

Accepted Manuscript



A journal for new directions in chemistry

This article can be cited before page numbers have been issued, to do this please use: M. Shaker and D. Elhamifar, *New J. Chem.*, 2020, DOI: 10.1039/C9NJ06250E.



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

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

You can find more information about Accepted Manuscripts in the Information for Authors.

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



rsc.li/njc

balisiland)

Core-shell structured magnetic mesoporous silica supported Schiffbase/Pd: An efficacious and reusable nanocatalyst

Masoumeh Shaker and Dawood Elhamifar*

Department of Chemistry, Yasouj University, Yasouj, 75918-74831, Iran E-mail: <u>d.elhamifar@yu.ac.ir</u>

Abstract: In this research, a novel Schiff-base/palladium complex containing magnetic ordered mesoporous silica (Fe₃O₄@MCM-41-SB/Pd) material with core-shell structure is perapred, characterized and its catalytic application is developed. The Fe₃O₄@MCM-41-SB/Pd nanocatalyst was characterized using FT-IR, TGA, SEM, VSM, PXRD and energy-dispersive X-ray (EDX) spectroscopy. This nanocatalyst showed high performance in Suzuki cross-coupling reaction under ultrasonic conditions and delivered corresponding products in high to excellent yield. The recovery study of the nanocatalyst proved that its activity is maintained during several stages of reuse. Moreover, the high stability of palladium species on the core-shell surface was confirmed by leaching and poisoning tests.

Keywords: Magnetic ordered mesoporous silica, Schiff-base/palladium complex, Coreshell, Biaryls, Suzuki cross-coupling.

1. Introduction

1 2 3

4 5 6

7 8

9

no paysilon 55

> 39 40 41

42 43

44 45 46

47 48

49 50 51

52 53

59 60

In recent years, the synthesis of metal oxide nanoparticles (NPs) has attracted much attention due to their important role in various sciences such as chemistry, physics, material, medicine, etc.¹⁻¹⁴ Among these, iron oxide NPs occupy a special position due to their easy preparation, easy separation, non-toxicity and inexpensive.^{15, 16} Also, the possibility of their surface modification with active biological compounds has increased the popularity of these particles.¹⁷⁻²¹ Accordingly, the iron oxide NPs are widely used in various fields such as magnetic resonance imaging (MRI),^{19, 20, 22-25} sensors,²⁶⁻²⁹ labeling and sorting of cells,³⁰ ferrofluid,^{31, 32} drug delivery,^{21, 24} and catalyst immobilization.^{3, 33, 34} In spite of the aforementioned advantages, uncoated Fe₃O₄ NPs have low chemical stability and lose much of their magnetic and chemical capacities in the presence of air and alkaline and acidic media. Also, these NPs have strong tendency for self-assembly, due to the existence of Van der Waals forces and the inherent magnetic interaction.^{35, 36} Hence, in recent years, different methods such as doping, functionalization and compositing have been used to coat a layer around MNPs and improve their stability.³⁷⁻³⁹ The coated layer can be species such as metal or metal oxides, groups and compounds of mineral, organic, sugar and peptide that surround the inner core and called as the shell. Between different shells, silica has become widely considered due to high biocompatibility, non-toxicity, poor chemical permeability and easy surface modification. In recent years, mesoporous silica shells have created a major revolution in the synthesis of core-shell nanostructures. due to their high adsorption capacity, relatively uniform and controllable pore size, easy

4 5

6 7 8

9

04. February 2020.

34 balsile 100

<u>ج</u> ج 38

> 39 40

48 49 50

51 52 53

54 55

56 57 58

59 60 are GdIO@mSiO₂@BNSCQD,⁵¹

Fe₃O₄@nSiO₂@mSiO₂⁵⁴

surface modification and high surface area.⁴⁰⁻⁵⁰ Some of recently developed magnetic nanostructures with mesoporous silica shells CuO/Silicalite-1@mSiO₂,⁵² Fe₃O₄-mSiO₂⁵³ Fe₃O₄@ZnO@mSiO₂⁵⁵ Fe₃O₄@mSiO₂ nanocapsules,⁵⁶ Fe₃O₄@nSiO₂@mSiO₂-APTES-VP16,57 Fe₃O₄@mSiO₂@ICG58 and DOX-Fe₃O₄@mSiO₂@Au.59 On the other hand, the Suzuki carbon-carbon coupling is a significant process that occurs between aryl halides/triflates and the arylboronic acids to give biaryl compounds. This reaction has been widely used in the synthesis of drugs, natural products, ligands for catalysts, nucleoside analogues and liquid crystalline materials. Traditionally, this has been accomplished in the presence of Pd-catalysts under homogeneous conditions. However, due to the restrictions of these systems such as catalyst and product separation, various heterogeneous catalysts have been reported for this reaction.⁶⁰⁻⁶⁴ Some of recently reported catalytic systems are Mag-IL-Pd,⁶² SMNP@NHC-Pd,⁶⁵ Fe₃O₄@SiO₂/isoniazide/Pd,⁶⁶

2. Experimental Section

1.2. Preparation of Fe₃O₄@MCM-41

For this, Fe_3O_4 ($aSiO_2$ NPs were first prepared according to a previous procedure.⁶⁹ The Fe_3O_4 (0.6 g) was then dispersed in a mixture of distilled water (80 mL) and ethanol (60

Fe₃O₄/DAG/Pd⁶⁷ and MNP@SPGMA@AP@Pd.⁶⁸ Following the above-mentioned

systems, in the present work a magnetic core-shell nanostructure modified with Schiff-

base/Pd complex is prepared for the Suzuki cross-coupling reaction under green conditions.

mL) at 40 °C. After that, aqueous ammonia (3 mL, 25% wt) and cetyltrimethylammonium bromide (CTAB, 1 g) were added and the resulted mixture was mechanically stirred at room temperature for 10 min. Then, TMOS (0.7 mL) was added and stirring was continued for 2 h at room temperature. The obtained combination was aged for 48 h at 100 °C. The resulted product was separated, washed with EtOH and dried at 70 °C for 6 h. Finally, the CTAB was eliminated *via* calcination at 500 °C for 6 h. This material was denoted as Fe₃O₄@MCM-41.

