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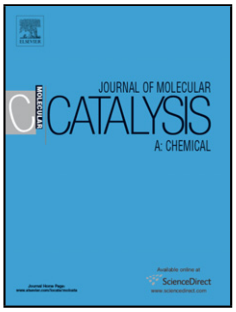

Title: Preparation of recoverable Fe_3O_4/PPy-Pd^{II} catalysts for carbonylative cross-coupling reactions

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PII: S1381-1169(14)00230-1
DOI: http://dx.doi.org/doi:10.1016/j.molcata.2014.05.024
Reference: MOLCAA 9124

To appear in: *Journal of Molecular Catalysis A: Chemical*

Received date: 12-12-2013
Revised date: 15-4-2014
Accepted date: 23-5-2014

Please cite this article as: J. Niu, M. Xie, X. Zhu, Y. Long, P. Wang, R. Li, J. Ma, Preparation of recoverable Fe_3O_4/PPy-Pd^{II} catalysts for carbonylative cross-coupling reactions, *Journal of Molecular Catalysis A: Chemical* (2014), http://dx.doi.org/10.1016/j.molcata.2014.05.024

Preparation of recoverable Fe_3O_4/PPy-Pd^{II} catalysts for carbonylative cross-coupling reactions

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Highlights

The preparation method meets the ideas of simpleness, fast and efficiency.
The catalyst was easily recovered.
The catalyst revealed high efficiency and high stability during recycling stages.

Abstract

The hierarchical porous Fe_3O_4/PPy-Pd^{II} catalyst has been synthesized using Fe_3O_4 microspheres both as chemical template and oxidant source under sonication. The catalyst characterized by TEM, XRD, FT-IR, XPS and vibrating sample magnetometry (VSM). The catalyst showed high reactivity for the carbonylative cross-coupling reaction of aryl iodides with arylboronic acids. This newly developed catalyst could be easily recovered and revealed high efficiency and high stability under the reaction conditions and during recycling stages.

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Keywords: carbonylative cross-coupling, environmental friendly, heterogeneous catalysis, palladium,

1. Introduction

It is well known that Pd-catalyzed carbonylative cross-coupling is of significant importance in modern chemical transformations, as these compounds are important moieties in many biologically active molecules, natural products, and pharmaceuticals [1]. Many palladium-based homogeneous catalysts, such as $Pd(tmhd)_2/Pd(OAc)_2$ [2], $Pd_2(dba)_3$ [3], $Pd(PPh_3)_4$ [4] and N-heterocyclic carbene palladium [5], have good activity in carbonylative cross-coupling reactions. Nevertheless, one key challenge for the practical use of homogeneous catalysts is the separation of product from the catalytic media. This process is often complicated and usually accomplished by means of complex work-up procedures [6]. Thus, more researches focus on heterogeneous palladium (immobilizing palladium complexes on various supports such as silica [7] and zeolites [8]) complexes as catalysts for Suzuki carbonylative coupling reactions. Cai et al. used MCM-41-2P-Pd^{II} [9] and MCM-41–2N–Pd^{II} [10] as catalysts for Suzuki carbonylative coupling reactions. Bhanage et al [11]. used Pd/C as a catalyst in Suzuki carbonylative coupling reactions. In our previous work for improving the recyclability, we immobilized Pd complexes on silica-coated magnetic nanoparticles (Fe_3O_4@SiO_2-SH-Pd^{II}) to catalyze Suzuki carbonylative coupling reactions, so that the catalyst (Fe_3O_4@SiO_2-SH-Pd^{II}) could be separated from the mother solutions by applying an external magnetic field [12]. Unfortunately, most of the conventional synthetic methods require long reaction time, toxic solvent and tedious synthetic steps.

