Revised: 30 August 2017

#### FULL PAPER

WILEY Applied Organometallic Chemistry

## Heck and oxidative boron Heck reactions employing Pd(II) supported amphiphilized polyethyleneimine-functionalized MCM-41 (MCM-41@aPEI-Pd) as an efficient and recyclable nanocatalyst

Seyed Farshad Motevalizadeh<sup>1†</sup> | Masoumeh Alipour<sup>2†</sup> | Fatemeh Ashori<sup>3</sup> | Alireza Samzadeh-Kermani<sup>4</sup> | Hosein Hamadi<sup>5</sup> | Mohammad Reza Ganjali<sup>6,7</sup> | Hamideh Aghahosseini<sup>8</sup> | Ali Ramazani<sup>8</sup> | Mehdi Khoobi<sup>2,9</sup> | Elham Gholibegloo<sup>8</sup>

<sup>1</sup> Particulate Fluids Processing Centre, School of Chemistry, The University of Melbourne, Melbourne, VIC 3010, Australia

<sup>2</sup>Nanobiomaterials Group, Pharmaceutical Sciences Research Center, Tehran University of Medical Sciences, Tehran 1417614411, Iran

<sup>3</sup>Department of Applied Chemistry, Faculty of Pharmaceutical Chemistry, Pharmaceutical Sciences Branch, Islamic Azad University, Tehran, Iran

<sup>4</sup>Department of Chemistry, Faculty of Sciences, University of Zabol, Zabol, Iran

<sup>5</sup>Department of Chemistry, College of Science, Shahid Chamran University, Ahvaz, Iran

<sup>6</sup>Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran

<sup>7</sup> Biosensor Research Center, Endocrinology & Metabolism Molecular-Cellular Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran

<sup>8</sup>Department of Chemistry, University of Zanjan, P.O. Box 45195-313, Zanjan, Iran

<sup>9</sup> Department of Pharmaceutical Biomaterials and Medical Biomaterials Research Center, Faculty of Pharmacy, Tehran University of Medical Sciences, Tehran, Iran A novel nanocatalyst was developed based on covalent surface functionalization of MCM-41 with polyethyleneimine (PEI) using [3-(2,3-Epoxypropoxy)propyl] trimethoxysilane (EPO) as a cross-linker. Amine functional groups on the surface of MCM-41 were then conjugated with iodododecane to render an amphiphilic property to the catalyst. Palladium (II) was finally immobilized onto the MCM-41@PEI-dodecane and the resulted MCM-41@aPEI-Pd nanocatalyst was characterized by FT-IR, TEM, ICP-AES and XPS. Our designed nanocatalyst with a distinguished core-shell structure and Pd<sup>2+</sup> ions as catalytic centers was explored as an efficient and recyclable catalyst for Heck and oxidative boron Heck coupling reactions. In Heck coupling reaction, the catalytic activity of MCM-41@aPEI-Pd in the presence of triethylamine as base led to very high yields and selectivity. Meanwhile, the MCM-41@aPEI-Pd as the first semi-heterogeneous palladium catalyst was examined in the C-4 regioselective arylation of coumarin via the direct C-H activation and the moderate to excellent yields were obtained toward different functional groups. Leaching test indicated the high stability of palladium on the surface of MCM-41@aPEI-Pd as it could be recycled for several runs without significant loss of its catalytic activity.

#### KEYWORDS

Heck coupling reaction, mesoporous structure, oxidative boron Heck coupling reaction, palladium, polyethyleneimine

This work is dedicated in memory of Prof. Abbas Shafiee (1937–2016).  $^\dagger These$  authors have the same contribution to this paper.

<sup>2 of 9</sup> WILEY-Organometallic Chemistry

Ali Ramazani, Department of Chemistry, University of Zanjan, P O Box 45195-313, Zanjan, Iran. Email: aliramazani@gmail.com Mehdi Khoobi, Department of Pharmaceutical Biomaterials and Medical Biomaterials Research Center, Faculty of Pharmacy, Tehran University of Medical Sciences, Tehran, Iran. Email: m-khoobi@tums.ac.ir

