

NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Preparation of recoverable $\text{Fe}_3\text{O}_4@\text{PANI-Pd}^{\text{II}}$ Core/Shell catalysts for Suzuki carbonylative cross-coupling reactions

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Xiaohang Zhu, Jianrui Niu, Fengwei Zhang, Jinghui Zhou, Xinzhe Li, and Jiantai Ma^{*[a]}

We report on synthesis, characterization and catalytic performances of a palladium-based superparamagnetic catalyst of $\text{Fe}_3\text{O}_4@\text{polyaniline}$ core/shell microspheres ($\text{Fe}_3\text{O}_4@\text{PANI-Pd}^{\text{II}}$). The material was characterized by TEM, FT-IR, vibrating sample magnetometer (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 direct-coupling product. The newly developed catalyst could be recovered from liquid phase easily by magnetic separation and recycled for 5 times without any significant loss of activity.

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.^[1] One general approach for the synthesis of biaryl ketones is the Friedel–Crafts acylation of substituted aromatic rings.^[2] However, Friedel–Crafts acylation has disadvantage for using Lewis acid, which is reactive with many functional groups and the regioselectivity is untunable. Another direct and convenient approach is using transition metal-catalyzed three-component cross-coupling reaction among arylmetal (Mg, Al, Si, Sn, Zn), carbon monoxide, and aryl electrophiles.^[3] But the generation of 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.^[4]

Many palladium-based homogeneous catalysts, such as $\text{Pd}(\text{tmhd})_2/\text{Pd}(\text{OAc})_2$,^[1a] $\text{Pd}_2(\text{dba})_3$,^[1b] $\text{Pd}(\text{PPh}_3)_4$,^[5] and N-heterocyclic carbene palladium,^[6] showed good activity in carbonylative cross-coupling reactions. However, the problem is that homogeneous catalysts are difficult to be separated from products and catalytic media, which limits homogeneous catalysts' commercial development and practical use. Thus, more research interests focus on heterogeneous palladium complexes as catalysts for Suzuki carbonylative coupling reactions. Cai et al. used $\text{MCM-41-2P-Pd}^{\text{II}}$ ^[7] and $\text{MCM-41-2N-Pd}^{\text{II}}$ ^[8] as catalysts for Suzuki carbonylative coupling reactions. Bhanage et al.^[4b] used Pd/C as a catalyst in Suzuki carbonylative coupling reactions. In order to improve the recyclability, we have immobilized Pd complexes on silica-coated magnetic nanoparticles ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH-Pd}^{\text{II}}$) to catalyze Suzuki carbonylative coupling reactions, so that the catalyst ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH-Pd}^{\text{II}}$) could be separated from the mother solutions by applying an external magnetic field.^[9] Core-shell structural superparamagnetic iron oxide hybrid nanoparticles have attracted increasing interest, as coatings can stabilize magnetic nanoparticles, leading to better dispersion and biocompatibility, and also can be further modified with

functional groups for divisive applications.^[10] Most of magnetic core-shell composite materials were prepared by coating Fe_3O_4 particles with functional shells.^[11] 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 property.^[12] Recently, Fe_3O_4 @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_3O_4 nanoparticles with core-shell structure via in-situ polymerization of aniline monomers in aqueous solution which contained Fe_3O_4 nanoparticles and surfactants. The fabrication of nanoscale ferromagnetic Fe_3O_4 -cross-linked PANI by an oxidative polymerization of aniline with ammonium peroxodisulfate as the oxidant was reported by Peng et al.^[12a] All Fe_3O_4 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_3O_4 .^[15]

In this paper, we report on synthesis of high superparamagnetic catalyst Fe_3O_4 @PANI-Pd^{II} with well-defined morphology. The superparamagnetic Fe_3O_4 @PANI microspheres have been synthesised via a simple in situ surface polymerization method. Pd^{II} can adhere strongly and disperse uniformly on the surface of Fe_3O_4 @PANI microspheres due to the covalent bonding between Pd^{II} 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 π - π conjugation between PANI shell and aromatic compounds. Fe_3O_4 @PANI-Pd^{II} was used to catalyze Suzuki carbonylative coupling reaction under mild conditions.