Polymers are commonly used as supports for catalyst loading. It can not only prevent the Fe_3O_4 NPs from aggregating but also provide a useful platform for further functionalization.[13] Among these systems, polypyrrole (PPy), with the advantages of good environmental stability, reversible redox and virtue of easy preparation by both chemical and electrochemical approaches, was used in many areas such as secondary batteries, catalysis, and biosensors.[14] Chen et al.[15] reported the preparation of a Fe_3O_4–Ppy–Au nanocomposite which exhibited excellent electrocatalytic activity. Koon Gee Neoh et al.[16] reported the functionalization of polypyrrole-Fe_3O_4 nanoparticles for applications in biomedicine to ascorbic acid. Xu et al.[17] reported Fe_3O_4/Ppy/Au nanocomposites with Core/shell/shell/structure. These catalysts exhibited good catalytic activity. However, it is difficult to synthesize magnetic-based polymer composite materials, since polymer such as polypyrrole is hydrophobic but the surfaces of magnetic particles are hydrophilic, Although surface modifiers such as PVP surfactant are commonly adopted, the development of facile methods to fabricate magnetic-based polymer composite materials is still a challenge.[18]A simple, fast and efficient method is therefore required for the construction magnetic nano-catalyst [19].

In order to meet the ideas of simpleness, fast and effectivity, we synthesize the magnetic polymer-supported catalyst by loading Pd on the surface of the orange-like Fe_3O_4/PPy composite microsphere using Fe_3O_4 microspheres both as chemical template and oxidant source under sonication and applied the catalyst in carbonylative cross-coupling reactions.

2. Experiment

2.1. Characterization

FT-IR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrometer with a DTGS detector and samples were measured with KBr pellets. XRD measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-Ka radiation as the X-ray source in the 2θ range of 5–90◦.The size and morphology of the magnetic nanoparticles were observed by a Tecnai G2 F30 transmission electron microscopy and samples were obtained by placing a drop of a colloidal solution onto a copper grid and evaporating the solvent in air at room temperature. Magnetic measurements of Fe_3O_4 and Fe_3O_4/PPy-Pd^{II} were investigated with Quantum Design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from -15 kOe to 15 kOe. X-Ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 instrument and the C1S line at 292.1 eV was used as the binding energy reference.

2.2. Catalyst preparation

2.2.1. Synthesis of Fe_3O_4 microspheres

The magnetic Fe_3O_4 particles were prepared through a solvothermal reaction. Typically, $FeCl_3{\cdot}6H_2O$ (1.35 g) and sodium acetate (3.6 g) were dissolved in ethylene glycol (40 mL) with magnetic stirring. The obtained homogeneous yellow solution was transferred to a Teflon-lined stainless-steel autoclave (60 mL) and heated at 200

℃for 10 h. The obtained black particles were washed with ethanol four times and then dried in a vacuum at 60 ℃ for 12 h.

2.2.2. Synthesis of Fe_3O_4/PPy composite microspheres [20]

Fe_3O_4 particles (0.30 g) were dispersed in 70 mL H_2O under sonication, and then pyrrole (3 mL) in alcohol (15 mL) and HCl solution (15 mL, 6 M) were added into the above solution in turn under sonication for 1.5 h. Finally, the black product was collected with the help of a magnet, washed with deionized water repeatedly to remove the residual pyrrole monomers and HCl acid, and then dried in a vacuum overnight. The corresponding PPy microspheres were obtained by treating Fe_3O_4/PPy composite microspheres in acidic solution.