### **1** | INTRODUCTION

Carbon-carbon bond coupling catalysed by transition metal is one of the most fundamental and important methodologies for the preparation of complex organic molecules like pharmaceuticals and natural products. Among different commonly used coupling reactions, Mizoroki-Heck coupling reaction (MHCR) has been attracted as one of the fascinating reactions for the formation of  $C(sp^2)$  –  $C(sp^2)$  from the catalytic aspects. This reaction has risen in popularity due to the high tolerance toward various commercial available starting materials, stability of the applied reagents during the reaction, and suitable regioselectivity of the products.<sup>[1-3]</sup> On the other hand, conventional MHCR bank on providing pre-activated coupling reagents causing a synthetic sequence to introduce the functionality, especially for the preparation of important biological molecules. Oxidative Heck reaction has opened a new way to overcome this obstacle and eliminate introducing protecting groups and reactive functionalities prior to C–C bond formation.<sup>[4–6]</sup> These types of reactions generally proceed in the presence of a homogeneous palladium catalyst, which makes its separation and recovery tedious, if not impossible, and might result in unacceptable palladium contamination of the products. However, the 'naked' Pd species have been postulated to be the true active catalytic species in many cases.<sup>[7–9]</sup> An example in this regard is the de Vries et al. work, which they employed ligand-free Pd(OAc)<sub>2</sub> (0.01–0.1 mol %) as a catalyst in the Heck reaction of aryl bromides.<sup>[7]</sup> At higher concentrations palladium black forms and the reaction stops. One of the strategies to overcome these drawbacks is their encapsulation or immobilization on porous solid matrices. Different types of supports were used to immobilize palladium and prepare environmental-friendly, efficient and simpler heterogeneous catalysts.<sup>[10–13]</sup> The immobilization of the metal on porous supports with high-surface area brings better stability and dispersity as well as recyclability of the catalyst.<sup>[14]</sup> Mesoporous materials have shown considerable activity as heterogeneous catalysts. The development of mesoporous catalysts and transition metal

tions are attractive approaches to find a new heterogeneous synthetic method.<sup>[15]</sup> Different methods were taken into account to stabilize nanometals on the support using various types of functional molecules such as polymers.<sup>[16-18]</sup> surfactants,<sup>[19]</sup> and different types of ligands<sup>[20]</sup> as capping agents. Both dendrimers and hyperbranched polymers covalently or noncovalently functionalized with catalytically active transition metal complexes are one of promising scaffolds with respect to catalyst recovery.<sup>[21-</sup> <sup>23]</sup> In many aspects, dendrimers can be replaced by hyperbranched polymers due to their similar properties,<sup>[24]</sup> such as low viscosity, high functionalities and spheroid-like shape. The silica-supported palladium nanoparticles-mediated organic transformations have been developed remarkably. Palladium nanoparticles were encapsulated in various forms of silica supports that were represented improved properties in carbon-carbon bondforming reactions gradually.<sup>[25-29]</sup> By now, catalytic activity of covalently or noncovalently functionalized hyperbranched macromolecules like hyperbranched polyethylenimine (HPEI) has received limited attention.<sup>[30–34]</sup> Therefore, it is worthwhile to develop a general, simple, and scalable approach to fabricate a reusable and stable nanocatalyst. In this work, we report a convenient methodology to stabilize palladium as a catalyst on a polyamine functionalized MCM-41 that leads to a reusable high-active semi-heterogeneous nanocatalyst for Heck coupling and oxidative Heck reactions (Scheme 1). To the best of our knowledge, there is no report about application of semi-heterogeneous palladium catalyst for direct arylation of coumarins.

supported mesoporous catalysts for various organic reac-

#### 2 | EXPERIMENTAL

Hyperbranched PEI (Mw = 60000) and EPO (98% purity) were purchased from Aldrich. The following materials were purchased from Merck: cetyl trimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), aqueous ammonia (28 wt. % solution), absolute ethanol (EtOH),



methanol (MeOH) and palladium chloride. Other reagents and solvents were obtained from Aldrich or Fluka and used without further purification.

Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets using a Bruker Equinox 55 (detector: DTGS) spectrophotometer. The morphology of the catalyst was studied by high resolution transmission electron microscopy (HRTEM) on a Philips CM30T (150– 300 kV). Thermogravimetric analysis (TGA) was carried out on a TGA Q50 with a heating rate of 10 °C min<sup>-1</sup> from 25 °C to 800 °C under a nitrogen atmosphere. The surface chemistry and chemical state of the supports were analysed by X-ray photoelectron spectroscopy (XPS; VG Escalab 250 iXL ESCA instrument, VG Scientific) using monochromatic Al-K $\alpha$  radiation of energy 1486.6 eV. A hemispherical analyser (Specs EA 10 Plus) under vacuum (10<sup>-9</sup> Torr) was used for energy analysis.