Experimental Section

Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), anhydrous sodium acetate, ethylene glycol, aniline, ammonium peroxodisulfate (APS), poly(vinylpyrrolidone) (PVP), 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_3O_4 particles

The magnetic Fe_3O_4 particles were synthesized via solvothermal reaction. Typically, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (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 vacuum at 60 °C overnight. Then Fe_3O_4 particles (0.2 g) and

APTES (4 mL) were dissolved in anhydrous ethanol to give a mixture solution (50 mL). The mixture was refluxed for 12 h under dry nitrogen. The resulting modified Fe_3O_4 particles were separated and then washed with ethanol. Finally, the product was dried in vacuum at 60 °C for 24 h and the amine-functionalized Fe_3O_4 particles (NH_2 - Fe_3O_4) were obtained.

Synthesis of Fe_3O_4 @PANI microspheres

The Fe_3O_4 @PANI microspheres were prepared by the in-situ surface polymerization method in the presence of PVP.^[16] Briefly, PVP (0.3 g) was dissolved in deionized water (600 mL), then the NH_2 - Fe_3O_4 particles (0.09 g) were added. The mixture was ultrasonically dispersed. After that, aniline (0.12 mL) and HCl (0.6 mL) was 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 vacuum at 60 °C for 24 h to obtain the desired Fe_3O_4 @PANI microspheres.

Loading of Pd on Fe_3O_4 @PANI microspheres (Fe_3O_4 @PANI-Pd^{II})

The as-synthesised Fe_3O_4 @PANI microspheres (300 mg) was 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_2 (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 the Fe_3O_4 @PANI-Pd^{II}, 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) were 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 diluted with 10 mL H_2O , followed by extraction with ethyl acetate (2×10 mL). The organic fraction was dried with MgSO_4 , the solvents evaporated under reduced pressure and the residue redissolved in 5 mL of ethanol. An aliquot was taken with a syringe and subjected to GC analysis. Yields were calculated against the consumption of the aryl iodides.

Characterization

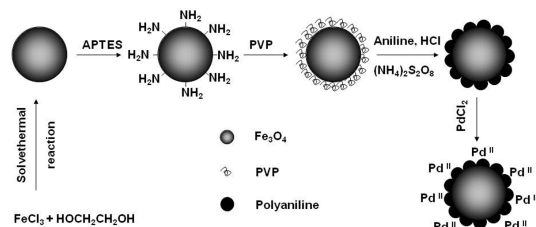
Transmission electron microscopy (TEM) images were characterized by Tecnai G2 F30 transmission electron microscopy. FT-IR spectra were recorded within a Nicolet NEXUS 670. Magnetic measurements of samples were performed by a vibrating sample magnetometer (Lake Shore

7304) at room temperature. X-ray-diffraction (PXRD) measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-K α radiation as the X-ray source in the 2θ range of 10–80°. X-Ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 instrument and the C_{1s} line at 292.1 eV was used as the binding energy reference.

Results and discuss

Catalyst preparation and characterization

The process for preparation of the catalyst Fe₃O₄@PANI-Pd^{II} is schematically described in Scheme 1. Firstly, Fe₃O₄ particles were prepared by the method given in previous reports.^[17] Secondly, Fe₃O₄ particles were modified with amine groups to enhance the growth of PANI. Afterwards, Fe₃O₄@PANI spheres were prepared by in-situ polymerization of aniline on the surface of Fe₃O₄ particles in the presence of PVP. Finally, PdCl₂ was anchored onto the surface of Fe₃O₄@PANI to afford the catalyst Fe₃O₄@PANI-Pd^{II}.



Scheme 1. Preparation of Fe₃O₄@PANI-Pd^{II}

The typical TEM image of Fe₃O₄@PANI microspheres prepared by the in-situ surface polymerization method at room temperature is showed in Figure 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 Fe₃O₄ microsphere cores and the thickness of the PANI shell was about 22 nm. The resultant Fe₃O₄@PANI composites had good dispersibility and spherical morphology. The TEM image of Fe₃O₄@PANI (Figure 1b) clearly showed that the magnetite particles were composed of plentiful nanocrystals with the size of about 16 nm. In the TEM image of Fe₃O₄@PANI-Pd^{II} (Figure 1c), it could be seen that the morphology of Fe₃O₄@PANI-Pd^{II} almost kept the same after loading PdCl₂ on Fe₃O₄@PANI microspheres.

