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Synthesis of Pd-Complex Supported on MCM-41 and Its Catalytic Activity for the C–C Coupling Reactions

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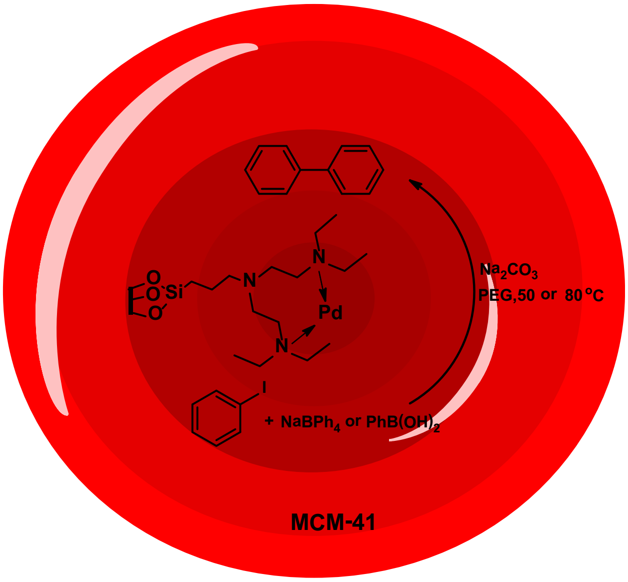
Abstract An efficient, novel and reusable heterogenized palladium catalyst was prepared on MCM-41 mesoporous. The prepared mesoporous catalyst was characterized by XRD, FT-IR, SEM, TGA, BET and ICP-OES techniques. This catalyst applied as an excellent nano catalyst for the Suzuki reactions in PEG and H_2O as an environmentally friendly solvents under phosphine-free conditions. The catalyst was easily recovered and reused for several times without significant loss of its catalytic efficiency. Also the turn over frequency effects of various reaction parameters on the Suzuki reactions and leaching of palladium are herein discussed.

Graphical Abstract



Keywords MCM-41 · Palladium · Carbon–carbon coupling · Suzuki reaction · Mesoporous · Biphenyl

1 Introduction

The Pd-catalyzed Suzuki reaction [1], is one of the most important routes to synthesize biaryl compounds through the cross-coupling of aryl halides with phenylboronic acids or its derivatives such as sodium tetraphenyl borate [2, 3]. These reactions have been frequently employed in the synthesis of natural products, agrochemicals, pharmaceuticals, biologically active compounds, herbicides, polymers, liquid crystals and advanced materials [4–7]. Suzuki

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reaction is typically carried out with phosphine-based or phosphine-free homogeneous Pd catalysts in organic solvents [8]. However, homogeneous catalysts have several drawbacks such as purification of the products, removal of palladium from organic products and recycling of the catalyst [9, 10]. Meanwhile, heterogeneous catalysts are the first option due to their inherent advantages of stability, simple separation, and better handling compared to homogeneous catalysts [11, 12]. However, immobilization of homogeneous catalysts decreases the catalytic activity or selectivity [13]. This drawback can be overcome by nanomaterials, because nanocatalysts can be used as a bridge gap between homogeneous and heterogeneous catalysts [14]. Among different nanoparticles, MCM-41, is commonly used as a heterogeneous support for the immobilization of homogeneous catalysts [15, 16]. Because of some advantages such as large specific surface area (>1000 m^2g^{-1}), high mechanical, chemical and thermal stability (up to 900 °C), homogeneous hexagonal pore arrays (between 20–100 Å), ease of functionalization, relatively hydrophobic nature and facile separation [17, 18]. Previously Pd-grafted functionalized various supported materials have been reported as catalyst in C–C coupling reactions. For example, biogenous iron oxide was used as a support for immobilized palladium and used in the Suzuki–Miyaura coupling reactions [19]. Also Poly(vinylidene dichloride)-diethylene triamine supported palladium complex was applied for the Heck reactions [20]. Herein a new Pd-based MCM-41 mesoporous catalyst has been reported for the Suzuki reactions.

