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A highly efficient and magnetically recoverable HMMS-SH-Pd^{II} has been developed for carbonylative cross-coupling and Suzuki coupling reactions

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ARTICLE TYPE

Stabilizing Pd^II on hollow magnetic mesoporous spheres: a highly active and recyclable catalyst for carbonylative cross-coupling and Suzuki coupling reactions

Jianrui Niu, Mengmeng Liu, Peng Wang, Yu Long, Miao Xie, Rong Li[*] and Jiantai Ma[*]

The hollow magnetic mesoporous spheres (HMMS) catalyst has been synthesized using polystyrene microspheres as chemical template. The catalyst characterized by TEM, XRD, XPS and vibrating sample magnetometry (VSM). The catalyst shows high activity for the carbonylative cross-coupling reaction of 10 aryl iodides with arylboronic acids and Suzuki coupling reaction. The newly developed catalyst is easy to be recovered and recycled by magnetic separation from liquid phase reactions. More importantly, the catalyst revealed high efficiency and high stability under the reaction conditions and during recycling stages.

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Introduction

The Suzuki coupling reaction has shown as an efficient method for construction of C-C bonds and plays an important role in pharmaceutical industry and organic synthesis. Furthermore,
5 biaryl ketones are important moieties in many biologically active molecules, natural products and pharmaceuticals. Various methods for the preparation of them have been reported[1]. Among them, the Suzuki carbonylative coupling reaction is one of the most promising methods for the direct synthesis of biaryl ketones
10 from carbon monoxide, aryl halides and arylboronic acids since a wide variety of functionalities can be tolerated on either partner and the arylboronic acids are generally nontoxic and thermally-, air- and moisture-stable[2]. To date, Pd catalyst has been widely used in the two reactions.
15 Nevertheless, one key challenge for the commercial development and practical use of homogeneous Pd-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[3]. To solve these problems and make the
20 process more "green", researchers have immobilized palladium complexes on various supports such as carbon[4], silica[5], hydroxyapatite[6], zeolites[7] and organic polymers[8] to create heterogeneous catalyst. On this occasion, the magnetic nanoparticles have drawn attention and widely used in various
25 fields. (such as drug delivery[9], magnetic resonance imaging[10], biomolecular sensors[11], bioseparation[12], and magneto-thermal therapy[13], catalytic system[14]). Due to magnetic separation is rapid and highly efficient. What is more, their special magnetic properties allow quick separation from aqueous systems in the
30 presence of an external magnetic field. To enhance the immobilization of the catalytically active metal on its surface whilst preventing their agglomeration, we always use functionalization of magnetic nanoparticles. Compared with the amine functionalization, the thiol-modified magnetic
35 nanoparticles has a higher affinity for Pd, which inspired by the work of Fryxell et al.[15] and Pinnavaia and Mercier[16], who demonstrated that thiol-modified mesoporous materials are remarkable scavengers for mercury, and by Kang et al.[17-18], who showed that SBA-15-SH has a higher affinity for Pd and Pt
40 compared to other metals.
In the latest decade, hollow magnetic mesoporous spheres (HMMS) represent a new class of powerful carrier because of their well-defined structures, uniform size, low density, large surface area, and wide range of potential applications. Compared
45 to the conventional mesoporous silica materials such as MCM-41, SBA-15, FSM-16 and MCF, HMS exhibited good catalyst loading properties for confined cooperative catalysis, as they could prevent aggregation of metallic nanoparticles and promote the mass diffusion and transport of reactants. Herein, we present a
50 reusable palladium catalyst with Fe_3O_4 nanoparticles embedded in the mesoporous shell for carbonylative cross-coupling and Suzuki coupling reactions.

