available monomers. This catalyst exhibits high activity for the Heck and Suzuki reactions in water, and can be used for six runs without significant loss of catalytic activity. Herein we wish to report this new work in detail.

2 Experimental

2.1 Materials

4-Vinyl pyridine (4-VP, $\geq 95\%$) was purchased from ACROS and was distilled under vacuum. Acrylic acid (AA, $\geq 99.5\%$) was provided by Tianjin Guangfu Fine Chemicals and purified by vacuum distillation. N,N'-Methylenebisacrylamide (BIS, $\geq 98\%$) was purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Azodiisobutyronitrile (AIBN, $\geq 99\%$) was obtained from Xi'an Chemical Reagent Factory and was purified by recrystallization from ethanol. Palladium(II) chloride (PdCl$_2$, $\geq 59.5\%$) was purchased from Shenyang Keda Reagents Company. Undecylenic acid (UA, $\geq 96\%$) was obtained from Beijing Reagents Company. Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O, $\geq 99.5\%$), iron chloride tetrahydrate (FeCl$_2$·4H$_2$O, $\geq 99\%$) and tetrabutyl ammonium bromide (TBAB, $\geq 99\%$) were purchased from Tianjin Guangfu Fine Chemicals and used as received. Other reagents were of analytical grade and used as received. Deionized water was used in the present experiments.

2.2 Characterization

The FT-IR spectra were collected on a NEXUS670 (Nicolet, USA) spectrophotometer using KBr pellets of samples. TEM micrographs were taken using a Tecnai-G2-F30 (FEI, USA) transmission electron microscope operating at 300 kV to obtain morphology and size of the nanoparticles. The palladium contents were determined by using an AA240 (Varian Corporation, USA) atomic absorption spectrometer (AAS). The magnetic properties of nanoparticles were recorded on a Model 7304 (Lake Shore, USA) vibrating sample magnetometer (VSM) at room temperature. X-ray diffraction (XRD) patterns of the samples were obtained with a Shimadzu XRD-6000 spectrometer using nickel-filter Cu Kα radiation (λ = 0.15418 nm). X-ray photo-electron spectroscopy (XPS) measurements were recorded by using an Axis Ultra DLD electron spectrometer (Kratos, UK) with contaminated C as the internal standard (C1s = 284.8 eV). The surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained in CDCl$_3$ or DMSO-d$_6$ on an AVANCE III 400 NMR spectrometer (Bruker, Germany) with TMS as the internal standard.

2.3 Synthesis of Fe$_3$O$_4$@UA magnetic nanoparticles

Undecylenic acid-coated magnetic nanoparticles (Fe$_3$O$_4$@UA) were prepared according to the literature method:[23] 2.35 g of FeCl$_3$·6H$_2$O and 0.86 g of FeCl$_2$·4H$_2$O were dissolved in 40 mL of deionized water under vigorous stirring. The solution was purged with argon gas for 30 min, and then the temperature was raised to 80 °C. A solution of undecylenic acid (0.1 g) in 5 mL of acetone was then added into the above solution,

followed by the addition of 5 mL of ammonium hydroxide (25 wt%). Another 1.0 g of undecylenic acid was added into the thus formed suspension in batches (5 × 0.2 g). The mixture was kept at 80 °C for 30 min, and then allowed to cool to ambient temperature. After using the mixed solvent of acetone and MeOH (volume ratio of 1 : 1) to precipitate the suspension, the black precipitate (Fe$_3$O$_4$@UA) was separated using a permanent magnet and washed repeatedly with the same mixed solvent, and then dried under vacuum overnight.

2.4 Synthesis of Fe$_3$O$_4$@PUVS magnetic nanoparticles

Fe$_3$O$_4$@poly(undecylenic acid-co-4-vinyl pyridine-co-sodium acrylate) (Fe$_3$O$_4$@PUVS) magnetic nanoparticles were synthesized using the following free radical polymerization method: 40 mg of Fe$_3$O$_4$@UA was dispersed in 30 mL of ethanol. After intense sonication for 30 min, 2.50 mL of sodium acrylate (SAA, 2 mol L^{-1}), 0.54 mL of 4-VP and 154 mg of BIS were added into the above mixture. After bubbling with argon gas for 30 min, the solution was heated to 70 °C under vigorous stirring, and then 16 mg of AIBN was added into it. The polymerization process was maintained for 8 hours. The product was collected by magnetic separation and washed with ethanol five times and dried under vacuum overnight.

