# NJC





Cite this: New J. Chem., 2014, 38, 4622

# Preparation of recoverable Fe<sub>3</sub>O<sub>4</sub>@PANI–Pd<sup>II</sup> core/shell catalysts for Suzuki carbonylative cross-coupling reactions†

Xiaohang Zhu, Jianrui Niu, Fengwei Zhang, Jinghui Zhou, Xinzhe Li and Jiantai Ma\*

We report on the synthesis, characterization and catalytic performance of a palladium-based superparamagnetic catalyst of  $Fe_3O_4$ @polyaniline core/shell microspheres ( $Fe_3O_4$ @PANI-Pd<sup>II</sup>). The

material was characterized by TEM, FT-IR, vibrating sample magnetometry (VSM), XRD, and XPS. The

catalyst showed high activity for the carbonylative cross-coupling reaction of aryl iodide with arylboronic acid. Moreover it could selectively reduce the formation of a direct-coupling product. The

newly developed catalyst could be recovered from the liquid phase easily by magnetic separation and

recycled 5 times without any significant loss of activity.

Received (in Porto Alegre, Brazil) 30th April 2014, Accepted 8th July 2014

DOI: 10.1039/c4nj00697f

www.rsc.org/njc

## Introduction

Synthesis of biaryl and heteroaryl carbonyl compounds has attracted considerable interest, as these compounds are important moieties in many biologically active molecules, natural products, and pharmaceuticals.<sup>1</sup> One general approach for the synthesis of biaryl ketones is the Friedel-Crafts acylation of substituted aromatic rings.<sup>2</sup> However, Friedel-Crafts acylation has the disadvantage of using Lewis acid, which is reactive towards many functional groups, and the regioselectivity is untunable. Another direct and convenient approach is transition metal-catalyzed three-component cross-coupling reaction among aryl metals (Mg, Al, Si, Sn, and Zn), carbon monoxide, and aryl electrophiles.<sup>3</sup> But the generation of a direct-coupling by-product without insertion of carbon monoxide is unavoidable. Among carbonylative cross-coupling reactions, Suzuki carbonylative coupling reaction is one of the most promising routes for the direct synthesis of biaryl ketones from carbon monoxide, as aryl halides and arylboronic acids with various functionalities can be tolerated on either partner and arylboronic acids are generally nontoxic and thermally-, air- and moisture-stable.<sup>4</sup>

Many palladium-based homogeneous catalysts, such as  $Pd(tmhd)_2/Pd(OAc)_2$ ,<sup>1a</sup>  $Pd_2(dba)_3$ ,<sup>1b</sup>  $Pd(PPh_3)_4^5$  and N-heterocyclic carbene palladium,<sup>6</sup> showed good activity in carbonylative cross-coupling reactions. However, the problem is that homogeneous catalysts are difficult to separate from products and catalytic media, which limits their commercial development and practical use. Thus, much research interest is focused on heterogeneous

palladium complexes as catalysts for Suzuki carbonylative coupling reactions. Cai *et al.* used MCM-41–2P–Pd<sup>II</sup> (ref. 7) and MCM-41– 2N–Pd<sup>II</sup> (ref. 8) as catalysts for Suzuki carbonylative coupling reactions. Bhanage *et al.*<sup>4b</sup> used Pd/C as a catalyst for Suzuki carbonylative coupling reactions. In order to improve recyclability, we have immobilized Pd complexes on silica-coated magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>–SH–Pd<sup>II</sup>) to catalyze Suzuki carbonylative coupling reactions, so that the catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>–SH–Pd<sup>II</sup>) could be separated from the mother solutions by applying an external magnetic field.<sup>9</sup>