Experimental

Synthesis of the hydrophobic magnetite nanoparticles (Fe_3O_4
55 NPs)

The Fe_3O_4 NPs were prepared using a published method with a slight modification16. First, 4.8 g of $FeCl_3 \cdot 6H_2O$, 2.0 g $FeCl_2 \cdot 4H_2O$ and 1.0 mL oleic acid were added to 40 mL of deionized water under vigorous stirring. Second, the mixture
60 solution was purged with nitrogen gas for 30 min under nitrogen atmosphere. Third, the mixture solution was heated to 90 ºC. Finally, 10 mL of ammonium hydroxide (28 wt%) was added rapidly to the solution, and it immediately turned black. The reaction was kept at 90 ºC for 2.5 h. The black precipitate was
65 obtained with the help of a magnet and dried at 323 K overnight.

Preparation of polystyrene latex with attached Fe_3O_4 nanoparticles

Briefly, carboxylic polystyrene (PS) latex was prepared by soap-free emulsion polymerization of St with AA. 1.5 g Fe_3O_4
70 nanoparticles and 2.5 g negatively charged PS latex were dispersed in 84 mL and 60 mL hydrochloric acid solution (pH = 2.3), respectively. Then the latter suspension was added dropwise into the former under vigorous stirring at room temperature. After 6 h, the heteroaggregates, i.e. Fe_3O_4 nanoparticles attached on the
75 surface of PS latex particles, were separated from the solution by an external magnet and washed several times with water until the pH value of the solution became close to 7.

Preparation of hollow magnetic mesoporous silica spheres (HMMS)

80 First, 2.0 g heteroaggregate of the PS latex and Fe_3O_4 nanoparticles were dispersed in a solution composed of 75 mL of ethanol, 5 mL of H_2O, and 3.8 mL of $NH_3 \cdot H_2O$ (28 wt %). After stirring for 10 min, 0.4 mL of TEOS and $C_{18}TMS$ mixture with a molar ratio of 4.7:1 were added dropwise under vigorous stirring.
85 Then, the reaction proceeded for 8 h at room temperature under stirring. The resultant particles were separated by centrifugation, purified by three cycles of magnetic separation/washing in ethanol, and dried at room temperature for 12 h. Finally, the as-prepared products were dried at 313 K overnight and calcined in
90 air at 823 K for 7 h.
Hollow magnetic mesoporous silica spherical magnetite nanoparticleswere synthesized via the versatile solvothermal reaction reported by Liao[24].

Preparation of thiol-modified hollow magnetic mesoporous
95 silica spheres (HMMS-SH)

The functionalization of the HMMS nanoparticles was carried out by adding 0.5 mL mercaptopropyl trimethoxysilane to 200 mL of dry toluene containing 500 mg of HMMS nanoparticles. The resulting solution was refluxed for 24 h and then washed with
100 toluene and acetone. The obtained solid material was dried in

vacuum at 50 ºC for 24 h

Loading of Pd on thiol-modified silica coated HMMS (HMMS-SH-Pd^{II})

500 mg of HMMS-SH samples were first dispersed in a 50 mL
5 ethanol solution under ultrasonication for 0.5 h. The formed black suspension was ultrasonically mixed with 0.188 mmol of a PdCl$_2$ solution for 1 h, then after 2 h of vigorous stirring, the products were obtained with the help of a magnet, washed thoroughly with deionized water and then dried in a vacuum at room temperature
10 overnight..

The preparation of the HMMS-SH-Pd^{II} catalyst follows the steps described in Scheme 1. Firstly, HMMS were prepared. Secondly, the functionalization of the silica coated HMMS with mercaptopropyltrimethoxysilane. Thirdly, under mechanical
15 stirring, palladium chloride was supported on the surface of ligand-modified magnetic nanoparticles.

Typical procedure for the carbonylative Suzuki coupling reaction

A mixture of aryl iodide (0.5 mmol), arylboronic acid (0.6
20 mmol), K$_2$CO$_3$ (1.5 mmol), and 1.5mol% palladium catalyst in anisole (5 mL) were stirred at 80 ºC under 1 atm pressure of CO. The reaction process was monitored by thin layer chromatography (TLC), and conversion was estimated by GC after separating the catalyst from the reaction mixture with a
25 magnet. The catalyst was then washed several times with ethanol and dried at room temperature for its reuse.