2.2. Preparation of Fe₃O₄@MCM-41-SB

1 2 3

4 5

6 7

8

9

34

persiperside and a second seco

41 42 43

44 45

46 47

59 60 For this, the Fe₃O₄@MCM-41 (1 g) was well-dispersed in toluene (30 mL). Then, (3aminopropyl)trimethoxysilane (1 mmol) was added and this mixture was refluxed for 24 h under argon. The product was magnetically separated, washed with EtOH (150 mL) and dried in oven at 80 °C for 6 h to yield Fe₃O₄@MCM-41-PrNH₂. Subsequently, the Fe₃O₄@MCM-41-PrNH₂ (1 g) was sonicated to disperse in dry toluene (40 mL). After adding of *o*-phthalaldehyde (3 mmol), the mixture was refluxed for 24 h. After completion of the reaction, the resulting product was collected, washed with EtOH and dried at 70 °C. This was denoted as Fe₃O₄@MCM-41-SB.

2.3. Preparation of Fe₃O₄@MCM-41-SB/Pd

At first, the Fe₃O₄@MCM-41-SB (1 g) was dispersed in DMSO (30 mL) at RT for 20 min. Then, Pd(OAc)₂(1.5 mmol) was added and this was stirred at RT for 24 h. The product was washed with EtOH/water (1:1, 200 mL), dried at 70 °C for 6 h and called as Fe₃O₄@MCM-41-SB/Pd.

4 5 6

7 8

9

no parsila 100 par

م 38 39

> 40 41

> 42 43 44

> 45 46

> 47 48

> 49 50

51 52 53

54 55

56 57 58

59 60

2.4. Procedure for the Suzuki cross-coupling using Fe₃O₄@MCM-41-SB/Pd nanocatalyst

For this, aryl halide (1 mmol), arylboronic acid (1.5 mmol), K₂CO₃ (2 mmol) and Fe₃O₄@MCM-41-SB/Pd (0.12 mol%) were added in distilled water (5 mL) in an ultrasonic bath at 50 °C. After completing of the reaction, ethyl acetate (5 mL) was added and the catalyst was magnetically removed. The organic phase was separated and dried over anhydrous Na₂SO₄. The pure Suzuki products were resulted using column chromatography on silica.

2.5. Procedure for the poisoning tests using mercury, triphenylphosphine and PMO-ILpropyl-SH

For this purpose, aryl halide (1 mmol), arylboronic acid (1.5 mmol), K_2CO_3 (2 mmol) and poisoning agent (in a ratio of 400 equivalents to the initial Pd amount) were added in distilled water (8 mL). This mixture was sonicated at 50 °C. In the next step, the Fe₃O₄@MCM-41-SB/Pd catalyst (0.12 mol%) was quickly added and the progress of reaction was monitored using TLC.

3. Results and discussion

Scheme 1 shows the overall procedure used to synthesize of Fe₃O₄@MCM-41-SB/Pd nanocatalyst. Firstly, $Fe_3O_4@SiO_2$ nanoparticles were prepared according to a previous procedure.⁶⁹ Subsequently, the second shell was created *via* alkaline hydrolysis and condensation of TMOS in the presence of CTAB. After removing of surfactant, the Fe₃O₄@MCM-41 was resulted. The shell surface of Fe_3O_4 (*a*) MCM-41 modified bv (3outer was aminopropyl)trimethoxysilane to give $Fe_3O_4@MCM-41$ -Pr-NH₂ nanomaterial. The latter material was treated first with o-phthalaldehyde and then with palladium acetate to deliver Fe₃O₄@MCM-41-SB/Pd nanocatalyst.

New Journal of Chemistry Accepted Manuscript



Scheme 1. Preparation of the Fe₃O₄@MCM-41-SB/Pd nanocatalyst

Determination and confirmation of the presence of different functional groups were carried out using FT-IR spectroscopy technique (Figure 1). The peak appeared at 568 cm⁻¹ is related to the stretching vibrations of Fe-O bonds. Furthermore, the broad band at approximately 3420 cm⁻¹ is due to O-H bonds. The FT-IR of Fe₃O₄@SiO₂, Fe₃O₄@MCM-41 and Fe₃O₄@MCM-41-SB/Pd showed the presence of Si-O-Si bonds at 823 and 1078 cm⁻¹. For Fe₃O₄@MCM-41-SB/Pd, the new signals appeared at 2965, 1625 and 1432 cm⁻¹ are related to stretching vibrations of C-H, C=N

balished

 View Article Online DOI: 10.1039/C9NJ06250E

and C=C bonds, respectively, indicating successful immobilization of the propyl Schiff-base groups on magnetic mesoporous silica nanoparticles.



Figure 1. FT-IR spectra of a) Fe_3O_4 , b) Fe_3O_4 ($@SiO_2$, c) Fe_3O_4 (@MCM-41 and d) Fe_3O_4 (@MCM-41-SB/Pd

The low-angle X-ray diffraction (LXRD) of the nanocatalyst is shown in Figure 2. The presence of a sharp peak at $20\approx2.24$ confirms the high order of the nanocatalyst structure. In fact, this peak is corresponded to mesoporous MCM-41 shell of designed material.^{59, 70-72} In the next step, the wide-angle X-ray diffraction (WXRD) was carried out to study the crystalline structure of the

magnetite nanoparticles (Figure 3). This showed six sharp peaks at 20 of 30.41, 35.88, 43.53, 53.80, 57.41 and 63.10 degrees corresponding to their Miller indices values (*hkl*).^{73, 74} This result clearly confirms that the crystalline structure of the magnetic iron oxide nanoparticles has been preserved during the modification processes.



