

# Magnetic Mesoporous Silica Nanocomposite Functionalized with Palladium Schiff Base Complex: Synthesis, Characterization, Catalytic Efficacy in the Suzuki–Miyaura Reaction and α-Amylase Immobilization

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#### Abstract

Magnetic mesoporous silica nanocomposite,  $Fe_3O_4$ -MCM-41, was functionalized with *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS) and then condensed with 5,5'-methylene bis(salicylaldehyde), followed by *N*(4)-phenylthiosemicarbazide to produce a ONS Schiff base grafted nanocomposite. Finally, by adding palladium(II) acetate, the palladium Schiff base complex was immobilized on magnetic nanocomposite. The characterization of new nanocomposites was carried out by means of several techniques such as FT-IR, XRD, FE-SEM, HRTEM, EDS, BET, VSM, XPS, DRS and TGA. The new nanocatalyst,  $Fe_3O_4$ @MCM-41-SB-Pd, was used in synthesis of symmetrical and unsymmetrical biaryl compounds via the Suzuki–Miyaura cross-coupling of phenylboronic acid with aryl halides. This catalyst was easily recovered by applying an external magnetic field and reused for several times without significant loss of its catalytic activity. Also the ability of synthesized mesoporous nanocomposites for enzyme immobilization was investigated and results showed that they efficiently immobilized  $\alpha$ -amylase enzyme.

#### **Graphic Abstract**



Keywords Magnetic mesoporous · Suzuki-Miyaura reaction · Enzyme immobilization · Schiff base

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# **1** Introduction

The nanoporous materials have holes in nanoscale and large volume that forms empty spaces in their structure. Based on the classification of IUPAC, these materials are divided into three categories: microporous (pore size less than 2 nm),

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mesoporous (pore size between 2 and 50 nm) and macroporous (pore size greater than 50 nm) [1]. Since the discovery of mesoporous silica materials in 1992, these materials have attracted a great deal of attention due to features such as tunable pore size, controlled size, extremely high surface area, chemical, thermal and mechanical stability and also ability of surface modification with various organic and inorganic groups. These materials are used as adsorbents, sensors, molecular sieves, catalysts, catalyst supports, ionexchangers, immobilization of enzymes, drug delivery and in many other related applications [2-11]. Mesoporous materials have a very high surface area and are used as substrates for different catalysts, so the design of mesoporous nanomaterials that have catalytic active centers on their surface, has always been of interest to researchers [10, 12-16]. Catalysts have an important role in the producing process for the synthesis of medicines, commercial chemicals, energy resources, fuels, biofuels and are divided into two general categories, heterogeneous and homogeneous. Homogeneous catalysts, due to their solubility in the reaction environment which increase the availability of catalytic site for the substrate, display higher catalytic activities than their heterogeneous counterparts. But, there are drawbacks in the separating and recycling of the homogeneous catalystsproduct mixture, which may contaminate the final product and greatly limit their applications in practice. To overcome these problems, heterogenization of homogeneous catalysts has been suggested. Among several methods recommended for this subject, the immobilization of homogeneous catalysts onto solid supports such as silica materials, zeolites, carbon materials, organosilica materials and layered compounds, is one of the most effective methods for preparation of heterogeneous catalysts with improved recovery and recyclability [11, 17, 18]. Since the surface of catalyst plays an important role in the catalytic reactions, materials having high surface area, such as mesoporous materials, are promising candidates as support for homogeneous catalysts. Heterogeneous catalysts usually are separated from the reaction medium through filtration and centrifugation. But, these procedures are tedious, time-consuming and inefficient. The use of magnetic nanoparticles as support for homogeneous catalyst immobilization is a suitable method for the facile separation and recycling of the catalyst from the reaction media by applying an external magnetic field [19–25].

The Suzuki–Miyaura cross-coupling reaction is an increasingly popular approach for the synthesis of biaryl compounds. The Suzuki reaction is catalyzed by palladium, which is one of the most expensive metals and cannot be efficiently isolated from the reaction medium. Therefore, immobilization of palladium complexes onto a solid support such as mesoporous silica leads to formation of heterogeneous catalyst and thus reducing Pd leaching into solution and

improvement the separating and recycling of the catalyst [26–29].

Due to the tunable and uniform pores of mesoporous materials, they have been also promising candidates for enzyme immobilization in recent years [30–35]. The use of mesoporous materials as support for immobilization of enzymes resolves some processing difficulties of natural enzymes and produces recoverable and stable heterogeneous biocatalysts [9, 11, 36].

In the present research work, we have used a dialdehyde to form bis-Schiff base with several chelating groups on Fe<sub>3</sub>O<sub>4</sub>@MCM-41 nanocomposite. Our aim is to propose a functionalized silica mesoporous nanomaterial with high chelating potency to immobilize large amounts of palladium and therefore improve catalytic activity along with low palladium leaching, also effectively immobilize enzyme. Hence, this hybrid nanocomposite, which have a combination of the magnetic properties of iron oxide nanoparticles, the high specific surface of mesoporous compounds and as well as the properties of Schiff base compounds, has been successfully used in Suzuki–Miyaura cross-coupling reactions and  $\alpha$ -amylase immobilization.

#### 2 Experimental

#### 2.1 Materials

All starting materials including tetraethylorthosilicate (TEOS), hexadecyltrimethyl ammonium bromide (CTAB, 99%), N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS), ammonia (25 wt%), Iron (III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), iron(II) chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O), ethanol and methanol, salicylaldehyde, 1,3,5-trioxane, sulphuric acid (98%), acetic acid (glacial), N(4)-phenylthiosemicarbazide, DMF, aryl halides, toluene, phenylboronic acid, potassium carbonate, n-hexane, CH<sub>3</sub>CN and palladium(II) acetate, were purchased from Merck chemical company and used without further purification. 5,5'-methylene-bis-salicylaldehyde was synthesized according to the previous method using 1,3,5-trioxane as starting material, in presence of catalytic amount of conc. H<sub>2</sub>SO<sub>4</sub> and in glacial CH<sub>3</sub>COOH as a solvent [37]. Deionized water was obtained from Millipore pure water system.