#### 2.1 | Preparation of mesoporous silica

The molar compositions of the reaction medium were applied at 1.0 for TEOS, 0.3 for CTAB, 11 for NH<sub>3</sub>, 144 for H<sub>2</sub>O and 28 for EtOH, where the mesoporous phase with high ordering degree was achieved.<sup>[35]</sup> A typical MCM-41 preparation procedure is described as follows: 13.0 g of CTAB was dissolved in 167.0 g of deionized water; then, 163.7 g of the aqueous ammonia and 131.5 g of the absolute ethanol was added to the surfactant solution. The solution was stirred for 15 min, and afterwards 24.8 g of TEOS was added. After 2 h of vigorous stirring with the mechanical stirrer at 1500 rpm and filtration, the white precipitate was successfully washed with plenty of deionized water and dried at 60 °C for 24 h. Before using MCM-41, a part of MCM-41 sample was calcined under oxygen atmosphere by applying a heating ramp of 1 °C /min up to 600 °C and then kept at this temperature for 6 h. The high-resolution TEM image of MCM-41 was provided which indicated its fine morphological structure with hexagonal array of uniform channels (Figure S1 a, b).

#### 2.2 | Preparation of MCM-41@PEI

MCM-41@PEI was synthesized according to the procedure reported previously.<sup>[36]</sup> To a stirred solution of 150 ml dry toluene containing 3.0 mmol of PEI, 1.0 mmol of 3-(2, 3-Epoxypropoxy) propyltrimethoxysilane was added. The resulting mixture was allowed to react at 80 °C for 24 h. To this solution, 2.5 g of calcined MCM-41<sup>[37]</sup> and 25 ml of EtOH were added and the solution was stirred at 80 °C for 24 h. The MCM-41@PEI was isolated by filtration and washed with MeOH and EtOH. Then, it was refluxed with EtOH during 1 h, filtered again and dried at 40 °C for two days. Low-angle X-ray diffraction, nitrogen sorption isotherms, specific surface area (as BET), pore volume, and pore diameter were measured for MCM-41 before and after grafting PEI (Figure S1 c-e, Table S1).

### 2.3 | Modifying of MCM-41@PEI with 1iodododecane

To a stirred solution of 200 ml dry Ethanol containing 4 g MCM-41@PEI, 13.5 mmol 1-iodododecane was added. The resulting mixture was allowed to reflux for 24 h. The MCM-41@PEI-dododecane was separated by evaporation of solvent and washed with MeOH and EtOH. The above procedure was repeated 3 times to obtain maximum modifying with 1-iodododecane.

### 2.4 | Palladium loading onto the MCM-41@PEI-dododecane

MCM-41@PEI-dododecane (300 mg) was charged into a round bottomed flask containing an acetonitrile solution (25 ml) of palladium chloride (0.6 mmol) and stirred under a nitrogen atmosphere for 48 h. The resultant residue was filtered off and washed with acetonitrile followed by acetone. The residue was dried in air for 24 h.<sup>[38]</sup>

# 2.5 | Heck coupling and oxidative Heck reactions

In a typical experiment, iodobenzene (1.1 mmol) and styrene (1.0 mmol) were added to *N*,*N*-dimethylformamide (DMF, 1 ml). MCM-41@aPEI-Pd as catalyst (1 mol % based on initial idobenzene) and triethylamine (1.5 mmol) were added to this system under stirring at 90 °C. After completion of the reaction, the catalyst was recovered by centrifugation and washed thoroughly with a mixed solvent of ethanol and water. The product was analysed by gas chromatography (GC).

In oxidative Heck reactions, coumarin was reacted with phenyl boronic acid. The feasibility of the reaction was investigated under the following conditions: coumarin (1 mmol), phenylboronic acid (1.2 mmol), Pd catalyst (4 mol %), ligand (20 mol %), O<sub>2</sub> (balloon pressure) in the solvent (0.4 M) were heated in a sealed tube at 100 °C for 24 h. After completion of the reaction, the catalyst was recovered by centrifugation and washed thoroughly with ethyl acetate and water. The structural properties of the recycled MCM-41@aPEI-Pd was monitored by BET and wide angle XRD analysis (Figure S2, S3 and Table S2).