2.5 Preparation of the Fe$_3$O$_4$@PUVS-Pd catalyst

4 mg of Fe$_3$O$_4$@PUVS was dispersed in 2.0 mL of aqueous solution of PdCl$_2$ (0.05 mM), and the mixture was stirred for 12 hours at room temperature. The Fe$_3$O$_4$@PUVS-Pd catalyst was isolated by applying a permanent magnet and was washed with deionized water three times. Then it was directly used as catalyst without further treatment.

2.6 General procedure for the Heck reactions in water

A 5 mL screw-capped tube was charged with aryl halides (1.0 mmol), acrylic acid (1.5 mmol), K$_2$CO$_3$ (3.0 mmol), Fe$_3$O$_4$@PUSA-Pd catalyst (0.09 mol% Pd based on aryl halide) and deionized water (2.0 mL). After the mixture was degassed under argon purge for 10 min, it was stirred vigorously at reflux temperature for a given time. Then the reaction mixture was cooled to room temperature, and the catalyst was separated by using a permanent magnet and washed with deionized water (3 × 2.0 mL). The aqueous phase was combined and acidified by the addition of HCl (1 mol L^{-1}) to reach a pH of 1–2. The products were filtered and purified by recrystallization. The obtained products were analyzed by ^{1}H NMR and ^{13}C NMR.

2.7 General procedure for the Suzuki reactions in water

A 5 mL screw-capped tube was charged with aryl halides (1.0 mmol), phenylboronic acid (1.5 mmol), K$_2$CO$_3$ (3.0 mmol), Fe$_3$O$_4$@PUVS-Pd catalyst (0.09 mol% Pd) and deionized water (2.0 mL). After the mixture was degassed under argon purge for 10 min, it was stirred vigorously at 90 °C for a given time. Then the reaction mixture was allowed to cool to room temperature. The catalyst was separated by using a permanent magnet and the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The organic phase was dried over MgSO$_4$, filtered, concentrated,

and the residual was purified by flash chromatography on silica gel to afford the pure products, which were analyzed by ^{1}H NMR and ^{13}C NMR.

2.8 General recycling procedure for the Heck reaction

The Heck reaction of iodobenzene (1.0 mmol) with acrylic acid (1.5 mmol) was performed following the procedure described above (Section 2.6). After completion of the reaction, the mixture was cooled to room temperature. The catalyst was separated with a permanent magnet and washed with deionized water (3 × 2.0 mL), and was directly used for the next run.

The procedure of Pd leaching is presented here as follows: after completion of the seventh run, the reaction mixture was allowed to cool to room temperature and the catalyst was separated by using a permanent magnet. 2.0 mL of aqua regia ($V_{HCl} : V_{HNO_3} = 3 : 1$) was added into the reaction solution, followed by the addition of 2.5 mL of DMF. The above solution was transferred to a 10 mL volumetric flask, diluted with water to volume, and the mixture was analyzed by AAS.

3 Result and discussion

3.1 Synthesis and characterization of Fe₃O₄@PUVS-Pd

The synthesis of Fe_3O_4@PUVS-Pd is illustrated in Scheme 1. Firstly, the Fe_3O_4@UA nanoparticles were prepared using a co-deposition method.[23] In the second step, Fe_3O_4@PUVS was synthesized by copolymerization of 4-vinyl pyridine (4-VP), sodium acrylate (SAA) and Fe_3O_4@undecylenic acid (UA). The Fe_3O_4@PUVS-Pd catalyst was obtained by immobilizing Pd(II) on Fe_3O_4@PUVS particles in water. The content of Pd loaded on Fe_3O_4@PUVS was measured to be 0.223 mmol g^{-1} based on AAS analysis.