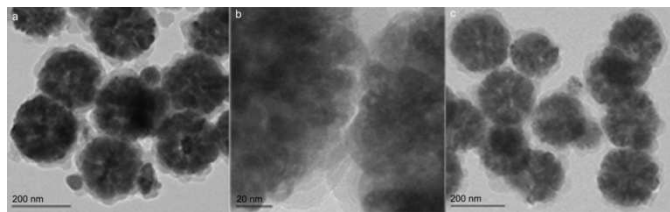


Figure 1. TEM images of (a), (b) Fe₃O₄@PANI, and (c) Fe₃O₄@PANI-Pd^{II}.

We also measured the Fourier transform infrared (FT-IR) spectra of Fe₃O₄@PANI and Fe₃O₄@PANI-Pd^{II}. In the FT-IR spectrum of Fe₃O₄@PANI (Figure 2a), the characteristic peaks at 1588 (C=C stretching deformation of quinoid and benzenoid ring, respectively), 1306 (C-N stretching of secondary aromatic amine), 1150, and 827 cm⁻¹ (out of plane deformation of C-H in the 1, 4-disubstituted benzene ring) showed that aniline was successfully polymerized onto the Fe₃O₄ core. The bands appeared at 574 and 3435 cm⁻¹ corresponded to the characteristic band of Fe-O vibration and -OH stretching vibration.^[11c] The FT-IR spectrum of Fe₃O₄@PANI-Pd^{II} (Figure 2b) was similar to that of Fe₃O₄@PANI, but the C-N stretching frequency shifted to lower frequency (around 1290 cm⁻¹), which was probably caused by N bonded to electron-deficient Pd to form the Pd complex.^[18]

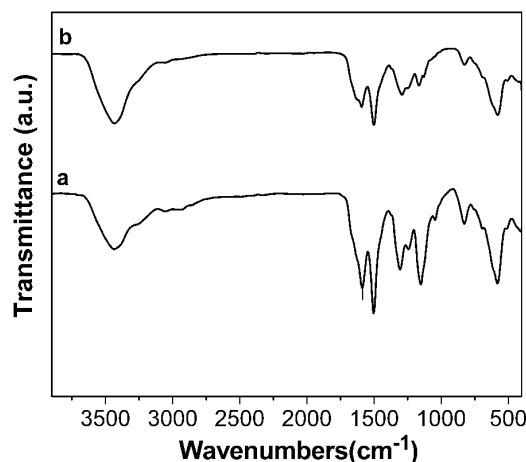


Figure 2. FT-IR spectra of (a) Fe₃O₄@PANI and (b) Fe₃O₄@PANI-Pd^{II}.

Magnetic measurements were performed using a vibrating sample magnetometer at room temperature. The magnetization curves for Fe₃O₄, Fe₃O₄@PANI and Fe₃O₄@PANI-Pd^{II} were compared in Figure 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.^[19] The measured saturation magnetizations were 71.8 emug⁻¹ for Fe₃O₄ particles, 46.5 emug⁻¹ for Fe₃O₄@PANI and 42.6 emug⁻¹ for Fe₃O₄@PANI-Pd^{II}. The saturation magnetization significantly decreased after aniline was polymerized onto Fe₃O₄ particles, and further decreased slightly after loading PdCl₂ on Fe₃O₄@PANI microspheres. However, the prepared Fe₃O₄@PANI-Pd^{II} microspheres still maintained good magnetic properties and could be completely and quickly separated from the aqueous solution when an external magnetic force was applied.

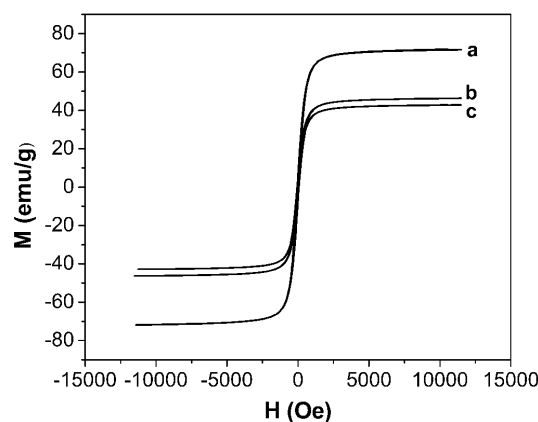


Figure 3. The magnetization curves of (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@\text{PANI}$, and (c) $\text{Fe}_3\text{O}_4@\text{PANI-Pd}^{\text{II}}$