## **3** | **RESULTS AND DISCUSSION**

. Ó EPO

The process for the preparation of MCM-41@aPEI-Pd is schematically described in Scheme 2. MCM-41@PEI was

prepared via a two steps reaction. First, PEI was attached to the EPO through the reaction of amine groups of PEI with epoxy groups of EPO. Then, PEI was grafted to the surface of MCM-41 through the reaction of trimethoxysilane part with hydroxyl groups of MCM-41. 1-Iodododecane was then used to render an amphiphilic character to the target catalyst providing a proper area for hydrophobic substrates. Palladium was finally loaded onto the catalyst via chelating by amine groups on the catalyst.

## 3.1 | FTIR spectroscopy

FT-IR spectra of MCM-41, MCM@PEI and MCM-41@aPEI-Pd are shown in Figure 1. The band at 1060 cm<sup>-1</sup>, 801 cm<sup>-1</sup> and 463 cm<sup>-1</sup> are attributed to asymetric stretching vibration, symmetric stretching vibration and bending vibration of Si-O-Si bonds in MCM-41, respectively.<sup>[38-40]</sup> The strong bands of OH related to the stretching and bending vibration indicate that a large number of OH groups are present on the surface of MCM-41 (3485 and 1639 cm<sup>-1</sup>, respectively). A comparison between the FT-IR spectra of MCM-41 and MCM@PEI reveals additional bands around 1465 and 2900  $\text{cm}^{-1}$  which could be due to the stretching vibration of the C-N and C-H bonds of polymer on the surface of MCM-41 (Figure 1a and 1b).<sup>[41]</sup> The modification with 1-iodododecane has increased the intensity of the peaks at about 2855 and 2927 cm<sup>-1</sup> which is assignable for the



PdCl<sub>2</sub>

odododecane 🐱

**SCHEME 2** Schematic representation of the formation of MCM-41@aPEI-Pd



**FIGURE 1** FT-IR spectra of (a) MCM-41, (b) MCM@PEI and (c) MCM@PEI-dodecane

stretching mode of CH(-CH  $_3$ ) and CH(-CH $_2$ -) groups of the 1-iodododecane species.

## 3.2 | Transmission electron microscopy (TEM)

Figure 2 shows the TEM image of MCM-41@aPEI-Pd presenting a core-shell structure with average size of about 300 nm. The thickness of the polymer layer was almost 20–30 nm.

#### 3.3 | Thermal analysis

Further experiments were carried out to prove the successful linking procedure and to estimate the percentage of functionalization in each step. Figure 3 showed the TGA measurement of the support after grafting with PEI and dodecyl moiety. As expected, there was no weight loss for MCM-41 till 600 °C. It is observed that the MCM-41 lose around 5% of its total weight because of the removal of adsorbed water below 150 °C. After the grafting reaction, the amount of the loaded PEI on MCM-41 was



FIGURE 2 TEM image of the MCM-41@aPEI-Pd nanocatalyst



FIGURE 3 TGA curves of the MCM@PEI and MCM@PEIdodecane nanocomposites

determined to be approximately 17%. In comparison with MCM-41@PEI, the TGA curve of MCM-41@PEIdodecane shows bigger decomposition at the temperature range from 200 to 800 °C than MCM-41@PEI, indicating the successful modifying procedure with dodecyl moiety. The weight loss of dodecyl part grafted MCM-41@PEI is observed to be around 22%. According to these results, it was concluded that identical amounts of PEI and dododecane are grafted onto the mesoporous silica materials.

# 3.4 | Quality and quantity of the palladium immobilized onto the MCM-41@aPEI-Pd

ICP-OES technique was used to identify the presence of palladium and quantify the amount of the metal onto the nanocatalyst. It was found that 10.56% of palladium was loaded onto the MCM-41@PEI-dodecane. For further confirmation, XPS was also used to investigate the elemental composition of the MCM-41@aPEI-Pd nanocatalyst (Figure 4). The XPS result showed



FIGURE 4 X-ray photoelectron spectroscopy pattern of the MCM-41@aPEI-Pd nanocatalyst

significant amounts of organic moiety on the surface of MCM-41@aPEI-Pd as indicated by the C  $1s_{1/2}$ , N  $1s_{1/2}$ , and O  $1s_{1/2}$  appeared at 285, 405, and 537 eV, respectively. [<sup>42,43]</sup> Two sharp peaks were indicated at 340 and 348 eV for Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$ , respectively, confirming the presence of Pd at +2 state.<sup>[44]</sup> Based on the observed XPS peaks, it can be concluded that, Pd<sup>+2</sup> ions were entrapped into the polymer layer through amine groups.