Fig. 1 shows the FT-IR spectra of magnetic nanoparticles: (a) Fe_3O_4@UA, (b) Fe_3O_4@PUVS and (c) fresh Fe_3O_4@PUVS-Pd catalyst. In Fig. 1a, the band at 588 cm^{-1} is attributed to Fe–O stretching vibration. The peak at 912 cm^{-1} corresponds to C–H out-of-plane bending vibration of the =CH₂ groups. The out-of-plane bending and stretching of C=C can be seen at 991 cm^{-1} and 1633 cm^{-1}, respectively. The bands at 2854 cm^{-1} and 2924 cm^{-1} are ascribed to the symmetric and asymmetric
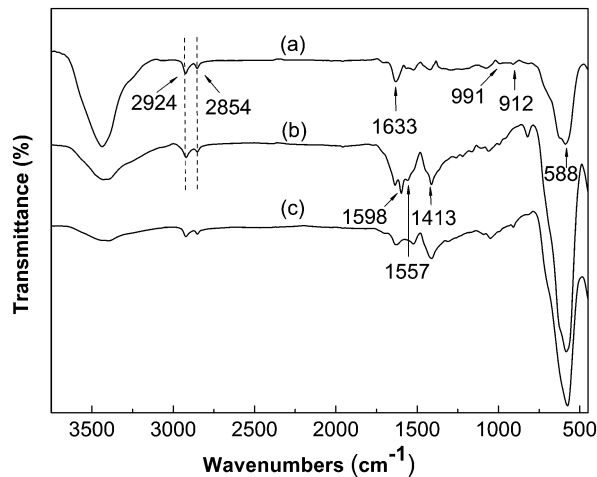

Fig. 1 FT-IR spectra of (a) Fe₃O₄@UA, (b) Fe₃O₄@PUVS and (c) fresh Fe₃O₄@PUVS-Pd catalyst.

stretching vibrations of aliphatic CH₂ groups. These data are consistent with the structural features of Fe_3O_4@UA nanoparticles.[24] Compared with Fig. 1a, three new bands appear in Fig. 1b at 1413 cm^{-1}, 1557 cm^{-1} and 1598 cm^{-1}. These bands are attributed to the characteristic absorptions of the pyridine ring. Specifically, the bands at 1413 cm^{-1} and 1557 cm^{-1} correspond to the stretching vibration absorptions of the C=C bond. The peak at 1598 cm^{-1} is attributed to the stretching vibration absorption of the C–N bond.[25] According to ref. 26, the bands of the C=O stretching vibrations of the ionized carboxyl group (–COO$^-$) appear at 1540 cm^{-1} and 1410 cm^{-1}. The band at 1410 cm^{-1} overlaps with the C=C adsorption band of the pyridine ring. In Fig. 1c, the intensity of the peak at about 1598 cm^{-1} is weaker than that of Fe_3O_4@PUVS (Fig. 1b) due to the formation of a metal–ligand bond. These characteristic absorption peaks confirm the successful synthesis of Fe_3O_4@PUVS and Fe_3O_4@PUVS-Pd.