2 Experimental

2.1 Preparation of Catalyst

The mesoporous MCM-41 was synthesized according to our reported procedure [21]. Then, 1 g of 3-choloropropyltriethoxysilane (CPTES) was added to a suspension of MCM-41 (1 g) in n-hexane (30 mL) and allowed to reflux for 24 h under N_2 atmosphere. Then, the reaction mixture was cooled down to room temperature, filtered and the resulting solid washed with n-hexane. The solid was dried under vacuum to get white solid (Cl-MCM-41). Then, for the Preparation of *N*,*N*,*N*”,*N*”-tetraethyldiethylenetriamine on MCM-41 (TEDETA-MCM-41), the above mentioned solid (1 g) was refluxed with 2 mmol of *N*,*N*,*N*”,*N*”-tetraethyldiethylenetriamine in toluene for 48 h under N_2 atmosphere. The resulting solid (TEDETA-MCM-41) was filtered, washed with ethanol and water and dried in vacuum. Finally, for Preparation of Pd-TEDETA-MCM-41, the TEDETA-MCM-41 (1 g) was mixed with 0.5 g of $Pd(OAc)_2$ in 15 mL of ethanol. The mixture was stirred at 80 °C for 24 h. The solid product was obtained by filtration, washed with ethanol and dried at 60 °C.

2.2 General Procedure for C–C Coupling Reaction Using Sodium Tetraphenyl Borate

A mixture of aryl halide (1 mmol), sodium tetraphenyl borate (0.5 mmol), Na_2CO_3 (1.5 mmol), and Pd-TEDETA-MCM-41 (0.002 g, 0.57 mol %) was stirred in PEG at 80 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled down to room temperature and catalyst was separated by simple filtration and washed with diethyl ether and the reaction mixture was extracted with H_2O and diethyl ether. The organic layer was dried over Na_2SO_4 (1.5 g). Then the solvent was evaporated and pure biphenyl derivatives were obtained in good to excellent yields. For more purification of biphenyls the preparative TLC plate was used in n-hexane/acetone (7:3). After desired biphenyl separated enough, ethyl acetate was used for recovering the product from silica gel and finally the pure biphenyls was obtained.

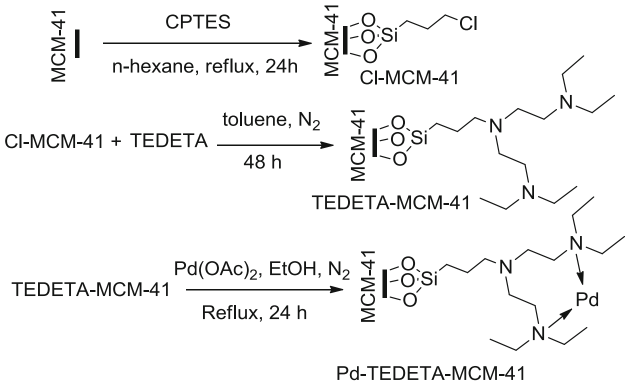
2.3 General Procedure for Coupling of Aryl Halides with Phenylboronic Acid

A mixture of aryl halide (1 mmol), phenylboronic acid (1 mmol), Na_2CO_3 (1.5 mmol), and Pd-TEDETA-MCM-41 (0.002 g, 0.57 mol %) were added to a reaction vessel. The resulting mixture was stirred in H_2O or PEG at 50 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by simple filtration and washed with ethylacetate and the reaction mixture was extracted with H_2O and diethylether and organic layer dried over anhydrous Na_2SO_4 (1.5 g). Then the solvent was evaporated and pure biphenyl derivatives were obtained in good to excellent yields. For more purification of biphenyls the preparative TLC plate was used in n-hexane/acetone (7:3). After desired biphenyl separated enough, ethyl acetate was used for recovering the product from silica gel and finally the pure biphenyls was obtained.

3 Results and Discussion

3.1 Catalyst Preparation

In continuation of our studies [14, 16, 21–23], herein, we report the Pd-TEDETA-MCM-41 as a recoverable and reusable catalyst for the C–C coupling reactions in PEG as green solvent. The catalyst was prepared by the concise route outlined in Scheme 1. Initially, the MCM-41



Scheme 1 Synthesis of Pd-TEDETA-MCM-41

mesoporous has been prepared according to new reported procedure [18] and subsequently was modified with 3-choloropropyltriethoxysilane (CPTES). The immobilized *N*,*N*,*N*",*N*"-tetraethyldiethylenetriamine on MCM-41 (TEDETA-MCM-41) was performed via substitution of NH instead supported-choloropropyl groups. Ultimately, the Pd-TEDETA-MCM-41 were prepared using reaction of TEDETA-MCM-41with palladium (II) acetate (Scheme 1). This catalyst has been characterized by FT-IR, SEM, TGA, BET and ICP-OES.