Figure 2. LXRD pattern of the Fe₃O₄@MCM-41-SB/Pd

Figure 3. WXRD pattern of the Fe₃O₄@MCM-41-SB/Pd nanocatalyst

Thermal stability of Fe₃O₄@MCM-41-SB/Pd was investigated by TGA (Figure 4). The immobilization of Schiff-base complex on the Fe₃O₄@MCM-41 nanostructure was well confirmed by this analysis. As shown, the initial weight loss (about 4%) from 34 to 130 °C is related to adsorbed water. The second weight loss (about 3%) from 134 to 280 °C is due to the elimination of the CTAB surfactant remained during catalyst preparation. Finally, the major part of the thermal degradation (about 10%) between 300 and 650 °C is related to the removal of propyl-Schiff base groups immobilized on the target nanostructure.

View Article Online DOI: 10.1039/C9NJ06250E

Figure 4.TG curve of the Fe₃O₄@MCM-41-SB/Pd nanocatalyst

balished

 The EDX spectrum of Fe₃O₄@MCM-41-SB nanocomposite demonstrated the presence of Fe, Si, C, N and O elements in the material proving successful incorporation and/or immobilization of silica and propyl-Schiff base moieties into/onto material framework (Figure 5).

Bublisked og 04 February 2020, Rowalonder Universiter Baris Descartes 0n 2/11/2020 1:22:35 PM. 2 9 5 4 6 7 1 0 6 8 2 9 5 7 0 0

Figure 5. EDX analysis of the Fe₃O₄@MCM-41-SB

To confirm the successful immobilization of Pd on Fe_3O_4 @MCM-41-SB nanocomposite, the final material was also characterized by EDX analysis. The appearance of Pd-signal in the latter analysis confirms well-immobilization of Pd species on Schiff base-modified material (Figure 6).

New Journal of Chemistry Accepted Manuscript

Figure 6. The EDX analysis of Fe₃O₄@MCM-41-SB/Pd nanocatalyst

The EDX mapping analysis was also done to show the distribution of elements in the nanocatalyst framework. This analysis showed that all elements are successfully and uniformly distributed in the Fe₃O₄@MCM-41-SB/Pd framework (Figure 7).

bished

Figure 7. The EDX mapping of the Fe₃O₄@MCM-41-SB/Pd nanocatalyst

Scanning electron microscopy (SEM) was performed to show the particle morphology at different stages of nanocatalyst synthesis. This showed that the particle morphology is spherical at all steps and the size of the NPs are increased at each step compared to the previous step (Figure 8). Especially, the SEM of the Fe₃O₄@MCM-41-SB/Pd clearly showed the presence of spherical particles with average size of 85 nm (Figure 8d).

balished

Figure 8. SEM images of a) $Fe_3O_4@MCM-41$, b) $Fe_3O_4@MCM-41/Pr-NH_2$, c) $Fe_3O_4@MCM-41-SB$ and d) $Fe_3O_4@MCM-41-SB/Pd$ nanomaterials

palsilar

 The VSM analysis confirmed that the Fe₃O₄@MCM-41-SB/Pd is paramagnetic (Figure 9). Based on this analysis, a saturation magnetization of 37.16 emu/g was found for the catalyst. These MNPs were dispersed in common solvents (H₂O, EtOH, DMF and toluene) and collected easily by an external magnet (Figure 9, inset Figure). This is a turning point in the synthesis of nanocatalyst.

Figure 9. VSM diagram of the Fe₃O₄@MCM-SB/Pd nanocatalyst

After synthesis and characterization of Fe_3O_4 @MCM-41-SB/Pd nanocatalyst, its catalytic application was investigated in the Suzuki reaction under ultrasonic media. To obtain the optimal conditions, the reaction between iodobenzene and phenylboronic acid was chosen as a test model (Table 1). In the first step, the effect of catalyst loading was investigated in the reaction progress. It was found that with increasing catalyst amount, the yield is increased and the best result was observed in the presence of 0.12 mol% of catalyst (Table

2 3 1, entries 1-5). The effect of temperature was also investigated. Based on this, it was 4 5 observed that the temperature has a great impact on the reaction, qua at 50 °C the highest 6 7 8 conversion was resulted (Table 1, entry 4 versus entries 6, 7). Therefore, this was selected 9 Bowulowder UNU INVERSIGN BASCARTES ON 2/11/2020 1:22:35 PM 8 2 9 5 4 2 2 1 0 6 8 2 9 5 4 2 7 1 0 as optimal temperature in subsequent studies. In another study, the reaction progress was studied in an oil bath that an unfortunate activity and yield in comparison to ultrasonic conditions were resulted (Table 1, entry 8). The reaction sensitivity to the base was also studied. According to the results, K₂CO₃ showed the best performance (Table 1, entry 4 versus entries 9-11). Importantly, the reaction did not perform under free base conditions (Table 1, entry 12). One of the most important goals in green chemistry is the use of environmentally friendly solvents in organic transformation. On the other hand, organic solvents, due to their high use, are the main source of chemical pollution. Fortunately, our 04. February 2020. study showed that the best result is obtained in water (Table 1, entry 4 versus entries 13-15). As stated in the introduction section, the presence of Pd catalyst, is mandatory for the 84 balsile 100 Suzuki reaction. To prove this, the model reaction was done using Pd-free Fe₃O₄@MCM-٩<u>5</u>7 38 41-SB and Fe₃O₄@SiO₂@MCM-41 materials, in which catalytic activity was not observed 39 40 (Table 1, entries 16, 17). According to these results, the use of 0.12 mol% of catalyst and 41 42 43 K_2CO_3 base in water at 50 °C were selected as optimal conditions. 44 45 46 47 48 49 50 51

1

Bublisked og 04 February 2020, Rowalonder Universiter Baris Descartes 0n 2/11/2020 1:22:35 PM. 2 9 5 4 6 7 1 0 6 8 2 9 5 7 0 0

