



# Recyclable Pd nanoparticles immobilized on amine functionalized LDH for the Suzuki–Miyaura cross-coupling reaction

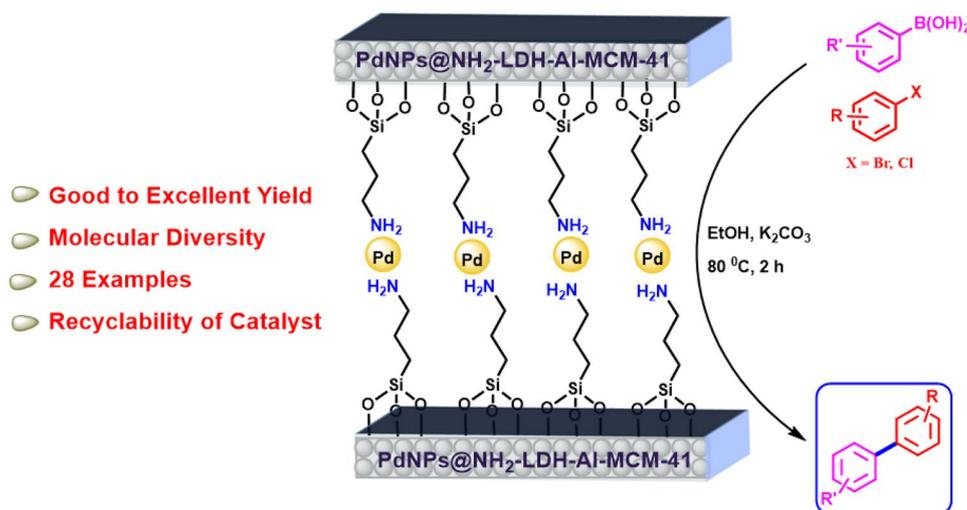
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## Abstract

In the present work, we invented a Pd nanoparticle immobilized on an amine-functionalized LDH catalyst (PdNP@NH<sub>2</sub>-LDH-Al-MCM-41) for cross-coupling reactions. The palladium was grafted onto the support by treating the Pd(OAc)<sub>2</sub> with NH<sub>2</sub>-LDH-Al-MCM-41 in acetone at room temperature. The prepared catalyst was characterized by FT-IR, SEM, TGA, TEM, and XPS techniques. The TEM characterization of the catalyst showed the uniform distribution of PdNPs with sizes ranging from 3 to 6 nm located inside the mesoporous. The Suzuki–Miyaura cross-coupling reaction was used to demonstrate the catalytic efficiency of the prepared PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 catalyst. The prepared and analyzed catalyst showed good to excellent activity in the Suzuki–Miyaura cross-coupling reaction of various aryl bromides with different aryl boronic acids in ethanol at 80 °C. The catalyst showed TON up to ~47 and TOF ~47 h<sup>-1</sup>. The catalytic results exhibited that the catalyst is completely recoverable with simple filtration. The catalytic efficiency shows a slight decrease in activity for the Suzuki–Miyaura cross-coupling reactions even after five repeated recycles. TEM images of the freshly prepared and reused catalysts (after five catalytic cycles) showed palladium nanoparticles remain unchanged at the end of the reactions.

## Graphical abstract



**Keywords** PdNPs · LDH · Suzuki–Miyaura coupling · Recyclability

Extended author information available on the last page of the article

## Introduction

Transition metal catalysts play a significant role in many areas of synthetic organic chemistry, mainly in catalysis (Magano and Dunetz 2011); (King and Yasuda 2004); (de Meijere et al. 2013). Many transition metals (Kambe et al. 2011); (Jeffery and Liebeskind 1996); (Brase et al. 1998), especially, the Pd catalysts offer relatively simple synthetic strategies and are widely used in many cross-coupling reactions for the synthesis of important organic molecules such as medicines, synthesis of bioactive natural products, manufacture of building blocks for supramolecular chemistry, organic materials, agrochemicals, and organic polymers (Noël and Buchwald 2011), (Nicolaou et al. 2005), (Rieger et al. 2003), (Skotheim and Reynolds 2006), (Sakamoto et al. 2009), (Surry and Buchwald 2011). Nowadays transition metals in the form of metal nanoparticles have attracted considerable attention in catalysis, due to their excellent electronic, optical, and increased number of catalytically active sites (Liu and Corma 2018), (Sawai et al. 2008), (Zhao et al. 2013), (Cherney et al. 2015). Particularly, owing to the high surface area, small particle size, high activity, and selectivity, palladium nanoparticles have intensively shown excellent catalytic activity for many chemical reactions, such as catalytic oxidation, hydrogenation, and different cross-coupling reactions (Trzeciak and Augustyniak 2019), (Chatterjee and Bhattacharya 2018), (Hong et al. 2020), (Balanta et al. 2011), (Nilsson et al. 2015), (Karimi et al. 2015). However, the aggregation of the PdNPs leads to the deactivation of the Pd metal. Furthermore, the difficulty in collecting PdNPs at the end of the reaction and their use for the next catalytic cycle limit their easy application in organic synthesis. Many efforts have been made to address these issues, such as immobilization of the PdNPs on high surface area solid supports such as metal oxides (Del Zotto and Zuccaccia 2017), mesoporous silica (Ncube et al. 2015), activated carbon (Jadhav et al. 2016), zeolites (Kumbhar et al. 2013b), biopolymers (Kumbhar et al. 2013a), (Jadhav et al. 2015a) and nanocomposites (Khan et al. 2020). Diaz-Sanchez et al. discussed the stability and recyclability of PdNPs and gives detailed applications and comparative studies around the solid support and role of ligands in the stability of PdNPs (Diaz-Sanchez et al.).