Core-shell structured superparamagnetic iron oxide hybrid nanoparticles have attracted increasing interest, as coatings can stabilize magnetic nanoparticles, leading to better dispersion and biocompatibility, and can also be further modified with functional groups for diverse applications.<sup>10</sup> Most of the magnetic core-shell composite materials were prepared by coating Fe<sub>3</sub>O<sub>4</sub> particles with functional shells.<sup>11</sup> Among these shell materials, polyaniline (PANI) has received more attention for its application prospects in many fields because of its high stability in air, solubility in various solvents, and its unique electrical properties.<sup>12</sup> Recently, Fe<sub>3</sub>O<sub>4</sub>@PANI nanocomposites have been developed intensively. Wan et al.13 reported a series of PANI composites containing nanomagnets prepared by chemical polymerization. Deng et al.14 reported the synthesis of PANI/Fe<sub>3</sub>O<sub>4</sub> nanoparticles with core-shell structure via in situ polymerization of aniline monomers in aqueous solution, which contained Fe<sub>3</sub>O<sub>4</sub> nanoparticles and surfactants. The fabrication of nanoscale ferromagnetic Fe<sub>3</sub>O<sub>4</sub>-cross-linked PANI by oxidative polymerization of aniline with ammonium peroxodisulfate as the oxidant was reported by Peng et al.<sup>12a</sup> All Fe<sub>3</sub>O<sub>4</sub> nanoparticles used in these studies have average diameters less than 10 nm. Unfortunately, these materials showed poor magnetic response due to the relatively low mass fraction of Fe<sub>3</sub>O<sub>4</sub>.<sup>15</sup>



**View Article Online** 

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, China. E-mail: majiantai@lzu.edu.cn

 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available. See DOI: 10.1039/ c4nj00697f

In this paper, we report on the synthesis of a high superparamagnetic catalyst  $Fe_3O_4$ @PANI-Pd<sup>II</sup> with well-defined morphology. The superparamagnetic  $Fe_3O_4$ @PANI microspheres have been synthesised *via* a simple *in situ* surface polymerization method. Pd<sup>II</sup> can adhere strongly and disperse uniformly on the surface of  $Fe_3O_4$ @PANI microspheres due to the covalent bonding between Pd<sup>II</sup> and amino groups of PANI shells. Furthermore, the PANI shells improved the dispersibility of the microspheres in aromatic solution. Meanwhile, aromatic reactants can access active sites easily because of the existence of  $\pi$ - $\pi$  conjugation between the PANI shell and aromatic compounds.  $Fe_3O_4$ @PANI-Pd<sup>II</sup> was used to catalyze Suzuki carbonylative coupling reaction under mild conditions.

## **Experimental section**

### Materials

Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), anhydrous sodium acetate, ethylene glycol, aniline, ammonium peroxodisulfate (APS), poly-(vinylpyrrolidone) (PVP), and 3-aminopropyltriethoxysilane (APTES) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used as received without further purification.

#### Synthesis and chemical modification of Fe<sub>3</sub>O<sub>4</sub> particles

The magnetic Fe<sub>3</sub>O<sub>4</sub> particles were synthesized *via* solvothermal reaction. Typically, FeCl<sub>3</sub>·6H<sub>2</sub>O (1.35 g) and sodium acetate (3.6 g) were dissolved in ethylene glycol (40 mL). The obtained homogeneous yellow solution was transferred to a Teflon-lined stainless-steel autoclave and sealed to heat at 200 °C. After reaction for 8 h, the autoclave was cooled to room temperature. The obtained black magnetite particles were washed with ethanol six times and then dried in a vacuum at 60 °C overnight. Then Fe<sub>3</sub>O<sub>4</sub> particles (0.2 g) and APTES (4 mL) were dissolved in anhydrous ethanol to give a mixed solution (50 mL). The mixture was refluxed for 12 h under dry nitrogen. The resulting modified Fe<sub>3</sub>O<sub>4</sub> particles were separated and then washed with ethanol. Finally, the product was dried in a vacuum at 60 °C for 24 h and the amine-functionalized Fe<sub>3</sub>O<sub>4</sub> particles (NH<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub>) were obtained.

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>@PANI microspheres

The Fe<sub>3</sub>O<sub>4</sub>@PANI microspheres were prepared by the *in situ* surface polymerization method in the presence of PVP.<sup>16</sup> Briefly, PVP (0.3 g) was dissolved in deionized water (600 mL), then the NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> particles (0.09 g) were added. The mixture was ultrasonically dispersed. After that, aniline (0.12 mL) and HCl (0.6 mL) were added into the mixture with vigorous stirring. After the mixture was stirred for 30 min, an aqueous solution (120 mL) of APS (1.2 g) was added into the above mixture instantly to start the oxidative polymerization. The reaction was performed under stirring for 3 h. The resulting precipitates were washed with deionized water and ethanol several times. Finally, the product was dried in a vacuum at 60 °C for 24 h to obtain the desired Fe<sub>3</sub>O<sub>4</sub>@PANI microspheres.

