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Synthesis and Characterization of Pd Schiff Base Complex Immobilized onto Functionalized Nanoporous MCM-41 and its Catalytic Efficacy in the Suzuki, Heck and Stille Coupling Reactions

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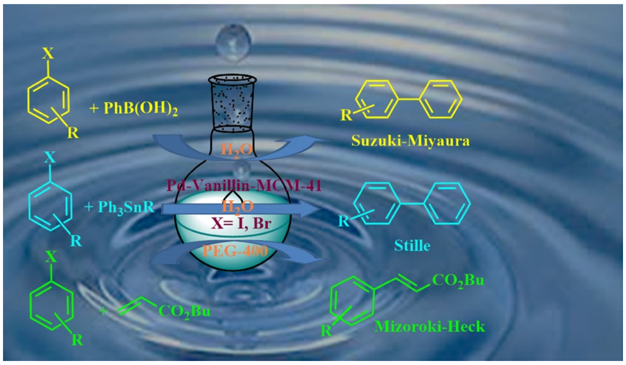
Abstract The present work describes the use of palladium-vanillin-Schiff-base complex immobilized on MCM-41 nanostructure as efficient catalyst for the Suzuki–Miyaura, Stille and Mizoroki–Heck reactions of several aryl halides under aerobic conditions. All the reactions were carried out in green solvents (H_2O and PEG-400). The developed procedure results bring several benefits such as uses of inexpensive and non-toxic ligand (vanillin), easy catalyst/product separation and catalyst recycling. The catalyst can be reused at least for five consecutive cycles without a significant loss of its catalytic activity or metal leaching.

Graphical Abstract



Keywords Suzuki · Heck · Stille · Cross coupling reactions · Mesoporous silica · Vanillin Palladium

1 Introduction

The synthesis of biaryl compounds, using the Heck, Stille and Suzuki–Miyaura reaction methods catalyzed by palladium complex have been recognized as a powerful synthetic tools and a major area of interest in multiple organic transformations for academic and industrial process including the pharmaceuticals, polymers and fabrication of herbicides [1–10]. The products of the latter reaction have been used for the synthesis of natural products, agrochemicals, several intermediates in pharmaceutical and fine chemicals. For example, the synthesis of taxol, one of active anticancer drugs, involves an intramolecular Heck reaction [11]. The use of Schiff base complexes containing transition metal ions is of significant importance due to their catalytic and biological properties [12, 13]. As a catalyst, Pd is very important in the pharmaceutical industry; however, this metal is expensive and cannot be separated from the reaction media efficiently. Therefore, to reduce the presence of Pd in the product solution, immobilization of Pd-catalysts onto a solid support allows formation of heterogeneous catalyst with decreased of Pd leaching into solution and improves the stability of the catalyst [14]. There are several reports of Pd-nanocatalyst immobilized on solid supports, such as zeolites [15], carbon [16], metal oxides [17, 18], polymers [19], graphite oxide [20] and mesoporous silica [21] for C–C coupling reactions. Current research focuses on the synthesis and application of modified mesoporous MCM-41 materials, which have an active species attached to the framework via host–guest interactions, creating discrete and uniform catalyst sites on the inner walls of the porous systems [22]. MCM-41 has a hexagonal arrangement of one-dimensional mesoporous with diameters ranging from 2 to 10 nm [23] and exhibits unique properties like high surface area, homogeneity of the pores, tunable and

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accessible pores. Likewise, When metal complexes immobilized onto surface of modified MCM-41, due to the stability of the metal complex, it is presumed that the metal will remain in its immobilized state when anchored to a support prior to reaction making it be less likely to leach into solution. Hence, MCM-41 has been focused in several research areas such as nanoscience [24], environmental purification [25], catalysis [26], drug delivery [27] and absorption [28]. The Pd immobilized on MCM-41 can be used as a catalyst for Suzuki–Miyaura and Stille cross-coupling reaction of aryl halides with phenylbronic acide or Ph_3SnCl in water and Mizoroki–Heck reaction with aryl halides and n-butyl acrylate in PEG-400 under thermal conditions. The catalytic system used here has several advantages like it is stable in air and moisture and the reaction can be done under environmentally benign conditions. Vanillin (4-Hydroxy-3-methoxybenzaldehyde), an aromatic flavor compound, is one of the most commonly used food flavoring agents and is extracted from pods of Vanilla planifolia. It holds tremendous industrial applications in food, pharmaceuticals, beverages, perfumes and as nutraceuticals. In this paper, we report synthesis and characterization of a Pd-vanillin Schiff base complex supported on functionalized nanostructured MCM-41 (Pd-Vanillin-MCM-41), which has been applied as a novel and efficient catalyst with excellent catalytic activity and stereoselectivity in C–C cross coupling reactions in green solvents.