3.2 Catalyst Characterization

The morphological and size of the catalyst was evaluated using scanning electron microscopy (SEM). The SEM image of the Pd-TEDETA-MCM-41 was shown in Fig. 1. The SEM image of Pd-TEDETA-MCM-41 was confirmed that the catalyst was formed in nanometer-sized with spherical morphology.

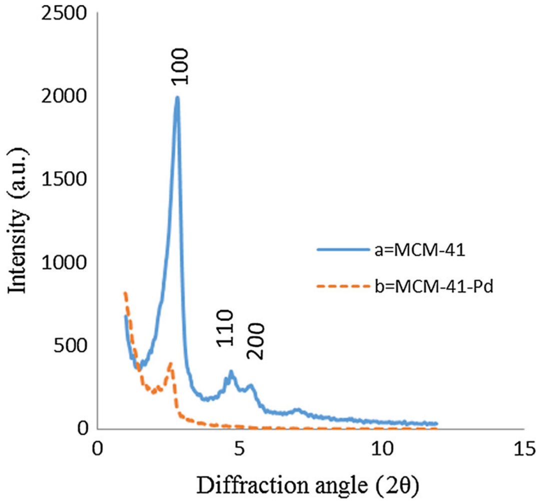


Fig. 2 XRD patterns of the MCM-41 and Pd-TEDETA-MCM-41

To extend the scope of catalyst characterization, we have determined the loading of Pd on MCM-41, by ICP-OES technique. The Pd amount of the immobilized catalyst on MCM-41 was found to be 0.0029 mol g^{-1} based on inductively coupled plasma atomic emission spectroscopy (ICP-OES). Also the mass percent of nitrogen is 2.95 % determined by CHN analysis. Figure 2 shows XRD patterns for MCM-41 and Pd-TEDETA-MCM-41. XRD patterns illustrate typical peaks corresponding to diffraction at (100), (110) and (200) plane of hexagonal phase. Diffraction peak at (100) reflects that the framework structure does not seriously deteriorate during the functionalization of MCM-41. Loss in the intensities of the peaks was observed after modification that providing further evidence of functionalization occurring mainly inside the mesopore

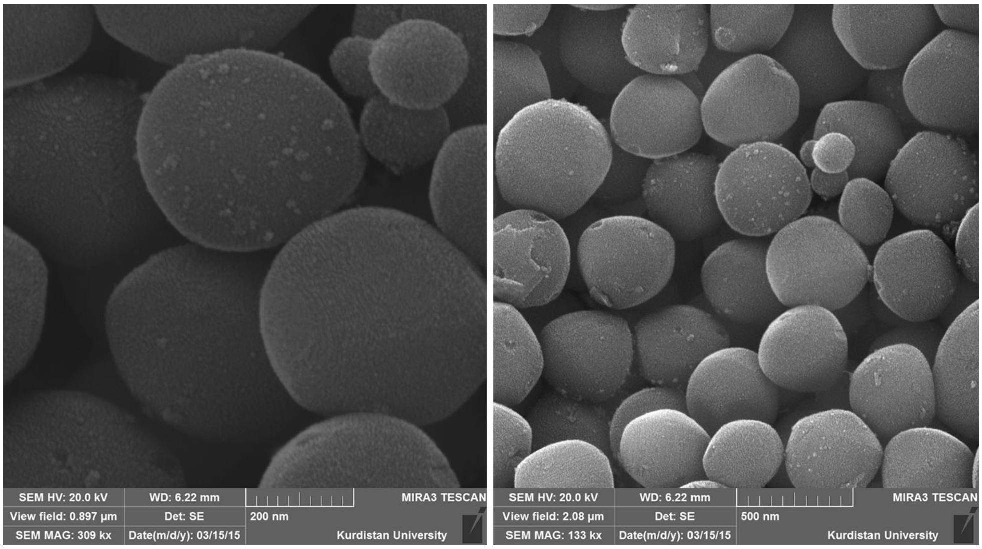


Fig. 1 SEM images of Pd-TEDETA-MCM-41

channels. Additionally, a unit cell parameter (the center-to-center pore distance), a_0, of 41.6 Å was obtained for MCM-41 by using d_{100}-spacing values according with the following equation:

