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Suzuki–Miyaura cross-coupling reactions catalyzed by efficient and recyclable Fe₃O₄@SiO₂@mSiO₂–Pd(II) catalyst

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Abstract

In this study, a novel Pd(II) complex functionalized core-shell magnetic mesoporous catalyst (Fe₃O₄@SiO₂@mSiO₂-Pd(II)) was synthesized by a simple cost effective procedure. It was characterized by transmission electron microscopy, X-ray Fourier transform infrared spectroscopy, X-ray photoelectron diffraction. spectroscopy, vibrating sample magnetometer, and nitrogen physical adsorption. The Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst offered high surface area and exhibited excellent activity towards Suzuki-Miyaura cross-coupling reaction of halides with aryl boronic acids in ethanol in air. The Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst was stable, reusable, and conveniently recovered by applying an external magnetic field. Moreover, it provided 91% conversion after the sixth catalytic run. The Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst examined in this study combined both the efficiency of a homogeneous catalyst and the durability of a heterogeneous catalyst. The results revealed that the Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst is promising as a candidate for various Pd-based catalytic applications.

Keywords: Suzuki coupling reaction; Palladium; Magnetic; Mesoporous; Recycling.

1. Introduction

The palladium (Pd) catalyzed Suzuki–Miyaura cross-coupling reaction of aryl halides with aryl boronic acids has emerged as an extremely powerful and highly efficient synthetic method for constructing biaryls that are important compounds in pharmaceutical, agrochemical, natural product, and advanced materials chemistry [1-4]. In general, Pd complexes containing ligands such as phosphine [5], dibenzylideneacetone [6], and carbenes [7] are widely employed as efficient homogeneous catalysts for Suzuki reaction [8-12]. These catalysts show high activity towards Suzuki–Miyaura cross-coupling reaction [13]. However, most of the phosphine ligands are air and moisture sensitive [14, 15]. The preparation of most of the homogeneous Pd complexes involves high cost, reuse of these catalysts is difficult; moreover, they are environmentally malignant. Therefore, the development of cost effective, moisture and air stable, and easily recyclable catalytic systems is highly desirable and has been one of the most interesting and challenging fields [16-18].

Recently, considerable efforts have been made to design new catalytic methods for Suzuki–Miyaura cross-coupling reaction. Owing to the inherent advantages of recovery and reuse, several Pd-based heterogeneous catalysts for Suzuki reaction have been developed. Various supports including carbon [19-21], magnetic nanoparticles [22], and mesoporous silica [23, 24] have been used for the immobilization of Pd

nanoparticles for Suzuki–Miyaura cross-coupling reactions. However, for all the reported catalysts, catalytic reactions occur only on the surface of the Pd nanoparticles and a large fraction of atoms in the core are catalytically inactive [25]. Therefore, to increase the availability of the Pd atoms to improve its catalytic performance, immobilization of Pd complexes on solid supports with large surface area is an effective approach. Magnetic nanoparticles-supported Pd catalyst plays a significant role in the Pd catalyzed reactions. In particular, Pd catalysts supported on magnetic mesoporous silica nanoparticles have attracted significant interest because of their unique physical properties such as high surface area, superparamagnetism, eco-friendly nature, reusability, and their potential applications in various fields [26-28].

Based on the aforementioned considerations, herein, we report the synthesis (Scheme 1) of a novel magnetic mesoporous silica nanoparticles-supported Pd(II) catalyst system having the following advantages: first, the preparation of the Pd complex was simple and cost effective; second, the palladium(II) complex could be permanently immobilized onto the surface of the support, and minimized the leaching of the palladium by cross-linking; third, magnetic mesoporous silica supports should be more favorable for the mass transfer of reactant molecules owing to their short pore channels [29]. Therefore, novel Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst was economical, eco-friendly, and could be easily separated from the reaction mixture for recycling. In this study, robust application of Suzuki–Miyaura cross-coupling reaction between aryl halide and aryl boronic acid has been demonstrated. Moreover, the as-prepared

catalyst exhibited long-life, significant activity, and high reusability without visible decrease in the catalytic performance even after six cycles.