Table	1. Effect of so	olvent, cataly	st loading, base a	nd temperature in th	ne Suzuki reaction	
		B(C	$(\text{PH})_2$ Fe ₃ O ₄ ($($	MCM-41@SB/Pd	\rightarrow	
	\checkmark	\checkmark)))		
Entry	Solvent	Base	Cat. (mol%)	T (°C)	Time (min)	Yield (%) ^a
1	H ₂ O	K ₂ CO ₃		50	60	
2	H ₂ O	K ₂ CO ₃	0.04	50	25	30
3	H ₂ O	K ₂ CO ₃	0.08	50	25	84
4	H ₂ O	K ₂ CO ₃	0.12	50	25	95
5	H ₂ O	K ₂ CO ₃	0.16	50	25	95
6	H ₂ O	K ₂ CO ₃	0.12	r.t.	25	Trace
7	H ₂ O	K ₂ CO ₃	0.12	35	25	45
8 ^b	H ₂ O	K ₂ CO ₃	0.12	50	25	70
9	H ₂ O	Na ₂ CO ₃	0.12	50	25	78
10	H ₂ O	NEt ₃	0.12	50	25	67
11	H ₂ O	NaOH	0.12	50	25	60
12	H ₂ O	Free base	0.12	50	60	Trace
13	EtOH	K ₂ CO ₃	0.12	50	25	82
14°	EtOH/H ₂ O	K ₂ CO ₃	0.12	50	25	88
15	Toluene	K ₂ CO ₃	0.12	50	25	55
16 ^d	H ₂ O	K ₂ CO ₃	0.003 g	50	60	
17e	H ₂ O	K ₂ CO ₃	0.003 g	50	60	
^a Isolat	ted yields. b	Oil bath. ^c	EtOH/H ₂ O $(1:1)$). d Fe ₃ O ₄ @MCM-	41@SB was used	as catalyst. ^e
Fe ₃ O ₄	MCM-41 w	as used as cat	alyst.			

After optimization of the conditions, the substrate scope of the catalyst was studied. According to Table 2, all reactions were performed at short time with excellent yield and high TON/TOF. As predicted, the activity of aryl halides was in the order of aryl iodides> aryl bromides> aryl chlorides. It is also important to note, no detectable homo-coupling byproduct was observed under applied conditions, confirming high selectivity of catalyst for cross-coupling reaction.

Table 2. Synthesis of Suzuki products in the presence of Fe ₃ O ₄ @MCM-41@SB/Pd									
		B(OH) ₂	Fe ₃ O ₄ @	MCM-41@SB/P	d (0.12 mol %)		$\bigwedge R^1$		
$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$			K ₂ CO ₃ , 50 °C, H ₂ O,)))			$R \xrightarrow{\langle} R$			
Entry	Aryl halide	Arylboronic acid	Time (min)	Yield (%) ^a	TON ^b	TOF (h ⁻¹) ^c	Found M.P. (°C)		
	I	B(OH) ₂							
1			25	95	791.6	1930.7	68-70		
_	Br L	B(OH) ₂							
2			40	91	758.3	1148.9	68-70		
		B(OH) ₂	-	0.5	7 00 0	(10.6	(0.70		
3			/0	85	/08.3	610.6	68-70		
	Çl	B(OH) ₂							
4			70	84	700	603.4	45-47		
		CH ₃							
	Cl	B(OH) ₂							
5			70	87	725	625	85-87		
	CN Br	B(OH) ₂							
6	CN		40	92	766.6	1161.5	35-37		
		B(OH) ₂							
7			65	87	725	671.2	112-114		
	NO ₂								
0		B(OH) ₂	20	04	792.2	15(((57.50		
8			30	94	/83.3	1300.0	57-39		
	Br	B(OH) ₂							
9			30	95	791.6	1583.2	106-108		
				~~	. /				
^a Isolated vields. ^b Turnover number [all TONs were calculated by this equation: Yield (%) /Cat. (mol %)]. ^c									
Turnover frequency [all TOFs were calculated by this equation: TON/Time (h)].									

New Journal of Chemistry Accepted Manuscript

Due to the unfathomable positive effects of catalyst in industries such as drug, paint, oil, gas, chemicals, *etc.*, its recoverability and reusability are important issues. Accordingly, these abilities of Fe₃O₄@MCM-41-SB/Pd in the coupling of PhB(OH)₂ and PhI, as a test model, were investigated. As shown in Table 3, the mentioned nanocatalyst was easily recycled and reused for at least eleven times with no significant decrease in its efficiency.

Table 3	3. Recoverability of	of the Fe ₃ O ₄ @MCM-4	1-SB/Pd	
	+ B(OH)	² Fe ₃ O ₄ @MCM-41@S	SB/Pd (0.12 mol %)	
		K ₂ CO ₃ , 50 °C	C, H ₂ O,)))	
Run	Time (min)	Yield (%)	TON	TOF (h ⁻¹)
1	25	95	791.6	1930.7
2	25	95	791.6	1930.7
3	25	93	775	1841.4
4	30	93	775	1550
5	30	93	775	1550
6	30	92	766.6	1533.2
7	37	92	766.6	1256.7
8	40	91	758.3	1148.9
9	40	88	733.3	1111
10	40	88	733.3	1111
11	42	85	708.3	1011.8
12	45	83	691.6	922.1

To confirm the chemical and structural stability of the nanocatalyst during applied conditions, the recycled nanocatalyst was characterized by XRD, ICP, EDX mapping and SEM techniques.

New Journal of Chemistry Accepted Manuscript

As shown in Figure 10, the appearance of crystal plates of 220, 311, 400, 422, 511 and 440 in the X-ray pattern, clearly confirms that the crystalline structure of the magnetic iron oxide nanoparticles has been preserved during applied conditions.

Figure 10. PXRD pattern of the recovered Fe₃O₄@MCM-41-SB/Pd nanocatalyst

As can be seen from the Figure 11, the EDX analysis of recovered nanocatalyst demonstrates the signals of Fe, Si, C, N, O and Pd elements in a pattern the same as its fresh parent proving high stability of the catalyst after several steps of recovery and reuse. According to this and also ICP analysis, the amount of Pd-leaching on the Fe₃O₄@MCM-41-SB nanostructure was negligible.