$$a_0 = \frac{2d_{100}}{\sqrt{3}} \tag{1}$$

Successful functionalization of the mesoporous MCM-41 can be inferred from FT-IR technique. Figure 3 shows FT-IR spectra for MCM-41, Cl-MCM-41, TEDETA-MCM-41 and Pd-TEDETA-MCM-41. The FT-IR spectrum for the MCM-41 shows two peaks at 793 and 1039 cm^{-1} corresponding to the symmetric and asymmetric Si–O–Si vibrations [22]. Modification of MCM-41 using 3-choloropropyltriethoxysilane was proved with the appearance of two peaks at 2922 and 2855 cm^{-1}, related to the C–H stretching vibrations, which C–H stretching vibrations is absent in FT-IR spectrum of MCM-41 and present in FT-IR spectrum TEDETA-MCM-41and Pd-TEDETA-MCM-41. Also, the stretching vibrations at 3460–3630 cm^{-1} are assigned to the both symmetrical and asymmetrical modes of the silanol groups (O–H) bonds that attached to the MCM-41 framework, which are absent in FT-IR spectrum of modified MCM-41 and Pd-TEDETA-MCM-41 [21].

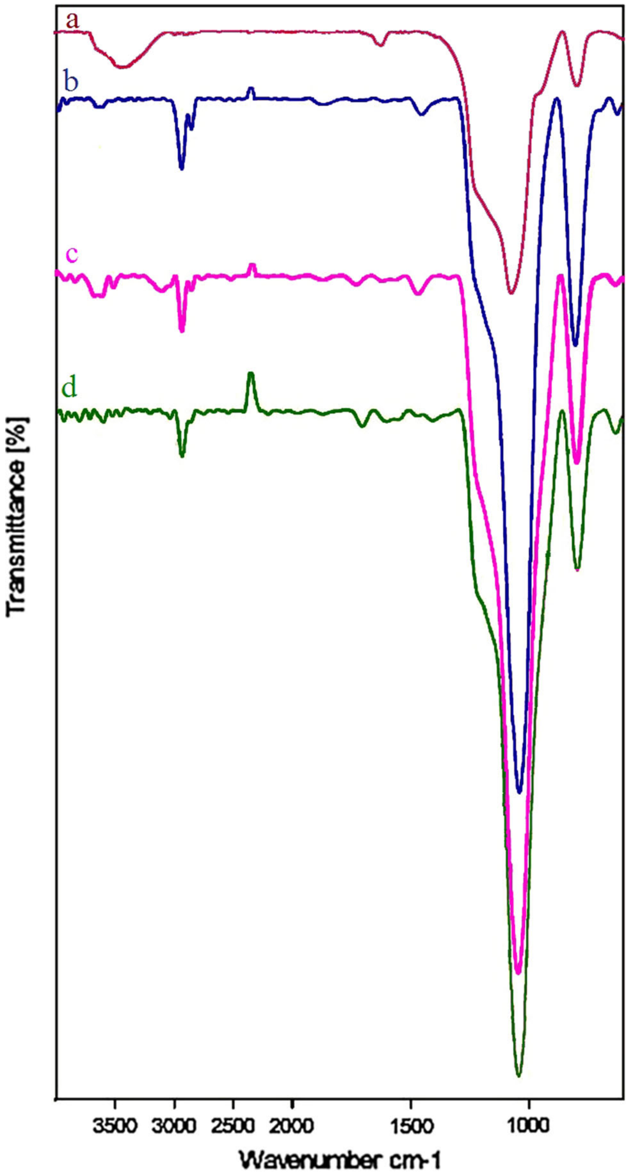


Fig. 3 FT-IR spectra of MCM-41 (*a*), Cl-MCM-41 (*b*), TEDETA-MCM-41 (*c*) and Pd-TEDETA-MCM-41 (***d***)

The thermogravimetric analysis (TGA) was applied to shown the percentage of chemisorbed organic layers onto the MCM-41 mesoporous. Figure 4 shows the TGA curves for MCM-41 and Pd-TEDETA-MCM-41. The TGA curve of the Pd-TEDETA-MCM-41 shows the mass loss of the organic functional groups as it decomposes upon heating. The TGA curve of the MCM-41 shows the small amount of weight loss of 5.7 % below 200 °C is due to desorption of physically adsorbed solvents and surface hydroxyl groups. Meanwhile, weight loss about 18 % from 200 to 500 °C is occurred for Pd-TEDETA-MCM-41, resulting from the decomposition of grafted Pd-complex and organic layers on the MCM-41. On the basis of this result, the well grafting of organic groups including palladium complex on the MCM-41 is verified.