Fig. 2 shows the typical TEM images of (a) Fe_3O_4@UA, (b) Fe_3O_4@PUVS and (c) fresh Fe_3O_4@PUVS-Pd catalyst. It can be clearly seen that the Fe_3O_4@UA, Fe_3O_4@PUVS and fresh Fe_3O_4@PUVS-Pd catalyst are quasi-spherical, with average diameters of 9.8 nm, 12.7 nm and 13.3 nm, respectively. Moreover, the Brunauer–Emmett–Teller (BET) surface area of Fe_3O_4@PUVS-Pd catalyst is determined to be 68.31 m² g^{-1} by nitrogen adsorption/desorption measurements. The nanoscale size and large BET surface area are beneficial to the catalytic activity of Fe_3O_4@PUVS-Pd catalyst.[11]
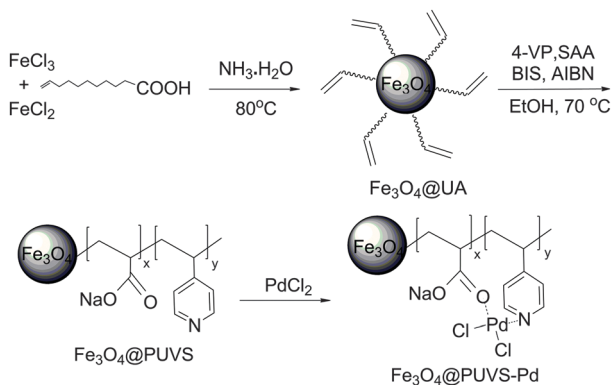
Scheme 1 Preparation of Fe₃O₄@PUVS-Pd catalyst.
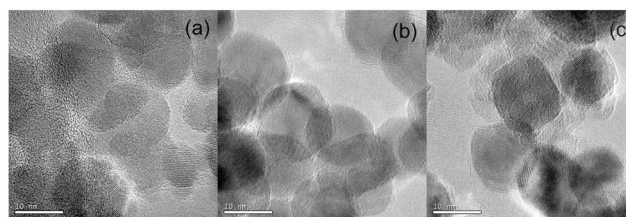
Fig. 2 TEM images of (a) Fe₃O₄@UA, (b) Fe₃O₄@PUVS, and (c) fresh Fe₃O₄@PUVS-Pd catalyst.

The magnetic properties of magnetic nanoparticles were measured by using a VSM at room temperature (300 K). As shown in Fig. 3, the magnetic nanoparticles (a) Fe_3O_4@UA, (b) Fe_3O_4@PUVS, and (c) fresh Fe_3O_4@PUVS-Pd catalyst have saturation magnetization values of 72.34, 61.23 and 57.40 emu g^{-1} respectively and possess superparamagnetic properties. The excellent magnetic properties are not only very conducive to dispersion and re-dispersion in the reaction medium, but will also facilitate the separation of catalyst and products with a permanent magnet (see the photograph in Fig. 3).

The magnetic nanoparticles were characterized by XRD. Fig. 4 shows the XRD patterns of (a) Fe_3O_4@UA, (b) Fe_3O_4@PUVS and (c) fresh Fe_3O_4@PUVS-Pd catalyst. All these species have six strong diffraction peaks ($2\theta = 30.1°$, $35.5°$, $43.3°$, $53.5°$, $56.9°$, $62.6°$) corresponding to the crystal face (220), (311), (400), (422), (511), (440) of Fe_3O_4.[27] In addition, no characteristic diffraction peaks of palladium(0) are observed in Fig. 4(c), indicating that the immobilized palladium is divalent in fresh Fe_3O_4@PUVS-Pd catalyst.

The supported catalyst Fe_3O_4@PUVS-Pd was also analyzed by using XPS to investigate the chemical oxidation state of the supported palladium species.[7] The XPS spectrum in Fig. 5a shows the doublet peaks at the binding energy of 336.6 eV and 341.2 eV, which can be assigned to electron transitions of $3d_{5/2}$ and $3d_{3/2}$ of Pd(II). This result confirms that the chemical state of palladium is divalent in fresh Fe_3O_4@PUVS-Pd. In Fig. 5(b), the binding energy at 335.0 eV and 340.1 eV corresponds to the typical absorption of Pd(0) for $3d_{5/2}$ and $3d_{3/2}$, respectively, showing that the Pd(II) can be reduced to metallic Pd(0) during the reaction process. This result is in accordance with the literature.[28,29]