2.2.3. Loading of Pd on Fe_3O_4/PPy (Fe_3O_4/PPy-Pd^{II})

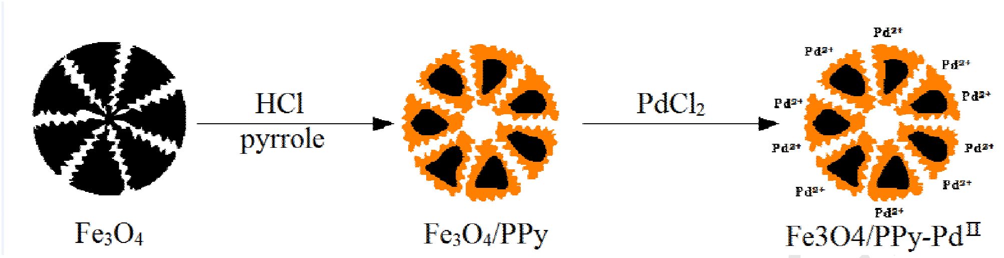
500 mg of Fe_3O_4/PPy samples were first dispersed in a 50 mL ethanol solution under ultrasonication for 0.5 h. The formed black suspension was ultrasonically mixed with 3.0 mmol of a $PdCl_2$ solution for 1 h. The solid product was filtered by suction, washed three times with ethanol, distilled water and ethanol successively, and dried at 50 ºC under vacuum for 24 h to give the palladium complex (Fe_3O_4/PPy-Pd^{II}).

2.2.4. Typical procedure for the carbonylative Suzuki coupling reaction

A mixture of aryl iodide (0.5 mmol), arylboronic acid (0.6 mmol), K_2CO_3 (1.5 mmol), and 2 mol% palladium catalyst in anisole (5 mL) were stirred at 80 ºC under 1 atm pressure of CO. An aliquot was taken with a syringe and subjected to GC analysis and ^1H NMR (See the supplementary material). Yields were calculated against the consumption of the aryl iodides.

3. Results and discussion

3.1. Catalyst preparation



Scheme 1 Preparation of Fe_3O_4/PPy-Pd^{II} catalyst.

The process for preparation of the catalyst Fe_3O_4/PPy-Pd^{II} is schematically described in Scheme 1. Firstly, Fe_3O_4 particles were prepared by the method given in previous reports. Secondly, in the strong acidic solution, the Fe^{3+} released from Fe_3O_4 microspheres and the polymerization of pyrrole monomers. A layer of polypyrrole was coated on the surface of Fe_3O_4 [20]. Thirdly, under magnetic stirrers, $PdCl_2$ was supported on the surface of polypyrrole.

3.2 Catalyst characterization

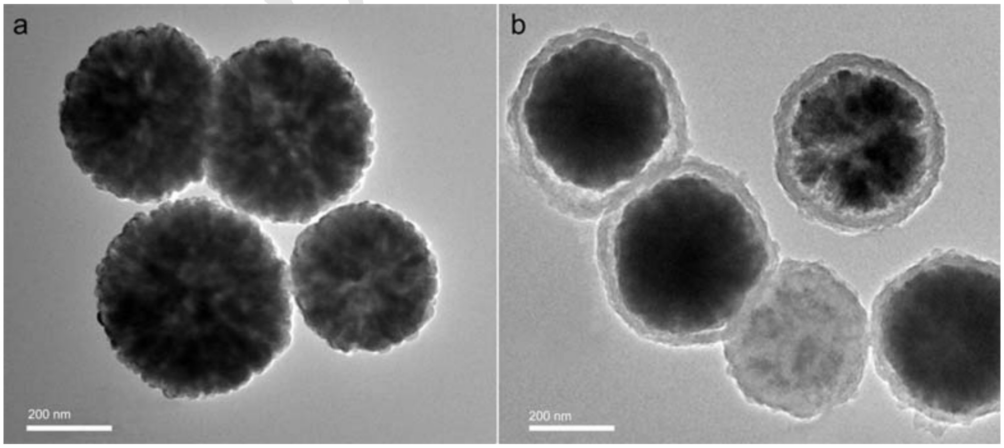


Fig. 1 TEM images of (a) Fe_3O_4 and (b) Fe_3O_4/PPy-Pd^{II}

The typical TEM image of Fe_3O_4, Fe_3O_4/PPy-Pd^{II} microspheres was showed in Fig. 1. The average diameter of the as-synthesized spherical particles was about 400 nm

(Figure 1a). A continuous layer of PPy could be observed on the outer shell of the Fe_3O_4 microsphere cores and the thickness of the PPy shell was about 25 nm. The resultant Fe_3O_4/PPy-Pd^{II} composites had good dispersibility and spherical morphology. In the TEM image of Fe_3O_4/PPy-Pd^{II} (Figure 1b), it could be seen that the morphology of Fe_3O_4/PPy-Pd^{II} almost kept spherical after coating process under acidic conditions and fastening $PdCl_2$ on the supporter.