The N_2 adsorption–desorption isotherms of MCM-41 and Pd-TEDETA-MCM-41samples were shown in Fig. 5. Based on the IUPAC classification, these materials display a typical type IV isotherm, which are the characteristics of mesoporous materia [21]. The Brunauer–Emmett–Teller (BET) surface area for MCM-41 and Pd-TEDETA-MCM-41 is 1372.3 and 908.6 m^2g^{-1}, respectively, and the BET large pore volume for MCM-41 and Pd-TEDETA-MCM-41 is 1.521 and 1.471 cm^3 g^{-1}, respectively. The pore volume of Pd-TEDETA-MCM-41 is lower than MCM-41. The decrease in pore volume and surface area of modified

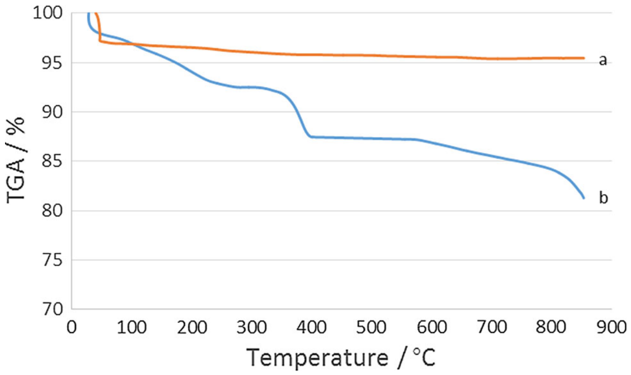


Fig. 4 TGA diagram of (*a*) MCM-41 and (*b*)Pd-TEDETA-MCM-41

MCM-41 was related to the immobilization of organic layers and Pd-complex onto the mesoporous wall. These results are demonstrated to the occupation of organic molecules on the inner surface of the pores.

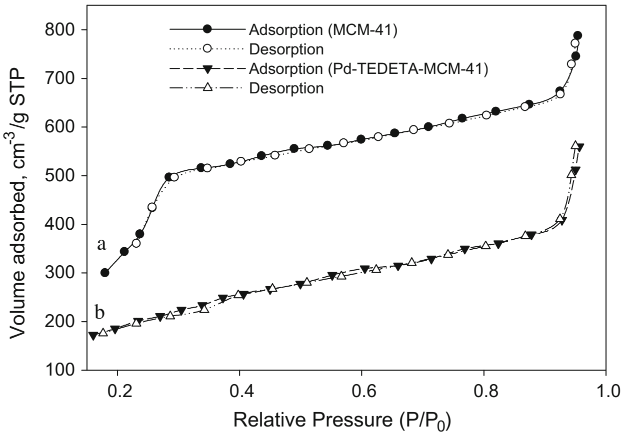


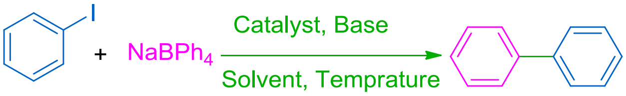
Fig. 5 BET curves for (*a*) MCM-41 and (*b*) Pd-TEDETA-MCM-41

3.3 Catalytic Study

In order to study the catalytic activity of Pd-TEDETA-MCM-41, carbon–carbon coupling reactions have been performed in the presence of this catalyst. In this light, we were interested in finding a simple and efficient method for the carbon–carbon coupling reaction in the presence of Pd-TEDETA-MCM-41 as an efficient nanocatalyst using $NaBPh_4$ or phenylboronic acid.