3.2 Heck reactions catalyzed by Fe_3O_4@PUVS-Pd in water

The Fe_3O_4@PUVS-Pd catalyst was then applied to the Heck reaction of aryl halides with acrylic acid to evaluate the catalytic performance. As it is known, both the base and catalyst dosage have a large influence on the Heck reaction.[30,31] Thus, in our
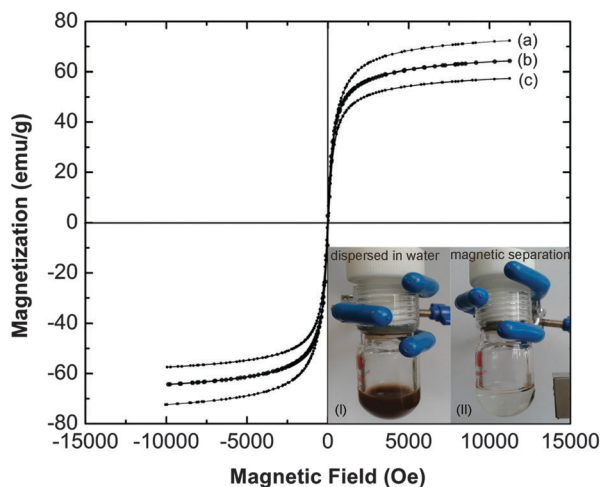

Fig. 4 XRD patterns of the (a) Fe_3O_4@UA, (b) Fe_3O_4@PUVS and (c) fresh Fe_3O_4@PUVS-Pd catalyst.
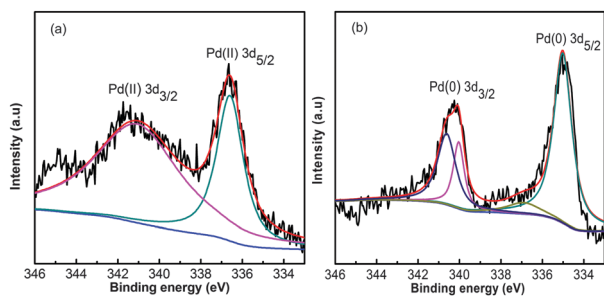
Fig. 5 XPS spectra of (a) fresh Fe_3O_4@PUVS-Pd catalyst and (b) Fe_3O_4@PUVS-Pd catalyst after its use in the Heck reaction.

preliminary investigations, conditions were optimized by varying the base and catalyst dosage through a model reaction of iodobenzene with acrylic acid. As illustrated in Table 1 (entries 1–4), inorganic bases such as sodium hydroxide (NaOH) and potassium carbonate (K_2CO_3) were more effective than the organic bases tributylamine and triethylamine. The effectiveness of inorganic bases is probably due to their good solubility in water. Of the two inorganic bases tested, K_2CO_3 is better than NaOH. With K_2CO_3 as the base, the effect of catalyst dosage was examined next at three different concentrations (entries 4–6). Under the

Fig. 3 Room temperature magnetization hysteresis loops of the (a) Fe_3O_4@UA, (b) Fe_3O_4@PUVS and (c) fresh Fe_3O_4@PUVS-Pd catalyst.

Table 1 Optimization of Heck reaction conditions[a]

Entry	Base	Catalyst[b] (mol%)	Yield[c] (%)
1	Et_3N	0.09	72
2	t-Bu_3N	0.09	41
3	NaOH	0.09	91
4	K_2CO_3	0.09	96
5	K_2CO_3	0.05	82
6	K_2CO_3	0.18	96

[a] Reaction conditions: iodobenzene (1.0 mmol), acrylic acid (1.5 mmol), base (3.0 mmol), H_2O (2.0 mL), at reflux for 12 hours. [b] Catalyst (relative to the amount of iodobenzene). [c] Isolated yield.

otherwise same conditions, increasing the amount of the catalyst from 0.05 mol% to 0.09 mol% remarkably raised the yield of the desired product from 82% to 96%, but the yield increased no more when the amount of the catalyst was further increased. Therefore, 0.09 mol% was taken as the optimal amount of Fe$_3$O$_4$@PUVS-Pd catalyst for the present Heck reaction.

Next, the kinetics of the reaction of iodobenzene with acrylic acid was investigated. As shown in Fig. 6(a), the yield of the product increased with reaction time until reaching 96% at the 12th hour, indicating that the reaction was complete in 12 hours.

With the optimized conditions in hand, the Heck reactions of a wide range of aryl halides with acrylic acid were examined subsequently. As illustrated in Table 2, the aryl iodides bearing either electron-withdrawing (entries 2, 3) or electron-donating groups (entries 4, 5, 7, 8) reacted efficiently, affording the corresponding coupling products in satisfactory yields (91–97%). Notably, even the sterically hindered 2-iodoanisole reacted with acrylic acid to give the product in 83% yield (entry 6) in 12 hours. In the latter case, the yield can be further increased to 94% by prolonging the reaction time to 24 hours.