Typical procedure for the Suzuki coupling reaction

In the Suzuki coupling reactions, 0.5 mmol of aryl halides, 0.7 mmol of phenyl boric acid and 1.5 mmol of base were taken into
30 5 mL of solvent. The amount of catalyst used in each reaction was 0.6 mol%, and the reaction mixture was refluxed at 343K. The reaction process was monitored by thin layer chromatography (TLC), and conversion was estimated by GC after separating the catalyst from the reaction mixture with a
35 magnet. The catalyst was then washed several times with ethanol and dried at room temperature for its reuse.

Results and discussions
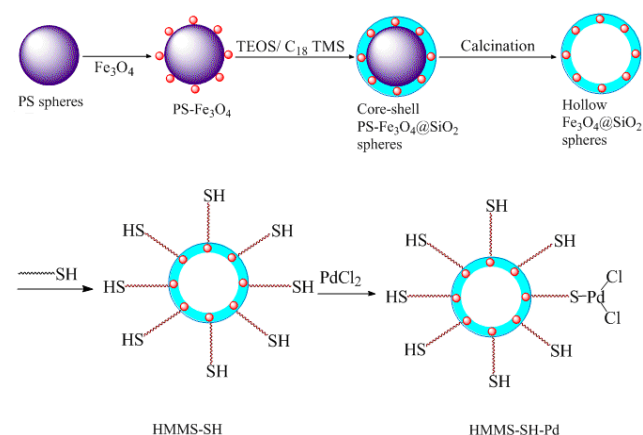
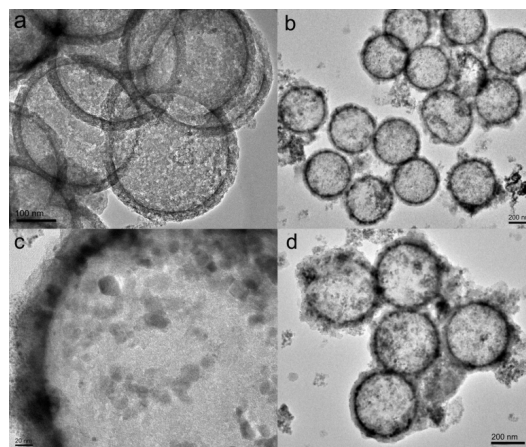**Scheme 1.** Preparation of catalyst

40
Figure 1 TEM images of (a) HMMS, (b, c) HMMS-SH and (d) HMMS-SH-Pd^{II}

Transmission electron microscopy (TEM) images were characterized by Tecnai G2F30 transmission electron
45 microscopy. The typical TEM image of the catalyst is showed in Figure 1. As shown in Fig 1 the average diameter of the as-synthesized spherical particles was about 250 nm and they were nearly monodisperse. A continuous layer of SiO$_2$ could be observed, and the thickness is about 30 nm. The TEM in Fig 1d
50 show that the HMMS-SH-Pd^{II} did not change the morphology after PdCl$_2$ coordinated to the surface of the hollow magnetic silica sphere.
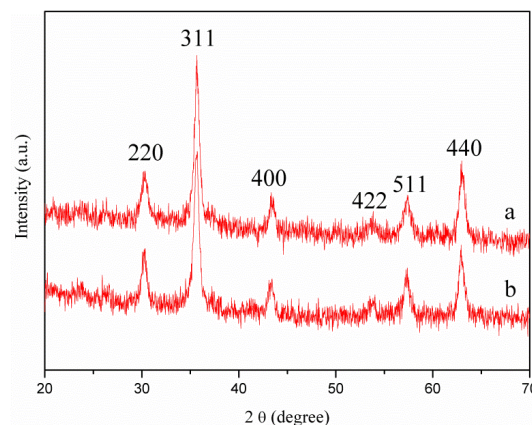
Figure 2 XRD patterns of (a) HMMS, (b) HMMS-SH-Pd^{II}