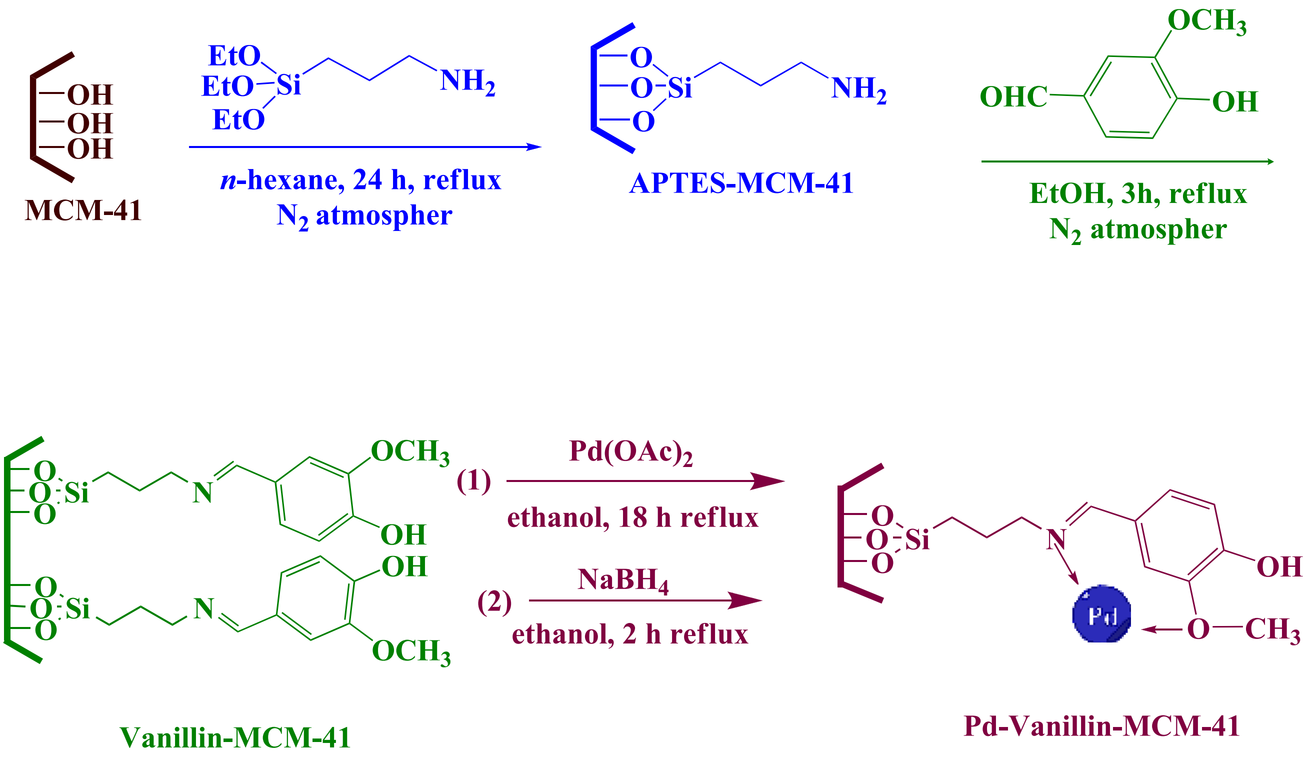
2 Experimental

2.1 Materials

The cationic surfactant cetyltrimethylammonium bromide (CTAB, 98%), tetraethylorthosilicate (TEOS, 98%), solvents and other materials were purchased from Merck, Aldrich or Fluka companies and used as received.

2.2 Techniques

IR (KBr) and Powder X-ray diffraction (PXRD) were recorded using a NICOLET impact 410 spectrometer and a Philips diffractometer with Co Kα radiation at 40 kV and 30 mA, respectively. The particle size and morphology were performed by a JEOLJEM-2010 scanning electron microscopy (SEM), on an accelerating voltage of 200 kV. The products component measurement was carried out by the energy dispersive spectroscopy (EDS) using a Tacnai TF20 high-resolution transmission electron microscope. Also, the content of Pd was measured by



Scheme 1 Schematic representation of the synthesis heterogeneous catalyst of Pd-Vanillin-MCM-41

inductively coupled plasma-optical emission spectrometry (ICP-OES). The thermogravimetric analysis (TGA) curves were collected using a PL-STA 1500 device manufactured by Thermal Sciences. The textural properties of the synthesized samples were evaluated by N_2 sorption–desorption technique (NOVA 1000). ^{1}H NMR spectra was recorded on a Bruker AVANCE300 spectrometer operating at 300.0 MHz. Melting point was measured with an Electrothermal 9100 apparatus.

2.3 Synthesis of MCM-41 Modified with (3-Aminopropyl)-triethoxysilane

To a mixture of NaOH solution (2 M) and deionized water (480 mL), 1 g of cetyltrimethyl ammonium bromide (CTAB) was added. Then, 5 mL tetraethylorthosilicate (TEOS) was continuously added and stirred at 80 °C. The resulting mixture was refluxed at the same temperature for another 2 h. The obtained product was washed with deionized water. MCM-41 was activated by heating at 70 °C in an oven for 20 °C. The resulting white product calcined at 823 K for 5 h with rate of 2 °C/min to remove the residual surfactant. Functionalization of MCM-41 was performed by refluxing 4.8 g of MCM-41 with 4.8 g of 3-aminopropyltriethoxysilane (3-APTES) in *n*-hexane under nitrogen atmosphere for 24 h. The resulting white solid of the functionalized MCM-41 (APTES-MCM-41) was filtered, washed with *n*-hexane and dried under vacuum.

2.4 Preparation of Heterogeneous Pd- Schiff Base Complex Grafted in Mesoporous Silica MCM-41 (Pd-Vanillin-MCM-41)

For the preparation of vanillin-MCM-41, 0.5 g APTES-MCM-41 and vanillin (0.182 g, 1.2 mmol) in ethanol was refluxed under N_2 atmosphere for 3 h. The resulting solid was washed with ethanol, collected by filtration and dried under vacuum and designated as vanillin-MCM-41. Ultimately, the Pd-Vanillin-MCM-41 was prepared by refluxing of $Pd(OAc)_2$ (0.168 g, 0.63 mmol) with 0.250 g vanillin-MCM-41 in ethanol (20 mL) for 18 h. For the reduction of Pd(II) present in the resulting catalyst, $NaBH_4$ (0.022 g, 0.057 mmol) was added and then refluxed for 2 h under the same conditions. The resulting black solid impregnated with the metal complex was filtered and washed with ethanol to give the grey Pd(0) complex. The detailed preparation route for Pd-Vanillin-MCM-41 is shown in Scheme 1.

2.5 General Procedure for the Synthesis of Biphenyl Derivatives

A mixture of aryl halide (1.0 mmol), $PhB(OH)_2$ or Ph_3SnCl (0.5 mmol), base (3 mmol) and Pd-Vanillin-MCM-41 were stirred in water at 80 °C for an appropriate time. The progress of reaction was monitored by TLC (eluent; *n*-hexane/acetone, 8:2). After completion of the reaction, the solution was allowed to cool to room temperature and was subsequently extracted with diethyl ether. Hereon, the pure product was obtained.

2.6 General Procedure for the Synthesis of Butyl Cinnamate Derivatives

The general protocol for Heck coupling reaction is described as follows: Aryl halide (1 mmol), butyl acrylate (1.2 mmol), base (3 mmol), and PEG-400 (3 mL) were added to a 25 mL round-bottom flask. After adding Pd-Vanillin-MCM-41 (4 mg, 0.71 mol %) catalyst, the reaction mixture was stirred at 120 °C for an appropriate time. After completion of the reaction [monitored by TLC (*n*-hexane/acetone, 8:2)], the catalyst was filtered off and the reaction mixture was separated with diethyl ether and water. After evaporation of the diethyl ether, the product was obtained.