2. Experimental section

2.1. Material

Tetraethoxysilane, 3-aminopropyltriethoxysilane (APTES), and Pd(II) acetate were purchased from Aladdin Chemical Co. Ltd. Aryl halides were purchased from Lanzhou Aihua Chemical Company. Aryl boronic acids were obtained from Shanghai Chemical Reagent Co. Ltd. Ethanol and other solvents were of analytical grade and used without further purification.

2.2. Synthesis of Magnetic Mesoporous Silica Nanocomposites (MMS)

Magnetic mesoporous silica nanocomposite was synthesized according to the literature method [30, 31] (supporting information).

2.3. Preparation of magnetic Pd(II) catalyst (Fe₃O₄@SiO₂@mSiO₂-Pd(II))

Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst was synthesized by the following procedure: 2,6-diformyl-4-methylphenol (0.16 g)was synthesized following the literature method [32]. APTES (0.45 g) was dissolved in toluene (50 mL) and refluxed at 105 °C for 6 h under nitrogen. Mesoporous material Fe₃O₄@SiO₂@mSiO₂ (1.5 g) was added to the solution and refluxed again at 105 °C for 6 h under nitrogen. Pd(OAc)₂ (0.15 g) was added to the solution, and the test flask was evacuated and backfilled with nitrogen. Ethanol was added to the solution via syringe under ultrasonication. After 30 min, the reaction system was refluxed under nitrogen for 14 h, resulting in the formation of the Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst. The catalyst was collected by filtration, washed

several times with ethanol, and dried overnight under vacuum at 80 °C.

2.4. Catalytic Suzuki reactions

After optimizing the reaction conditions (Table 1), Suzuki coupling reactions were performed by placing aryl halide (0.5 mmol), phenyl boronic acid (0.75 mmol), K_2CO_3 (1.0 mmol), EtOH (5.0 mL), and $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ catalyst (0.5 mol% Pd) in a 10 mL round bottom flask. The mixture was stirred at 80 °C for required time under air. After the completion of the reaction, the mixture was cooled to room temperature and the $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ catalyst was separated by applying an external magnetic field. The reaction mixtures were analyzed by Gas chromatography (GC) or GC–mass spectrometry (GC-MS).

2.5. Catalytic recycling in Suzuki reaction

A mixture of Iodobenzene (0.5 mmol), 4-Chlorophenyl boronic acid (0.75 mmol), K_2CO_3 (1 mmol), EtOH (5.0 mL), and $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ catalyst (0.5 mol% Pd) was stirred at 80 °C under air. After being cooled to room temperature towards the end of the reaction, the $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ catalyst was separated by strong magnetic suction. The separated catalyst was washed with ethanol and water, respectively, dried under vacuum at 50 °C, and reused.

2.6. Characterization

Powder X-ray diffraction (XRD) spectra were obtained by a Rigaku D/max-2400 diffractometer using Cu-K α radiation in the 2 θ range of 20–80°. Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Nexus 670 FT-IR spectrometer equipped with a deuterated triglycine sulfate pyroelectric detector using KBr pellets.

X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 and the C1S line at 291.4 eV was used as the binding energy reference. Magnetic measurement of $Fe_3O_4@SiO_2@mSiO_2$ and $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ was performed using a quantum design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from -15 to 15 KOe. Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 F30, FEI, USA. The Brunauer–Emmett–Teller (BET) surface area and pore-size distribution were obtained by measuring N₂ adsorption isotherms at 77 K using a TriStar 3020 (Micromeritics). The reaction conversion was estimated using GC (P.E. AutoSystem XL) or GC–MS (Shimadzu QP2010S).

3. Results and discussion

3.1. Catalyst preparation and characterization

Fig. 1a shows the FT-IR spectra of the core–shell magnetic mesoporous $Fe_3O_4@SiO_2@mSiO_2$ microspheres and magnetic mesoporous microspheres of the catalyst $Fe_3O_4@SiO_2@mSiO_2=Pd(II)$. The adsorption peaks at 1081.5 and 796.6 cm⁻¹ correspond to the antisymmetric and symmetric stretching vibration of Si–O–Si bond in oxygen-silica tetrahedron, respectively. The peaks at 963.9, 460, and 574.9 cm⁻¹ correspond to Si–OH, Si–O, and Fe–O stretching, respectively [33]. The strong peaks at 3438.6 and 1638 cm⁻¹ explain that a large number of –OH groups and structural water molecules prove to be advantageous for the modification Pd(II) complex by hydrogen bonds. The major peaks for the Pd(II) complex (Fig. 1a, red line) at 2981.6, 2936.3, 1545.1, 1405.1, and 1164.5 cm⁻¹ correspond to –CH₃, –CH₂, –C–N, –C=N,

and -C-O stretching, respectively.