To illustrate the catalytic activity of Pd-TEDETA-MCM-41, initially we were selected the coupling of iodobenzene with $NaBPh_4$ as a model reaction and the effect of various parameters such as temperature, solvents, bases and amount of catalyst were examined for this reaction (Table 1). We found the reaction did not performed in the absence of Pd-TEDETA-MCM-41 (Table 1, entry 1). In order to choose the reaction media, different solvents (Table 1, entries 2–8) and different amount of Pd-TEDETA-MCM-41 (Table 1, entries 1–3) were examined and the best results were observed in PEG using 0.002 g (0.57 mol %) of catalyst (Table 1, entry 2). Also, the model reaction was examined using different bases such as $NaHCO_3$, K_2CO_3, Na_2CO_3, and Et_3N (Table 1, entries 2

Table 1 Optimization of reaction conditions for the C–C coupling reaction of iodobenzene with sodium tetraphenyl borate in the presence of Pd-TEDETA-MCM-41



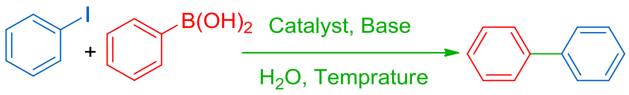
Entry	Catalyst (mg)	Solvent	Base	Amounts of base (mmol)	Temperature (°C)	Time (min)	Yield (%)[a]
1	–	PEG	Na_2CO_3	1.5	80	24 h	–[b]
2	2	PEG	Na_2CO_3	1.5	80	70	94
3	5	PEG	Na_2CO_3	1.5	80	35	96
4	2	H_2O	Na_2CO_3	1.5	80	100	22[c]
5	2	DMF	Na_2CO_3	1.5	80	100	67[c]
6	2	DMSO	Na_2CO_3	1.5	80	100	13[c]
7	2	EtOH	Na_2CO_3	1.5	80	100	15[c]
8	2	n-Hexane	Na_2CO_3	1.5	80	100	–[b]
9	2	PEG	Et_3N	1.5	80	100	60[c]
10	2	PEG	NaHCO3	1.5	80	100	91
11	2	PEG	K_2CO_3	1.5	80	100	92
12	2	PEG	Na_2CO_3	3	r.t.	80	Trace
13	2	PEG	Na_2CO_3	1.5	40	80	35[c]
14	2	PEG	Na_2CO_3	1.5	60	80	63[c]
15	2	PEG	Na_2CO_3	1.5	100	40	95

[a] Isolated yield

[b] No reaction

[c] Purification by preparative TLC

Table 2 Optimization of Suzuki reaction conditions for the coupling of iodobenzene with phenylboronic acid in the presence of Pd-TEDETA-MCM-41 in water



Entry	Catalyst (mg)	Base	Temperature (°C)	Time (min)	Yield (%)[a]
1	–	Na_2CO_3	50	24 h	–[b]
2	1	Na_2CO_3	50	70	75[c]
3	2	Na_2CO_3	50	70	92
4	3	Na_2CO_3	50	55	94
5	2	Na_2CO_3	r.t.	70	Trace
6	2	Et_3N	50	70	80[c]
7	2	$NaHCO_3$	50	70	86
8	2	K_2CO_3	50	70	89

[a] Isolated yield

[b] No reaction

[c] Purification by preparative TLC

Table 3 Catalytic C–C coupling reaction of aryl halides using sodium tetraphenyl borate or phenylboronic acid in the presence of Pd-TEDETA-MCM-41 (0.002 g, 0.57 mol%) under optimized conditions