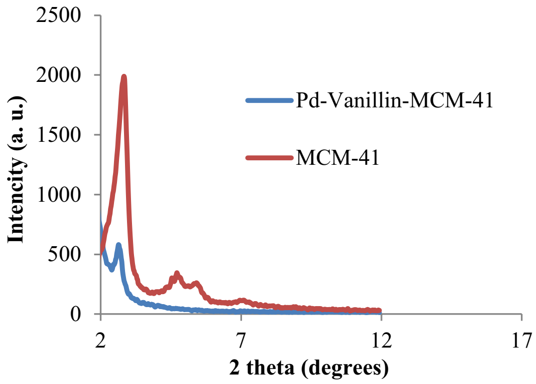


Fig. 1 Small angle XRD patterns of: MCM-41 and Pd-Vanillin-MCM-41

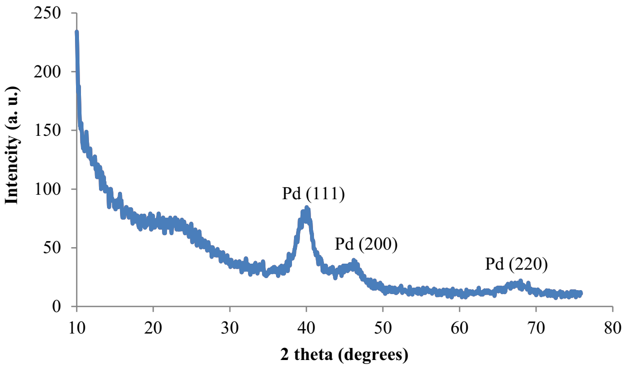


Fig. 2 XRD pattern of Pd-Vanillin-MCM-41 at high degree 2θ

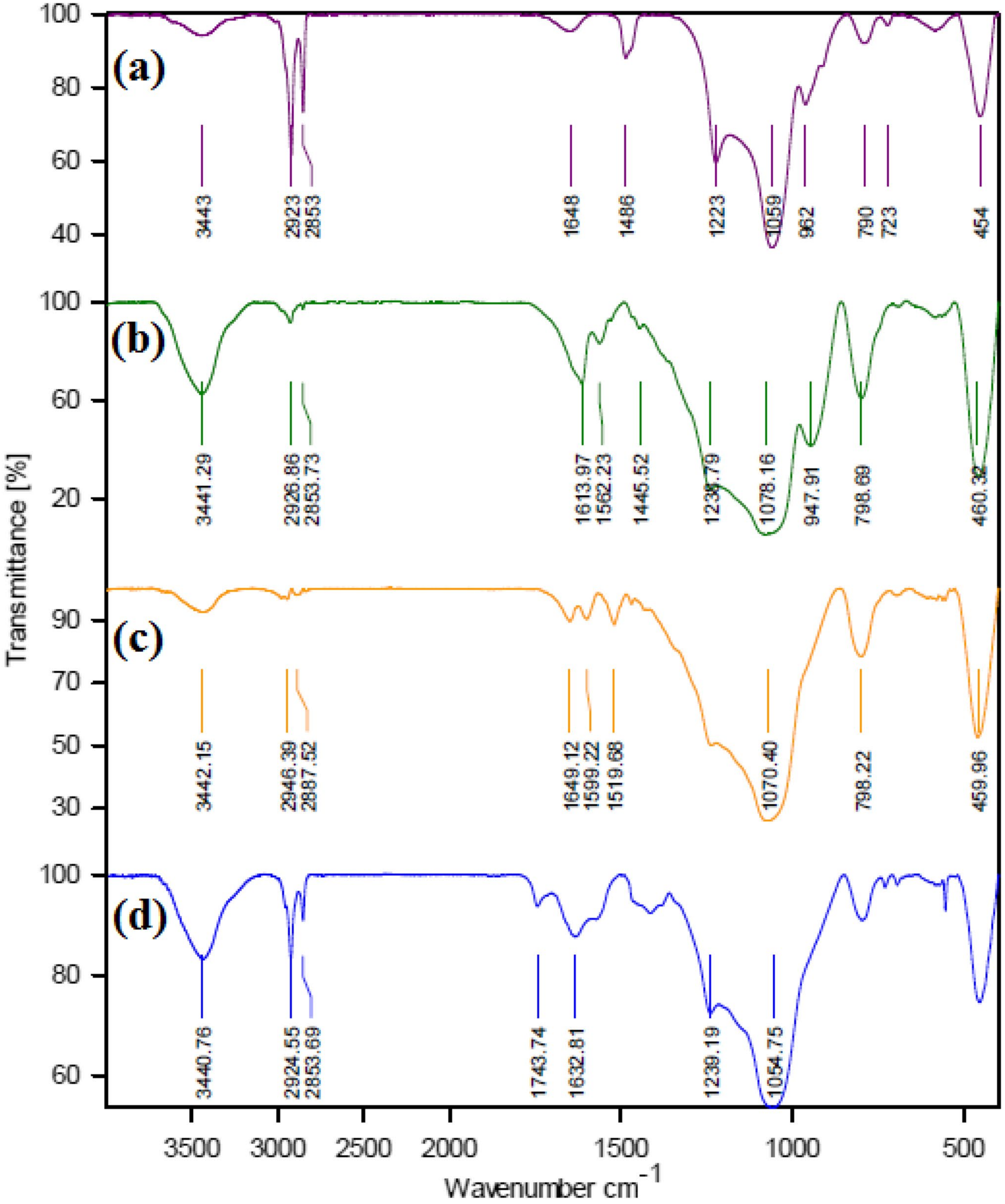


Fig. 3 FT-IR spectra of, *a* MCM-41, *b* APTES-MCM-41, *c* Vanillin-MCM-41 and *d* Pd-Vanillin-MCM-41