## Loading of Pd on Fe<sub>3</sub>O<sub>4</sub>@PANI microspheres (Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup>)

The as-synthesised Fe<sub>3</sub>O<sub>4</sub>@PANI microspheres (300 mg) were first dispersed in ethanol solution (100 mL) under ultrasonication for 0.5 h. The formed black suspension was ultrasonically mixed with 31 mg of PdCl<sub>2</sub> (0.174 mmol) dispersed in deionized water. After the mixture was stirred at room temperature for 24 h, the resulting precipitates were then thoroughly rinsed with deionized water and ethanol, and then vacuum dried at 60 °C overnight. The weight percentage of Pd in Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup>, as determined by atomic absorption spectroscopic (AAS) analysis, was 4.8 wt%.

# Typical procedure for the Suzuki carbonylative coupling reaction

A mixture of aryl iodide (0.5 mmol), arylboronic acid (0.6 mmol),  $K_2CO_3$  (1.5 mmol), and 1 mol% palladium catalyst in anisole (5 mL) was stirred at 80 °C under 1 atm pressure of CO. After the reaction, the mixture was cooled down to room temperature, separated by magnetic decantation, and the resultant residual mixture was diluted with 10 mL of  $H_2O$ , followed by extraction with ethyl acetate (2 × 10 mL). The organic fraction was dried with MgSO<sub>4</sub>, the solvents were evaporated under reduced pressure and the residue was redissolved in 5 mL of ethanol. An aliquot was taken using a syringe and subjected to GC analysis. Yields were calculated against the consumption of the aryl iodides.

#### Characterization

Transmission electron microscopy (TEM) images were characterized using a Tecnai G2 F30 transmission electron microscope. FT-IR spectra were recorded using a Nicolet NEXUS 670. Magnetic measurements of samples were performed using a vibrating sample magnetometer (Lake Shore 7304) at room temperature. X-ray-diffraction (PXRD) measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-K $\alpha$  radiation as the X-ray source in the 2 $\theta$  range of 10°–80°. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 instrument and the C<sub>1S</sub> line at 292.1 eV was used as the binding energy reference.

## Results and discussion

#### Catalyst preparation and characterization

The process of preparation of the catalyst  $Fe_3O_4$ @PANI-Pd<sup>II</sup> is schematically described in Scheme 1. Firstly,  $Fe_3O_4$  particles were prepared by the method given in a previous report.<sup>17</sup> Secondly,  $Fe_3O_4$  particles were modified with amine groups to enhance the growth of PANI. Afterwards,  $Fe_3O_4$ @PANI spheres were prepared by *in situ* polymerization of aniline on the surface of  $Fe_3O_4$  particles in the presence of PVP. Finally, PdCl<sub>2</sub> was anchored onto the surface of  $Fe_3O_4$ @PANI to afford the catalyst  $Fe_3O_4$ @PANI-Pd<sup>II</sup>.

The typical TEM image of  $Fe_3O_4$ @PANI microspheres prepared by the *in situ* surface polymerization method at room temperature is shown in Fig. 1a. The average diameter of the as-synthesized spherical particles was about 240 nm. A continuous layer of PANI could be observed on the outer shell of the  $Fe_3O_4$  microsphere NJC



Scheme 1 Preparation of Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup>



Fig. 1 TEM images of (a), (b)  $Fe_3O_4@PANI$ , and (c)  $Fe_3O_4@PANI-Pd^{II}$ .

cores and the thickness of the PANI shell was about 22 nm. The resultant Fe<sub>3</sub>O<sub>4</sub>@PANI composites had good dispersibility and spherical morphology. The TEM image of Fe<sub>3</sub>O<sub>4</sub>@PANI (Fig. 1b) clearly showed that the magnetite particles were composed of plentiful nanocrystals with the size of about 16 nm. From the TEM image of Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup> (Fig. 1c), it could be seen that the morphology of Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup> almost remained the same after loading PdCl<sub>2</sub> on Fe<sub>3</sub>O<sub>4</sub>@PANI microspheres.