Figure 11. The EDX analysis of the recoverd Fe₃O₄@MCM-41-SB/Pd nanocatalyst

Moreover, the EDX mapping analysis confirmed the uniform distribution of aforementioned elements onto/into material network (Figure 12).

palsilang page 1

Figure 12. The EDX mapping of the recoverd Fe₃O₄@MCM-41-SB/Pd nanocatalyst

The SEM image of the recovered nanocatalyst also demonstrated a uniform spherical structure the same as its fresh parent confirming high stability of material structure during applied conditions (Figure 13).

New Journal of Chemistry Accepted Manuscript

Figure 13. The SEM image of the recovered Fe₃O₄@MCM-41-SB/Pd nanocatalyst

In the next study, a filtration test was carried out to prove the heterogeneity of the catalyst. For this purpose, after the development of about 40% of the coupling process, the catalyst was removed using a magnetic field and the progress of the residue mixture was monitored. Interestingly, no further conversion was observed in this case. Accordingly, we conclude that the catalyst operates in a heterogeneous manner and no leaching of active palladium species performs under applied conditions.

The mechanism of this reaction is presented in Scheme 2. The first step includes insertion and oxidative addition of Pd (0) into C-X bond of aryl halide to give intermediate **1**. Subsequently, the intermediate **2** is delivered through a transmetalation process. In the final step, a reductive elimination reaction is occurred to regenerate the catalyst and produce Suzuki cross-coupling product.^{75, 76}

41-SB/Pd

Bublished an GLFebruary 2020 Rowalowded by Universite Barks Descartes on 2/11/2020 12:22:32 PM. 2 9 5 4 8 7 1 0 6 8 2 9 5 7 0 0

Poisoning test is another technique that was performed to prove the heterogeneity of our catalytic system. According to the results of Table 4, our catalyst kept up its relative activity in the presence of all poisonous agents (Hg, PPh₃ and PMO-IL-propyl-SH), in which the model reaction showed a good yield. These results confirm that the Fe₃O₄@MCM-41-SB/Pd catalyst is stable under applied conditions and amount of Pd-leaching on the designed support is negligible.

Table 4. The effect of poisoning agents in the activity of Fe ₃ O ₄ @MCM-41-SB/Pd				
I B(OH) ₂	Fe ₃ O ₄ @MCM-41@SB/Pd (0.12 mo			
	K ₂ CO ₃ , 50 °C, H ₂ O,)))			
Entry	Poisoning additive	Yield (%)		
1	Free poisoning additive	95		
2	Hg	88		
3	PPh ₃	92		
4	PMO-IL-propyl-SH	91		

At the end of this study, we compared the efficiency of $Fe_3O_4@MCM-41-SB/Pd$ catalyst with some of the catalysts used recently in the Suzuki reaction. According to Table 5, $Fe_3O_4@MCM-$ 41-SB/Pd nanocatalyst is more favorable than the other catalysts in terms of temperature, TOF, reaction time and recycling times. These findings confirm high efficiency, stability and durability of designed catalyst.

Table 5. Comparative study of the efficiency of our catalyst with that of previously reported					
catalytic systems in Suzuki cross-coupling reaction					
$ \overset{\text{Br}}{\longleftarrow} + \overset{\text{B(OH)}_2}{\longrightarrow} \checkmark \checkmark$					
Catalyst	Conditions	Time	Recovery times	TOF (h ⁻¹)	Ref.
MNP-CD-Pd	Cat. 0.03 mol %, reflux, H ₂ O, K ₂ CO ₃	4 h	6	591.6	77
IL@SBA-15-Pd	Cat. 0.05 mol %, 60 °C, H ₂ O, K ₃ PO ₄ , TBAB	4 h	4	500	78
Mag-IL-Pd	Cat. 0.025 mol %, 60 °C, H ₂ O, K ₃ PO ₄	7.5 h	10	633.3	62
KCC-1-NH ₂ /Pd	Cat. 0.5 mol %, 100 °C, EtOH/H ₂ O, K ₃ PO ₄	4 h	7	43	79
hollow Pd spheres	Cat. 0.015 mol %, reflux EtOH, K ₃ PO ₄	24 h	7	250	80
Fe ₃ O ₄ @MCM-41- SB/Pd	Cat. 0.12 mol %, 50 °C,))), H ₂ O, K ₂ CO ₃	40 min	11	1148.9	This work

4. Conclusion

In this work, a Schiff-base/palladium complex was covalently immobilized on a magnetic ordered mesoporous silica to form a novel $Fe_3O_4@MCM-41-SB/Pd$ nanocatalyst. The FT-IR, TG and EDX analyses clearly confirmed well immobilization of this complex onto material framework. The low angle PXRD analysis showed a highly ordered two-dimensional hexagonal mesostructure for this material. The crystalline structure of magnetic NPs was confirmed by the wide angle PXRD technique. The VSM analysis showed good magnetic properties for the nanocatalyst. The SEM image illustrated a uniform spherical morphology for this nanocatalyst. The performance and activity of the $Fe_3O_4@MCM-41-SB/Pd$ nanocatalyst were examined in the Suzuki coupling reaction to produce biaryl compounds in water as green solvent. This catalyst demonstrated high efficiency and selectivity in the desired reaction. The $Fe_3O_4@MCM-41-SB/Pd$ was recycled and reused for several times with no noticeable decrease in performance.

Datisited (

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

The authors thank the Yasouj University and the Iran National Science Foundation (INSF) for supporting this work.