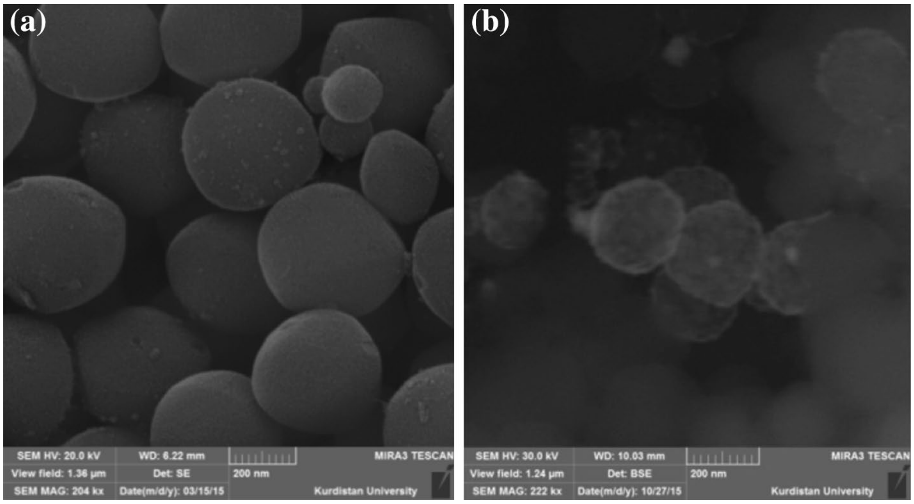


Fig. 4 SEM images of, **a** MCM-41 and **b** Pd-Vanillin-MCM-41

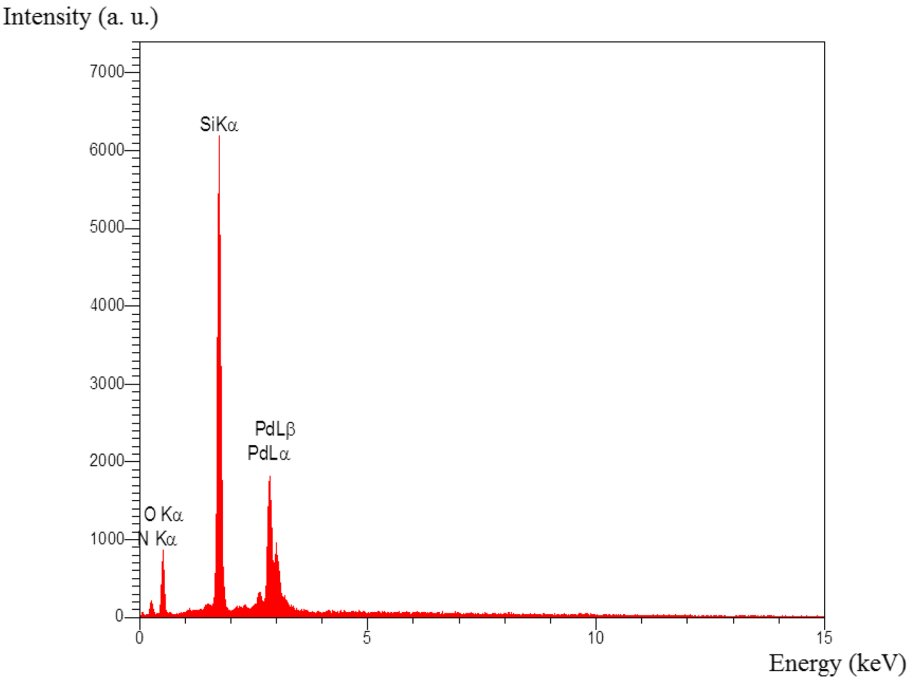


Fig. 5 The EDS spectrum of Pd-Vanillin-MCM-41

2.7 Selected Spectral Data

1,1′-Biphenyl (Table 3, entry 1): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.41–7.37$ (tt, $J = 7.6$, 1.2 Hz, 2 H), 7.50–7.40 (m, 4 H), $\delta_H =$ 7.64–7.62 (m, 4 H) ppm.

4-Methoxy-1,1′-biphenyl (Table 3, entry 4): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta_H = 3.88$ (s, 3 H), 7.03–7.0 (dt, $J = 8.8$, 2.4 Hz, 2 H), 7.35–7.31 (tt, $J = 7.6$, 1.2 Hz, 1 H), 7.46–7.41 (t, $J = 7.6$ Hz, 2 H), 7.60–7.55 (m, 4 H) ppm.

Butyl cinnamate (Table 7, entry 1): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta_H = 1.01–0.97$ (t, $J = 7.6$ Hz, 3 H), 1.50–1.44 (m, 2 H), 1.75–1.69 (m, 2 H), 4.25–4.22 (t, $J = 6.4$ Hz, 2 H), 6.50–6.46 (d, $J = 16$ Hz, 1 H), 7.43–7.40 (m, 3 H), 7.56–7.54 (m, 2 H), 7.74–7.70 (d, $J = 16$ Hz, 1 H) ppm.

Butyl 3-(4-methoxyphenyl)acrylate (Table 7, entry 4): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta_H = 1.01–0.97$ (t, $J = 7.6$ Hz, 3 H), 1.50–1.41 (sixt, $J = 8$ Hz, 2 H), 1.72–1.66 (quint, $J = 6.8$ Hz, 2 H), 3.85 (s, 3 H), 4.23–4.20 (t, $J = 6.4$ Hz, 2 H), 6.35–6.31 (d, $J = 16$ Hz, 1 H), 6.92–6.91 (d, $J = 7.2$ Hz, 2 H), 7.50–7.48 (d, $J = 6.8$ Hz, 2 H), 7.67–7.63 (d, $J = 15.6$ Hz, 1 H) ppm.

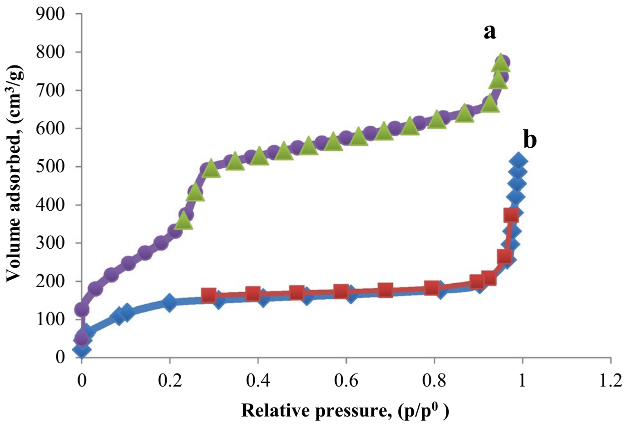


Fig. 6 Nitrogen adsorption–desorption isotherms for, **a** bulk MCM-41 and **b** Pd-Vanillin-MCM-41

Table 1 Textural parameters deduced from nitrogen sorption isotherms

Sample	S_{BET} (m^2/g)	Pore diam. by BJH method (nm)	Pore vol. (cm^3/g)
MCM-41	1372.27	2.45	1.521
Pd-Vanillin-MCM-41	464.18	1.21	0.6466