55 X-ray-diffraction (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 20-70°. The XRD pattern of the HMMS (See Figure 2a) shows characteristic peaks of magnetite nanoparticles and the sharp, strong peaks confirm the products
60 are well crystallized and detected diffraction peaks in every pattern could be indexed as cubic Fe$_3$O$_4$ (JCPDS card No. 82-1533). In Figure 2b, the main peaks of the HMMS-SH-Pd^{II} composite were similar to the HMMS, which illustrated decorating thiol and immobilizing PdCl$_2$ on the surface of
65 HMMS did not influence the feature of the HMMS.

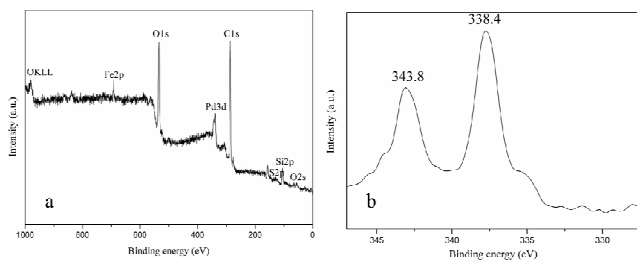**Figure 3** (a) XPS spectrum of the elemental survey scan of HMMS-SH-Pd^{II} and (b) XPS spectrum of the HMMS-SH-Pd^{II} showing Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ binding energies

[5] 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. The XPS elemental survey scans of the surface of HMMS-SH-Pd^{II} the catalyst are showed in Figure 3. Peaks corresponding to iron, oxygen, sulfur, palladium, silicon [10] and carbon were clearly observed. To ascertain the oxidation state of the Pd, X-ray photoelectron spectroscopy (XPS) studies were carried out. In Figure 3b, the Pd binding energy of HMMS-SH-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. [15] These values agreed with the Pd^{II} binding energy of PdCl$_2$.
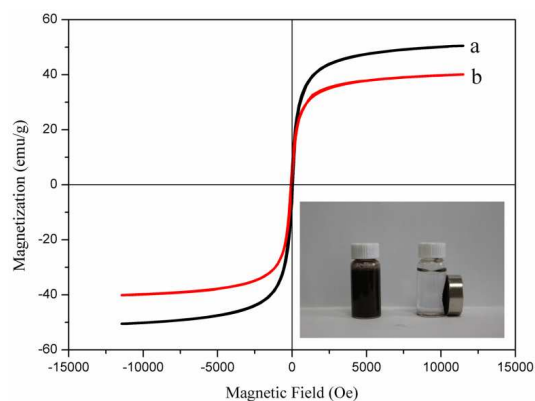

Figure 4 Magnetization curves of (a) HMMS-SH, (b) HMMS-SH-Pd^{II}

Magnetic measurements of samples were performed by a vibrating sample magnetometer (Lake Shore 7304) at room [20] temperature. The magnetization curves measured for HMMS-SH and HMMS-SH-Pd^{II} are compared in Fig 4, which showed no detectable hysteresis loop, neither coercivity nor remanence was observed, suggesting that the two nanoparticles are superparamagnetic. Furthermore, it was obviously observed that [25] its saturation magnetization were 50.53 and 40.08 emu/g for HMMS-SH and HMMS-SH-Pd^{II}. The decrease of the saturation magnetization suggests the presence of some palladium particles on the surface of the magnetic supports. Even with this reduction in the saturation magnetization, the nanomaterials still could be [30] efficiently separated from the solution by placing a magnet near the vessels.