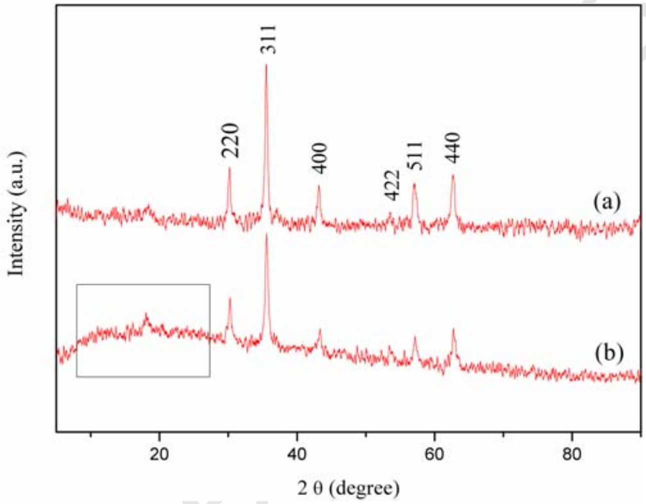


Fig. 2 XRD patterns of (a) Fe_3O_4 and (b) Fe_3O_4/PPy-Pd^{II}

The crystalline structure of the resulting products was investigated by X-ray powder diffraction (XRD). In Figure 2, the main peaks of the Fe_3O_4/PPy-Pd^{II} composite were similar to the Fe_3O_4. It exhibited that the coating process under acidic conditions and fastening $PdCl_2$ on the supporter did not affect the structure of Fe_3O_4. Both of the two patterns showed strong peaks which confirmed the products were well-crystallized and detected diffraction peaks in every pattern could be indexed as cubic Fe_3O_4 (JCPDS card No. 82-1533). A broad peak was observed at $2\theta = 10^{\circ}$- 30°, which suggested newly generating a layer of PPy [21].

Magnetic measurements were performed using a vibrating sample magnetometer

(VSM) at room temperature. The magnetization curves for Fe_3O_4 particles and Fe_3O_4/PPy-Pd^{II} were compared in Figure S1. There was no hysteresis in the magnetization for the two types of particles. Additionally, neither coercivity nor remanence could be observed, which suggested that the two particles were superparamagnetic[22]. The measured saturation magnetizations were 76.2 emug^{-1} for Fe_3O_4 particles and 22 emug^{-1} for Fe_3O_4/PPy-Pd^{II}, respectively. The saturation magnetization significantly decreased after pyrrole monomer was polymerized and $PdCl_2$ was loaded onto Fe_3O_4 particles microspheres. However, the prepared Fe_3O_4/PPy-Pd^{II} microspheres still maintained good magnetic properties and could be completely and quickly separated from the solvent when an external magnetic force was applied.