The catalyst also exhibited high activity toward various aryl bromides (entries 9–19). Excellent yields were obtained for aryl bromides bearing electron-withdrawing substituents (entries 10–14). Reaction of the aryl bromide bearing a methoxy group also delivered the coupling product in high yield (entry 15). For the methyl-substituted aryl bromides (entries 16–19), the position of the methyl group has a large influence on the reaction, and the yield was only moderate under standard conditions when the methyl group was at the *meta* or *ortho* position. Nevertheless, in these cases, the yield was greatly improved on extending the reaction time or on adding TBAB (tetrabutyl ammonium bromide) into the reaction mixture. Furthermore, electron-deficient aryl chlorides also reacted satisfactorily under the present conditions: the coupling of 4-nitrochlorobenzene and 4-chlorobenzoic acid
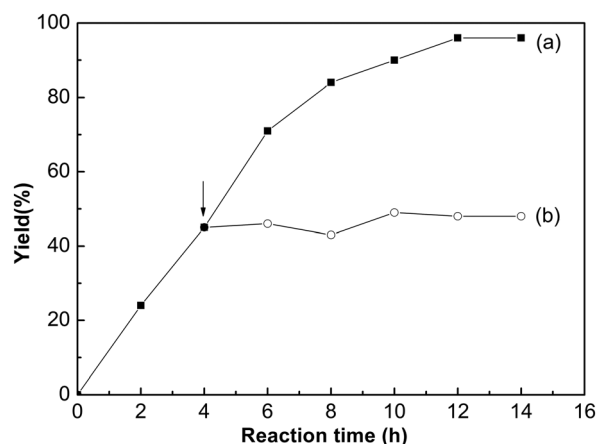
Fig. 6 Kinetic profiles of the Fe$_3$O$_4$@PUVS-Pd catalyst in the Heck reaction. (a) Normal reaction kinetics; (b) reaction kinetics after the catalyst was removed from the reaction at 4 hours. Reaction conditions: iodobenzene (1.0 mmol), acrylic acid (1.5 mmol), 0.09 mol% Fe$_3$O$_4$@PUVS-Pd catalyst, K$_2$CO$_3$ (3.0 mmol), H$_2$O (2.0 mL), at reflux.

Table 2 Heck reactions of various aryl halides with acrylic acid[a]

Entry	Aryl halide	Product	Time (h)	Yield[b] (%)
1			12	96
2			12	97
3			12	95
4			12	93
5			12	92
6			12 / 24	83 / 94
7			12	91
8			12	93
9			12	93
10			12	95
11			12	92
12			12 / 24	68 / 94
13			12	92
14			12	89
15			12	90
16			12	91
17			12 / 12 / 24	48 / 93[c] / 86

Table 2 (continued)

Entry	Aryl halide	Product	Time (h)	Yield[b] (%)
18	Br (2-CH₃)	COOH (2-CH₃)	12 / 24	90[c] / 84
19	Br (3,5-diCH₃)	COOH (3,5-diCH₃)	12	89
20	Cl–NO₂ (para)	O₂N–COOH (para)	12 / 24	81 / 93
21	Cl–COOH (para)	HOOC–COOH (para)	24	82
22	Cl	COOH	24	Trace
23	Cl (3-NO₂)	COOH (2-NO₂)	24	Trace

[a] Reaction conditions: aryl halides (1.0 mmol), acrylic acid (1.5 mmol), 0.09 mol% of Fe₃O₄@PUVS-Pd catalyst, K₂CO₃ (3.0 mmol), H₂O (2.0 mL), at reflux. [b] Isolated yield. [c] In the presence of 1 mmol TBAB.

with acrylic acid (entries 20, 21) generated the corresponding products in 93% and 82% yield, respectively. However, for chlorobenzene and 3-chloronitrobenzene (entries 22, 23), the reaction hardly took place.