We also measured the Fourier transform infrared (FT-IR) spectra of  $Fe_3O_4$ @PANI and  $Fe_3O_4$ @PANI-Pd<sup>II</sup>. In the FT-IR spectrum of  $Fe_3O_4$ @PANI (Fig. 2a), the characteristic peaks at 1588 (C=C stretching deformation of the quinoid and benzenoid ring, respectively), 1306 (C-N stretching of secondary aromatic amine), 1150, and 827 cm<sup>-1</sup> (out of plane deformation of C-H in the 1,4-disubstituted benzene ring) showed that aniline was successfully polymerized onto the  $Fe_3O_4$  core. The bands at 574 and 3435 cm<sup>-1</sup> corresponded to the characteristic band of Fe-O vibration and -OH stretching vibration.<sup>11c</sup> The FT-IR spectrum of



Fig. 2 FT-IR spectra of (a) Fe<sub>3</sub>O<sub>4</sub>@PANI and (b) Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup>.



Fig. 3 The magnetization curves of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>@PANI, and (c) Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup>.

 $Fe_3O_4$ @PANI-Pd<sup>II</sup> (Fig. 2b) was similar to that of  $Fe_3O_4$ @PANI, but the C-N stretching frequency shifted to a lower frequency (around 1290 cm<sup>-1</sup>), which was probably caused by N bonded to electron-deficient Pd to form the Pd complex.<sup>18</sup>

Magnetic measurements were performed using a vibrating sample magnetometer at room temperature. The magnetization curves of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>(a)PANI and Fe<sub>3</sub>O<sub>4</sub>(a)PANI-Pd<sup>II</sup> are compared in Fig. 3. There was no hysteresis in the magnetization for the three types of particles. Additionally, neither coercivity nor remanence could be observed, which suggested that the three particles were superparamagnetic.<sup>19</sup> The measured saturation magnetization values were 71.8 emu  $g^{-1}$  for Fe<sub>3</sub>O<sub>4</sub> particles, 46.5 emu  $g^{-1}$  for  $Fe_3O_4$ @PANI and 42.6 emu g<sup>-1</sup> for  $Fe_3O_4$ @PANI-Pd<sup>II</sup>. The saturation magnetization significantly decreased after aniline was polymerized onto Fe<sub>3</sub>O<sub>4</sub> particles, and further decreased slightly after loading PdCl2 on Fe3O4@PANI microspheres. However, the prepared Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup> microspheres still maintained good magnetic properties and could be completely and quickly separated from the aqueous solution when an external magnetic force was applied.

The XRD patterns of  $Fe_3O_4$ @PANI and  $Fe_3O_4$ @PANI-Pd<sup>II</sup> are shown in Fig. 4. The main peaks of the  $Fe_3O_4$ @PANI-Pd<sup>II</sup> composite were similar to  $Fe_3O_4$ @PANI, which revealed that immobilizing PdCl<sub>2</sub> on the surface of  $Fe_3O_4$ @PANI did not affect the structure of  $Fe_3O_4$ @PANI. Both the patterns showed strong peaks, which confirmed that the products were crystallized well after the coating process under acidic conditions and the detected diffraction peaks in every pattern could be indexed as cubic  $Fe_3O_4$  (JCPDS card No. 82-1533). According to the Debye–Scherrer formula, the nanocrystal size of magnetite particles was calculated to be 16.3 nm, in good agreement with the TEM observations.

The XPS elemental survey scans of the surface of the  $Fe_3O_4$ @PANI-Pd<sup>II</sup> catalyst are shown in Fig. 5. Peaks corresponding to oxygen, carbon, nitrogen, palladium and iron were clearly observed. To ascertain the oxidation state of Pd, X-ray photoelectron spectroscopy (XPS) studies were carried out. In Fig. 6, the Pd binding energy of  $Fe_3O_4$ @PANI-Pd<sup>II</sup> exhibited two strong peaks centered at 342.8 and 337.5 eV, which were

Paper



Fig. 4 XRD patterns of (a) Fe<sub>3</sub>O<sub>4</sub>@PANI and (b) Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup>.