Entry	Aryl halide	Phenylatig reagent	Solvent	Time (min)	Yield (%)[a]	TOF (h^{-1})	M.P. (°C) [Reference]
1	Iodobenzene	Sodium tetraphenyl borate	PEG	70	94	141.35	64–66 [24]
2	Iodobenzene	Phenylboronic acid	H_2O	70	92	138.34	64–68 [24]
3	4-Iodotoluene	Sodium tetraphenyl borate	PEG	45	95	222.22	42–43 [25]
4	4-Iodotoluene	Phenylboronic acid	H_2O	45	90	210.53	42–45 [25]
5	4-Iodoanisole	Sodium tetraphenyl borate	PEG	90	96	112.28	81–83 [26]
6	4-Iodoanisole	Phenylboronic acid	PEG	90	87	101.75	81–83 [26]
7	4-Bromotoluene	Sodium tetraphenyl borate	PEG	60	96	168.42	42–45 [25]
8	4-Bromotoluene	Phenylboronic acid	H_2O	80	92	121.05	40–43 [25]
9	4-Bromoanisole	Sodium tetraphenyl borate	PEG	120	87[b]	30.63	84–85 [26]
10	4-Bromoanisole	Phenylboronic acid	PEG	360	98	28.65	83–85 [26]
11	4-Bromophenol	Phenylboronic acid	H_2O	170	94	58.20	162–163 [27]
12	Bromobenzene	Sodium tetraphenyl borate	PEG	75	95	133.33	65–68 [24]
13	Bromobenzene	Phenylboronic acid	H_2O	100	98	103.16	64–68 [24]
14	1-Bromonaphthalene	Sodium tetraphenyl borate	PEG	24 h	58[c]	1.056	Oil [27]
15	1-Bromonaphthalene	Phenylboronic acid	H_2O	24 h	60	4.386	Oil [27]
16	4-Bromonitrobenzene	Sodium tetraphenyl borate	PEG	100	90	94.74	110–111 [26]
17	4-Bromonitrobenzene	Phenylboronic acid	PEG	420	91	22.81	111–113 [26]
18	1-Bromo-3-(trifluoromethyl)benzene	Sodium tetraphenyl borate	PEG	40	97[b]	102.46	Oil [28]
19	1-Bromo-3-(trifluoromethyl)benzene	Phenylboronic acid	H_2O	85	96	118.88	Oil [28]
20	4-Bromochlorobenzene	Sodium tetraphenyl borate	PEG	120	91[b]	32.04	69–73 [24]
21	4-Bromochlorobenzene	Phenylboronic acid	H_2O	60	90	157.89	70–72 [24]
22	4-Bromobenzonitrile	Sodium tetraphenyl borate	PEG	100	92[b]	38.87	80–82 [27]
23	4-Chloronitrobenzene	Sodium tetraphenyl borate	PEG	90	96[b]	45.07	108–111 [25]
24	4-Chlorobenzonitrile	Sodium tetraphenyl borate	PEG	110	82	78.47	79–82 [27]
25	Chlorobenzene	Sodium tetraphenyl borate	PEG	120	92[b]	32.39	64–66 [26]
26	Chlorobenzene	Phenylboronic acid	H_2O	165	90	57.41	70–72 [26]

[a] Isolated yield

[b] In the presence of Pd-TEDETA-MCM-41 (5 mg, 1.42 mol%)

[c] In the presence of Pd-TEDETA-MCM-41 (8 mg, 2.28 mol%)

and 9–11), among them, the best results were obtained using 1.5 mmol of Na_2CO_3. Because the coupling reaction yields were depended to temperature, the effect of temperature were studied (Table 1, entries 2 and 12–15) and the best results were obtained at 80 °C. Therefore, the best result was obtained by carrying out the reaction with the Pd-TEDETA-MCM-41 (0.002 g, 0.57 mol %), sodium tetraphenyl borate (0.5 mmol), iodobenzene (1 mmol) and Na_2CO_3 (1.5 mmol) in PEG at 80 °C (Table 1, entry 2).

In order to extend the catalytic application of Pd-TEDETA-MCM-41, Suzuki reaction with phenylboronic acid was studied. In order to establish the optimum conditions, the reaction of iodobenzene with phenylboronic acid was selected as a model reaction, and was examined under different reaction parameters such as base, solvent, temperature and amount of Pd-TEDETA-MCM-41 (Table 2). As expected, in the absence of a catalyst, the reaction was not proceed (Table 2, entry 1). Initially, the model reaction was examined in the presence of different amount of catalyst and it was found that 0.002 g (0.57 mol %) of catalyst in H_2O gave the best yield (Table 2, entries 1–4). Next, we examined the effect of the bases (Table 2, entries 3 and 6–8). Therefore, the best result was obtained with the use of Na_2CO_3 as the base in the presence of 0.002 g (0.57 mol%) of Pd-TEDETA-MCM-41 at 50 °C (Table 2, entry 3).

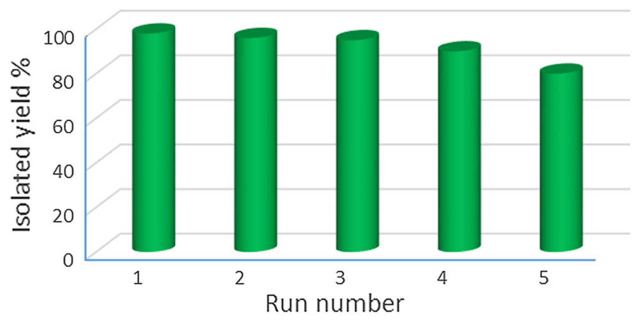


Fig. 6 Recyclability of Pd-TEDETA-MCM-41 in the: coupling of iodobenzene (1 mmol) with $NaBPh_4$ (0.5 mmol) under the reaction conditions