Recently, layered double hydroxides (LDH) have been acting as bridges between organic and inorganic composites and are widely used as heterogeneous support for many catalysts (Xu and Wei 2018), (Heravi and Mohammadi 2022), (Choudary et al. 2002) as LDH mainly ensures good dispersions and distribution of MNPs. In addition, LDH is cost-effective, thermally, and chemically stable, enabling catalytic reactions in various experimental conditions without a change in structure. Despite the vast versatility

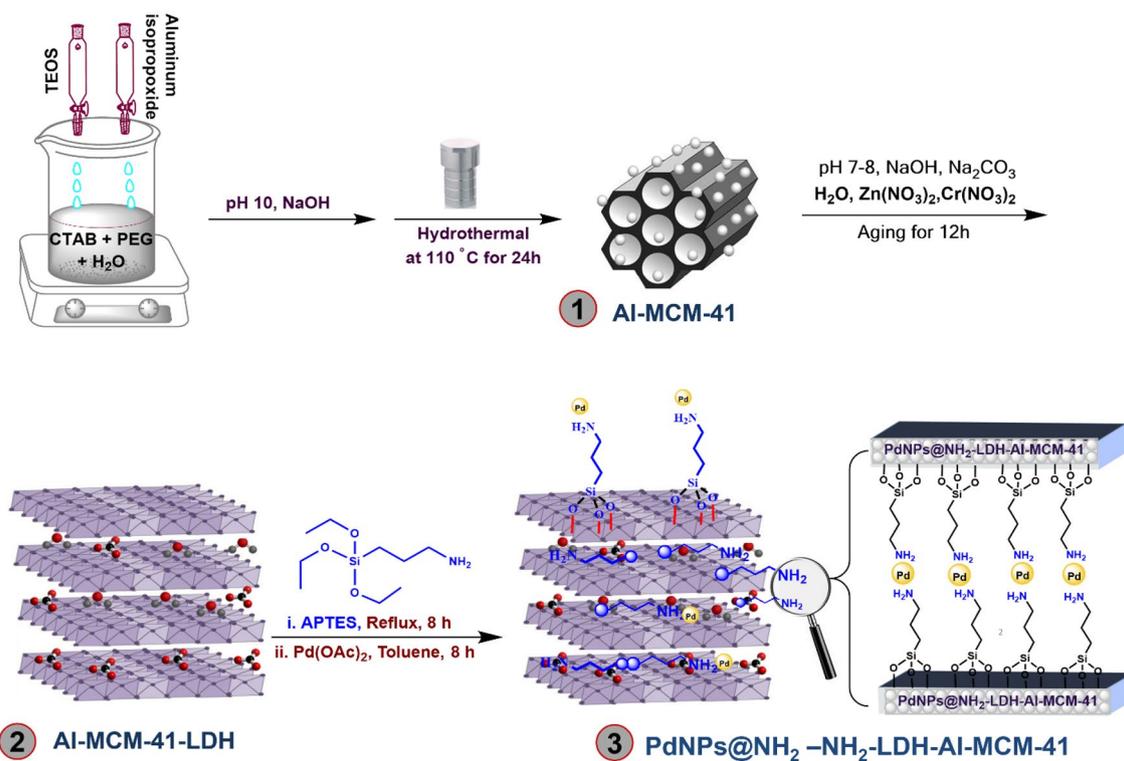
of characteristic ligands in coupling reactions, most of the reports of Pd-catalyzed coupling reactions have made use of phosphine-based compounds as excellent ligands (Martin and Buchwald 2008), (Jadhav and Rode 2017). Due to the strong donation by N favoring oxidative addition and reductive elimination steps in the catalytic cycle, chemists have focused on using N-based ligands (Kumbhar 2019), (Kumbhar 2017), (Diaz-Sanchez et al. 2021). In this regard, modification of the support with organic functionalities containing nitrogen as a donor atom is a widely used strategy in catalysis (Kumbhar 2019), (Kumbhar 2017). In this connection previously, Parida et al. used PdNPs supported diamine functionalized LDH for Suzuki coupling reaction of aryl halides with excellent catalytic activity (Singha et al. 2011).