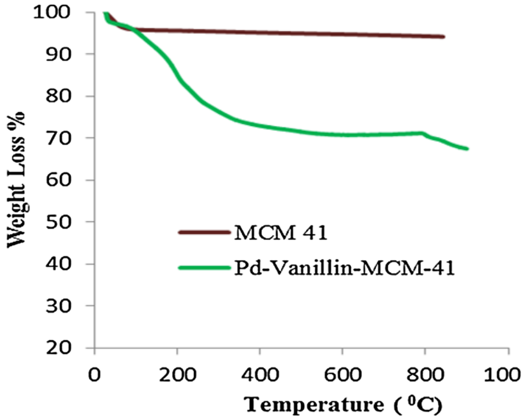


Fig. 7 TGA thermograms of MCM-41 and Pd-Vanillin-MCM-41

3 Result and Discussion

3.1 X-ray Diffraction

Figure 1 shows low-angle XRD patterns of the obtained MCM-41 and Pd-Vanillin-MCM-41. Three characteristic peaks $2\theta = 2.77$, 4.67 and 5.13 assigned to (100), (110) and (200) reflections were observed respectively for the MCM-41 sample. The intensities of the XRD peaks for Pd-Vanillin-MCM-41 are decreased insofar as for 110 and 200 reflections close to disappear in comparison with XRD peaks of MCM-41. These intensity decreases indicating that the palladium metal is highly dispersed on the inner channel pores of MCM-41 [22]. In order to prove that the Pd(0) is dispersed onto surface of MCM-41, the high angle XRD test was conducted. As shown in Fig. 2, in higher angle range three diffraction peaks can be observed at $2\theta = 39.51$, 45.65 and 66.57 corresponding to $d_{1\,1\,1}$, $d_{2\,0\,0}$ and $d_{2\,2\,0}$ planes respectively [29, 30]. These observations indicated that the Pd(0) is immobilized on the inner channel pores.

3.2 FT-IR Spectroscopy

Figure 3 shows the FT-IR spectra of the synthesized MCM-41, APTES-MCM-41, Vanillin-MCM-41 and Pd-Vanillin-MCM-41, respectively. For the MCM-41 sample (Fig. 3a) the peaks at 1059, 962 and 454 cm^{-1} corresponded to asymmetric stretching, symmetric stretching and bending vibrations of Si-O–Si respectively. The broad band at 3441 cm^{-1}, can be assigned to the hydrogen-bonding silanol groups and adsorbed water and the band about 2900 cm^{-1} is associated with the CH_2 vibrations corresponding to the C–H stretching (Fig. 3b). The appearance of the ν(C=N) (1649 cm^{-1}) and ν (C=C) (1519 cm^{-1}) bands support the formation of the Schiff base ligand and shows that amine groups of 4-hydroxy-3-methoxybenzaldehyde rings (vanillin) anchored onto MCM-41 (Fig. 3c). The band at 1599 cm^{-1} assigned to (NH_2) in the ligand is shifted towards 1632 cm^{-1} in the Pd-Vanillin-MCM-41 identified the Pd-ligand bond formation (Fig. 3d).

3.3 SEM, EDS and ICP-OES

Figure 4 shows the scanning electron microscopy (SEM) images of MCM-41 and Pd-Vanillin-MCM-41. This study showed the morphologies of the MCM-41 and Pd-Vanillin-MCM-41 are agglomerations of small spherical with uniform nanometre sized particles (Fig. 4). The energy dispersive spectrum (EDS) evidently shows the presence of Pd in the catalyst (Fig. 5). The ICP-OES results showed that the loading amount of Pd on Pd-Vanillin-MCM-41 was 1.77×10^{-3} mol/g.

3.4 N_2 Adsorption–Desorption Studies

Nitrogen adsorption–desorption isotherms of the prepared MCM-41 and Pd-Vanillin-MCM-41 show in Fig. 6. Pore volume, surface areas, and average pore size were calculated by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models. The BET data and

Table 2 Optimization of the solvent, base, temperature and concentration of catalyst for the synthesis of biphenyl in Suzuki reaction

Entry	Temperature (°C)	Solvent	Base (eq.)	Catalyst (mol%)	Time(min)	Yield[a]
1	80	H_2O	K_2CO_3	0	5 h	–[b]
2	80	H_2O	K_2CO_3	0.88	15	94
3	80	H_2O	K_2CO_3	0.71	15	94
4	80	H_2O	K_2CO_3	0.53	15	90
5	70	H_2O	K_2CO_3	0.71	15	90
6	60	H_2O	K_2CO_3	0.71	15	83
7	50	H_2O	K_2CO_3	0.71	15	66
8	25	H_2O	K_2CO_3	0.71	15	43
9	80	EtOH	K_2CO_3	0.71	15	56
10	80	1,4-dioxane	K_2CO_3	0.71	15	40
11	80	PEG-400	K_2CO_3	0.71	15	94
12	80	H_2O	Na_2CO_3	0.71	15	90
13	80	H_2O	KOH	0.71	15	30
14	80	H_2O	Et_3N	0.71	15	91
15	80	H_2O	$NaHCO_3$	0.71	15	93

Reaction conditions: Aryl halide (1 mmol), $PhB(OH)_2$ (1 mmol), base (3 mmol), solvent (3 mL). Reaction time was 15 min

[a] Isolated yield

[b] No reaction

BJH data of prepared materials are illustrated in Table 1. The original pore volume of 1.521 $cm^3\ g^{-1}$ and surface area of 1372 $m^2\ g^{-1}$ are reduced to 0.646 and 464 $m^2\ g^{-1}$, after increasing substance anchored on the surface of MCM-41. Hence, this decrease of surface areas, pore volume and average pore size of mesoporous materials were seen with incorporation of Pd nanoparticles in the framework of MCM-41 (Fig. 6b).