Nitrogen, carbon, hydrogen content were 1.60%, 14.27%, 2.22% measured by elementar analysis, respectively. The FT-IR spectra and elementar analysis data revealed that the complex is successfully grafted on the magnetic mesoporous surface.

XRD patterns of Fe₃O₄@SiO₂@mSiO₂ and Fe₃O₄@SiO₂@mSiO₂-Pd(II) samples are shown in Fig. 1b. The broad peak between 20-30° corresponds to amorphous silica, indicating that the silica was successfully coated on the surface of Fe₃O₄ nanoparticles. The XRD patterns of Fe₃O₄ nanoparticles show five characteristic diffraction peaks at $2\theta = 30.2^{\circ}$, 35.6° , 43.3° , 57.3° , and 63.0° corresponding to (220), (311), (400), (511), and (440), respectively [34]. The XRD pattern of the Pd(II) catalyst demonstrates that almost no change occurs after modification of Pd(II) complex the magnetic mesoporous nanoparticle surface. The on Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst involved Pd(II) rather than Pd(0), therefore XRD patterns did not show the characteristic peak of Pd.

Fig. presents XPS elemental survey of the surface 2 scans Fe₃O₄@SiO₂@mSiO₂-Pd(II) of the catalyst. Peaks corresponding to oxygen, silica, carbon, nitrogen and palladium are clearly observed. The presence of N1s (398 eV) provides evidence for the successful complex onto the surface of Fe₃O₄@SiO₂@mSiO₂. In the inset figure, Pd species in the Fe₃O₄@SiO₂@mSiO₂-Pd(II) were present in +2 oxidation state rather than in metallic state, corresponding to the binding envergy of 336.5 and 341.5 eV in the Pd $3d_{5/2}$ and Pd 3d_{3/2} levels [29], respectively. The XPS reveals that the Pd(II) complex is

successfully grafted on the magnetic mesoporous surface.

The mesoporous silica shell and the Fe_3O_4 nanoparticles core are present in the microspheres of magnetic mesoporous catalyst as shown in the high resolution TEM image of $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ catalyst. Moreover, the image indicates that the $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ particle size is approximately 100 nm (Fig. 3a), and the pore diameter is about 2.2 nm (Fig. 3b).

The characterization of N₂ adsorption/desorption was carried out to obtain the structural information about the Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst on a mesoscopic scale. Fig. 4a shows the N₂ adsorption/desorption isotherms of Fe₃O₄@SiO₂@mSiO₂-Pd(II exhibiting typical IV-type isotherm with H₁-hysteresis loops according to the IUPAC classification [35], indicating the presence of the catalyst mesopores. The results showed that the BET surface area, pore volume, and pore diameter were 491.62 m²g⁻¹, 0.28 cm³g⁻¹ and 2.24 nm, respectively. The abovementioned data indicated that the Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst had large surface area and pore volume; thus, making it beneficial for the adsorption of reactant molecules owing to their short pore channels.

Magnetic measurements were carried out by VSM at room temperature. The magnetization curves measured for $Fe_3O_4@SiO_2@mSiO_2$ and $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ catalyst are shown in Fig. 4b. The magnetic saturation values of the two samples are 5.0 and 4.8 emug⁻¹, respectively. The decrease in the saturation magnetization was due to the modification of the Pd(II) complex on the surface of the magnetic supports. Moreover, Fig. 4b shows the separation-redispersion

process of the Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst demonstrating that the catalyst is drawn from the solution to the sidewall of the vial by applying an external magnetic field and disperses rapidly with a slight shake once the magnetic field is removed. Therefore, the abovementioned result indicated an easy and efficient way to separate and recycle the Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst from the solution by applying an external magnetic force.

3.2. Suzuki-Mayaura cross coupling reaction by Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst.

The weight percent of Pd in the $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ catalyst, as determined by atomic absorption spectroscopic analysis, was 3.93 wt%.