#### 2.2 Characterization Methods

FT-IR spectra were recorded by a Perkin Elmer spectrophotometer model spectrum two within the 400–4000 cm<sup>-1</sup> range using the KBr pellets. X-ray powder diffraction (XRD) spectra of the catalyst were recorded with a PW 1730 X-ray diffractometer model X Pert Pro using monochromatic Cu K $\alpha$  radiation at 40 kv and 30 mA. The particle size and morphology of the catalyst was performed by a field emission scanning electron microscope (FE-SEM) equipped with EDX analyzer model Mira 3-XMU and with an accelerating voltage of 15 kv. High resolution transmission electron microscopy (HRTEM) images were carried out on a HR-TEM FEI TEC9G20 (200 kV). The nitrogen adsorption-desorption isotherms were measured using a Belsorp mini II instrument at liquid N<sub>2</sub> temperature. Samples were evacuated for 15 h at 120 °C prior to adsorption measurements. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area, and pore size distribution and pore volume were estimated by applying the Barrett-Joyner-Halenda (BJH) method. The saturated magnetization of the synthesized nanoparticles was determined by means of vibrating sample magnetometer with the magnetic field range of between + 12,000 and - 12,000Oe at room temperature. The metal amount of the catalyst was measured by atomic absorption spectrometer model Analytikjena-contrAA 700. Thermogravimetric analysis (TGA) of the prepared catalyst was performed on a STA 1500 thermal analyzer under N<sub>2</sub> atmosphere from 25 to 800 °C and heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) analysis was conducted by an 8025-Bes Tec instrument. UV-Visible diffuse reflectance spectrum (UV-DRS) of catalyst was recorded by Avaspec 2048 Thech spectrophotometer.

# 2.3 Synthesis of Fe<sub>3</sub>O<sub>4</sub> Superparamagnetic Nanoparticles

Magnetic nanoparticles of  $Fe_3O_4$  were prepared by co-precipitating of  $Fe^{3+}$  and  $Fe^{2+}$  ions in water solution with a molar ratio of 2:1. In this way, 1.35 g  $FeCl_3 \cdot 6H_2O$  and 0.5 g  $FeCl_2 \cdot 4H_2O$  were dissolved in 50 mL of deionized water under N<sub>2</sub> with vigorous shaking at 85 °C. The solution was stirred for 1 h. Thereafter, 7 mL of ammonia solution was dropped into the mixed solution to adjust the pH value to 10. The addition of the ammonia solution changed the color of solution from orange to black immediately. The reaction mixture was stirred at the same temperature for another 1 h. After completion of the reaction, the formed magnetite precipitates were separated from the reaction medium using an external magnet, washed several times with deionized water and dried under vacuum at 60 °C.

# 2.4 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@MCM-41 Nanocomposites

A mixture of  $\text{Fe}_3\text{O}_4$  MNPs (1.0 g), deionized water (60 mL) and ethanol (75 mL) were dispersed by ultrasonic vibration for 30 min. Then 5 mL of ammonia aqueous solution was added to the mixture during 10 min and allowed to stir for 1 h at room temperature under an N<sub>2</sub> atmosphere. To form the framework of mesoporous, 20 mL of CTAB solution (100 mmol/L), as surfactant agent, was slowly added to above solution and stirred for 1 h. Afterwards, 1.2 mL of tetraethylorthosilicate (TEOS) was added dropwise to the solution and the reaction mixture was stirred for 24 h. The black precipitates were separated from the solution by an external magnet, washed several times with ethanol/deionized water mixture and then dried in oven at 60 °C for 24 h. In the next step, CTAB was removed from the product by calcining in air at 550 °C for 6 h to produce the mesoporous material.

#### 2.5 Synthesis of Amine-Functionalized Fe<sub>3</sub>O<sub>4</sub>@MCM-41 Nanocomposites (Fe<sub>3</sub>O<sub>4</sub>@ MCM-41-AEAPS)

0.5 g of mesostructured composite of Fe<sub>3</sub>O<sub>4</sub>@MCM-41 was dispersed for 30 min in 35 mL of anhydrous toluene with an ultrasonic bath. Then, AEAPS (4 mL) was added dropwise and the mixture was refluxed at 110 °C under N<sub>2</sub> atmosphere for 12 h. The reaction mixture was cooled and aminofunctionalized nanoparticles were collected by an external magnet, washed with plenty of toluene and methanol, and subsequently dried in an oven at 60 °C for 24 h.

# 2.6 Synthesis of Aldehyde-Functionalized Fe<sub>3</sub>O<sub>4</sub>@ MCM-41 Nanocomposites (Fe<sub>3</sub>O<sub>4</sub>@MCM-41-ald)

The amino-functionalized magnetic nanoparticles (1 g) were sonicated for 30 min in 20 mL of ethanol. Then, a solution of 5,5'-methylene bis(salicylaldehyde) (4 mmol) in EtOH was added to it and the mixture was refluxed for 24 h under a nitrogen gas. The product was separated by an external magnet, washed with ethanol and finally dried in oven overnight.

# 2.7 Synthesis of Schiff Base-Functionalized Fe<sub>3</sub>O<sub>4</sub>@ MCM-41 Nanocomposites (Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB)

The aldehyde-functionalized  $\text{Fe}_3\text{O}_4$ @MCM-41 nanocomposites (1 g) were added to round-bottom flask comprising absolute ethanol (20 mL) and were homogeneously dispersed. After 30 min of ultrasonication, N(4)-phenylthiosemicarbazide (4 mmol) in EtOH was added into the mixture and refluxed for 24 h. At the end of the reaction, Schiff base functionalized mesoporous materials were collected using an external magnet, washed with ethanol, and dried in oven at 60 °C.