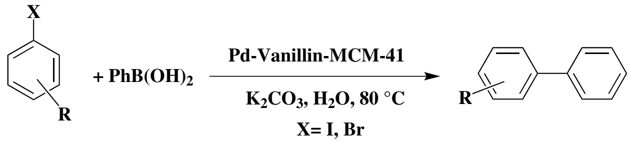
3.5 Thermogravimetric Analysis

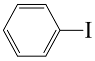
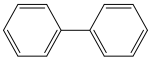
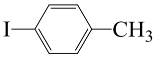
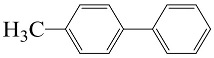
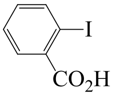
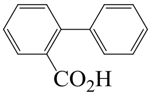
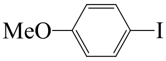
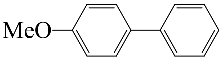
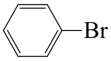
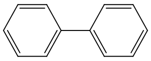
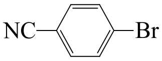
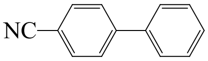
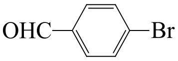
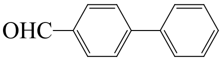
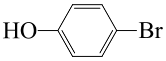
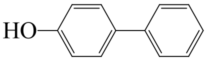
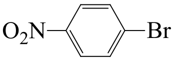
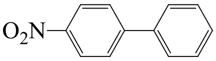
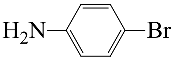
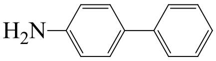
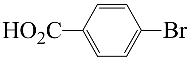
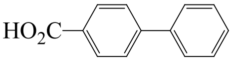
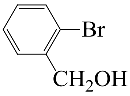
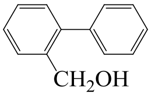
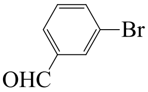
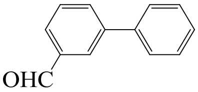
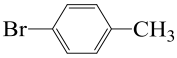
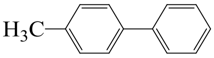
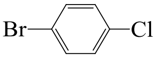
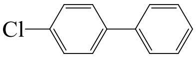
The thermogravimetric analysis (TGA) curves of MCM-41 and Pd-Vanillin-MCM-41 are shown in Fig. 7. The TGA of the synthesized MCM-41 shows 3% weight loss in one step at 25–100 °C due to desorption of water. Pd-Vanillin-MCM-41 sample showed several weight loss steps. A mass loss below 200 °C is due to the removal of physically adsorbed water and solvent inside the pores channels. Pd-Vanillin-MCM-41 showed the second step mass loss (25%) within the temperature range of 200–500 °C, which is chiefly related to the decomposition of organically modified framework. The third weight loss above 800 °C is likely associated with the decomposition of the silanol groups. As a result, TGA diagram of Pd-Vanillin-MCM-41 showed several steps of weight loss that confirmed the formation of Palladium Schiff-base complex.

In continuation of our investigations on different organic transformation [31–33], we were interested in finding a simple and efficient method for C–C cross coupling reactions via the reaction of phenylboronic acid or Ph_3SnCl with an aryl halide for synthesis of biphenyl derivatives and aryl halides with n-butyl acrylate in model of Heck reaction under the influence of Pd-Vanillin-MCM-41 as a non-toxic reusable and heterogeneous catalyst with short reaction times with good to excellent yields in green solvents under aerobic conditions.

At the onset of our work, the catalytic activity of complex was evaluated in Suzuki–Miyaura cross coupling reactions. For this propose the reaction between phenylboronic acid (1 mmol) and phenyl iodide (1 mmol) using K_2CO_3 as a base at 80 °C was chosen as model reaction. When the experiments were carried out in the absence of catalyst, the desired product was not achieved after 5 h (Table 2, entry 1). Thus, we tested different amount of catalyst (0.53, 0.71 and 0.88 mol%) (Table 2, entries 2–4). As shown in (Table 2, entry 3) the best amount of catalyst was found 4 mg (0.71 mol%) for this reaction. In the next step, the influence of temperature on conversion and product selectivity in the presence Pd-Vanillin-MCM-41 was examined. When reaction temperature was increased gradually from room temperature to 80 °C, the rate of the reaction increased (Table 2, entries 3, 5–8).

Table 3 C–C Coupling of aryl halides with phenylboronic acid in the presence of Pd-Vanillin-MCM-41 (4 mg, 0.71 mol%) in water at 80 °C



Entry	Substrate	Product	Time (min)	Yield (%)[a]	Melting point (ºC) [references]	TOF (h^{-1})
1			15	94	65–67 [34]	529.3
2			20	92	45–47 [34]	388.7
3			35	90	107–108 [35]	217.3
4			15	95	83–85 [34]	535.2
5			25	94	64–66 [34]	317.7
6			55	85	82–84 [35]	130.6
7			60	87	55–57 [36]	122.5
8			55	92	161–164 [34]	141.3
9			40	80	113–114 [37]	136.3
10			45	89	51–54 [38]	167.1
11			55	93	125–127 [38]	142.89
12			60	90	60–63 [39]	126.7
13			45	91	Oil [40]	169.0
14			35	87	44–46 [34]	210.0
15			25	90	71–74 [34]	304.2

[a] Isolated yield

Table 4 Catalytic results for the Stille reaction

Entry	Temperature (°C)	Solvent	Base (eq.)	Catalyst (mol%)	Time (min)	Yield[a]
1	80	H_2O	K_2CO_3	0	10 h	–[b]
2	80	H_2O	K_2CO_3	0.71	40	76
3	80	H_2O	K_2CO_3	0.88	40	87
4	80	H_2O	K_2CO_3	1.06	40	92
5	80	H_2O	Et_3N	1.06	40	91
6	80	H_2O	KOH	1.06	40	Trace
7	80	H_2O	Na_2CO_3	1.06	40	90
8	80	H_2O	$NaHCO_3$	1.06	40	90
9	80	DMSO	K_2CO_3	1.06	40	30
10	80	EtOH	K_2CO_3	1.06	40	Trace
11	80	1,4-dioxane	K_2CO_3	1.06	40	–[b]
12	80	PEG-400	K_2CO_3	1.06	40	90
13	70	H_2O	K_2CO_3	1.06	40	82
14	60	H_2O	K_2CO_3	1.06	40	40
15	25	H_2O	K_2CO_3	1.06	40	–[b]

The reaction mixture consisted of phenyl iodide (1.0 mmol), Ph_3SnCl (0.5 mmol), base (K_2CO_3, 3 mmol) and 3 mL of solvent. Reaction time was 40 min

[a] Isolated yield

[b] No reaction

Later, various solvents were applied for this reaction. Ethanol and 1,4-dioxane were found to be ineffective under the present reaction conditions (Table 2, entries 9–11), whereas, PEG-400 and highly polar solvents like water were found to give excellent yields (Table 2, entries 3, 11). Interestingly, the reaction proceeded smoothly in water providing an excellent yield (94%). Also, a variety of bases were employed to give desired product at 80 °C in the presence of 0.71 mmol% catalyst (Table 2, entries 12–15). Using K_2CO_3 as a base, the reaction had proceeded in high yield (Table 2, entry 3). The results illustrated in Table 2.

To examine the utility and generality of this approach, we have performed the reaction under optimized reaction conditions for the synthesis of a wide variety of biphenyls. The biphenyl derivatives were obtained in high yields (Table 3, entries 1–15).