Fig. 5 XPS spectrum of the elemental survey scan of Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup>



Pd  $3d_{3/2}$  binding energies.

assigned to Pd 3d 3/2 and Pd 3d 5/2, respectively. These values agreed with the  $Pd^{II}$  binding energy of  $PdCl_2$ .<sup>20</sup>

#### The Suzuki carbonylative coupling reaction

The carbonylative cross-coupling reaction of phenylboronic acid with 4-iodoacetophenone under an atmospheric pressure of carbon monoxide was chosen as the model reaction, to optimize temperature, solvent and base applied in the reaction. The results are summarized in Table 1. At 40 and 60 °C, the yield of the desired product was low (Table 1, entries 1 and 2). Increasing the temperature up to 80 °C, high yield of the desired product (95%) was obtained (Table 1, entry 3). However, when the temperature increased to 100 °C, the yield of the desired product (94%) did not increase (Table 1, entry 4). Therefore, the optimum reaction temperature was 80 °C. According to the evaluated results of solvents, anisole was found to be the best (Table 1, entry 3). As less polar solvents, such as anisole, dioxane, and toluene, were used in the reaction, a relatively good yield of the carbonylative cross-coupling product, 4-methoxybenzophenone, could be obtained. However, the yield of the carbonylative cross-coupling product was relatively low in polar solvent, such as DMF, as a significant amount of the direct coupling product, 4-methoxybiphenyl (72%), was produced (Table 1, entry 7). The inorganic bases used in the carbonylative Suzuki coupling reaction (Na<sub>2</sub>CO<sub>3</sub>,  $K_2CO_3$ ,  $Cs_2CO_3$ , and  $K_3PO_4$ ) could affect the selectivity of the products. Cs<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub> had a strong tendency to produce the direct coupling product (Table 1, entries 9 and 10). Unfortunately, Na<sub>2</sub>CO<sub>3</sub> showed the lowest activity compared to the other three inorganic bases (Table 1, entry 8). As a result, K<sub>2</sub>CO<sub>3</sub> was the most efficient base. Therefore, the optimized reaction conditions are: 80 °C, anisole, and K<sub>2</sub>CO<sub>3</sub>.

To investigate the substrate scope of this carbonylative cross-coupling reaction, a variety of arylboronic acids and aryl iodides were investigated under optimized reaction conditions. As shown in Table 2, the carbonylative cross-coupling reaction could proceed smoothly under mild conditions to afford the corresponding carbonylative coupling products in high yields, whether using arylboronic acids and aryl iodides containing either electron-withdrawing groups or electron-donating

Table 1 The carbonylative cross-coupling of phenylboronic acid with 4-iodoacetophenone under different conditions<sup>a</sup>

$ \begin{array}{c} & & & \\ & & & \\ $					
				Yield	° (%)
Entry	Solvent	Base	Temp./°C	1	2
1	Anisole	K <sub>2</sub> CO <sub>3</sub>	40	21	21
2	Anisole	$K_2CO_3$	60	66	10
3	Anisole	$K_2CO_3$	80	95	2
4	Anisole	$K_2CO_3$	100	94	5
5	Toluene	$K_2CO_3$	80	55	8
6	Dioxane	$K_2CO_3$	80	76	5
7	DMF	$K_2CO_3$	80	24	72
8	Anisole	Na <sub>2</sub> CO <sub>3</sub>	80	21	5
9	Anisole	$Cs_2CO_3$	80	48	23
10	Anisole	K <sub>3</sub> PO <sub>4</sub>	80	46	43

<sup>*a*</sup> The reactions were carried out using 4-iodoacetophenone (0.5 mmol), arylboronic acid (0.6 mmol), CO (1 atm), base (1.5 mmol), solvent (5 mL), and 1 mol% palladium catalyst. <sup>*b*</sup> Determined by GC.

 Table 2
 The synthesis of unsymmetrical biaryl ketones<sup>a</sup>

				Yield <sup>b</sup>	Yield <sup><math>b</math></sup> (%)	
Entry	R <sub>1</sub>	$R_2$	t/h	1	2	
1	4-CH <sub>3</sub> CO	Н	6	95	2	
2	4-CH <sub>3</sub> CO	$4-CH_3$	6	90	5	
3	4-CH <sub>3</sub> CO	4-Cl	6	92	3	
4	$2-NO_2$	Н	6	98	0.7	
5	$2-NO_2$	$4-CH_3$	6	97	2	
6	$2-NO_2$	4-Cl	6	97	0.3	
7	Н	Н	8	97	3	
8	Н	$4-CH_3$	8	94	5	
9	Н	4-Cl	8	97	1	
10	$4-CH_3$	Н	8	95	3	
11	$4-CH_3$	$4-CH_3$	8	92	4	
12	$4-CH_3$	4-Cl	8	88	2	
13	4-CH <sub>3</sub> O	Н	8	95	2	
14	4-CH <sub>3</sub> O	$4-CH_3$	8	90	2	
15	4-CH <sub>3</sub> O	4-Cl	8	87	2	
16	$2-NH_2$	Н	12	96	1	
17	$2-NH_2$	$4-CH_3$	12	98	1	
18	$2-NH_2$	4-Cl	12	97	0.6	