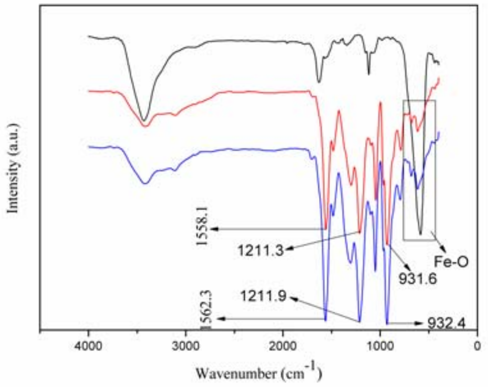


Fig. 3 FT-IR of (a) Fe_3O_4, (b) Fe_3O_4/PPy and (c) Fe_3O_4/PPy-Pd^{II}

The compositions of Fe_3O_4/PPy-Pd^{II} composite microsphere were confirmed by FT-IR (Figure 3). For comparison Fe_3O_4 and Fe_3O_4/PPy were also shown in the picture. From the spectrogram, the peaks at around 1560 cm^{-1}, 1200 cm^{-1} and 930 cm^{-1} were attributed to C=C stretching vibrations, C-N stretching vibrations and C-H stretching vibrations, respectively. From the Fe_3O_4/PPy-Pd^{II} pattern, we can see the C=C, C-N, C-H stretching vibrations take place blue shift, which exhibited $PdCl_2$ was fastened on the supporter.

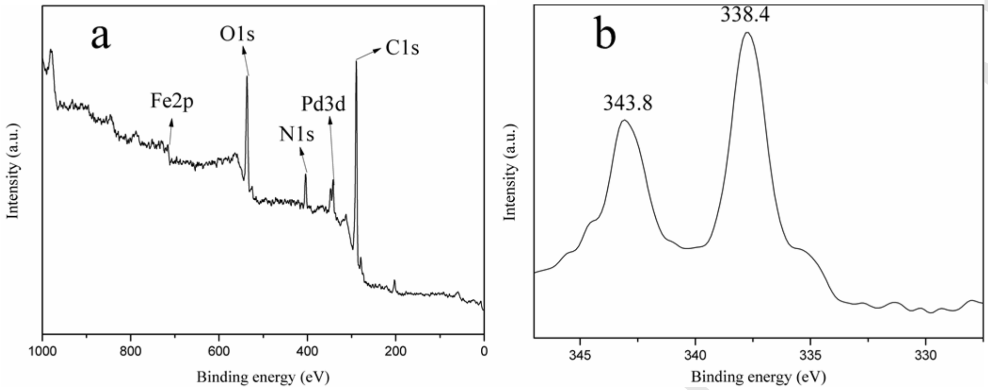


Fig. 4 XPS spectra for (a) Fe_3O_4/PPy-Pd^{II} and (b) Fe_3O_4/PPy-Pd^{II} showing Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies

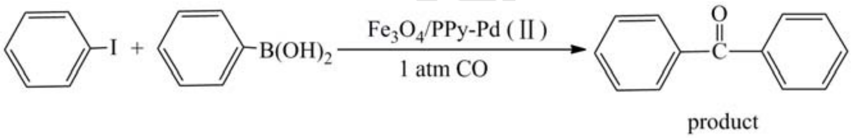
The XPS elemental survey scans of the surface of the Fe_3O_4/PPy-Pd^{II} catalyst were showed in Figure 4a. Peaks corresponding to iron, oxygen, nitrogen, palladium and carbon were clearly observed. To ascertain the oxidation state of the Pd, X-ray photoelectron spectroscopy (XPS) studies were carried out. In Figure 4b, the Pd binding energy of Fe_3O_4/PPy-Pd^{II} exhibited two strong peaks centered at 343.8 and 338.4 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 $PdCl_2$.

3.3 Catalytic Carbonylative Suzuki coupling reaction

To explore the optimal reaction conditions, the coupling of iodobenzene with phenylboronic acid was determined at the model reaction (Table 1). The preliminary results indicated that temperature, base and solvent had a significant effect on the coupling reaction. From Table 1, when the temperature increased from 60 °C to 80 °C high yield of the desired product (92%) was obtained (Table 1, entry 1-2). But at the temperature of 100 °C (Table 1, entry 3), the yield of the desired product (90%) was decreased. Therefore, the best temperature was 80°C. According to the evaluated results of solvents, anisole was found to be the best (Table 1, entry 2, 4-6). Under the optimized reaction temperature and solvent, several bases were examined, such as NaOAc, K_3PO_4, Cs_2CO_3 and K_2CO_3(Table 1, entry 2, 7-9). As a result, the most used base K_2CO_3 was the most efficient base to produce carbonylative cross-coupling product. Therefore, the optimized reaction conditions are: 80 °C, anisole, and K_2CO_3.