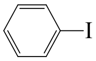
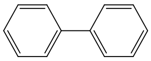
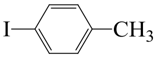
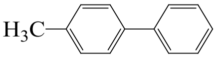
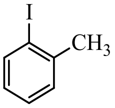
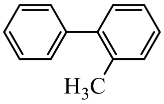
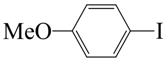
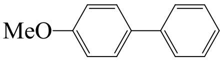
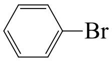
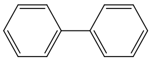
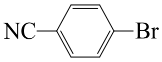
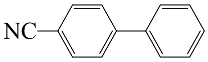
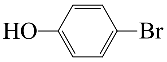
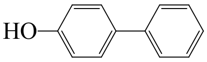
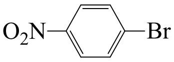
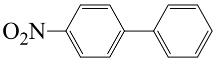
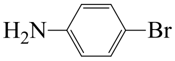
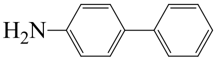
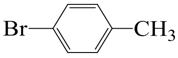
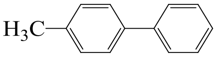
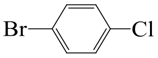
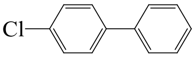
The activity of the catalyst was also examined in the Stille cross-coupling reactions. For this purpose, the reaction between the phenyl iodide (1.0 mmol) and Ph_3SnCl (0.5 mmol) in the presence of base (3 mmol) was probed as a model reaction. The catalytic reactions were first carried out in the absence of catalyst, which did not give a quantitative yield of biphenyl after 10 h (Table 4, entry 1). To investigate the effect of the catalyst, systematic studies were carried out in the presence of different amounts of the catalyst (0.71, 0.88, 1.06 mol%) in water (Table 4, entries 2–4). Hereon, we chose 1.06% mol% to be the proper catalyst loading. Also, the effect of a series of organic and inorganic bases on the activity of Pd-Vanillin-MCM-41 catalyst was studied and Na_2CO_3 was selected as the proper base under optimization reaction conditions (Table 4, entries 5–8). Beside, in order to find appropriate solvent, we designed this reaction in different solvents (Table 4, entries 9–11). However, H_2O proved to be the best solvent. Further optimization was performed at different temperatures (Table 4, entries 12–15). A high conversion of biphenyl can be achieved at 80 °C. The results of the screening process have been summarized in Table 3. Notably, the combination of H_2O as solvent and K_2CO_3 as base at 80 °C appeared to be suitable for this coupling reaction in presence of our developed Pd catalyst.

After optimization, the Stille reaction of aryl halides with Ph_3SnCl in the presence of heterogeneous Pd-Vanillin-MCM-41 catalyst (6 mg. 1.06 mol%) in water at 80 °C were carried out and the obtained results are listed in Table 5.

Also, the ability of Pd-Vanillin-MCM-41 to act as an efficient catalyst in Heck reactions has been examined. The reaction of aryl halides with n-butyl acrylate have been employed as the model reaction. There are several parameters which have been tuned to get the optimized yield. The reactions have been performed with 1.0 mmol of phenyl

Table 5 The Stille reaction of aryl halides with Ph_3SnCl using heterogeneous Pd-Vanillin-MCM-41 catalyst (6 mg. 1.06 mol%) in water at 80 °C

$$\mathbf{Ph_3SnR} \;+\; \mathbf{R'X} \xrightarrow[\substack{\mathbf{K_2CO_3,\ H_2O} \\ \mathbf{X=\ I,\ Br}}]{\mathbf{Pd\text{-}Vanillin\text{-}MCM\text{-}41}} \mathbf{R\text{-}R'}$$

Entry	Substrate	Product	Time (min)	Yield (%)[a]	Melting point (°C) [references]	TOF (h^{-1})
1			40	92	64–66 [34]	130.1
2			45	93	45–47 [34]	116.9
3			55	94	Oil [34]	96.7
4			55	85	86–89 [34]	87.4
5			50	90	63–66 [34]	101.8
6			145	89	83–85 [35]	34.7
7			70	86	162–164 [34]	69.5
8			75	94	112–114 [37]	70.9
9			80	85	53–55 [38]	60.1
10			65	87	44–46 [34]	75.7
11			160	89	71–73 [34]	31.4

[a] Isolated yield

iodide and 1.2 mmol of *n*-butyl acrylate in the presence of 3 mmol of base under varying conditions, e.g. using different solvents, temperature and various bases. As shown in Table 6, when the reaction was carried out in the absence of Pd-Vanillin-MCM-41, the low yield of product was obtained (Table 6, entry 1). As shown in Table 6, among the different amount of catalyst tested, 4 mg of Pd-Vanillin-MCM-41 was found to be the most effective catalytic amount since it gave the highest yield of the product. On the other hand, when the amount of catalyst was reduced, the yield of the product catalysed was decreased (Table 6, entries 2–4). As entries 5–7 show in Table 6, the reaction temperature plays an important role in the Pd-Vanillin-MCM-41 catalysed Heck reaction, with the maximum conversion reaching at 120 °C. Solvents play an essential role in the selectivity and reactivity performance, thus, the choice of a proper solvent is necessary. To investigate the effect of solvent, systematic studies are carried out in the presence of different solvents (Table 6, entry 8–10). Thus, the best yield is found in the presence of PEG-400 as solvent. Then, a variety of bases were essayed to give desired product in the presence of 0.71 mmol% complex. Using K_2CO_3 as a base, the reaction had proceeded in high yield (Table 6, entries 11–14). Finally, we found the following optimized conditions: the reaction proceeded in 91% yield with K_2CO_3 as a base in the presence of 4 mg (0.71 mol%) of catalyst in PEG-400 at 120 °C under stirring.

The reaction of various aryl halide derivatives, including electron-donating and electron-withdrawing groups on the aromatic ring, with *n*-butyl acrylate was then investigated to confirm the generality of the present method. The results of this study are summarized in Table 7.

Table 6 Catalytic results for the Heck reaction

Entry	Temperature (°C)	Solvent	Base (eq.)	Catalyst (mol%)	Time (min)	Yield[a]
1	120	PEG-400	K_2CO_3	0	10 h	–[b]
2	120	PEG-400	K_2CO_3	0.53	25	72
3	120	PEG-400	K_2CO_3	0.71	25	91
4	120	PEG-400	K_2CO_3	0.88	25	91
5	130	PEG-400	K_2CO_3	0.71	25	91
6	110	PEG-400	K_2CO_3	0.71	25	80
7	100	PEG-400	K_2CO_3	0.71	25	63
8	120	EtOH	K_2CO_3	0.71	25	–[b]
9	120	H_2O	K_2CO_3	0.71	25	75
10	120	DMF	K_2CO_3	0.71	25	83
11	120	PEG-400	Et_3N	0.71	25	90
12	120	PEG-400	$NaHCO_3$	0.71	25	75
13	120	PEG-400	Na_2CO_3	0.71	25	88
14	120	PEG-400	KOH	0.71	25	35