<sup>*a*</sup> The reactions were carried out using aryl iodide (0.5 mmol), arylboronic acid (0.6 mmol), CO (1 atm),  $K_2CO_3$  (1.5 mmol) and 1 mol% palladium catalyst in anisole (5 mL) at 80 °C. <sup>*b*</sup> Determined by GC.

groups (Table 2, entries 1-18). Aryl iodides substituted with electron-withdrawing groups, such as 4-CH<sub>3</sub>CO and 2-NO<sub>2</sub> (Table 2, entries 1-6), were found to be the most active reagents in carbonylative cross-coupling, as high yields were obtained in the shortest time (6 h). According to the proposed reaction mechanism (Scheme 2), the existence of electron-withdrawing groups could promote the oxidative addition of the organic halide to palladium(0) (step 1). Comparing the reaction using aryl boronic acid with the same substituent (Table 2, entries 1-18), we found that changing the electronic properties of boronic acid would affect the selectivity for the direct coupling products. It could be seen that aryl boronic acid containing the electron-attracting group, -Cl, produced the lowest yields of the direct coupling product. In contrast, aryl boronic acid containing the electron-donating group, -CH<sub>3</sub>, gave the highest yields of the direct coupling product. Since transmetalation (step 2) was slow with aryl boronic acid containing the electron-attracting group, direct coupling was hindered. In contrast, aryl boronic acid containing the electron-donating group could promote direct coupling.<sup>5a</sup> Unfortunately, the derivatives of bromobenzene and bromobenzene can not react with phenylboronic acid.



Scheme 2 Catalytic cycles of carbonylative cross-coupling reaction.

Table 3 The carbonylative cross-coupling of phenylboronic acid with 4-iodoacetophenone using different catalysts<sup>a</sup>

$ \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \end{array} \rightarrow \begin{array}{c} \\ \end{array} \rightarrow \begin{array}{c} \\ & \\ \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \begin{array}{c} \\ \end{array} \rightarrow \begin{array}{c} \\ \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \begin{array}{c} \\ \end{array} \rightarrow \begin{array}{c} \\ \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \begin{array}{c} \\ \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \begin{array}{c} \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \begin{array} \end{array} \rightarrow \end{array} \rightarrow \end{array} \rightarrow \begin{array} \rightarrow \end{array} \rightarrow \end{array}$					
Entry	Catalyst	Catalyst amount (mol%)	Time/ h	°C	Yield (%)
1	Fe <sub>3</sub> O <sub>4</sub> @PANI-Pd <sup>II</sup>	1	6	80	95
2	MCM-41-2P-Pd <sup>II</sup>	2	5	80	85
3	$Pd/C^b$	2	8	100	85
4	MCM-41-2N-Pd <sup>II</sup>	2	6	80	86
5	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SH-Pd <sup>II</sup>	1	6	80	92
6	ImmPd–IL <sup>c</sup>	2	8	100	76

<sup>a</sup> Reaction conditions: CO (1 atm), anisole. <sup>b</sup> Reaction conditions: CO (200 psi), anisole. <sup>c</sup> Reaction conditions: CO (1 MPa), toluene.

The catalytic activities of heterogeneous catalysts, MCM-41-2P-Pd<sup>II</sup>,<sup>7</sup> Pd/C,<sup>4b</sup> MCM-41-2N-Pd<sup>II</sup>,<sup>8</sup> Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SH-Pd<sup>II</sup>,<sup>9</sup> and ImmPd-IL,<sup>21</sup> for Suzuki carbonylative coupling reaction in literature are also shown in Table 3. Compared with those heterogeneous catalysts, Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup> showed the highest activity. There are two possible reasons for the high activity: firstly, the covalent bonding between Pd<sup>II</sup> and amino groups of PANI can make Pd<sup>II</sup> adhere strongly and disperse uniformly on the surfaces of supports. Secondly, there existed  $\pi$ - $\pi$  conjugation between the PANI shell and aromatic compounds, so Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup> has good dispersibility in anisole and aromatic reactants can access active sites easily. The main drawback of Suzuki carbonylative coupling reaction is the formation of a lot of direct-coupling products. The carbonylative crosscoupling reaction catalyzed by Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup> produced only little amounts of direct coupling product (Table 2). The route of transmetalation without migratory insertion of carbon monoxide and direct reductive elimination should account for the formation of the direct coupling product (step 3). The  $\pi$ - $\pi$ conjugation between the PANI shell and the aromatic substrate would lead to a lower reaction rate of reductive elimination. In this case, carbon monoxide insertion occurring after transmetalation was promoted (step 4), so only a small amount of direct coupling products was produced.