# 2.8 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd Nanocomposites

500 mg of  $Fe_3O_4@MCM-41-SB$  was dispersed in methanol (50 mL) and a solution of  $Pd(OAc)_2$  (1 mmol, 0.224 g) in acetone (10 mL) was added dropwise. This mixture was



Fig. 1 The route for synthesis of the functionalized magnetic mesoporous silica nanocomposite

refluxed under  $N_2$  atmosphere for 24 h. The resulting catalyst was magnetically separated, washed with acetone and methanol and finally dried in oven at 60 °C for 10 h.

# 2.9 General Procedure for the Suzuki–Miyaura Cross-Coupling Reaction Using Fe<sub>3</sub>O<sub>4</sub>@ MCM-41-SB-Pd as Catalyst

2 mg of the nano-catalyst ( $Fe_3O_4@MCM-41-SB-Pd$ ) was dispersed in DMF (5 mL) using sonication for 30 min at room temperature. Then, aryl halide (1 mmol),

phenylboronic acid (1.2 mmol) and  $K_2CO_3$  (1.2 mmol) were added to the reaction flask and the mixture was refluxed at 120 °C. The progress of the reaction was checked by TLC (*n*-hexane/EtOAc). After completion of the reaction, the reaction mixture was cooled to the room temperature. The catalyst was separated by an external magnet and washed with ethyl acetate. The resultant mixture was extracted with n-hexane to isolate the product and then the crude product was recrystalized from n-hexane.

#### 2.10 Enzyme Immobilization

2 mg of  $\alpha$ -amylase enzyme was dissolved in 1 mL of phosphate buffer saline (PBS) and then 20 mg of each sample, Fe<sub>3</sub>O<sub>4</sub>@MCM-41, Fe<sub>3</sub>O<sub>4</sub>@MCM-41-NH<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@MCM-41-ald and Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd was added to this solution. The mixture was incubated with continuous shaking (75 rpm) at 37 °C for 24 h. Then the mesoporous nanocomposites loaded with  $\alpha$ -amylase enzyme were separated using high-speed centrifuging with 10,000 rpm for 5 min and washed three times with PBS. In the following, these nanocomposites were dispersed in phosphate buffer saline  $(500 \ \mu L)$  and the paper disks were saturated with these solutions. Saturated paper disks were placed on plates containing starch 10%. Also, a disc saturated with the third wash solution was considered as a control for each compound. Finally, plates were incubated at 37 °C for 24 h. Then the area of inhibition around each disc was measured after addition of iodine solution.

#### **3** Results and Discussion

#### 3.1 Preparation and Characterization

Figure 1 illustrates the synthesis pathway of the  $Fe_3O_4@$ MCM-41-SB-Pd nanocomposite. First, Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were synthesized by a conventional co-precipitation method. Subsequently, to increase the stability and activity of the magnetic nanoparticles, silica was coated on the surface of Fe<sub>3</sub>O<sub>4</sub> by basic hydrolysis of TEOS in the presence of CTAB. After the removal of CTAB, Fe<sub>3</sub>O<sub>4</sub>@MCM-41 nanoparticles were surface-modified with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS). In this reaction, -NH<sub>2</sub> groups were introduced on the support by treatment of the methoxy groups of AEAPS with the active silanol groups on Fe<sub>3</sub>O<sub>4</sub>@MCM-41. Schiff base was covalently anchored to the surface of magnetic nanoparticles in two steps using condensation of the carbonyl groups of the dialdehyde with terminal amine of AEAPS and then with the amine group of the N(4)-phenylthiosemicarbazide. Finally, incorporation of palladium onto the nanoparticles was carried by reaction of the Pd(OAc)<sub>2</sub> with functionalized Fe<sub>3</sub>O<sub>4</sub>@MCM-41. The concentration of palladium (0/II) was 9.5 wt% (0.89 mmol/g), which was determined by AAS. It is noteworthy that due to presence of several good coordination sites on the bis-Schiff base ligand including imine, amine, thiol and hydroxyl groups, high amount of palladium was loaded on the catalyst. The synthesized new heterogeneous catalyst was characterized by FT-IR, TGA, XRD, FE-SEM, HRTEM, EDX, VSM, XPS and DRS techniques and N<sub>2</sub> adsorption-desorption isotherms.

Figure 2 shows the FT-IR spectra of all synthesized nanocomposites which are in agreement with the proposed structure shown in Fig. 1. In Fig. 2a, the bands appearing at 3406 and 1626 cm<sup>-1</sup> were attributed to the vibrational modes of water molecules adsorbed to the surface. The sharp peak at about 585 cm<sup>-1</sup> that is observable in all spectra, was assigned to stretching vibrations of Fe-O bonds in tetrahedral sites of iron oxide [38]. The strong absorption bands at 1075, 805 and 453  $cm^{-1}$  in Figs. 2b-g are corresponding to the asymmetric and symmetric stretching of Si-O-Si framework vibrations and Si-O-Si or O-Si-O bending modes, respectively [39-41]. In the IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@ MCM-41-CTAB (Fig. 2b), the strong bands at 2919 and 2850 cm<sup>-1</sup> were related to the C-H stretching vibrations of CTAB. These bands were completely eliminated at the spectrum of Fe<sub>3</sub>O<sub>4</sub>@ MCM-41, which confirms the complete removal the template. In the FT-IR spectra of  $Fe_3O_4@$ MCM-41-AEAPS, the presence of the anchored n-propylamine groups are confirmed by new bands at 2936 and 2882 cm<sup>-1</sup> assigned to the C-H stretching vibrations, and the band at 1630 cm<sup>-1</sup> related to NH/NH<sub>2</sub> bending vibration. In the IR spectrum of  $Fe_3O_4@MCM-41$ -ald and  $Fe_3O_4@$ MCM-41-SB, a sharp band at  $1635 \text{ cm}^{-1}$  is appeared which attributed to the stretching vibration of the imine group (C=N) and confirms successful formation of Schiff base. In the FT-IR spectrum of  $Fe_3O_4$ @MCM-41-SB-Pd, the C=N stretching vibration slightly shifts to lower frequencies and appears at 1628  $\text{cm}^{-1}$ . This shift confirms the coordination of the imine nitrogen atom to palladium and reveals that the catalyst has been successfully synthesized.