3.3 Suzuki reactions catalyzed by Fe₃O₄@PUVS-Pd in water

Following its application to the Heck reaction, the effectiveness of Fe₃O₄@PUVS-Pd for the Suzuki reactions in water was investigated next. As shown in Table 3, bromobenzene, 4-nitrobromobenzene and 4-bromotoluene reacted well with phenylboronic acid (entries 1, 2, 5), affording the desired products in excellent yields. The reaction of 3-nitrobromobenzene was less satisfactory, but the result was greatly improved by the addition of TBAB (entry 3). TBAB can also improve the reaction of 2-nitrobromobenzene, 3-bromotoluene and 1-bromo-3,5-dimethylbenzene (entries 4, 6, 7). In addition, this catalyst is applicable to the coupling reactions involving chlorobenzene. For example, the reaction of 4-nitrochlorobenzene with phenylboronic acid proceeded well to give the coupling product in 87% yield (entry 8). 4-Chlorobenzoic acid (entry 9) also reacted efficiently with phenylboronic acid, affording the corresponding product in 82% yield. For the coupling of chlorobenzene (entry 10) with phenylboronic acid, the yield of the coupling product was low (36%) in water, but it can be raised to 73% by using a mixed solvent of water–DMF.

To further evaluate the catalytic performance of Fe₃O₄@PUVS-Pd, a comparison was made with several literature-reported magnetic nanoparticle-supported catalysts. The reactions of bromobenzene with acrylic acid and phenylboronic acid were

Table 3 Suzuki reactions of various aryl halides with phenylboronic acid[a]

Entry	Aryl halide	Product	Time (h)	Yield[b] (%)
1	Br	biphenyl	1	93
2	Br–NO₂ (para)	biphenyl-NO₂ (para)	1	97
3	Br (3-NO₂)	biphenyl-NO₂ (3)	3 / 3	72 / 95[c]
4	Br (2-NO₂)	biphenyl-NO₂ (2)	5	87[c]
5	Br–CH₃ (para)	biphenyl-CH₃ (para)	4	94
6	Br (3-CH₃)	biphenyl-CH₃ (3)	4	95[c]
7	Br (3,5-diCH₃)	biphenyl (3,5-diCH₃)	6	89[c]
8	Cl–NO₂ (para)	biphenyl-NO₂ (para)	4 / 4	61 / 87[c]
9	Cl–COOH (para)	biphenyl-COOH (para)	6	82[d]
10	Cl	biphenyl	24 / 18	36[e] / 73[f]

[a] Reaction conditions: aryl halides (1.0 mmol), phenylboronic acid (1.5 mmol), 0.09 mol% Fe₃O₄@PUVS-Pd catalyst, K₂CO₃ (3.0 mmol), H₂O (2.0 mL), at 90 °C. [b] Isolated yield. [c] In the presence of 1 mmol TBAB. [d] At reflux. [e] In the presence of 2 mmol TBAB. [f] H₂O/DMF = 1 : 1 (2.0 mL).

taken as the standard reactions, and the results are listed in Table 4. It can be clearly seen that for the Heck reaction of bromobenzene with acrylic acid, the current Fe₃O₄@PUVS-Pd is superior to others in terms of catalytic efficiency. Moreover, this Fe₃O₄@PUVS-Pd catalyst also proved to be the most efficacious in activity for the Suzuki reaction of bromobenzene with phenylboronic acid, as reflected from its high TOF value (1033 h⁻¹). It should be noted that the Fe₃O₄@PUVS-Pd-catalyzed Heck and Suzuki reactions were carried out in water in the absence of organic solvents, which makes this catalytic capacity more impressive.