### Recyclability of Fe<sub>3</sub>O<sub>4</sub>@PANI-Pd<sup>II</sup>

After the first cycle of the reaction, the catalyst was recovered successively by placing a magnet near the reaction vessel and washed with distilled water and ethanol several times and then dried at room temperature. As shown in Table 4, the catalyst

Table 4 The carbonylative cross-coupling reaction of 4-iodoaceto-phenone with phenylboronic acid catalyzed by the recycled catalyst<sup>a</sup>

в(он), + 1-	COCH <sub>3</sub> - Fe,O2@PANEPd'' 1 abm CO, K,CO3 +	сна +
Recycle	Catalyst cycle	Yield (%)
1	1	95
5	5	92

<sup>*a*</sup> The reactions were carried out using 4-iodoacetophenone (0.5 mmol), PhB(OH)<sub>2</sub> (0.6 mmol), CO (1 atm), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), and the Pd catalyst (1 mol%) in anisole (5 mL) at 80  $^{\circ}$ C.

was recycled in the carbonylative cross-coupling reactions of 4-iodoacetophenone with phenylboronic acid.  $Fe_3O_4$ @PANI-Pd<sup>II</sup> still maintained high activity and selectivity after being reused for five runs. The weight percentage of Pd in the reused catalyst, as determined by atomic absorption spectroscopic (AAS) analysis, was 3.9 wt%.

## Conclusions

In summary, we have developed a novel and practical heterogeneous catalyst for the Suzuki carbonylative coupling reaction under mild reaction conditions. This novel Pd catalyst exhibits higher activity for the Suzuki carbonylative coupling reaction than many other heterogeneous catalysts, such as MCM-41–2P–Pd<sup>II</sup>, Pd/C, MCM-41–2N–Pd<sup>II</sup>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>–SH–Pd<sup>II</sup>, and ImmPd–IL, reported in literature. Furthermore, a significant reduction in the formation of the direct coupling product could be observed when Fe<sub>3</sub>O<sub>4</sub>@PANI–Pd<sup>II</sup> was used to catalyze the Suzuki carbonylative coupling reaction. This catalyst can be reused five times without significant loss in catalytic activity. In addition, the Fe<sub>3</sub>O<sub>4</sub>@PANI–Pd<sup>II</sup> catalyst avoids the use of phosphine ligands, which makes it more environmentally friendly.

## Acknowledgements

The authors are grateful to the Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization, Gansu Province, for financial support.

# Notes and references

- (a) P. J. Tambade, Y. P. Patil, A. G. Panda and B. M. Bhanage, *Eur. J. Org. Chem.*, 2009, 3022–3025; (b) H. L. Li, M. Yang, Y. X. Qi and J. J. Xue, *Eur. J. Org. Chem.*, 2011, 2662–2667; (c) N. De Kimpe, M. Keppens and G. Froncg, *Chem. Commun.*, 1996, 635–636.
- 2 (a) C. E. Song, W. H. Shim, E. J. Roh and J. H. Choi, *Chem. Commun.*, 2000, 1695–1696; (b) S. Gmouh, H. Yang and M. Vaultier, *Org. Lett.*, 2003, 5, 2219–2222; (c) A. Furstner, D. Voigtlander, W. Schrader, D. Giebel and M. T. Reetz, *Org. Lett.*, 2001, 3, 417–420.
- 3 (a) B. M. O'Keefe, N. Simmons and S. F. Martin, *Tetrahedron*, 2011, **67**, 4344–4351; (b) X. F. Wu, H. Neumann and M. Beller, *Adv. Synth. Catal.*, 2011, 353, 788–792; (c) M. Dai, B. Liang, C. H. Wang, Z. J. You, J. Xiang, G. B. Dong, J. H. Chen and Z. Yang, *Adv. Synth. Catal.*, 2004, 346, 1669–1673.