Fig.2 FT-IR spectra of synthesized nanocomposites **a**  $Fe_3O_4$ , **b**  $Fe_3O_4$ @ MCM-41-CTAB, **c**  $Fe_3O_4$ @ MCM-41, **d**  $Fe_3O_4$ @ MCM-41-AEAPS, **e**  $Fe_3O_4$ @MCM-41-ald **f**  $Fe_3O_4$ @MCM-41-SB and **g**  $Fe_3O_4$ @MCM-41-SB-Pd



Fig. 3 FE-SEM images of the magnetic nanoparticles: a  $Fe_3O_4$  b  $Fe_3O_4$  @ MCM-41 c  $Fe_3O_4$ @MCM-41-SB-Pd, d, e TEM images of  $Fe_3O_4$ @ MCM-41-SB-Pd

The morphology and size of  $Fe_3O_4$ ,  $Fe_3O_4$ @ MCM-41 and  $Fe_3O_4$ @MCM-41-SB-Pd nanoparticles were studied by field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) analysis (Fig. 3). FE-SEM and TEM images show that the prepared composites are about uniform spherical nanoparticles with a diameter in the range of 12–30 nm. TEM images confirm a core–shell structure of the catalyst.

The chemical composition of the  $Fe_3O_4@MCM-41-SB-Pd$  nanocatalyst was determined by energy-dispersive X-ray spectrum (EDX) analysis. The results have been shown in Fig. 4. This analysis exhibits that the  $Fe_3O_4@MCM-41-SB-Pd$  contains Fe, Si, Pd, N, C, S and O elements, which confirms the immobilization of Schiff base complex on silica coated  $Fe_3O_4$  nanoparticles. The presence and distribution of elements were as well as determined by EDX mapping (Fig. 5).



Fig. 4 The elemental composition of  $Fe_3O_4@MCM-41-SB-Pd$  determined by EDX analysis



Fig. 5 Elemental mapping of Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd

The wide angle XRD (WAXRD) patterns of bare  $Fe_3O_4$ nanoparticles,  $Fe_3O_4$ @ MCM-41,  $Fe_3O_4$ @MCM-41-ald,  $Fe_3O_4$ @MCM-41-SB-Pd are given in Fig. 6. In the XRD pattern of bare  $Fe_3O_4$  nanoparticles, the characteristic peaks observed at  $2\theta = 30.50^\circ$ ,  $35.87^\circ$ , 43.51,  $53.88^\circ$ ,  $57.43^\circ$ ,  $63.00^\circ$  and  $74.55^\circ$  are assigned to the crystalline planes (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) of magnetite, respectively, which agrees with the standard  $Fe_3O_4$  XRD spectrum of highly crystalline cubic spinel structure [42–44]. All diffraction peaks of pure  $Fe_3O_4$  were also observed in the XRD patterns of  $Fe_3O_4@$  MCM-41,  $Fe_3O_4@$ MCM-41-ald and  $Fe_3O_4@$ MCM-41-SB-Pd, suggesting that the magnetic core has been preserved during the surface modification. In the XRD pattern of the  $Fe_3O_4@$ MCM-41-SB-Pd, the appearance of the new peaks at  $2\theta = 40.40^\circ$ ,  $46.59^\circ$  and  $68.11^\circ$  corresponding to  $(1\ 1\ 1)$ ,  $(2\ 0\ 0)$  and  $(2\ 2\ 0)$  planes, respectively, is related to the fcc palladium [45–49]. Therefore, Pd nanoparticles were formed



Fig.6 Wide angle X-ray diffraction patterns of bare  $Fe_3O_4$  nanoparticles,  $Fe_3O_4@$  MCM-41,  $Fe_3O_4@$ MCM-41-ald,  $Fe_3O_4@$ MCM-41-SB-Pd and reused  $Fe_3O_4@$ MCM-41-SB-Pd



Fig.7 Low angle X-ray diffraction patterns of  $Fe_3O_4@$  MCM-41 and  $Fe_3O_4@MCM-41\text{-SB-Pd}$ 

in the absence of any additional reducing agent [50]. Figure 7 shows the low-angle XRD patterns of the Fe<sub>3</sub>O<sub>4</sub>@ MCM-41 and Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd. A single intense peak at  $2\theta = 2.13$  and two weak peaks at  $2\theta = 3.54$  and 4.35 are appeared in the XRD pattern of Fe<sub>3</sub>O<sub>4</sub>@ MCM-41 which are assigned to reflections from the (1 0 0), (1 1 0) and (2 0 0) planes, respectively. These peaks are the characteristic of the ordered hexagonal mesoporous structure of MCM-41 type MSN (mesoporous silica nanoparticles) [30, 51–56]. Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd gives only one broad Bragg peak at low angle corresponding to (1 0 0) plane. This broadening and disappearing of XRD peaks are due to functionalization that decreases the regularity of hexagonal mesostructure [30, 57]. The decrease in the intensity of the (1 0 0) peak in anchoring of palladium complex provides an evidence that functionalization occurs also inside the mesopore channels [58].