# 3.5 | Application of the catalyst in Heck coupling reaction

The MCM-41@aPEI-Pd nanocatalyst was first evaluated for the C-C bond formation via Heck coupling reaction. For initial assessment, the Suzuki coupling reaction of iodobenzene and styrene was chosen as a model reaction to optimize the reaction conditions (Table 1). Variation of temperature in the range 75-100 °C revealed that the optimum temperature for the reaction is 90 °C (Table 1, entries 1-3). In addition, further experiments showed that 10 mg of the catalyst was sufficient to guarantee a good conversion (Table 1, entry 4). It was found that the highest yield could be achieved in the presence of DMF; while, the highset selectivity was obtained in DMSO (Table 1, entries 5 and 2). The reaction did not proceed successfully in the presence of inorganic bases like sodium acetate (data not shown) or nonpolar solvents like xylene and protic solvent like water and EtOH. But, clearly polar solvents showed proper efficiency for the reaction (Table 1, entries 4–6). With these results in hand, triethylamine and DMSO were chosen as best base and solvent, respectively.

To investigate the scope of the reaction, the ability of the nanocatalyst for Heck coupling reaction was further studied by using other styrene derivatives (Table 2). As illustrated in Table 3, it could be concluded that the catalyst could successfully catalyse both styrene and acrylate derivatives. The percentage of conversion and selectivity were in the range of 65–100%. Excellent yield was achieved for the reaction between iodobenzene and butyl acrylate, and the product was obtained in highest selectivity.

## 3.6 | Reusability of the catalyst

Leaching test was also applied to obtain the amount of the metal desorption from the solid catalyst. In order to determine metal species desorbed from the solid catalyst,

**TABLE 2** Using different styrene derivatives in the Heck coupling reaction

			Conversion	Selectivity %
Entry <sup>a</sup>	ArX	Substrate	%	(trans)
1	PhI	Styrene	96	91
2	PhI	4-methylstyrene	88	95
3	PhI	Acrylonitrile	82	86
4	PhI	Methyl acrylate	90	87
5	PhI	Butyl acrylate	100	100
6	PhI	Ethyl methyl acrylate	65	90

<sup>a</sup>**Condition:** ArI (1 mmol), trietylemine (1.5 mmol), styrene derivatives (1.1 mmol); temperature: 90 °C; time: 9 h; Catalyst: MCM-41@aPEI-Pd.

$1 \qquad 2 \qquad \underbrace{condition}_{(E)-isomer} + \underbrace{4}_{(Z)-isomer}$						
Entry <sup>a</sup>	Catalyst (g)	Solvent	Base	Temperature	Conversion %	Selectivity %(3)
1	0.05	DMSO	Triethylamine	75	78	94
2	0.05	DMSO	Triethylamine	90	89	98
3	0.05	DMSO	Triethylamine	120	83	96
4	0.01	DMSO	Triethylamine	90	75	90
5	0.05	DMF	Triethylamine	90	96	91
6	0.05	$DMA^b$	Triethylamine	90	92	89
7	0.05	CH <sub>3</sub> CN	Triethylamine	90	73	92
8	0.05	<i>p</i> -xylene	Triethylamine	90	2	51

**TABLE 1** Optimization of the reaction conditions for Heck coupling reaction

<sup>a</sup>Condition: iodobenzene (1 mmol), trietylemine (1.5 mmol), styrene (1.1 mmol), catalyst: MCM-41@aPEI-Pd. Time: 9 h. Conversion and selectivity were determined by GC analysis.

<sup>b</sup>DMA: dimethylacetamide.

-WILEY-Organometallic 7 of 9 Chemistry

**TABLE 3** Quantity of the leached palladium which obtained

 from ICP analysis and reusability of the catalyst in coupling reaction

Entry	Pd (ppm)	Yield (%)
Run 1	<0.2	95
Run 2	<0.1	94
Run 3	<0.1	92
Run 4	<0.015	92
Run 5	<0.010	91
% trans-product after fifth run		86

<sup>a</sup>**Condition:** PhI (1 mmol), trietylemine (1.5 mmol), styrene (1.1 mmol), temperature 90 °C, time 9 h. Catalyst: MCM-41@aPEI-Pd.