The XRD patterns of $\text{Fe}_3\text{O}_4@\text{PANI}$ and $\text{Fe}_3\text{O}_4@\text{PANI-Pd}^{\text{II}}$ are shown in Figure 4. The main peaks of the $\text{Fe}_3\text{O}_4@\text{PANI-Pd}^{\text{II}}$ composite were similar to the $\text{Fe}_3\text{O}_4@\text{PANI}$, which revealed that immobilizing PdCl_2 on the surface of $\text{Fe}_3\text{O}_4@\text{PANI}$ did not affect the structure of $\text{Fe}_3\text{O}_4@\text{PANI}$. Both of the two patterns showed strong peaks which confirmed the products were still well-crystallized after the coating process under acidic conditions and 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 well agreement with the TEM observations.

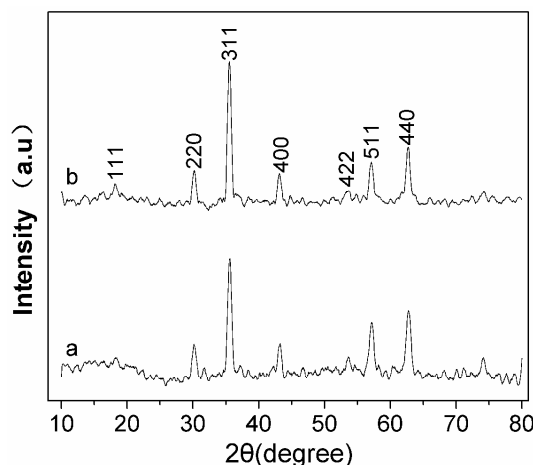


Figure 4. XRD patterns of (a) $\text{Fe}_3\text{O}_4@\text{PANI}$ and (b) $\text{Fe}_3\text{O}_4@\text{PANI-Pd}^{\text{II}}$.

The XPS elemental survey scans of the surface of the $\text{Fe}_3\text{O}_4@\text{PANI-Pd}^{\text{II}}$ catalyst are showed in Figure 5. Peaks corresponding to oxygen, carbon, nitrogen, palladium and iron were clearly observed. To ascertain the oxidation state of the Pd, X-ray photoelectron spectroscopy (XPS) studies were carried out. In Figure 6, the Pd binding energy of $\text{Fe}_3\text{O}_4@\text{PANI-Pd}^{\text{II}}$ exhibited two strong peaks centered at 342.8 and 337.5 eV, which were assigned to Pd 3d $3/2$ and Pd 3d $5/2$, respectively. These values agreed with the Pd^{II} binding energy of PdCl_2 .^[20]

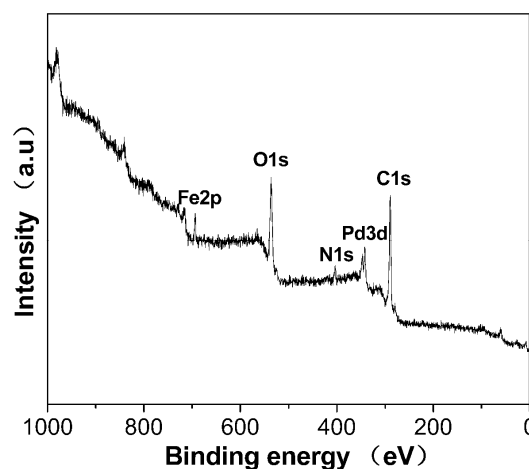


Figure 5. XPS spectrum of the elemental survey scan of $\text{Fe}_3\text{O}_4@\text{PANI-Pd}^{\text{II}}$

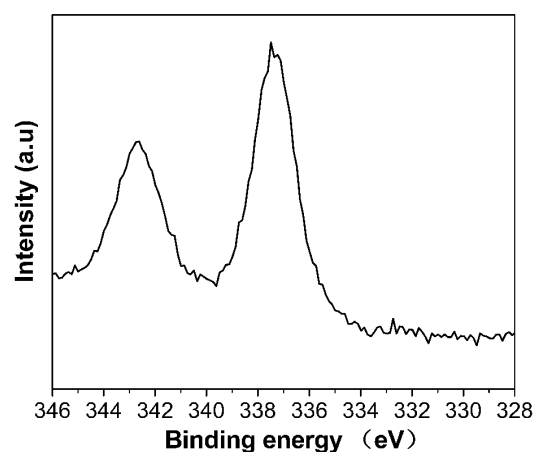


Figure 6. XPS spectrum of the $\text{Fe}_3\text{O}_4@\text{PANI-Pd}^{\text{II}}$, which shows the Pd 3d $_{5/2}$ and Pd 3d $_{3/2}$ binding energies.