Table 1

Carbonylative Suzuki coupling reaction under diffident conditions. [a]



Entry	Solvent	Base	Temp./°C	Time/h	Yield [b] (%)
1	Anisole	K_2CO_3	60	8	41
2	Anisole	K_2CO_3	80	8	92
3	Anisole	K_2CO_3	100	8	90
4	Toluene	K_2CO_3	80	8	69
5	Dioxane	K_2CO_3	80	8	78
6	DMF	K_2CO_3	80	8	70
7	Anisole	NaOAc	80	8	0
8	Anisole	Cs_2CO_3	80	8	63
9	Anisole	K_3PO_4	80	8	69

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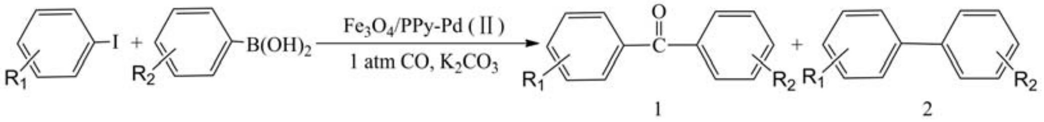
[a] The reactions were carried out with iodobenzene (0.5 mmol), arylboronic acid (0.6 mmol), CO (1 atm), base (1.5 mmol), solvent (5 mL), and 2 mol% palladium catalyst.

[b] Determined by GC.

The activity of palladium-complexes immobilized on Fe_3O_4/PPy was tested in the Suzuki carbonylative coupling reactions of aryl halides, namely the reactivity of aryl halides with arylboronic acids using K_2CO_3 as a base under balloon pressure of CO in anisole. Firstly, The Suzuki carbonylative reaction of iodobenzene with phenylboronic acid was chosen as the model reaction to evaluate the reaction time. To our delight, the catalyst was active for it and with 92% conversion in 8 h and the products of the diphenyl ketone were highly selective (Table 2, entries 1, 2, 3). Further investigation of the substrate scope was carried out under the optimized reaction conditions. In Table 2, various aryl iodides as well as arylboronic acids were examined and good functional group tolerance of the Fe_3O_4/PPy-Pd^{II} catalytic system was observed. For example, aryl iodides containing electron-withdrawing groups including 4-CH_3CO and 2-NO_2 produced desired ketones in excellent yields (Table 2, entries 15-20), the reason should be that the existence of electron-withdrawing groups could promote the oxidative addition of the organic halide to palladium (0) (Scheme S2 step 1) . It was noteworthy that up to 98 % yield of unsymmetrical biaryl ketone was obtained for 4-chlorobenzeneboronic acid with the 4-iodonitrobenzene (Table 2, Entry 17). In addition, both 4-methylbenzeneboronic acid and 4-chlorophenylboronic acid reacted smoothly with aryl iodides to give unsymmetrical biaryl ketones in high yields (Table 2, Entries 4, 5, 7, 8, 10, 11, 13, 14, 16, 17, 19 and 20).