MCM-41@aPEI-Pd was stirred in aqueous media for 1 day. After separation of the catalyst, the solution was concentrated and tested for verification of the leached metal ion by ICP analysis and the isolated catalyst was also used for the next five runs under the above-mentioned condition. ICP analysis was revealed that the amount of the leached palladium from the catalyst is less than 0.2 ppm for the first run and less than 0.010 ppm even after the fifth run (Table 3). These results can imply that palladium was strongly chelated by MCM-41@PEIdodecane. To confirm the reusability of MCM-41@aPEI-Pd, we next run five-cycle reusability test of MCM-41@aPEI-Pd in the reaction between PhI and styrene. At the end of each run, the nanocatalyst was recovered, washed, and then dried before being used for the next run. The results confirmed the potential of the catalyst for at least five next runs without detectable loss in the yield of the product and selectivity.

# 3.7 | Application of the catalyst in oxidative Heck coupling reaction

Synthesis of 4-arylcoumarins via direct-arylation of inactivated coumarins has also attracted a great attention due to their diverse biological activities. Direct functionalization of desired scaffold through regioselective C-H bond activation provides an efficient cost-effective and atom-economical entry to these compounds as it eliminates the need for introducing protecting groups and reactive functionalities prior to C-C formation.<sup>[5]</sup> Therefore, development of general, atom-economical and regioselective arylation methods merits further considerations. Catalytic activity of MCM-41@aPEI-Pd nanocomposite was also investigated in oxidative Heck reaction of coumarins 5 with phenylboronic acid 6. To begin, coumarin was chosen as the test substrate in the oxidative Heck reaction with phenylboronic acid. We checked optimal conditions by screening various palladium sources. Fortunately, the reaction was efficiently catalysed in the presence of only 4 mol% of MCM-41@aPEI-Pd as optimized amount of the catalyst to achieve 4-phenylcoumarin 7 with only 5% of homo-coupling product 8 (Table 4, entry 1). But, the presence of phenantroline as ligand was necessary to perform the reaction, as in ligand free conditions, biphenyl 8 was

TABLE 4	Screening of reaction conditions for the intermolecular oxidative heck-reaction of coumarin and phenylboronic acid	

	<b>5</b> 0.1 mmol	$\begin{array}{c} \text{Lig.(20mol\%)}\\ \text{B(OH)}_2 & \text{Cat.(4mol\%)}\\ \hline \\ \textbf{DMF(0.3cc)}\\ \textbf{6}\\ 1.2 \text{ eq} \end{array}$			
Entry <sup>a</sup>	Cat.	Lig.	Solv.	Yield	
				3	4
1	MCM-41@aPEI-Pd	Phenantroline	DMF	87%	<5%
2	MCM-41@aPEI-Pd	Free ligand	DMF	-	40%
3	MCM-41@aPEI-Pd	Phenantroline	Toluene	20%	<5%
4	MCM-41@aPEI-Pd	Phenantroline	1,4-Dioxane	10%	<5%
5	MCM-41@aPEI-Pd	Phenantroline	CH <sub>3</sub> CN	5%	<5%
6	MCM-41@aPEI-Pd	Phenantroline	EtOH	40%	10%
7	MCM-41@aPEI-Pd	Phenantroline	DMF/H <sub>2</sub> O(80/20)	50%	10%
8 <sup>b</sup>	$Pd(OAc)_2$	Phenantroline	DMF	53%	10%
9 <sup>b</sup>	MCM/Pd	Phenantroline	DMF	-	37%

<sup>a</sup>Condition: coumarin (1 eq.), phenylboronic acid (1.2 eq.), Pd catalyst (4 mol%), ligand (20 mol%), O<sub>2</sub> (balloon pressure) in the corresponding solvent (0.4 M) were heated in a sealed tube at 100 °C for 24 h.

<sup>b</sup>10 mol% of Pd catalyst was used in the reaction.

**TABLE 5** Scope of the regioselective arylation of coumarins<sup>a</sup>



 $^a\textbf{Conditions:}$  coumarin 1(1 equiv.), arylboronic acid 2(1.1 mmol), MCM-41@aPEI-Pd (4 mol%), 1,10-phenanthroline (20 mol%), O\_2 (balloon pressure) in DMF (0.4 M) were heated in a sealed tube at 100 °C for 24 h.

constructed in 40% yield and 4-phenylcoumarin **7** was not detected at all (Table 4, entries 2). Solvents screening was also revealed that replacing DMF with other solvents such as 1,4-dioxane, acetonitrile, ethanol, and toluene result in lower yields (Table 5, entries 3–7). Pd(OAc)<sub>2</sub> and MCM/Pd showed unsatisfactorily low yield even in the presence of 10 mol% of the catalyst (Table 4, entries 8 and 9). When MCM/Pd was employed as catalyst, only trace amount of the desired product **7** was detected, while biphenyl **8** was obtained in 37% (Table 4, entry 2).