After the optimization of the reaction condition, we extended the catalytic activity of Pd-TEDETA-MCM-41 for various substrates and the results are summarized in Table 3. Therefore, various aryl iodides (Table 3, entries 1–6), bromides (Table 3, entries 7–13) and chlorides (Table 3, entries 14–16) were coupled with $NaBPh_4$ or phenylboronic acid and corresponding biphenyls were obtained in good to excellent yields. The reaction of the various aryl halide derivatives, including electron-donating (Table 3, entries 2–5) and electron-withdrawing (Table 3, entries 7, 8) groups on aromatic ring with sodium tetraphenyl borate or phenylboronic acid were then investigated to confirm the generality of the present method. Therefore, this methodology is effective for a wide range of aryl halide including Cl, Br and I.

The recovery and recyclability of Pd-TEDETA-MCM-41 was studied in the coupling reaction of iodobenzene with sodium tetraphenyl borate. In a typical reaction after completion the reaction, the reaction mixture was centrifuged in ethyl acetate. The catalyst was separated by centrifuge easily and washed with ethyl acetate and then water several times and dried at 50 °C for overnight. Then, the recovered catalyst was subjected to the next step. As shown in Fig. 6, the catalyst can be reused over five times without any significant loss of its catalytic activity. The average isolated yield for five successive cycles was 91.8 %, which clearly demonstrates the practical recyclability of this catalyst.

In order to shown the analysis of leaching in catalyst, amount of Pd in Pd-TEDETA-MCM-41 was determined by ICP-OES after recycled that was found to be

Table 4 Comparison results of Pd-TEDETA-MCM-41 with other catalysts for the coupling of iodobenzene with phenylboronic acid

Entry	Catalyst (mol % of Pd)	Condition	Time (min)	Yield (%)[a]	Reference.
1	Polymer anchored Pd(II) Schiff base complex (0.5 mol %)	K_2CO_3, DMF: H_2O (1:1), 80 °C	5 h	99	[4]
2	$Fe_3O_4@SiO_2@mSiO_2$-Pd (II) (0.5 mol %)	EtOH, K_2CO_3, 80 °C	180	98	[29]
3	PVP–PdNPs (0.8×10^{-3} mol %)	K_2PO_4, 90 °C EtOH/H_2O,	120	94	[30]
4	Pd NP (1.0 mol %)	H_2O, KOH, 100 °C	12 h	95	[31]
5	CA/Pd(0) (0.5-2.0 mol %)	H_2O, K_2CO_3, 100 °C	120	94	[32]
6	$PdCl_2$ (0.05 mol %)	DMF, Cs_2CO_3, 130 °C	120	95	[33]
7	Pd/Au NPs (4.0 mol %)	EtOH/H_2O, K_2CO_3, 80 °C	24 h	88	[34]
8	PANI-Pd (2.2 mol %)	K_2CO_3, 1,4-dioxane: H_2O (1:1), 95 °C	4 h	91	[35]
9	Pd-TEDETA-MCM-41 (0.57 mol %)	H_2O, Na_2CO_3, 50 °C	70	92	This work

[a] Isolated yield

0.0028 mol g^{-1} (1.52 % leaching). The results from ICP-OES technique were showed that leaching of palladium during the reaction is negligible, so the catalyst can be recovered and reused several times.

To show the merit of Pd-TEDETA-MCM-41 in comparison with other reported catalysts, we compared the results of the coupling of iodobenzene with phenylboronic acid (Table 4) with the previous reported in the literature. This catalyst showed short reaction time and good yield compared to the other catalysts.

4 Conclusion

In conclusion an efficient heterogeneous catalyst (Pd-TEDETA-MCM-41) was synthesized from loading palladium acetate onto functionalized MCM-41. This catalyst was characterized using several techniques such as FT-IR, BET, TGA, SEM and ICP-OES. The Pd-TEDETA-MCM-41 exhibit an excellent catalytic activity, high reusability and air or moisture stability for the Suzuki reaction with good yields. The negligible leaching of Palladium obtained from ICP-OES after the coupling reaction. Also the catalyst can be reused more than five times without any significant loss of its activity.

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