Table 2

Carbonylative Suzuki coupling reaction of various aryl iodides with arylboronic acids in the presence of the Fe_3O_4/PPy-Pd^{II} catalyst. [a]



Entry	R_1	R_2	t/h	Yield[b] (%)		TOF (h^{-1})
				1	2	
1	H	H	4	40	5	5.00
2	H	H	6	63	9	5.25
3	H	H	8	92	6	5.75
4	H	4-CH_3	8	88	9	5.50
5	H	4-Cl	8	84	6	5.25
6	4-CH_3	H	8	89	6	5.56
7	4-CH_3	4-CH_3	8	87	10	5.43
8	4-CH_3	4-Cl	8	90	5	5.63
9	4-CH_3O	H	8	91	6.7	5.69
10	4-CH_3O	4-CH_3	8	89	9	5.56
11	4-CH_3O	4-Cl	8	92.5	2	5.78
12	2-NH_2	H	12	85	9	3.54
13	2-NH_2	4-CH_3	12	80	11	3.33
14	2-NH_2	4-Cl	12	88	10	3.67
15	2-NO_2	H	6	99	0.5	8.25
16	2-NO_2	4-CH_3	6	100	0	8.33

17	2-NO_2	4-Cl	6	98	<0.1	8.17
18	4-CH_3CO	H	6	93	6	7.75
19	4-CH_3CO	4-CH_3	6	89	10	7.42
20	4-CH_3CO	4-Cl	6	90	7	7.50

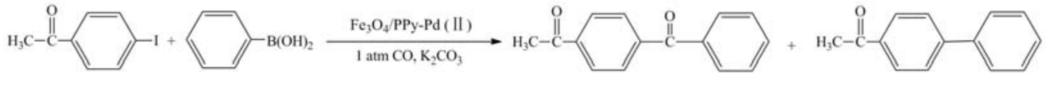
[a] The reactions were carried out with iodobenzene (0.5 mmol), arylboronic acid (0.6 mmol), CO (1 atm), K_2CO_3 (1.5 mmol), solvent (5mL) and 2 mol% palladium catalyst.

[b] Determined by GC and ^1H NMR.

Furthermore, we investigated the recyclability of the Fe_3O_4/PPy-Pd^{II}. After the first cycle of the reaction, the catalyst was recovered with the help of a magnet, successively washed with distilled water (to remove excess of base), ethanol, and dried at room temperature ready for the next cycle. The carbonylative cross-coupling reaction of 4-Iodoacetophenone with phenylboronic acid catalyzed by recycled catalyst were displayed in Table 3. The weight percentage of Pd in the Fe_3O_4/PPy, determined by atomic absorption spectroscopic (AAS) analysis, was 4.21 wt% before and 3.1 % after four cycles.

Table 3

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



1 2

Recycle	Catalyst cycle	Yield (%)

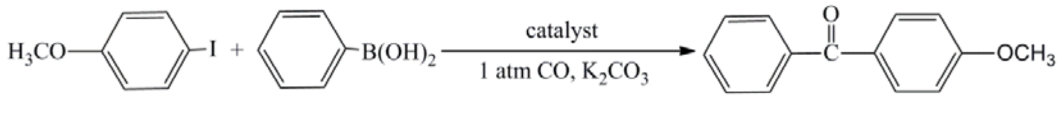
		1	2
1	1	93	6
4	4	80	10

[a] The reactions were carried out with 4-Iodoacetophenone (0.5 mmol), $PhB(OH)_2$ (0.6 mmol), CO (1 atm), K_2CO_3 (1.5 mmol) and 2 mol% palladium catalyst in anisole (5 mL) at 80 ºC.

As a comparison, we compared the results achieved in this work with those reported elsewhere over many supported catalysts. Take phenylboronic acid with 4-iodoanisole as an example, the results were listed in Table 4. What was worth mentioning, the Fe_3O_4/PPy-Pd^{II} was outstanding over the other heterogeneous catalysts. In contrast with the catalysts of Pd/C [11] and Imm Pd-IL [23], our catalyst took less reaction time and in a mild environment towards the carbonylative cross-coupling(Table 4 entries 2, 4, 5). Although the catalysts of MCM-41-2P-PdII [9] and MCM-41-2N-PdII [10] give a good yields in a short time and 80℃, the yield is lower than the catalyst of Fe_3O_4/PPy-Pd^{II} (Table 4 entries 1, 3, 5).