References

9

84

balsile 100

<u>ج</u>7

38

39

40 41

42

43

44

45

46

47

48

49 50

51

52

53

54

55

- 1 S. Joshi, I. Ghosh, S. Pokhrel, L. Mädler and W. M. Nau, *ACS nano*, 2012, **6**, 5668-5679.
- 2 J. Hou, H. Liu, L. Wang, L. Duan, S. Li and X. Wang, *Environ. Sci. Technol.*, 2018, **52**, 7996-8004.
- 3 R. N. Baig and R. S. Varma, *Chem. Commun.*, 2013, **49**, 752-770.
- 4 R. Liu, L. Chi, X. Wang, Y. Sui, Y. Wang and H. Arandiyan, J. Environ. Chem. Eng., 2018.
- 5 A. Sabareeswaran, E. B. Ansar, P. R. V. H. Varma, P. V. Mohanan and T. V. Kumary, *Nanomedicine*, 2016, **12**, 1523-1533.
- 6 D. Ling, N. Lee and T. Hyeon, Acc. Chem. Res., 2015, 48, 1276-1285.
- Y. Kazemzadeh, S. E. Eshraghi, M. Riazi and S. Zendehboudi, *J. of Supercritical Fluids*, 2018, 135, 1 7.
- 8 C. Kaweeteerawat, A. Ivask, R. Liu, H. Zhang, C. H. Chang, C. Low-Kam, H. Fischer, Z. Ji, S. Pokhrel and Y. Cohen, *Environ. Sci. Technol.*, 2015, **49**, 1105-1112.
- 9 J. Lee, J. C. Park and H. Song, *Adv. Mater.*, 2008, **20**, 1523-1528.
- 10 C. A. Falaschetti, T. Paunesku, J. Kurepa, D. Nanavati, S. S. Chou, M. De, M. Song, J.-t. Jang, A. Wu and V. P. Dravid, *ACS nano*, 2013, **7**, 7759-7772.
- 11 Y. J. Hong, M. Y. Son and Y. C. Kang, *Adv. Mater.*, 2013, **25**, 2279-2283.
- 12 H.-L. Jiang, T. Akita, T. Ishida, M. Haruta and Q. Xu, J. Am. Chem. Soc., 2011, **133**, 1304-1306.
- S. Rostamnia, B. Zeynizadeh, E. Doustkhah, A. Baghban and K. O. Aghbash, *Catal. Commun.*, 2015, 68, 77-83.
- J. Xu, X. Shen, L. Jia, Z. Ge, D. Zhou, Y. Yang, T. Ma, Y. Luo and T. Zhu, ACS Biomater. Sci. Eng., 2018,
 5, 996-1004.
- 15 Y. Hu, S. Mignani, J.-P. Majoral, M. Shen and X. Shi, *Chem. Soc. Rev.*, 2018, **47**, 1874-1900.
- 16 W. Wu, C. Z. Jiang and V. A. Roy, *Nanoscale*, 2016, **8**, 19421-19474.
- 17 D. C. Bock, C. J. Pelliccione, W. Zhang, J. Timoshenko, K. Knehr, A. C. West, F. Wang, Y. Li, A. I. Frenkel and E. S. Takeuchi, *Phys. Chem. Chem. Phys.*, 2017, **19**, 20867-20880.
- 18 X. Zhang, Z. Hu, X. Xiao, L. Sun, S. Han, D. Chen and X. Liu, *New J. Chem.*, 2015, **39**, 3435-3443.
- 19 Y. Hu, Y. Zhou, N. Zhao, F. Liu and F. J. Xu, *Small*, 2016, **12**, 2459-2468.
- H. Cai, K. Li, J. Li, S. Wen, Q. Chen, M. Shen, L. Zheng, G. Zhang and X. Shi, Small, 2015, 11, 4584 4593.
- 21 Y. Zhu, T. Ikoma, N. Hanagata and S. Kaskel, *Small*, 2010, **6**, 471-478.
- 22 N. Lee, H. R. Cho, M. H. Oh, S. H. Lee, K. Kim, B. H. Kim, K. Shin, T.-Y. Ahn, J. W. Choi and Y.-W. Kim, *J. Am. Chem. Soc.*, 2012, **134**, 10309-10312.
- 23 Y.-w. Jun, Y.-M. Huh, J.-s. Choi, J.-H. Lee, H.-T. Song, S. Kim, S. Kim, S. Yoon, K.-S. Kim and J.-S. Shin, J. Am. Chem. Soc., 2005, **127**, 5732-5733.
- 24 J. E. Lee, N. Lee, H. Kim, J. Kim, S. H. Choi, J. H. Kim, T. Kim, I. C. Song, S. P. Park and W. K. Moon, J. Am. Chem. Soc., 2009, **132**, 552-557.
- T. Zhu, X. Ma, R. Chen, Z. Ge, J. Xu, X. Shen, L. Jia, T. Zhou, Y. Luo and T. Ma, *Biomater. Sci.*, 2017, 5, 1090-1100.
- 26 S. Capone, M. Manera, A. Taurino, P. Siciliano, R. Rella, S. Luby, M. Benkovicova, P. Siffalovic and E. Majkova, *Langmuir*, 2014, **30**, 1190-1197.
- 27 M. S. Lin and H. J. Leu, *Electroanalysis*, 2005, **17**, 2068-2073.
- 28 C. Yu, L. Gou, X. Zhou, N. Bao and H. Gu, *Electrochim. Acta*, 2011, **56**, 9056-9063.
- 57 58 59
- 60