Using the optimized conditions, we then studied the scope and limitations of the oxidative Heck arylation of coumarins with various aryl boronic acids. Various electron-rich and electron-poor coumarins were tested in their reaction with phenylboronic acids (Table 5, entries 1–8). The desired products were obtained in high yields and the reactions were highly regioselective. However, 3-nitrophenylboronic acid did not react under the optimized reaction conditions (entry 6).

### 4 | CONCLUSION

In summary, we fabricated MCM-41@aPEI-Pd through a simple and reproducible two steps method. The catalyst showed proper efficacy for Heck and oxidative boron Heck coupling reactions with reusability for at least five runs with negligible yield dropping or palladium leaching. The reactions needed exceptionally small amount of the catalyst to achieve desired products with excellent selectivity. The high stability, simple recoverability, efficient

reusability and selectivity for the preparation of the desired products are some of advantages of this semi-heterogeneous nanocatalyst. Based on the above mentioned results, it could be concluded that this green and costeffective catalyst, with convenient experimental procedure, could be a valuable alternative for Heck and oxidative Heck coupling reaction.

#### ACKNOWLEDGEMENTS

This work was supported financially by the grants from Tehran University of Medical Sciences and Iran Science Elite Federation (ISEF), Tehran, Iran.

#### ORCID

Ali Ramazani D http://orcid.org/0000-0003-3072-7924

#### REFERENCES

- L. Ackermann, R. Born, *The Mizoroki-Heck Reaction*, Wiley, Chichester 2009 345.
- [2] M. Hosseini-Sarvari, A. Khanivar, F. Moeini, J. Iran. Chem. Soc. 2016, 13, 45.
- [3] R. Martinez, F. Voica, J. P. Genet, S. Darses, Org. Lett. 2007, 9, 3213.
- [4] I. S. Young, P. S. Baran, Nat. Chem. 2009, 1, 193.
- [5] M. Khoobi, M. Alipour, S. Zarei, F. Jafarpour, A. Shafiee, Chem. Commun. 2012, 48, 2985.
- [6] F. Jafarpour, H. Hazrati, N. Mohasselyazdi, M. Khoobi, A. Shafiee, *Chem. Commun.* 2013, 49, 10935.
- [7] A. H. De Vries, J. M. Mulders, J. H. Mommers, H. J. Henderickx, J. G. De Vries, Org. lett. 2003, 5, 3285.
- [8] A. H. de Vries, F. J. Parlevliet, L. Schmieder-van de Vondervoort, J. H. Mommers, H. J. Henderickx, M. A. Walet, J. G. de Vries, *Adv. Synth. Catal.* **2002**, *344*, 996.
- [9] J. G. De Vries, Dalton Trans. 2006, 421.
- [10] M. Pagliaro, V. Pandarus, R. Ciriminna, F. Béland, P. Demma Carà, Chem. Cat. Chem. 2012, 4, 432.
- [11] K. Niknam, M. Sadeghi Habibabad, A. Deris, F. Panahi, M. R. Hormozi Nezhad, J. Iran. Chem. Soc. 2013, 10, 527.
- [12] Á. Molnár, Chem. Rev. 2011, 111, 2251.
- [13] L. Yin, J. Liebscher, Chem. Rev. 2007, 107, 133.
- [14] X. S. Zhao, X. Y. Bao, W. Guo, F. Y. Lee, Mater. Today 2006, 9, 32.
- [15] H. Tüysüz, F. Schüth, Adv. Catal. 2012, 55, 127.
- [16] S. F. Motevalizadeh, M. Khoobi, A. Sadighi, M. Khalilvand-Sedagheh, M. Pazhouhandeh, A. Ramazani, M. A. Faramarzi, A. Shafiee, J. Mol. Catal. B: Enzym. 2015, 120, 75.
- [17] M. Khoobi, S. F. Motevalizadeh, Z. Asadgol, H. Forootanfar, A. Shafiee, M. A. Faramarzi, J. Magn. Magn. Mater. 2015, 375, 217.
- [18] R. J. White, R. Luque, V. L. Budarin, J. H. Clark, D. J. Macquarrie, *Chem. Soc. Rev.* 2009, *38*, 481.