Table 4

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



Entry	Catalyst	Catalyst amount (mol%)	Time/h	Temp./°C	Yield (%)
1	MCM-41-2P-Pd^{II}	2	5	80	85

2	Pd/C[b]	2	8	100	85
3	MCM-41-2N-Pd^{II}	2	6	80	86
4	ImmPd-IL[c]	2	8	100	76
5	Fe_3O_4/PPy-Pd^{II}	2	6	80	93

[a] Reaction conditions: CO (1 atm), anisole.

[b] Reaction conditions: CO (200 psi), anisole.

c Reaction conditions: CO (1 MPa), toluene.

4 Conclusions

We have developed a hierarchical porous, practial and economic heterogeneous catalytic system for the Suzuki carbonylative cross-coupling reaction by using PPy modified MNPs that were supported on Pd as the catalyst in anisole under an atmospheric pressure of carbon monoxide. This novel Pd catalyst can be conveniently prepared by using Fe_3O_4 microspheres both as chemical template and oxidant source under sonication; it exhibited high activity and selectivity for the Suzuki carbonylative coupling reaction. The catalyst revealed high efficiency and high stability under the reaction conditions and during recycling stages. Our catalyst used the polymer as ligands, which renders it more environmentally friendly.

5 Acknowledgements

The authors are grateful to the Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization, Gansu Province for financial supports. Additionally, we are also very thank you for the Scholarship Award for Excellent Doctoral Student granted by Lanzhou University

6 Appendix A. Supplementary data

Supplementary data to this article can be found at the supplementary material.

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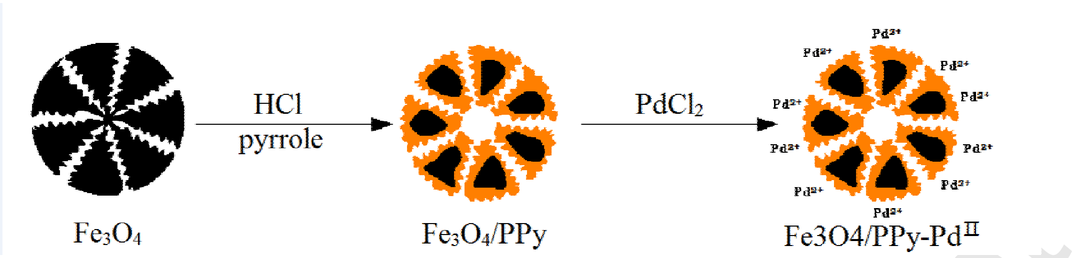
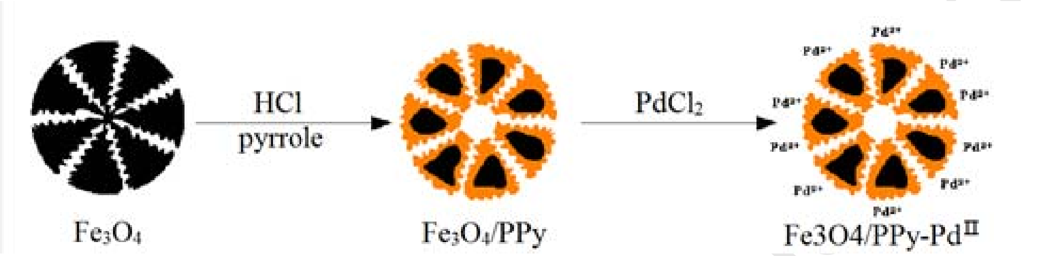

HCl
pyrrole
PdCl₂
Fe₃O₄
Fe₃O₄/PPy
Fe3O4/PPy-Pdᴵᴵ
Pd²⁺


HCl
pyrrole
PdCl₂
Fe₃O₄
Fe₃O₄/PPy
Fe3O4/PPy-Pdᴵᴵ
Pd²⁺