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, relatively good yield of carbonylative cross-coupling product, 4-methoxybenzophenone, could be obtained. However, the yield of carbonylative cross-coupling product was relatively low in polar solvent, such as DMF, as significant amounts 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_2CO_3 , K_2CO_3 , Cs_2CO_3 , and K_3PO_4) could affect the selectivity of the products. Cs_2CO_3 and K_3PO_4 had a strong tendency in producing the direct coupling product (Table 1, entries 9 and 10). Unfortunately, Na_2CO_3 showed the lowest activity compared to other three inorganic bases (Table 1, entry 8). As a result, K_2CO_3 was the most efficient base. Therefore, the optimized reaction conditions are: 80 °C, anisole, and K_2CO_3 .

Table 1. The carbonylative cross-coupling of phenylboronic acid with 4-iodoacetophenone under different conditions^[a]

Entry	Solvent	Base	Temp./°C	Yield ^[b] (%)	
				1	2
1	Anisole	K_2CO_3	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_2CO_3	80	21	5
9	Anisole	Cs_2CO_3	80	48	23
10	Anisole	K_3PO_4	80	46	43

[a] The reactions were carried out with 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. [b] Determined by GC.

To investigate the substrate scope of this carbonylative cross-coupling reaction, a variety of arylboronic acids and aryl iodides were performed 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

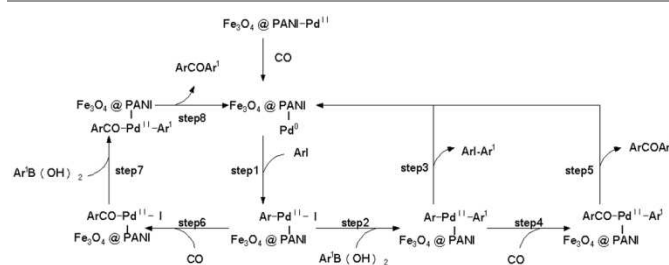
groups, (Table 2, entries 1-18). Aryl iodides substituted with electron-withdrawing groups, such as 4- CH_3CO and 2- NO_2 (Table 2, entries 1-3 and 4-6), were found to be the most active reagents in the carbonylative cross-coupling, as high yields were obtained in the shortest time (6 h). According to the proposed reaction mechanism for the reactions (scheme 2), the reason should be that the existence of electron-withdrawing groups could promote the oxidative addition of the organic halide to palladium (0) (step 1). Comparing the reaction used the aryl boronic acid with the same substituent (Table 2, entries 1-3, 4-6, 7-9, 10-12, 13-15, and 16-18), we found changing the electronic properties of the boronic acid would affect the selectivity to the direct coupling products. It could be seen that aryl boronic acid containing electron-attracting group, -Cl, produced the lowest yields of the direct coupling product. On the contrary, aryl boronic acid containing electron-donating group, - CH_3 , gave the highest yields of the direct coupling product. Since, the transmetalation (step 2) was slow when aryl boronic acid containing electron-attracting group, so direct coupling was hindered. On the contrary, aryl boronic acid containing electron-donating group could promote direct coupling.^[5a]

Table 2. The synthesis of unsymmetrical biaryl ketones^[a]

Entry	R ₁	R ₂	t/h	Yield ^[b] (%)	
				1	2
1	4-CH ₃ CO	H	6	95	2
2	4-CH ₃ CO	4-CH ₃	6	90	5
3	4-CH ₃ CO	4-Cl	6	92	3
4	2-NO ₂	H	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	H	H	8	97	3
8	H	4-CH ₃	8	94	5
9	H	4-Cl	8	97	1
10	4-CH ₃	H	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 ₃ O	H	8	95	2
14	4-CH ₃ O	4-CH ₃	8	90	2
15	4-CH ₃ O	4-Cl	8	87	2
16	2-NH ₂	H	12	96	1
17	2-NH ₂	4-CH ₃	12	98	1
18	2-NH ₂	4-Cl	12	97	0.6

[a] The reactions were carried out with aryl iodide (0.5 mmol), arylboronic acid (0.6 mmol), CO (1 atm), K₂CO₃ (1.5 mmol) and 1 mol% palladium

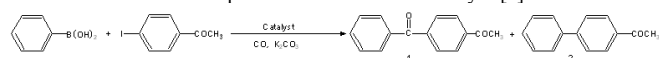
catalyst in anisole (5 mL) at 80 °C.[b]Determined by GC.