The nitrogen adsorption–desorption isotherms of  $Fe_3O_4@$ MCM-41 and  $Fe_3O_4@MCM-41$ -SB-Pd are shown in Fig. 8. BET and BJH data of  $Fe_3O_4@$  MCM-41 in comparison to  $Fe_3O_4@MCM-41$ -SB-Pd are shown in Table 1. According to the IUPAC classification, these materials show a typical type IV isotherm, which is a characteristic of mesoporous materials. The results display the BET surface area, pore volume and pore size for  $Fe_3O_4@$  MCM-41 is 481.13 m<sup>2</sup>/g, 0.505 cm<sup>3</sup>/g and 3.22 nm, respectively. After the grafting of palladium complex, these value change to 28.16 m<sup>2</sup>/g, 0.162 cm<sup>3</sup>/g and 10.09 nm, respectively, consistent with the presence of complexes in the pore channels [30, 57, 59].

The magnetic properties of the synthesized nanomaterials were investigated at room temperature in the applied magnetic field sweeping from – 12,000 to 12,000 Oe using vibrating sample magnetometry (VSM), as shown in Fig. 9. The saturation magnetization values for  $Fe_3O_4$ ,  $Fe_3O_4$ @ MCM-41,  $Fe_3O_4$ @MCM-41-SB and  $Fe_3O_4$ @MCM-41-SB-Pd were 80.5, 55.8, 51.3 and 36.9 emu/g, respectively. As it obvious in Fig. 9, after addition of the SiO<sub>2</sub> and then functionalization with palladium Schiff base complex, the saturation magnetization of the  $Fe_3O_4$  decreased considerably from 80.5 to 36.9 emu/g. Nevertheless, the synthesized catalyst can still be separated from the reaction medium easily by applying an external magnetic field.

The thermogravimetric analysis (TGA) of  $Fe_3O_4@MCM-41$ ,  $Fe_3O_4@MCM-41$ -SB and  $Fe_3O_4@MCM-41$ -SB-Pd are shown in Fig. 10.  $Fe_3O_4@MCM-41$  shows only a small weight loss due to the removal of physically adsorbed water.  $Fe_3O_4@MCM-41$ -SB and  $Fe_3O_4@MCM-41$ -SB-Pd nanocomposites also show a first weight loss below 200 °C due to the removal of physically adsorbed water and solvent inside the pores channels [30, 60]. Then, the main weight loss in the temperature range of 200–800 °C corresponds to the thermal degradation of immobilized organic materials on  $Fe_3O_4@MCM-41$  surface.

The oxidation state of palladium in catalyst was determined by XPS (Fig. 11). Figure 11a shows C, N, O, S, Fe and Pd peaks and Fig. 11b gives the high-resolution Pd 3d XPS signals. The characteristic peaks at 335.36 and 341.04 eV can be indexed to the Pd (0) state and the other set of peaks at 337.32 and 343.18 eV are related to the Pd (II) oxidation state [61, 62]. The integration areas of these peaks indicate that Pd (0) is the major phase on the catalyst.

The optical properties of  $Fe_3O_4@MCM-41-SB-Pd$  have been studied through UV–Visible DRS spectrum in the range of 200–800 nm (Fig. 12). A broad absorbance band at range of 500–800 nm may be related to the charge-transfer transitions from nitrogen or sulfur lone pair to vacant d-orbitals of the metal [63]. This strong absorbance in the



Fig. 8 N<sub>2</sub> adsorption-desorption isotherms of a Fe<sub>3</sub>O<sub>4</sub>@ MCM-41 and b Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd

| Table 1 | BET and BJI | I data of Fe <sub>3</sub> C | 0 <sub>4</sub> @ MCM-41 | and Fe <sub>3</sub> O <sub>4</sub> | @MCM- |
|---------|-------------|-----------------------------|-------------------------|------------------------------------|-------|
| 41-SB-I | Pd          |                             |                         |                                    |       |

| Sample                                       | BET surface<br>area (m <sup>2</sup> /g) | Pore<br>volume<br>(cm <sup>3</sup> /g) | Pore size (nm) |
|--|---|--|----------------|
| Fe <sub>3</sub> O <sub>4</sub> @ MCM-41      | 481.13                                  | 0.505                                  | 3.22           |
| Fe <sub>3</sub> O <sub>4</sub> @MCM-41-SB-Pd | 28.16                                   | 0.162                                  | 10.09          |



Fig. 9 Magnetization curves at 300 K for  $Fe_3O_4$ ,  $Fe_3O_4$ @MCM-41,  $Fe_3O_4$ @MCM-41-SB and  $Fe_3O_4$ @MCM-41-SB-Pd

visible light region may be also due to the surface plasmon resonance (SPR) of Pd nanoparticles [64]. The absorptions at lower wavelength range is due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of aromatic phenyl moieties (C=C) and imine systems



Fig. 10 The TGA curve of the a  $Fe_3O_4@MCM-41$  b  $Fe_3O_4@MCM-41-SB$  and c  $Fe_3O_4@MCM-41-SB-Pd$ 

(C=N), respectively, and also spin-allowed d–d transition of palladium [63–66].

#### 3.2 Catalytic Reaction

Catalytic performance of  $Fe_3O_4$ @MCM-41-SB-Pd nanocatalyst was evaluated through the Suzuki–Miyaura coupling reaction. In order to optimize the reaction conditions, the coupling of bromobenzene with phenylboronic acid has been chosen as a model reaction and various parameters including catalyst and base dose, solvent and temperature were optimized. The reactions were monitored using TLC and the yields were reported after isolation of product.