The reaction mixture consisted of aryl halide (1.0 mmol), n-butyl acrylate (1.2 mmol), base (K_2CO_3, 3 mmol), and 3 mL of solvent, reaction time was 25 min

[a] Isolated yield

[b] No reaction

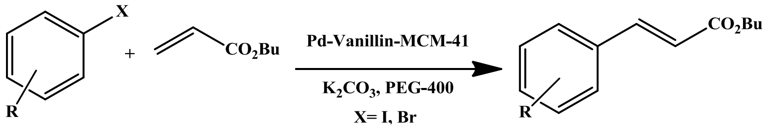
The catalyst was tested for their recyclability in these reactions. For each cycle, the amounts of solvent and reagents were adjusted depending on the amount of catalyst that had been recovered from the previous run. The results are presented in Fig. 8. In Suzuki coupling reaction, the reusing possibility of the recovered catalyst was investigated using phenyl iodide (5 mmol) and phenylboronic acid (5 mmol) or Ph_3SnCl (2.5 mmol) as a model reaction. After each run, the supported catalyst was separated by filtration, then dried, and used directly for the next run (Fig. 8, column a, b). In Mizoroki–Heck reaction, the reusing possibility of the recovered catalyst was investigated using phenyl iodide and butyl acrylate as substrates. After each run, the supported catalyst was extracted by filtration and used directly for the next run (Fig. 8, column c). The result showed that catalyst is recoverable and recycled for at least five times without significant loss of its catalytic activity (Fig. 8).

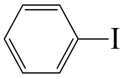
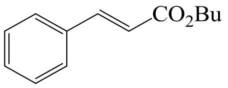
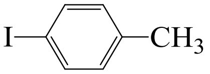
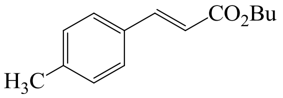
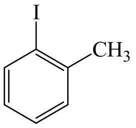
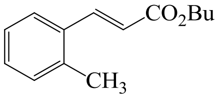
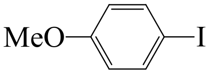
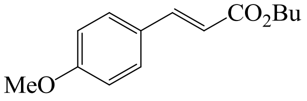
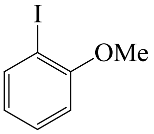
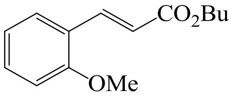
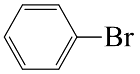
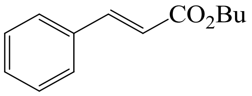
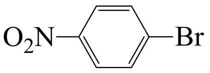
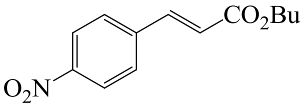
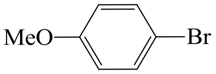
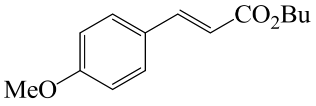
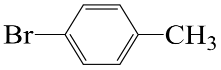
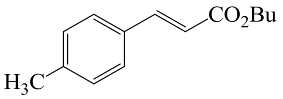
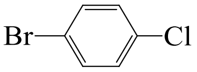
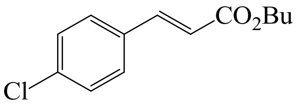
Finally, hot filtration test was investigated to check if the leached metal species are responsible for the catalytic activity in Mizoroki–Heck reaction of phenyl iodide with butyl acrylate as a model substrate in the presence of Pd-Vanillin-MCM-41 (4 mg, 0.71 mol%) at 120 °C in PEG-400. During the catalytic reaction, the solid catalyst was removed from the reaction mixture by filtration after 10 min and the determined conversion was 53%. The residual solution was, then, allowed to react for the further 15 min and the obtained conversion was the same (53%). And also, the hot filtration test was applied for syntheses of biphenyl from reaction of phenyl iodide (1 mmol) and $PhB(OH)_2$ (1 mmol) in water at 80 °C as model reaction in the presence of catalyst (4 mg, 0.71 mol%). After completion of 50% of the coupling reaction the liquid phase is collected by filtration at the reaction temperature. The mixture was continued to be stirred at the same temperature, but the coupling reaction dose not proceed further after the separation of the Pd-Vanillin-MCM-41 from the mixture.

4 Conclusions

In summary, palladium Schiff base complexes consisting of mesoporous MCM-41 has been prepared by means of Post-Grafting procedure and characterized using various analytical techniques. The results indicated Pd-Vanillin-MCM-41 catalyst was a highly efficient and recyclable catalyst for C–C coupling reactions with variety aryl halides under mild conditions. Phenyl iodides and phenyl bromides showed good reactivity to generate the corresponding products in good to excellent yields for all reactions. Short reaction times, easy purification, high yields, recyclability and very low Pd leaching are main characteristic of the process.

Table 7 The Heck reaction of aryl halides with olefin using heterogeneous Pd-Vanillin-MCM-41 catalysts (0.71 mol%) at 120 °C in PEG-400



Entry	Substrate	Product	Time (min)	Yield (%)[a]	References	TOF (h^{-1})
1			25	91	Xu et al. [41]	304.2
2			60	90	Xu et al. [41]	126.7
3			45	89	Xu et al. [41]	167.3
4			30	91	Xu et al. [41]	256.3
5			25	86	Xu et al. [41]	290.7
6			40	90	Xu et al. [41]	190.14
7			45	90	Xu et al. [41]	169.0
8			55	85	Xu et al. [41]	130.6
9			70	75	Xu et al. [41]	90.54
10			60	89	Xu et al. [41]	125.35

[a] Isolated yield

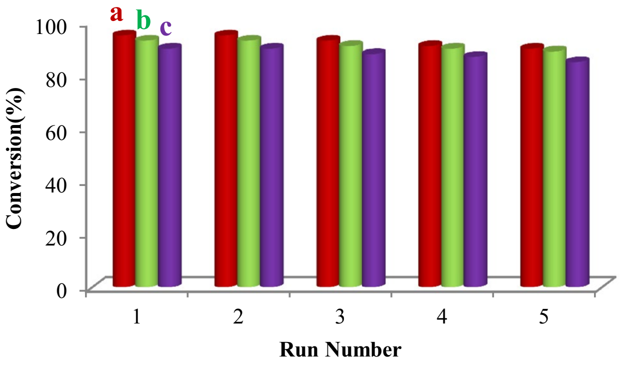


Fig. 8 Reusability of Pd-Vanillin-MCM-41 catalyst for the Suzuki reaction (column *a*), Stille reaction (column *b*) and Heck reaction (column *c*)

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