Scheme 2. catalytic cycles of carbonylative cross-coupling reaction.

The catalytic activities of heterogeneous catalysts, MCM-41-2P-PdII[7], Pd/C[4b], MCM-41-2N-PdII,[8] Fe₃O₄@SiO₂-SH-PdII,[9] and ImmPd-IL,[21] for Suzuki carbonylative coupling reaction in literatures were also showed in Table 3. Compared with those heterogeneous catalysts, Fe₃O₄@PANI-PdII showed the highest activity. There are two responsible reasons for the high activity: Firstly, the covalent bonding between the PdII and amino groups of PANI can make PdII adhere strongly and disperse uniformly on the surfaces of supporters. Secondly, there existed π - π conjugation between PANI shell and aromatic compounds, so Fe₃O₄@PANI-PdII has good dispersibility in anisole and aromatic reactants can access active sites easily. The main drawback of Suzuki carbonylative coupling reaction is formation of a lot of direct-coupling product. The carbonylative cross-coupling reaction catalyzed by Fe₃O₄@PANI-PdII produced only little amounts of direct coupling product (Table 2). The route of transmetalation without migratory insertion of carbon monoxide and directly reductive elimination should account for the formation of direct coupling product (step 3). The π - π conjugation between PANI shell and aromatic substrate would lead to lower reaction rate of reductive elimination. In this case, carbon monoxide insertion occurred after transmetalation were promoted (step 4), so only a small amount of direct coupling products were produced.

Table 3. The carbonylative cross-coupling of phenylboronic acid with 4-iodoacetophenone with different catalysts[a]

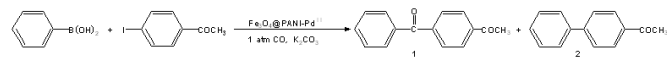


Entry	Catalyst	Catalyst amount (mol%)	Time/h	Temp./°C	Yield (%)
1	Fe ₃ O ₄ @PANI-Pd ^{II}	1	6	80	95
2	MCM-41-2P-Pd ^{II}	2	5	80	85
3	Pd/C ^[b]	2	8	100	85
4	MCM-41-2N-Pd ^{II}	2	6	80	86
5	Fe ₃ O ₄ @SiO ₂ -SH-Pd ^{II}	1	6	80	92
6	ImmPd-IL ^[c]	2	8	100	76

[a] Reaction conditions: CO (1 atm), anisole. [b] Reaction conditions: CO (200 psi), anisole. [c] Reaction conditions: CO (1 MPa), toluene.

Recyclability of Fe₃O₄@PANI-Pd^{II}

After the first cycle of the reaction, the catalyst was recovered successively by placing a magnet near the reaction vessels and washed with distilled water and ethanol several times and then dried at room temperature. As shown in Table 4, the catalyst was recycled in the carbonylative cross-coupling reactions of 4-iodoacetophenone with phenylboronic acid. Fe₃O₄@PANI-Pd^{II} 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%.

Table 4. The carbonylative cross-coupling reaction of 4-Iodoacetophenone with phenylboronic acid catalyzed by recycled catalyst^[a]

Recycle	Catalyst cycle	Yield (%)
1	1	95
5	5	92

[a] The reactions were carried out with 4-iodoacetophenone (0.5 mmol), PhB(OH)₂ (0.6 mmol), CO (1 atm), K₂CO₃ (1.5 mmol), and Pd catalyst (1 mol %) in anisole (5 mL) at 80 °C.