Fig. 11 a XPS spectrum of Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd catalyst and b high-resolution XPS Pd 3d spectrum



Fig. 12 UV–Visible DRS spectrum of  $Fe_3O_4@MCM-41-SB-Pd$ 

Table 2 Influence of amount of catalyst (Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd) on Suzuki reaction

| Entry | Amount of catalyst (mg) | Pd content<br>(mol%) | Yield (%) <sup>a</sup> |
|-------|-------------------------|----------------------|------------------------|
| 1     | 1                       | 0.089                | 70                     |
| 2     | 2                       | 0.18                 | 98                     |
| 3     | 3                       | 0.27                 | 98                     |
| 4     | 5                       | 0.45                 | 98                     |

Reaction carried out with 1 mmol of bromobenzene, 1.2 mmol of phenylboronic acid, 2 mmol of K2CO3 and 5 mL of DMF at 120 °C <sup>a</sup>Isolated yield

The results are summarized in Tables 2, 3, and 4. Table 2 illustrates the effect of catalyst molar ratio on the reaction time of bromobenzene as a model substrate at 120 °C in DMF. The optimum amount of the catalyst was found to be 2 mg (0.18 mol% of Pd) in current conditions (Table 2,

Table 3 Influence of different solvents and temperature on Suzuki reaction

| Entry | Solvent               | Temperature (°C) | Yield (%) <sup>a</sup> |
|-------|-----------------------|------------------|------------------------|
| 1     | H <sub>2</sub> O      | 100              | Trace                  |
| 2     | EtOH                  | 80               | 30                     |
| 3     | H <sub>2</sub> O-EtOH | 78               | 40                     |
| 4     | DMF                   | 120              | 98                     |
| 5     | DMF                   | 100              | 60                     |
| 6     | DMF                   | 75               | 35                     |
| 7     | DMF                   | 25               | Trace                  |

Reaction carried out with 1 mmol of bromobenzene, 1.2 mmol of phenylboronic acid, 2 mg of catalyst, 1.2 mmol of K<sub>2</sub>CO<sub>3</sub> and 5 mL of solvent

<sup>a</sup>Isolated yield

| Table 4Influence of amountof base ( $K_2CO_3$ ) on Suzukireaction | Entry                                       | Amount<br>of base<br>(mmol)                                       | Yield (%) <sup>a</sup>                                       |
|---|---|---|--|
|   | 1   | 1   | 80   |
|   | 2   | 1.2   | 98   |
|   | 3   | 1.5   | 98   |
|   | 4   | 2   | 98   |
|   | Reacti<br>1 mi<br>1.2 r<br>acid, 2<br>of DM | on carried<br>mol of b<br>nmol of<br>2 mg of cata<br>IF at 120 °C | l out with<br>romobenzene,<br>phenylboronic<br>lyst and 5 mL |

<sup>a</sup>Isolated yield

entry 2). According to the results shown in Table 3, biphenyl product was detected in trace-40% yield when the reaction was carried out in water, EtOH and H<sub>2</sub>O-EtOH (1:1) (Table 3, entries 1-3). When *N*,*N*-dimethylformamide (DMF) was used as solvent, an excellent yield (98%) was

| Table 5 Suzuki reaction catalyzed by v | arious ca | atalysts |
|--|-----------|----------|
|--|-----------|----------|

| Entry | Catalyst  | Time (h) | Yield (%) <sup>d</sup> |
|-------|---|----------|------------------------|
| 1     | None <sup>a</sup>   | 24       | 0                      |
| 2     | Fe <sub>3</sub> O <sub>4</sub> @MCM-41 <sup>a</sup>       | 24       | 0                      |
| 3     | Fe <sub>3</sub> O <sub>4</sub> @MCM-41-SB <sup>a</sup>    | 24       | 0                      |
| 4     | Fe <sub>3</sub> O <sub>4</sub> <sup>a</sup>               | 24       | 0                      |
| 5     | $Pd(OAc)_2^b$   | 4        | 40                     |
| 6     | Fe <sub>3</sub> O <sub>4</sub> @MCM-41-SB-Pd <sup>c</sup> | 0.17     | 98                     |

Reaction carried out with 1 mmol of bromobenzene, 1.2 mmol of phenylboronic acid and 5 mL of DMF at 120 °C. <sup>a</sup>2 mg, <sup>b</sup>0.4 mg, <sup>c</sup>2 mg of catalyst (9.5 wt% Pd), <sup>d</sup>Isolated yield

detected (Table 3, entry 4). As the result of the tables, after a series of optimization experiments, the best outcome was achieved with 1.2 mmol of K<sub>2</sub>CO<sub>3</sub> (Table 4) in the presence of 2 mg of catalyst (0.18 mol% Pd) and in DMF as solvent at 120 °C. To investigate the effective component of the catalyst, a series of control experiments were conducted. The results were summarized in Table 5. In the absence of any catalyst, or in the presence of only Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@MCM-41 or Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB as a control, hardly any reaction occurred (Table 5, entries 1-4). The results indicated that the Suzuki reaction could not proceed in the absence of Pd. In the presence of only  $Pd(OAc)_2$  as a catalyst, low yield was obtained at a longer time (Table 5, entry 5). While using the supported catalyst, Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd, yield is up to 98% (Table 5, entry 6). Therefore, supporting of palladium on functionalized mesoporous silica promoted the Suzuki reaction and made the catalyst achieve excellent catalytic performance.