29 30 31 32 33 34 35 36	 J. Xu, XK. Shen, L. Jia, JL. Cao, Y. Wang, XL. Zhao, N. Bi, SL. Guo and TY. Ma, <i>J. Mater. Chem.</i> <i>B</i>, 2019, 7, 734-743. B. D. Plouffe, S. K. Murthy and L. H. Lewis, <i>Rep. Prog. Phys.</i>, 2014, 78, 016601. T. Guo, X. Bian and C. Yang, <i>Physica A</i>, 2015, 438, 560-567. R. Hong, T. Pan, Y. Han, H. Li, J. Ding and S. Han, <i>J. Magn. Magn. Mater.</i>, 2007, 310, 37-47. J. Safari and Z. Zarnegar, <i>J. Mol. Catal. A: Chem.</i>, 2013, 379, 269-276. T. Zeng, L. Yang, R. Hudson, G. Song, A. R. Moores and CJ. Li, <i>Org. Lett.</i>, 2010, 13, 442-445. X. Y. Chen, B. H. Liu and Z. P. Li, <i>Solid State Ion.</i>, 2014, 261, 45-52. B. Kakavandi, A. Takdastan, N. Jaafarzadeh, M. Azizi, A. Mirzaei and A. Azari, <i>J. Photochem.</i>
30 31 32 33 34 35 36	 B. D. Plouffe, S. K. Murthy and L. H. Lewis, <i>Rep. Prog. Phys.</i>, 2014, 78, 016601. T. Guo, X. Bian and C. Yang, <i>Physica A</i>, 2015, 438, 560-567. R. Hong, T. Pan, Y. Han, H. Li, J. Ding and S. Han, <i>J. Magn. Magn. Mater.</i>, 2007, 310, 37-47. J. Safari and Z. Zarnegar, <i>J. Mol. Catal. A: Chem.</i>, 2013, 379, 269-276. T. Zeng, L. Yang, R. Hudson, G. Song, A. R. Moores and CJ. Li, <i>Org. Lett.</i>, 2010, 13, 442-445. X. Y. Chen, B. H. Liu and Z. P. Li, <i>Solid State Ion.</i>, 2014, 261, 45-52. B. Kakavandi, A. Takdastan, N. Jaafarzadeh, M. Azizi, A. Mirzaei and A. Azari, <i>J. Photochem.</i>
31 32 33 34 35 36	 T. Guo, X. Bian and C. Yang, <i>Physica A</i>, 2015, 438, 560-567. R. Hong, T. Pan, Y. Han, H. Li, J. Ding and S. Han, <i>J. Magn. Magn. Mater.</i>, 2007, 310, 37-47. J. Safari and Z. Zarnegar, <i>J. Mol. Catal. A: Chem.</i>, 2013, 379, 269-276. T. Zeng, L. Yang, R. Hudson, G. Song, A. R. Moores and CJ. Li, <i>Org. Lett.</i>, 2010, 13, 442-445. X. Y. Chen, B. H. Liu and Z. P. Li, <i>Solid State Ion.</i>, 2014, 261, 45-52. B. Kakavandi, A. Takdastan, N. Jaafarzadeh, M. Azizi, A. Mirzaei and A. Azari, <i>J. Photochem.</i>
32 33 34 35 36	 R. Hong, T. Pan, Y. Han, H. Li, J. Ding and S. Han, <i>J. Magn. Magn. Mater.</i>, 2007, 310, 37-47. J. Safari and Z. Zarnegar, <i>J. Mol. Catal. A: Chem.</i>, 2013, 379, 269-276. T. Zeng, L. Yang, R. Hudson, G. Song, A. R. Moores and CJ. Li, <i>Org. Lett.</i>, 2010, 13, 442-445. X. Y. Chen, B. H. Liu and Z. P. Li, <i>Solid State Ion.</i>, 2014, 261, 45-52. B. Kakavandi, A. Takdastan, N. Jaafarzadeh, M. Azizi, A. Mirzaei and A. Azari, <i>J. Photochem.</i>
33 34 35 36	 J. Safari and Z. Zarnegar, <i>J. Mol. Catal. A: Chem.</i>, 2013, 379, 269-276. T. Zeng, L. Yang, R. Hudson, G. Song, A. R. Moores and CJ. Li, <i>Org. Lett.</i>, 2010, 13, 442-445. X. Y. Chen, B. H. Liu and Z. P. Li, <i>Solid State Ion.</i>, 2014, 261, 45-52. B. Kakavandi, A. Takdastan, N. Jaafarzadeh, M. Azizi, A. Mirzaei and A. Azari, <i>J. Photochem</i>.
34 35 36	 T. Zeng, L. Yang, R. Hudson, G. Song, A. R. Moores and CJ. Li, <i>Org. Lett.</i>, 2010, 13, 442-445. X. Y. Chen, B. H. Liu and Z. P. Li, <i>Solid State Ion.</i>, 2014, 261, 45-52. B. Kakavandi, A. Takdastan, N. Jaafarzadeh, M. Azizi, A. Mirzaei and A. Azari, <i>J. Photochem.</i>
35 36	X. Y. Chen, B. H. Liu and Z. P. Li, <i>Solid State Ion.</i> , 2014, 261 , 45-52. B. Kakavandi, A. Takdastan, N. Jaafarzadeh, M. Azizi, A. Mirzaei and A. Azari, <i>J. Photochem</i> .
36	B. Kakavandi, A. Takdastan, N. Jaafarzadeh, M. Azizi, A. Mirzaei and A. Azari, <i>J. Photochem.</i>
	Dhatahial A: Cham 2016 211 179 199
37	Z. Y. Ma, D. Dosev, M. Nichkova, S. J. Gee, B. D. Hammock and I. M. Kennedy, J. Mater. Chem.,
38	2009, 19 , 4695-4700. C. Mi, J. Zhang, H. Gao, X. Wu, M. Wang, Y. Wu, Y. Di, Z. Xu, C. Mao and S. Xu, <i>Nanoscale</i> , 2010, 2 ,
	1141-1148.
39	J. Li, L. Zheng, H. Cai, W. Sun, M. Shen, G. Zhang and X. Shi, ACS Appl. Mater. Interfaces, 2013, 5, 10357-10366.
40	C. Hui, C. Shen, J. Tian, L. Bao, H. Ding, C. Li, Y. Tian, X. Shi and HJ. Gao, <i>Nanoscale</i> , 2011, 3 , 701- 705
41	H. Yang, Q. Hou, S. Wang, D. Guo, G. Hu, Y. Xu, J. Tai, X. Wu, D. Yu and J. Wang, <i>Chem. Commun.</i> ,
10	2010, 54 , 10075-10002. D. Lowandowski M. Cogłowski M. Smoluch E. Boszko, J. Silberring and C. Schroeder, <i>Microper</i>
42	Mesopor. Mat., 2017, 240 , 80-90.
43	L. Xiong, J. Bi, Y. Tang and S. Z. Qiao, <i>Small</i> , 2016, 12 , 4735-4742.
44	H. Matsushita, S. Mizukami, F. Sugihara, Y. Nakanishi, Y. Yoshioka and K. Kikuchi, Angew. Chem.,
	2014, 126 , 1026-1029.
45	J. Kim, H. S. Kim, N. Lee, T. Kim, H. Kim, T. Yu, I. C. Song, W. K. Moon and T. Hyeon, <i>Angew. Chem.</i> , 2008, 120 , 8566-8569.
46	J. Liu, S. Z. Qiao, Q. H. Hu and G. Q. Lu. <i>Small</i> . 2011. 7 . 425-443.
47	J. Mondal, T. Sen and A. Bhaumik. <i>Dalton Trans.</i> , 2012, 41 , 6173-6181.
48	R. Mirbagheri, D. Elhamifar and M. Norouzi, <i>New J. Chem.</i> , 2018. 42 , 10741-10750.
49	M. Vahidian, D. Elhamifar and M. Shaker, <i>Polyhedron</i> , 2020, 178 , 114326.
50	M. Nevsi, A. Zarnegarvan and D. Elhamifar. New J. Chem., 2019. 43, 12283-12291.
51	R. K. Das, A. Pramanik, M. Maihi and S. Mohapatra, <i>Langmuir</i> , 2018, 34 , 5253-5262.
52	X Cheng H Zhao W Huang I Chen S Wang I-P Dong and Y Deng <i>Janamuir</i> 2018
53	D. Patiño-Ruiz, L. Sanchez-Botero, I. Hinestroza and A. Herrera. <i>Phys. Status Solidi</i> , 2018, 1800266.
54	Y Deng D Oi C Deng X Zhang and D Zhao J Am Chem Soc 2008 130 28-29
55	H. Qiu, B. Cui, G. Li, J. Yang, H. Peng, Y. Wang, N. Li, R. Gao, Z. Chang and Y. Wang, <i>J. Phys. Chem.</i>
ГС	C, 2014, 110 , 14929-14937.
50	Y. Chen, H. Chen, D. Zeng, Y. Han, F. Chen, J. Feng and J. Shi, ACS <i>Julio</i> , 2010, 4, 6001-6013.
57	W. Zildo, B. Cul, H. Pelig, H. Qiu aliu Y. Walig, J. Phys. Chem. 4, 2015, 119 , 4579-4580.
58	J. LI, H. Jiang, Z. Yu, H. Xia, G. Zou, Q. Zhang and Y. Yu, <i>Chem.: Asian J.</i> , 2013, 8 , 385-391.
59	L. Cul, H. Lin, C. Yang, X. Han, T. Zhang and F. Qu, <i>Eur. J. Inorg. Chem.</i> , 2014, 2014 , 6156-6164.
60	Q. Liang, P. Xing, Z. Huang, J. Dong, K. B. Snarpiess, X. Li and B. Jiang, <i>Org. Lett.</i> , 2015, 17 , 1942- 1945.
61	A. K. Rathi, M. B. Gawande, J. Pechousek, J. Tucek, C. Aparicio, M. Petr, O. Tomanec, R. Krikavova,
	Z. Travnicek and R. S. Varma, Green Chem., 2016, 18 , 2363-2373.
62	B. Karimi, F. Mansouri and H. Vali, Green Chem., 2014, 16, 2587-2596.