In continuation of our previous work related to N-based materials in Pd-catalyzed cross-coupling reactions (Kumbhar et al. 2013a), (Jadhav et al. 2015a), the present work demonstrates the fabrication of easily separable Pd catalyst (PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41) based on amine-functionalized LDH. The catalyst was fully characterized by various analytical techniques like IR, SEM, TEM, EDS, and XPS. Moreover, their efficiency was tested for the Suzuki coupling reaction in the presence of K<sub>2</sub>CO<sub>3</sub> as a base in ethanol at 80 °C.

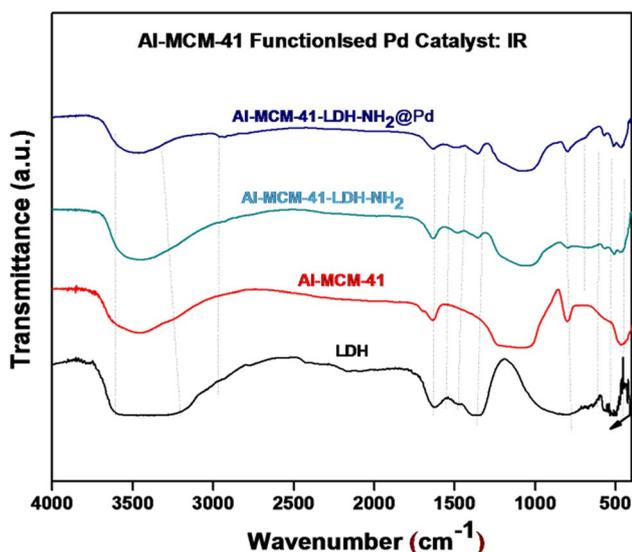
## Results and discussion

### Synthesis of PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 catalyst

The complete preparation route for the synthesis of the catalyst includes three steps (Scheme 1). The Al-MCM-41 was prepared by hydrothermal method (Mello et al. 2011), (Nale et al. 2016), (Hong and Zaera 2012), (Vinu et al. 2005), (Parida and Rath 2009), (Cauvel et al. 1997), (Pujari et al. 2014), and LDH-Al-MCM-41 was prepared by a simple in situ co-precipitation method (Fan et al. 2014), (Fu et al. 2015). The amine-functionalized LDH-Al-MCM-41 (NH<sub>2</sub>-LDH-Al-MCM-41) was synthesized by the standard reflux method (Mello et al. 2011), (Parida and Rath 2009), (Cauvel et al. 1997). In a typical procedure, the LDH-Al-MCM-41 was suspended in refluxing toluene taken in a round-bottom flask, and treated with aminopropyl triethoxy silane (APTES). Finally, the obtained NH<sub>2</sub>-LDH-Al-MCM-41 (1 g) was treated with Pd(OAc)<sub>2</sub> (0.0226 g) in dry acetone (10 mL) at room temperature. The resulting solid was washed with acetone (3 × 5 mL) and dried under a vacuum generating PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41. The anchored Pd content on NH<sub>2</sub>-LDH-Al-MCM-41 was found to be 0.076 mmol g<sup>-1</sup> as determined by ICP-AES analysis.



**Scheme 1** Synthetic route for the preparation of PdNPs@NH<sub>2</sub>-LDH-AI-MCM-41 catalyst



**Fig. 1** IR spectrum of PdNPs@NH<sub>2</sub>-LDH-AI-MCM-41 catalyst

### Characterization of PdNPs@NH<sub>2</sub>-LDH-AI-MCM-41 catalyst

To further verify the presence and amount of the Pd on the support, the obtained PdNPs@NH<sub>2</sub>-LDH-AI-MCM-41