After the optimization of the reaction conditions, the reaction of the various aryl halides, even aryl chloride, containing electron-donating and electron-withdrawing groups with phenylboronic acid were carried out under optimized conditions and the results were summarized in Table 6. The results show that the catalyst system is very efficient and the biphenyl derivatives were obtained in a short time with high yields. Suzuki-Miyaura reactions of activated aryl bromides including 4-bromotolune, 4-bromoanisole and 4-bromophenol proceeded with high yields of 98%, 85% and 80%, in short reaction time and high turnover frequencies (TOF) of 32.02 h<sup>-1</sup>, 9.44 h<sup>-1</sup>, and 13.47 h<sup>-1</sup>, respectively, (Table 6, entries 2-4). The Suzuki reaction of deactivated aryl bromides with different substituents also gave high yields but in longer reaction times and lower TOF than activated aryl bromides (Table 6, entries 5 and 6). The reactions of sterically hindered ortho and meta-position halides with phenylboronic acid also produced the desired biaryls under the optimized reaction conditions (Table 6, entries 7 and 8). Based on these data, 2-bromotoluene which is sterically hindered could be coupled in good yield of 75% in 1 h and 4.02  $h^{-1}$ 

TOF (Table 6, entry 7) and the reaction of 3-bromotoluene proceeds with high yield of 95% in 10 min and 31.05  $h^{-1}$  TOF. Also aryl iodides react much faster than aryl bromides with higher TOF (Table 6, entries 9–11). Chlorobenzene was also successfully coupled with phenylboronic acid in the presence of this catalyst with high yield of 98% in 0.5 h and 10.88  $h^{-1}$  TOF (Table 6, entry 12).

The catalytic performance of the  $Fe_3O_4@MCM-41-SB-Pd$  is compared with some Pd-based heterogeneous catalysts reported in the literature for the model reaction (Table 7) [46, 49, 67–71]. The results show that the high loading of palladium on  $Fe_3O_4@MCM-41-SB$  effectively makes performing the reaction with only a small amount of the catalyst and a higher reaction yield within shorter time. Furthermore, the catalyst is easily recovered using an external magnetic field.

In order to investigate the reusability of the magnetic heterogeneous palladium catalyst, a set of experiments were performed under optimized conditions for the reaction of bromobenzene with phenylboronic acid. After each run, the reaction mixture was cooled at room temperature and the catalyst was extracted by applying an external magnet, washed several times with water and ethyl acetate and finally dried under vacuum for the next run. As shown in Fig. 13, the Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd catalyst is recycled for five times without significant decreasing in the catalytic activity. FT-IR spectroscopy also confirmed that the structure of the catalyst after 5 cycles has not changed (Fig. 14). Furthermore, XRD pattern of recovered catalyst (Fig. 6) demonstrates that the catalyst can be recycled several times without any considerable change in the structure. The measurement of palladium by atomic absorption before (9.5 wt%) and after (9.2 wt%) catalytic reaction also showed that palladium leaching was negligible, probably due to excellent binding of the amine, imine, thiol and hydroxyl groups [72]. This result proves a strong interaction between the support material and palladium. These analyses clearly demonstrate that the catalyst is stable, recoverable and the crystalline structure of it did not change after several runs.

#### 3.3 Enzyme Immobilization

The results of  $\alpha$ -amylase enzyme immobilization on the Fe<sub>3</sub>O<sub>4</sub>@MCM-41 and functionalized Fe<sub>3</sub>O<sub>4</sub>@MCM-41 nanocomposites are shown in Fig. 15 and listed in Table 8. The results show that the  $\alpha$ -amylase was immobilized on all composites, but the functionalized composites more successfully load the enzyme. Immobilization of enzymes on a support occurs by covalent or noncovalent interactions through binding to a support, encapsulation and cross-linking [73–75]. Hydroxyl groups on Fe<sub>3</sub>O<sub>4</sub>@MCM-41 may interact with OH groups of  $\alpha$ -amylase by hydrogen bonding. Functionalized nanocomposites have amine, imine, carbonyl or

|       | X +                  | B(OH) <sub>2</sub> Fe <sub>3</sub> O <sub>4</sub> @MCM- | 41-SB-Pd   |                        |                  |                                     |
|-------|----------------------|---|------------|------------------------|------------------|-------------------------------------|
|       | G'/                  | K <sub>2</sub> CO <sub>3</sub> , DMF,                   | 120 °C     | G∕∕ ∖∖                 | //               |                                     |
| Entry | Aryl halide          | Product   | Time (min) | Yield (%) <sup>a</sup> | TON <sup>b</sup> | TOF (h <sup>-1</sup> ) <sup>c</sup> |
| 1     | ⟨Br                  |   | 10         | 98                     | 5.44             | 32.02                               |
| 2     | H <sub>3</sub> C-Br  | H <sub>3</sub> C  | 10         | 98                     | 5.44             | 32.02                               |
| 3     | H <sub>3</sub> CO-Br | H <sub>3</sub> CO-                                      | 30         | 85                     | 4.72             | 9.44                                |
| 4     | HO                   | но-   | 20         | 80                     | 4.44             | 13.47                               |
| 5     | OHC Br               | онс-  | 40         | 90                     | 5.00             | 7.46                                |
| 6     | H <sub>3</sub> CC Br |   | 60         | 90                     | 5.00             | 5.00                                |
| 7     | CH <sub>3</sub>      |   | 60         | 75                     | 4.02             | 4.02                                |
| 8     | H <sub>3</sub> C     | H <sub>3</sub> C  | 10         | 95                     | 5.28             | 31.05                               |
| 9     |                      |   | 5          | 98                     | 5.44             | 68.06                               |
| 10    | H <sub>3</sub> CO-   | H <sub>3</sub> CO-                                      | 15         | 85                     | 4.72             | 18.89                               |
| 11    | O <sub>2</sub> N-    | 0 <sub>2</sub> N-                                       | 5          | 98                     | 5.44             | 68.06                               |
| 12    | СІ                   |   | 30         | 98                     | 5.44             | 10.88                               |

| Table 6 | Suzuki-Miyaura | reaction of aryl halides | with phenylboronic a | acid catalysed by Fe <sub>3</sub> 0 | O <sub>4</sub> @MCM-41-SB-Pd |
|---------|----------------|--------------------------|----------------------|-------------------------------------|------------------------------|
|---------|----------------|--------------------------|----------------------|-------------------------------------|------------------------------|