Table 1 The carbonylative cross-coupling of phenylboronic acid with iodobenzene under different conditions[a]


[35]
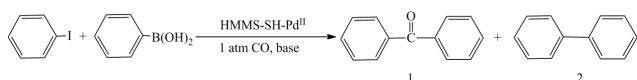
Entry	Solvent	Base	Temp./°C	Time/h	Yield [b] 1	Yield [b] 2
1	Anisole	K$_2$CO$_3$	60	9h	60	8
2	Anisole	K$_2$CO$_3$	80	9h	94	3
3	Anisole	K$_2$CO$_3$	100	9h	90	10
4	Toluene	K$_2$CO$_3$	80	9h	54	12
5	Dioxane	K$_2$CO$_3$	80	9h	51	13
6	DMF	K$_2$CO$_3$	80	9h	68	5
7	Anisole	NaAc	80	9h	0	0
8	Anisole	Cs$_2$CO$_3$	80	9h	8	9
9	Anisole	K$_3$PO$_4$	80	9h	88	11
10	Anisole	Na$_2$CO$_3$	80	9h	87	10

[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 1.5 mol% palladium catalyst.
[b] Determined by GC.

To explore the optimal reaction conditions, the coupling of iodobenzene with phenylboronic acid was determined at the model reaction (See Table 1). The preliminary results indicated that temperature, base and solvent had a significant effect on the [40] coupling reaction. From table 1, when the temperature increased from 60 °C to 80 °C high yield of the desired product (94%) 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, due to the product of direct coupling increasing. [45] 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 NaAc, K$_3$PO$_4$, Ce$_2$CO$_3$, Na$_2$CO$_3$ and K$_2$CO$_3$ (Table 1, entry 2, 7-10). As a result, [50] the most used base K$_2$CO$_3$ was the most efficient base to produce carbonylative cross-coupling product. Therefore, the optimized reaction conditions are: 80 °C, anisole, and K$_2$CO$_3$.

Table 2 Carbonylative Suzuki coupling reaction of various aryl iodides with arylboronic acids in the presence of the HMMS-SH-Pd^{II} catalyst [a]

[55]
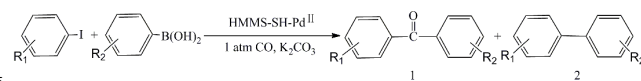
Entry	R_1	R_2	t/h	Yield[b] (%)		TON	TOF (h^{-1})
				1	2		
1	H	H	9	94	3	62.6	6.96
2	H	4-CH$_3$	9	87	11.3	58.0	6.44
3	H	4-Cl	9	91	6	60.6	6.73
4	4-CH$_3$	H	9	91	3.3	60.6	6.73
5	4-CH$_3$	4-CH$_3$	9	89	10.1	59.3	6.59
6	4-CH$_3$	4-Cl	9	85	5	56.7	6.30
7	4-CH$_3$O	H	9	93	6.7	62.0	6.89
8	4-CH$_3$O	4-CH$_3$	9	90	9	60.0	6.67
9	4-CH$_3$O	4-Cl	9	86	2	57.3	6.37
10	2-NH$_2$	H	12	95	1.3	63.3	5.28
11	2-NH$_2$	4-CH$_3$	12	90	2	60.0	5.00
12	2-NH$_2$	4-Cl	12	99	0.6	66.0	5.50
13	2-NO$_2$	H	7	97	0.5	66.0	9.43
14	2-NO$_2$	4-CH$_3$	7	97	<0.1	64.7	9.24
15	2-NO$_2$	4-Cl	7	99	<0.1	66.0	9.43
16	4-CH$_3$CO	H	7	90	4	60.0	8.57
17	4-CH$_3$CO	4-CH$_3$	7	87	12	58.0	8.29
18	4-CH$_3$CO	4-Cl	7	92	5	61.3	8.76