To standardize the reaction conditions, a series of reactions were performed using several bases, solvents, temperatures, and catalyst concentration to obtain the best possible combination. Initially, the experiment was performed using Suzuki–Miyaura cross-coupling reaction of 1-iodo-4-nitrobenzene (0.5 mmol) with phenyl boronic acid (0.75 mmol) in the presence of Fe₃O₄@SiO₂@mSiO₂–Pd(II) (0.5 mol% Pd) catalyst, K₂CO₃ (1 mmol) and ethanol 5 mL at 80 °C for 3 h. The corresponding product was obtained in 95.5% yield (Table 1, entry 1). When the reaction was carried out in methyl alcohol, acetone, isopropanol, and ethyl acetate under the same reaction conditions, the products were obtained in poor to moderate yields of 60.8%, 24.9%, 45.7%, and 62.3% (Table 1, entries 2–5). The reaction conditions were also optimized with respect to the base. The reactions were carried out under similar conditions using different bases such as Na₂CO₃, KOH, and NaOH and the yields were 72.5%, 88.8%,

and 86.5%, respectively (Table 1, entries 6–8). For the reactions at room temperature, 40 °C, and 60 °C corresponding products were obtained in the following yields: 56.3%, 74.0%, and 89.1%, respectively (Table 1, 9–11). The best catalytic activity of the Fe₃O₄@SiO₂@mSiO₂–Pd(II) catalyst was observed using ethanol as solvent , and K_2CO_3 as base at 80 °C (Table 1).

optimizing conditions, catalytic activity After the reaction the of Fe₃O₄@SiO₂@mSiO₂-Pd(II) for Suzuki-Miyaura reaction was explored with respect to various aryl halides and phenyl boronic acids or 4-chlorophenyl boronic acid. As listed in Table 2, when the coupling of aryl iodides and phenyl boronic proceeded at 80 °C for 3 h, the corresponding products were obtained in high yields (Table 2, entries 1–8). Further exploration of the catalytic activity revealed that for the coupling between aryl bromides and aryl boronic acids, the reaction times approached 8 h to yield Suzuki products in high yields (Table 2, entries 9-14). However, for the reactions of 1-bromo-2-nitrobenzene poor yields (Table 2, entries 11 and 12) were obtained, due to the electron-withdrawing -NO₂ group in the ortho position. Further, for the reaction of aryl iodides and aryl bromides with electron-donating -CH₃ group, the products were obtained in higher yields. To test the feasibility of the aforementioned protocol for challenging substrates, several aryl chlorides with aryl boronic acids were employed and the reaction time was increased to 10 h. However, the products were obtained in low yields (Table 2, entries 15–17). The results indicated that the reactivity of aryl iodides was greater than aryl bromides, which in turn was greater than aryl chlorides.

For practical applications of heterogeneous systems, the recyclability of catalyst is an important factor. To investigate the reusability of the $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ catalyst, the catalyst was recycled in Suzuki–Mayaura cross-coupling reaction between 4-chlorophenyl boronic acid and iodobenzene as shown in Fig. 5. The recovered catalyst was added each time to the reaction mixture under the same conditions for six cycles without significant loss in activity. Metal leaching of the catalyst before and after was studied by atomic absorption spectroscopic analysis. The Pd content was found to be 3.93 wt.% before reaction and 3.68 wt.% after six reaction cycles, which confirmed negligible Pd leaching. Moreover, the catalyst was easily separated magnetically from the reaction mixture, washed with alcohol, water, and finally dried for the next run. The results confirmed the significant recyclability of the $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ catalyst.

4. Conclusions

A novel magnetic mesoporous Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst was synthesized, offering high surface area and exhibiting significant activity towards Suzuki coupling reaction between any halide and any boronic acid. The catalyst was chemically stable, could be easily recovered by applying an external magnetic field, and reused. Moreover, good vield was obtained even after the Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst was reused six times. Therefore, high surface area, chemical stability, superparamagnetism, eco-friendly nature, convenient recovery and ease of use, make Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst a promising candidate for potential applications in industrial synthesis.

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Scheme. 1 Preparation of the Fe₃O₄@SiO₂@mSiO₂-Pd(II) catalyst.