- [19] T. Maegawa, Y. Kitamura, S. Sako, T. Udzu, A. Sakurai, A. Tanaka, Y. Kobayashi, K. Endo, U. Bora, T. Kurita, A. Kozaki, Y. Monguchi, H. Sajiki, *Chem. Eur. J.* 2007, *13*, 5937.
- [20] K. A. Flanagan, J. A. Sullivan, H. Müeller-Bunz, Langmuir 2007, 23, 12508.
- [21] K. R. Kumar, J. N. Kizhakkedathu, D. E. Brooks, *Macromol. Chem. Phys.* 2004, 205, 567.
- [22] M. Q. Slagt, S. E. Stiriba, H. Kautz, R. J. M. Klein Gebbink, H. Frey, G. V. Koten, Organometallics 2004, 23, 1525.
- [23] Z. Shen, Y. Chen, H. Frey, S. E. Stiriba, *Macromolecules* 2006, 39, 2092.
- [24] C. M. Nunez, B. S. Chiou, A. L. Andrady, S. A. Khan, *Macro-molecules* 2000, 33, 1720.
- [25] P. Veerakumar, P. Thanasekaran, K. -L. Lu, S. -B. Liu, S. Rajagopal, ACS Sustain. Chem. Eng. 2017, https://doi.org/ 10.1021/acssuschemeng.7b00921.
- [26] P. Ncube, T. Hlabathe, R. Meijboom, J. Cluster Sci. 2015, 26, 1873.
- [27] R. L. Oliveira, W. He, R. J. K. Gebbink, K. P. de Jong, *Catal. Sci. Tech.* 2015, 5, 1919.
- [28] F. Farjadian, M. Hosseini, S. Ghasemi, B. Tamami, RSC Adv. 2015, 5, 79976.
- [29] P. Puthiaraj, K. Pitchumani, Green Chem. 2014, 16, 4223.
- [30] C. Schlenk, A. W. Kleij, H. Frey, G. Koten, Angew. Chem., Int. Ed. 2000, 39, 3445.
- [31] S. E. Stiriba, M. Q. Slagt, H. Kautz, R. J. M. K. Gebbink, H. Frey, G. Koten, *Organometallics* **2004**, *23*, 1525.
- [32] S. E. Stiriba, M. Q. Slagt, H. Kautz, R. J. M. K. Gebbink, R. Thomann, H. Frey, G. Koten, *Chem. – Eur. J.* 2004, *10*, 1267.
- [33] M. Q. Slagt, S. E. Stiriba, R. J. M. K. Gebbink, H. Kautz, H. Frey, G. Koten, *Macromolecules* **2002**, *35*, 5734.
- [34] R. Salazar, L. Fomina, S. Fomine, Polym. Bull. (Berlin). 2001, 47, 151.

#### [35] H. Chen, Y. Wang, Ceram. Int. 2002, 28, 541.

[36] M. Khoobi, S. F. Motevalizadeh, Z. Asadgol, H. Forootanfar, A. Shafiee, M. A. Faramarzi, *Biochem. Eng. J.* 2014, *88*, 131.

nnlied

Organometallic Chemistry 9 of 9

- [37] L. Martins, D. Cardoso, Micro. Meso. Mater. 2007, 106, 8.
- [38] M. L. Kantam, M. Roy, S. Roy, B. Sreedhar, S. S. Madhavendra, B. M. Choudary, R. L. De, *Tetrahedron* 2007, 63, 8002.
- [39] Z. Ying, Z. Li, Z. Yong, S. Xiaonv, L. Liangxu, Mater. Lett. 2006, 60, 3221.
- [40] S. C. Laha, P. Mukherjee, S. R. Sainkar, R. Kumar, J. Catal. 2002, 207, 213.
- [41] Y. Yang, J. Hu, J. He, Sci. Rep. 2016, 6, 28749.
- [42] M. Kruk, M. Jaroniec, J. Phys. Chem. B. 1997, 101, 583.
- [43] Y. Ren, J. G. Rivera, L. He, H. Kulkarni, D. K. Lee, P. B. Messersmith, BMC Biotechnology. 2011, 11, 63.
- [44] Q. Zhao, Y. Zhu, Z. Sun, Y. Li, G. Zhang, F. Zhang, X. Fan, J. Mater. Chem. A 2015, 3, 2609.

#### SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

**How to cite this article:** Motevalizadeh SF, Alipour M, Ashori F, et al. Heck and oxidative boron Heck reactions employing Pd(II) supported amphiphilized polyethyleneimine-functionalized MCM-41 (MCM-41@aPEI-Pd) as an efficient and recyclable nanocatalyst. *Appl Organometal Chem*. 2017;e4123. https://doi.org/10.1002/aoc.4123