- 4 (a) T. Ishiyama, H. Kizaki, T. Hayashi, A. Suzuki and N. Miyaura, *J. Org. Chem.*, 1998, 63, 4726–4731; (b) M. V. Khedkar, P. J. Tambade, Z. S. Qureshi and B. M. Bhanage, *Eur. J. Org. Chem.*, 2010, 6981–6986.
- 5 (a) M. Medio-Simon, C. Mollar, N. Rodriguez and G. Asensio, *Org. Lett.*, 2005, 7, 4669–4672; (b) P. Prediqer, A. V. Moro, C. W. Noqueira, L. Saveqnaqo, P. H. Menezes, J. B. Rocha and G. Zeni, *J. Org. Chem.*, 2006, 71, 3786–3792.
- 6 B. M. Okeefe, N. Simmons and S. F. Martin, *Org. Lett.*, 2008, 10, 5301–5304.
- 7 M. Z. Cai, G. M. Zheng, L. F. Zha and J. Peng, *Eur. J. Org. Chem.*, 2009, 1585–1591.
- 8 M. Z. Cai, J. Peng, W. Y. Hao and G. D. Ding, *Green Chem.*, 2011, **13**, 190–196.
- 9 J. R. Niu, X. Huo, F. W. Zhang, H. B. Wang, P. Zhao, W. Q. Hu, J. T. Ma and R. Li, *ChemCatChem*, 2013, 5, 349–354.
- 10 L. L. Zhou, J. Y. Yuan and Y. Wei, *J. Mater. Chem.*, 2011, **21**, 2823–2840.
- 11 (a) S. H. Xuan, Y. X. J. Wang, J. C. Yu and K. C. F. Leung, Langmuir, 2009, 25, 11835–11843; (b) Y. H. Deng, Y. Cai,
  Z. K. Sun, J. Liu, C. Liu, J. Wei, W. Li, C. Liu, Y. Wang and
  D. Y. Zhao, J. Am. Chem. Soc., 2010, 132, 8466–8473; (c) Y. Lu,
  Y. Yin, B. T. Mayers and Y. Xia, Nano Lett., 2002, 2, 183–186.
- (a) J. Deng, X. Ding, W. Zhang, Y. Peng, J. Wang, X. Long, P. Li and A. S. C. Chan, *Polymer*, 2002, 43, 2179–2184; (b) D. P. He, C. Zeng, C. Xu, N. C. Cheng, H. G. Li, S. C. Mu and M. Pan, *Langmuir*, 2011, 27, 5582–5588; (c) F. Wu, J. Chen, L. Li, T. Zhao and R. Chen, *J. Phys. Chem. C*, 2011, 115, 24411–24417.
- 13 M. X. Wan and W. G. Li, J. Polym. Sci., Part A: Polym. Chem., 1997, 35, 2129–2136.
- 14 J. G. Deng, C. L. He, Y. X. Peng, J. H. Wang, X. P. Long, P. Li and A. S. C. Chan, *Synth. Met.*, 2003, **139**, 295–299.
- 15 Y. H. Deng, D. W. Qi, C. H. Deng, X. G. Zhang and D. Y. Zhao, J. Am. Chem. Soc., 2008, 130, 28–29.
- 16 S. H. Xuan, Y. X. J. Wang, K. C.-F. Leung and K. Y. Shu, J. Phys. Chem. C, 2008, 112, 18804–18809.
- 17 H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen and Y. D. Li, Angew. Chem., Int. Ed., 2005, 117, 2842–2845.
- 18 S. Y. Wei, Z. Y. Ma, P. Wang, Z. P. Dong and J. T. Ma, J. Mol. Catal. A: Chem., 2013, 370, 175–181.
- 19 S. H. Xuan, L. Y. Hao, W. Q. Jiang, X. L. Gong, Y. Hu and Z. Y. Chen, *J. Magn. Magn. Mater.*, 2007, **308**, 210–213.
- 20 M. Ranjbar, S. Fardindoost, S. M. Mahdavi, A. Iraji zad and N. Tah-masebi Garavand, *Sol. Energy Mater. Sol. Cells*, 2011, 95, 2335–2340.
- 21 M. V. Khedkar, T. Sasaki and B. M. Bhanage, *RSC Adv.*, 2013, 3, 7791–7797.