[a] The reactions were carried out with iodide (0.5 mmol), arylboronic acid (0.6 mmol), CO (1 atm), base (1.5 mmol), solvent (5mL), and 1.5 mol% palladium catalyst.
[b] Determined by GC.
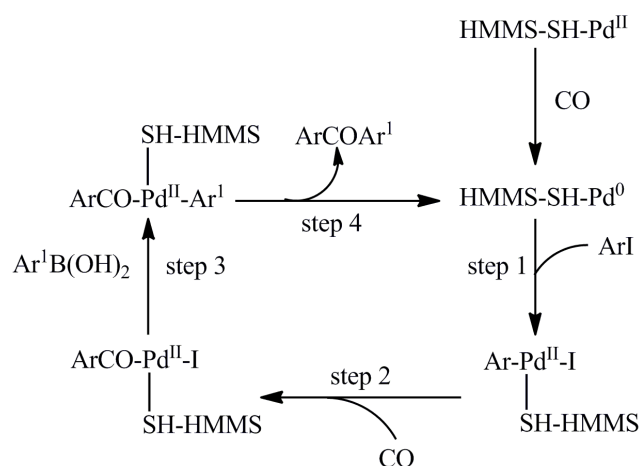
Scheme 2. Reaction mechanism of carbonylative cross-coupling reaction

The reaction mechanism may proceed through a catalytic cycle (See Scheme 2). Oxidative addition of ArI to a Pd^0 complex
5 provides Ar-Pd-I (step 1), which is followed by migratory insertion of carbon monoxide giving ArCO-Pd-I (step 2). Subsequent transmetalatioon and reductive elimination of ketone from ArCO-Pd-Ar^1 reproduce the Pd^0 species[3a]. And the activity of palladium-complexes immobilized on HMMS-SH was tested
10 in the Suzuki carbonylative coupling reactions of aryl halides, namely the reactivity of aryl halides with arylboronic acids using K$_2$CO$_3$ as a base under balloon pressure of CO in anisole. As shown in Table 2, a variety of arylboronic acids and aryl iodidescould proceed smoothly under mild conditions to afford
15 the corresponding carbonylative coupling products in high yields whether using arylboronic acids and aryl iodides containing either electron-withdrawing groups or electron-donating groups. Yields of the products are almost >90% (Table 2, entries 1-18).It's worth noting that aryl iodides containing electron-withdrawing groups,
20 such as 4-CH$_3$CO and 2-NO$_2$(Table 2, entries 13-18), were found to be the most active (7h) than aryl iodides containing electron-donating groups(9h, 12h), such as 4-CH$_3$, 4-CH$_3$O and 2-NH$_2$(Table 2, entries 4-12). According to the proposed reaction mechanism for the reactions, the reason should be that the
25 existence of electron-withdrawing groups could promote the oxidative addition of the organic halide to palladium (0) (Scheme 2 step 1). In one word, HMMS-SH-Pd^{II} is an efficient catalyst for carbonylative cross-coupling reactions.

30 **Table 3** Suzuki coupling reaction of various arylbromobenzene witharylboronic acids in the presence of the HMMS-SH-Pd^{II}catalyst[a]

Entry	R_1	X	R_2	T	Yield[b](%)	TON	TOF (h^{-1})
1	-H	Br	H	6 h	96	160.3	26.7
2[c]	H	CH$_2$Br	H	4 h	98	163.3	40.8

3	-H	Br	CH_3	8 h	99	165.0	20.6
4	$-NH_2$	Br	H	14 h	95	158.3	11.3
5	$-NH_2$	Br	CH_3	16 h	90	150.0	9.4
6	$-COCH_3$	Br	H	60 min	99	165.0	165.0
7	$-COCH_3$	Br	CH_3	45 min	98	163.3	217.3
8	$-CH_3$	Br	H	11 h	97	161.7	14.7
9	$-CH_3$	Br	CH_3	14 h	99	165.0	11.8
10	$-NO_2$	Br	H	60 min	98	163.3	163.3
11	$-NO_2$	Br	CH_3	90 min	90	150.0	100.0
12	-H	Cl	H	16h	60	100.0	6.3

[a] The reaction was carried out with 0.5 mmol of arylhalides, 0.7 mmol of phenylboronic acids or 4-methylphenylboronic adid, 1 mmol of K_2CO_3, 0.6 mol% of catalyst and ethanol :water = 1 : 1.
[b] Determined by GC or GC-MS.
[c] The product was diphenylmethane