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^{II}, Pd/C, MCM-41-2N-Pd^{II}, Fe₃O₄@SiO₂-SH-Pd^{II}, and ImmPd-IL, reported in literatures. Furthermore, a significant reduction in the formation of direct coupling product could be observed when Fe₃O₄@PANI-Pd^{II} was used to catalyze the Suzuki carbonylative coupling reaction. This catalyst can be reused five times without significant loss in catalytic activity. More than that, the catalyst Fe₃O₄@PANI-Pd^{II} 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

- [1] a) P.J. Tambade, Y.P. Patil, A.G. Panda, B.M. Bhanage, *Eur. J. Org. Chem.* 2009, **2009**, 3022-3025; b) H.L. Li, M. Yang, Y.X. Qi, J.J. Xue, *Eur. J. Org. Chem.* 2011, **2011**, 2662-2667; c) N. De Kimpe, M. Keppens, G. Froncg, *Chem. Commun.* 1996, 635-636.
- [2] a) C.E. Song, W.H. Shim, E.J. Roh, J.H. Choi, *Chem. Commun.* 2000, 1695-1696; b) S. Gmouh, H. Yang, M. Vaultier, *Org. Lett.* 2003, **5**, 2219-2222; c) A. Furstner, D. Voigtlander, W. Schrader, D. Giebel, M.T. Reetz, *Org. Lett.* 2001, **3**, 417-420.
- [3] a) B.M. O'Keefe, N. Simmons, S.F. Martin, *Tetrahedron*. 2011, **67**, 4344-4351; b) X.F. Wu, H. Neumann, M. Beller, *Adv. Synth. Catal.* 2011, **353**, 788-792; c) Dai Mingji, B. Liang, C.H. Wang, Z.J. You, J. Xiang, G.B. Dong, J.H. Chen, Z. Yang, *Adv. Synth. Catal.* 2004, **346**, 1669-1673;
- [4] a) T. Ishiyama, H. Kizaki, T. Hayashi, A. Suzuki, N. Miyaura, *J. Org. Chem.* 1998, **63**, 4726-4731; b) M.V. Khedkar, P.J. Tambade, Z.S. Qureshi, B.M. Bhanage, *Eur. J. Org. Chem.* 2010, **2010**, 6981-6986.
- [5] a) M. Medio-Simon, C. Mollar, N. Rodriguez, 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, G. Zeni, *J. Org. Chem.* 2006, **71**, 3786-3792.
- [6] B.M. Okeefe, N. Simmons, S.F. Martin, *Org. Lett.* 2008, **10**, 5301-5304.
- [7] M.Z. Cai, G.M. Zheng, L.F. Zha, J. Peng, *Eur. J. Org. Chem.* 2009, **2009**, 1585-1591.
- [8] M.Z. Cai, J. Peng, W.Y. Hao, 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, R. Li, *ChemCatChem*. 2013, **5**, 349-354.
- [10] L.L. Zhou, J.Y. Yuan, Y. Wei, *J. Mater. Chem.* 2011, **21**, 2823-2840.

- [11] a) S.H. Xuan, Y.X.J. Wang, J.C. Yu, 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, D.Y. Zhao, *J. Am. Chem. Soc.* 2010, **132**, 8466-8473; c) Lu, Y.; Yin, Y.; Mayers, B. T.; Xia, Y. *Nano Lett.* 2002, **2**, 183-186.
- [12] a) J. Deng, X. Ding, W. Zhang, Y. Peng, J. Wang, X. Long, P. Li, 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, M. Pan, *Langmuir*. 2011, **27**, 5582-5588; c) Feng Wu, Junzheng Chen, Li Li, Teng Zhao, Renjie Chen, *J. Phys. Chem. C*. 2011, **115**, 24411-24417.
- [13] M.X. Wan, 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, A.S.C. Chan, *Synth. Met.* 2003, **139**, 295-299.
- [15] Y.H. Deng, D.W. Qi, C.H. Deng, X.G. Zhang, D.Y. Zhao, *J. Am. Chem. Soc.* 2008, **130**, 28-29.
- [16] Xuan, S. H.; Wang, Y. X. J.; Leung, K. C.-F.; Shu, K. Y. *J. Phys. Chem. C* 2008, **112**, 18804-18809.
- [17] H. Deng, X.L. Li, Q. Peng, X. Wang, J.P. Chen, Y.D. Li, *Angew. Chem.* 2005, **117**, 2842-2845.
- [18] S.Y. Wei, Z.Y. Ma, P. Wang, Z.P. Dong, 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, Z.Y. Chen, *J. Magn. Magn. Mater.* 2007, **308**, 210-213.
- [20] M. Ranjbar, S. Fardindoost, S.M. Mahdavi, A. Irajizad, N. Tahmasebi Garavand, *Sol. Energy Mater. Sol. Cells*. 2011, **95**, 2335-2340.
- [21] M.V. Khedkar, T. Sasaki, B.M. Bhanage, *RSC Advances*. 2013, **3**, 7791-7797.