3.4 Recyclability of the Fe₃O₄@PUVS-Pd catalyst

Recyclability is a crucial parameter for the evaluation of supported catalysts in practical applications.[7] The recycling performance of Fe₃O₄@PUVS-Pd was examined by applying it to the Heck reaction of iodobenzene with acrylic acid. After the reaction was

Table 4 Performance of different nanoparticle-supported catalysts for Heck and Suzuki reactions

Entry	Pd catalyst (mol%)	Solvent/temperature/time	Yield^a (%)	TOF^b (h^{-1})	Ref.
		$\text{PhBr} + \text{CH}_2=\text{CHCOOH} \xrightarrow[\text{base,solvent}]{\text{catalyst}} \text{PhCH=CHCOOH}$			
1	Fe$_3$O$_4$@PUVS-Pd (0.09)	H$_2$O/reflux/12 h	93	86.1	This work
2	Fe$_3$O$_4$/SiO$_2$/HPG-OPPh$_2$-PNP (0.95)	DMF/100 °C/1.5 h	84	58.9	18
3	Fe$_3$O$_4$/P(GMA-MMA-AA)Pd (0.5)	DMF/95 °C/3 h	8.2	5.5	32
4	Fe$_3$O$_4$-NH$_2$-Pd (0.5)	DMF/95 °C/3 h	12.4	8.3	33
5	Fe$_3$O$_4$/SiO$_2$/HPG-Pd (3)	DMF/140 °C/12 h	67	1.9	34
		$\text{PhBr} + \text{PhB(OH)}_2 \xrightarrow[\text{base,solvent}]{\text{catalyst}} \text{Ph-Ph}$			
6	Fe$_3$O$_4$@PUVS-Pd(0.09)	H$_2$O/90 °C/1 h	93	1033.3	This work
7	Fe$_3$O$_4$@PUNP-Pd (0.1)	H$_2$O/90 °C/1 h	95	950	22
8	Pd/MFC (0.308)	EtOH/reflux/1 h	98	16.3	35
9	Fe$_3$O$_4$/P(GMA-AA-MMA-Pd) (0.2)	EtOH/H$_2$O/80 °C/3 h	96	160	36
10	Fe@Pd/C (0.5)	EtOH/H$_2$O/80 °C/0.5 h	97^c	194	37

^{a} Isolated yield. ^{b} The TOF was defined as mol product mol^{-1} Pd h^{-1}. ^{c} GC yield.

Table 5 Reusability of Fe$_3$O$_4$@PUVS-Pd catalyst^a

Runs	1	2	3	4	5	6	7	8
Yield^b (%)	96	96	94	91	91	88 (92^c)	79 (86^c)	79^c

^{a} Reaction conditions: iodobenzene (1.0 mmol), acrylic acid (1.5 mmol), 0.09 mol% Fe$_3$O$_4$@PUVS-Pd catalyst, K$_2$CO$_3$ (3.0 mmol), H$_2$O (2.0 mL), at reflux for 12 hours. ^{b} Isolated yield. ^{c} Reaction time is 24 hours.

completed, the Fe$_3$O$_4$@PUVS-Pd catalyst was separated by using a permanent magnet and washed with deionized water, and then the catalyst was directly reused for the next run of the reaction. As shown in Table 5, the yield did not decrease much (96–91%) for the first five runs, and reached 92% and 86% at the sixth and seventh runs respectively when the reaction time was prolonged to 24 hours. After the seventh run, the aqueous solution was analyzed, and the leaching of Pd was found to be only 0.56 ppm, indicating that the catalyst was stable during the reaction.

The impact of palladium leaching was also tested by the following experiment set up on the basis of the aforementioned kinetics analysis (Fig. 6): the catalyst was removed from the reaction mixture after 4 hours and the aqueous phase was monitored from then on. As shown in Fig. 6b, after the catalyst was removed, the yield remained almost constant (43–48%) within the next 10 hours. This result further demonstrated that the palladium leaching was insignificant and the Fe$_3$O$_4$@PUVS catalyst is stable.

4 Conclusions

In summary, we have developed a new magnetically responsive heterogeneous palladium catalyst (Fe$_3$O$_4$@PUVS-Pd) which is applicable to the Heck and Suzuki reactions in water. This catalyst exhibits high catalytic activity as well as good stability. It can be easily recovered and used consecutively for six runs without significant loss of catalytic activity. Besides, this catalyst can be conveniently prepared from readily available materials, and thus is advantageous in terms of practical usefulness and synthetic economy.

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