- 63 L. Jia, T. Zhou, J. Xu, F. Li, Z. Xu, B. Zhang, S. Guo, X. Shen and W. Zhang, *Nanomaterials*, 2017, **7**, 333.
- L. Jia, W. Zhang, J. Xu, J. Cao, Z. Xu and Y. Wang, *Nanomaterials*, 2018, **8**, 409.
- 65 Q. Deng, Y. Shen, H. Zhu and T. Tu, *Chem. Commun.*, 2017, **53**, 13063-13066.
- 66 F. Heidari, M. Hekmati and H. Veisi, J. Colloid Interface Sci., 2017, 501, 175-184.
- 67 H. Veisi, J. Gholami, H. Ueda, P. Mohammadi and M. Noroozi, *J. Mol. Catal. A: Chem.*, 2015, **396**, 216-223.
- A. Pourjavadi, A. Motamedi, Z. Marvdashti and S. H. Hosseini, *Catal. Commun.*, 2017, **97**, 27-31.
- 69 Y. S. Kang, S. Risbud, J. F. Rabolt and P. Stroeve, *Chem. Mater.*, 1996, **8**, 2209-2211.
- 70 X. Dong, X. Zhang, P. Wu, Y. Zhang, B. Liu, H. Hu and G. Xue, *ChemCatChem*, 2016, **8**, 3680-3687.
- 71 W. Feng, H. Dong, L. Niu, X. Wen, L. Huo and G. Bai, *J. Mater. Chem. A*, 2015, **3**, 19807-19814.
- 72 M. Norouzi and D. Elhamifar, *Compos. B. Eng.*, 2019, **176**, 107308.

4

5

6

7

8

9

- 73 S. Abaeezadeh, D. Elhamifar, M. Norouzi and M. Shaker, *Appl. Organomet. Chem.*, 2019, **33**, e4862.
- R. Mirbagheri and D. Elhamifar, J. Alloys Compd., 2019, **790**, 783-791.
- 75 A. J. Lennox and G. C. Lloyd-Jones, *Chem. Soc. Rev.*, 2014, **43**, 412-443.
- A. R. Hajipour, K. Karami and A. Pirisedigh, *Inorganica Chim. Acta*, 2011, **370**, 531-535.
- 77 H. Salemi, B. Kaboudin, F. Kazemi and T. Yokomatsu, *RSC Adv.*, 2016, **6**, 52656-52664.
- 78 B. Karimi and A. Zamani, *Org. Biomol. Chem.*, 2012, **10**, 4531-4536.
- A. Fihri, D. Cha, M. Bouhrara, N. Almana and V. Polshettiwar, *ChemSusChem*, 2012, **5**, 85-89.
- 80 S.-W. Kim, M. Kim, W. Y. Lee and T. Hyeon, *J. Am. Chem. Soc.*, 2002, **124**, 7642-7643.

Graphical abstract

Preparation, characterization and catalytic application of a novel magnetic ordered mesoporous silica supported Schiff-base/Pd (Fe₃O₄@MCM-41-SB/Pd) are developed.