Reaction conditions: aryl halides (1.0 mmol), phenylboronic acid (1.2 mmol),  $K_2CO_3$  (1.2 mmol),  $Fe_3O_4@MCM-41$ -SB-Pd (2 mg, 0.18 mol% Pd) and DMF (5 mL) at 120 °C

<sup>a</sup>Isolated yield

<sup>b</sup>TON, turnover number, moles of aryl halides converted per mole of Pd

<sup>c</sup>TOF, turnover frequencies, TON/time of reaction

| Entry | Catalyst  | Solvent                             | Temp. (°C) | Time (h) | Yield (%) | References   |
|-------|---|-------------------------------------|------------|----------|-----------|--------------|
| 1     | SBA-15/AO/Pd(II) <sup>a</sup>   | H <sub>2</sub> O:EtOH               | 50         | 1        | 98        | [46]         |
| 2     | Anchored Pd(II)–Schiff base complex <sup>b</sup>  | H <sub>2</sub> O                    | 50         | 0.5      | 100       | [49]         |
| 3     | [PdCl(PC(CH <sub>2</sub> ) <sub>5</sub> CP) (CH <sub>3</sub> CN)]BF <sub>4</sub> <sup>c</sup> | DMF                                 | 120        | 12       | 80        | [61]         |
| 4     | Fe <sub>3</sub> O <sub>4</sub> @C-Pd-550 <sup>d</sup>   | EtOH                                | 75         | 6        | 92.22     | [62]         |
| 5     | Pd@imine-SiO <sub>2</sub> <sup>e</sup>  | H <sub>2</sub> O: <sup>i</sup> PrOH | 60         | 2        | 98        | [63]         |
| 6     | $Fe_3O_4@SiO2@mSiO_2-Pd(0)^f$   | <sup>i</sup> PrOH                   | 80         | 6        | 97.23     | [64]         |
| 7     | MNP@SPGMA@AP@Pd <sup>g</sup>  | DMF:H <sub>2</sub> O                | 70         | 1        | 96        | [65]         |
| 8     | $Fe_3O_4@MCM-41-SB-Pd^h$  | DMF                                 | 120        | 0.16     | 98        | Present work |

Table 7 Catalytic performance of different Pd-based catalysts in the coupling of bromobenzene and phenyl boronic acid

<sup>a</sup>Pd immobilized on amidoxime-functionalized Mesoporous SBA-15 (0.010 g cat., 0.002 mol% Pd)

<sup>b</sup>Nanosilica (derived from rice husk)-anchored Pd(II)–Schiff base complex (10 mg)

<sup>c</sup>Silver(I) and palladium(II) complexes of pentamethylene-functionalized bis-imidazolium dication ligands (0.1 mol% Pd complex)

<sup>d</sup>Core-shell magnetic composite catalyst (10 mg)

eSilica supported palladium Schiff base catalyst (0.02 g cat., 0.08 mol% Pd)

 $^{\rm f}$ Immobilized palladium on the amine-modified core-shell magnetic mesoporous Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mSiO<sub>2</sub>microspheres (0.075 mol% cat.)

<sup>g</sup> Palladium loaded magnetic nanocomposite based on natural polysaccharide salep modified with poly (amino pyridine) (0.1 mol% cat.)

<sup>h</sup> Magnetic mesoporous silica nanocomposite functionalized with palladium Schiff base complex (2 mg cat., 0.18 mol% Pd)



Fig. 13 Reusability of catalyst in Suzuki reaction of bromobenzene with phenylboronic acid



thiocarbonyl groups that can interact with functional groups of amylase by hydrogen bonding or covalent bond formation. Free probable coordination sites on the palladium may also be suitable for binding of  $Fe_3O_4$ @MCM-41-SB-Pd with enzyme. In view of the importance of biocatalysts, these modified magnetic mesoporous silica nanoparticles can be good candidates for enzyme immobilization.

# Fig. 14 Comparison of the IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd composite **a** before catalytic reaction and **b** after recycling five times

#### 4 Conclusion

Magnetic mesoporous silica nanocomposites were synthesized and functionalized with an ONS donor Schiff Base and then loaded with relatively large amounts of palladium (9.5 wt%). Nanocomposites were characterized by various methods. Then, Fe<sub>3</sub>O<sub>4</sub>@MCM-41-SB-Pd was successfully used for the Suzuki–Miyaura coupling reaction and



Fig. 15 Starch hydrolysis zone diameter (mm) following the effect of a  $Fe_3O_4@MCM-41$ , b  $Fe_3O_4@MCM-41-NH_2$ , c  $Fe_3O_4@MCM-41$ -ald and d  $Fe_3O_4@MCM-41-SB-Pd$ 

 Table 8
 Starch hydrolysis zone diameter (mm) following the effect of synthesized composites

|             | Fe <sub>3</sub> O <sub>4</sub> @<br>MCM-41 | Fe <sub>3</sub> O <sub>4</sub> @<br>MCM-<br>41-NH <sub>2</sub> | Fe <sub>3</sub> O <sub>4</sub> @<br>MCM-41-ald | Fe <sub>3</sub> O <sub>4</sub> @<br>MCM-<br>41-SB-Pd |
|-------------|--|--|--|--|
| Effect zone | 16   | 20   | 26   | 26   |

showed excellent catalytic performance for the synthesis of substituted biaryls. The recovery of the catalyst is easily performed using an external magnetic field and also can be reused several times without considerable loss of its catalytic activities. Synthesized mesoporous nanocomposites were also investigated for immobilization of amylase enzyme and the good results were achieved. According to our results, high chelating ability of imine, amine, thiol and hydroxyl groups of bis-Schiff base ligand can load large amounts of palladium, restrict palladium leaching in the catalysis process and also effectively immobilize amylase enzyme.

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