The activity of HMMS-SH-Pd[II] catalyst was also investigated for the Suzuki coupling reaction. Table 3 displays the results of the Suzuki cross-coupling reaction of aryl halides with phenylboronic or 4-methylphenylboronic acid. At the 0.6 mol% of catalyst, HMMS-SH-Pd[II]afforded satisfactory biaryl yields (97-99%) for aryl bromides with substituents such as $-CH3$, $-NH_2$, $-COCH_3$ and $-NO_2$, complete conversions were observed and the corresponding biaryl products in 90-99% yields were achieved within 45 min-16 h (Table 3). Aryl bromides bearing strong electron-withdrawing groups need a relatively shorter time to obtain a moderate yield (Table 3 entry 6, 7, 10, 11). Aryl bromides bearing strong electron donating groups need a relatively longer time to obtain a moderate yield (Table 3 entry 4, 5, 8, 9). Comparing the reactions of bromobenzeneand benzyl bromide with benzene boric acid (Table 3 entry 1, 2), the yield of benzyl bromide with benzene boric acid was higher (98%) and the reaction needed shorter time (4 h). This is possible because the Ph-X bond energy (Ph-Br 86.0 kcal/mol) is generally superior to the corresponding $PhCH_2$-X bond energy ($PhCH_2$-Br 57.2 kcal/mol)[19].
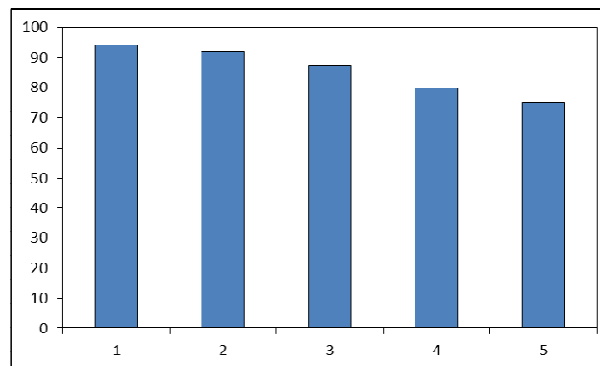

Figure 5 The carbonylative cross-coupling reaction of iodobenzene with phenylboronic acid catalyzed by recycled catalyst.

Further, we investigated the recyclability of the catalyst. 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 iodobenzene with phenylboronic acid catalyzed by recycled catalyst is displayed in Figure 5. The weight percentage of Pd in the HMMS-SH-Pd, as determined by atomic absorption spectroscopic (AAS) analysis, was 5.21 wt% before and 4.17 % after five cycles

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	HMMS-SH-Pd[II]	1.5	7	80	90

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

As a comparison, we compared the results achieved in this work with those reported elsewhere over many supported cataylsts. Take phenylboronic acid with 4-iodoanisole as an example, the results were listed in Table 4. What is worth mentioning, the HMMS-SH-Pd[II] is outstanding over the other heterogeneous catalysts. In contrast with the catalysts of Pd/C[20] and Imm Pd-IL [21], our catalyst takes less reaction timeand in a mild environment towards the carbonylative cross-coupling(Table 4 entry 2, 4, 5).Although the catalysts of MCM-41-2P-Pd[II22] and MCM-41-2N-Pd[II23] give a good yields in a short time and 80°C, the amount

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of Pd is consumed more than the catalyst of HMMS-SH-Pd[II] (Table 4 entry 1, 3, 5).

Conclusion

In conclusion, we gathered the advantages of heterogeneous catalysis, magnetic separation and enhanced catalytic activity of palladium promoted by mercaptopropyl ligands to synthesize a hollow magnetic mesoporous spheres catalyst. In this system, the magnetite nanomaterials play two important roles: one is in increasing the stability of the nanoparticles and the other is preventing Pd (0) leaching during the reaction, because of their surface thiol groups. The catalyst was successfully applied to carbonylative cross-coupling and Suzuki reactions with the fascinating nature of both a high activity and durability.

Acknowledgements

Notes and references

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