Fig. 1 (a) FT-IR spectra of $Fe_3O_4@SiO_2@mSiO_2$ (black) and $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ (red). (b) The wide-angle XRD of $Fe_3O_4@SiO_2@mSiO_2(red)$ and $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ (blue).



Fig. 2 XPS spectrum of the $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ (inset: high resolution spectrum of Pd 3d).



Fig. 3 HRTEM images of Fe₃O₄@SiO₂@mSiO₂-Pd(II).

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Fig. 4 (a) N_2 adsorption/ desorption isotherms of $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$. (b) Rom temperature magnetization curves of $Fe_3O_4@SiO_2@mSiO_2$ (black) and $Fe_3O_4@SiO_2@mSiO_2-Pd(II)$ (red).

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Fig. 5 Recycling experiment.

Table 1

The effects of solvent, base and temperature on the Suzuki coupling of 1-Iodo-4-nitrobenzene with phenylboronic acid using Pd(II) catalyst.

Entry	Solvent	Base	Temp(°C)	Yield(%)
1	Ethanol	K ₂ CO ₃	80	95.5
2	Methyl alcohol	K ₂ CO ₃	80	60.8
3	Acetone	K ₂ CO ₃	80	24.9
4	Isopropanol	K ₂ CO ₃	80	45.7
5	Ethyl acetate	K ₂ CO ₃	80	62.3
6	Ethanol	Na ₂ CO ₃	80	72.5
7	Ethanol	КОН	80	88.8
8	Ethanol	NaOH	80	86.5
9	Ethanol	K ₂ CO ₃	25	56.3
10	Ethanol	K ₂ CO ₃	40	74.0
11	Ethanol	K ₂ CO ₃	60	89.1

^a Reaction condition: aryl halide (0.5mmol), arylboronic acid (0.75mmol), base (1.0 mmol),

solvent 5.0 mL, Pd(II) catalyst (0.5 mol%), in air, 3 h.

^bYield was determined by GC-MS or GC analysis.

Table 2

The Suzuki - Miyaura cross coupling reactions of aryl halides with arylboronic acids using Fe $_3O_4@SiO_2@mSiO_2-Pd(II)$ catalyst.

	$\begin{array}{c} \begin{array}{c} Pd(II) Catalysis, K_2CO_3 \\ \hline R_1 \end{array} \end{array} \\ \hline \\ \\ \hline \end{array} \\ \\ \\ \end{array} \\ \\ \\ \hline \end{array} \\ \\ \\ \\$						
Entry	Aryl halide	Arylboronic acid	Product	Time/	Yield(%)		
1	-	CI-B(OH)2		3	99.5		
2		CI-B(OH)2	CI-CI	3	98.0		
3	ОН	CI-B(OH)2	но-С-С	3	95.0		
4		CI-B(OH)2	0 ₂ NCI	3	97.5		
5		B(OH) ₂		3	98.0		
6		B(OH) ₂	0 ₂ N-	3	98.5		
7		B(OH) ₂		3	99.5		
8	но-	B(OH) ₂	но-	3	94.0		
9	Br	CI-B(OH)2	-<	8	98.0		
10	──B r	CI-B(OH)2	∠→−CI	8	97.0		
11	NO ₂ Br		NO ₂	8	28.0		
12	NO ₂ Br	B(OH) ₂		8	33.0		
13	Br	B(OH) ₂		8	95.0		
14	Br	B(OH) ₂		8	96.0		
15		CI-B(OH)2	CI	10	16.0		
16	-Cl	CI-B(OH)2	-CI	10	25.0		
17	СІ	CI-B(OH)2	C-C-CI	10	64.0		

^a Reaction condition: aryl halide (0.5mmol), arylboronic acid (0.75mmol), K_2CO_3 (1.0mmol), EtOH 5.0 mL, Pd(II) catalyst (0.5 mol%), and 80 °C, in air.

^bYield was determined by GC-MS or GC analysis.

Highlights :

- 1. The Pd(II) catalyst is easy to prepare with low cost.
- 2. This new catalyst can be easily separated from the reaction mixture to reuse.
- 3. The catalyst showed high activity for the Suzuki-Miyaura cross coupling reaction.

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