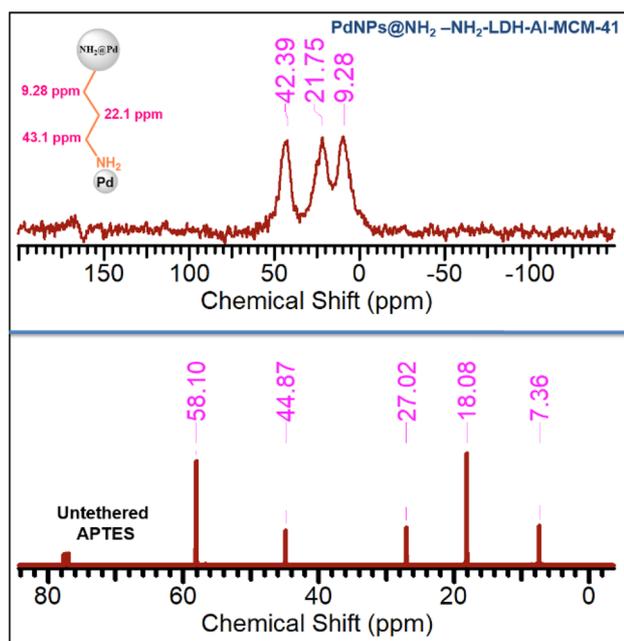
catalyst was characterized using IR, SEM-EDS, BET, TEM, XRD, TGA, and XPS techniques.

### IR analysis

The FTIR spectral data for LDH, LAM, AI-MCM-41, NH<sub>2</sub>-LDH-AI-MCM-41, and PdNPs@NH<sub>2</sub>-LDH-AI-MCM-41 are shown in Fig. 1. The band at 690 cm<sup>-1</sup> (N-H bending vibration) and 1532 cm<sup>-1</sup> (–NH<sub>2</sub> symmetric bending vibration) confirmed the successful grafting of organic –NH<sub>2</sub> amine on the surface of AI-MCM-41 nanocomposite. This is also supported by the characteristic asymmetric vibration of the –CH<sub>2</sub> group of propyl chain in APTES observed at 2927 cm<sup>-1</sup> (Weng et al. 2018).

### <sup>13</sup>C CP/MAS NMR Spectrum

The chemical structure of PdNPs@NH<sub>2</sub>-LDH-AI-MCM-41 catalyst was established by solid-state <sup>13</sup>C NMR (Fig. 2). As designated, the three methylene groups present in the catalyst, showed distinct signals with equal intensities at 9.28, 21.75 and 42.39 ppm (Weng et al. 2018) (Li 2005), (Mehdi et al. 2005).



**Fig. 2**  $^{13}\text{C}$  CP/MAS NMR spectrum of PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 catalyst

**Table 1** N<sub>2</sub> Adsorption–desorption isotherms data summary

Catalysts	$A/\text{m}^2 \text{g}^{-1}$	$V_T/\text{cm}^3 \text{g}^{-1}$	$\langle d \rangle/\text{nm}$
ZnCrLDH	56	–	3–5
Al-MCM-41	1089	0.61	6.63
LDH	305.7	0.35	4.59
Catalyst	121.3	0.10	2.98

### BET analysis

The prepared catalyst's specific surface area and pore-size distribution were estimated by Brunauer–Emmett–Teller (BET) method (Table 1). The specific surface area of the catalyst was 121.3 m<sup>2</sup>/g which is 10 times lower than Al-MCM-41, due to the immobilization of organic functionality on support. Moreover, the catalyst displayed a mesoporous property with an average pore size of 2.98 nm (Fan et al. 2014), (Fu et al. 2015).

### SEM–EDS analysis

Initially, we tried to find direct evidence of the occurrence of PdNPs by using SEM coupled to the EDS of the catalyst (Fig. 3). In SEM analysis, PdNPs were not observed as PdNPs were positioned inside the support. However, the EDS spectrum of the catalyst indicated that, in addition to Si and Al, there are signals for Pd, which indicates the presence of substantial amounts of Pd on the support material.

### TEM analysis

To gain exact information about the size of PdNPs, TEM analysis of PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 was carried out (Fig. 4). The typical TEM images of the catalyst showed that the diameter of the prepared PdNPs was about 3–5 nm with a thin size distribution. The decent dispersion of PdNPs on support should be attributed to the strengthened metal-support interaction of amino groups on support and PdNPs. From these results observed that the -NH<sub>2</sub> functional groups performed as adsorption and coordination centers for PdNPs.

### XPS analysis

The XPS is the most significant technique used to determine the oxidation state of surface elements in materials. The XPS spectrum of PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 (Fig. 5) shows the survey of the surface of the catalyst. The observed peak of the Pd 3d orbit is located at binding energy around 335.5 eV and 342.7 eV arising from the Pd3d<sub>5/2</sub> and Pd3d<sub>3/2</sub> orbital, respectively, which are the typical peaks of Pd metal. The two binding energy peaks observed at 335.5 eV and 342.7 eV are assigned to Pd(0) in the PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 composite (Liu et al. 2018), (Jadhav et al. 2015b). The above result indicated that the Pd<sup>2+</sup> is reduced to the Pd(0).

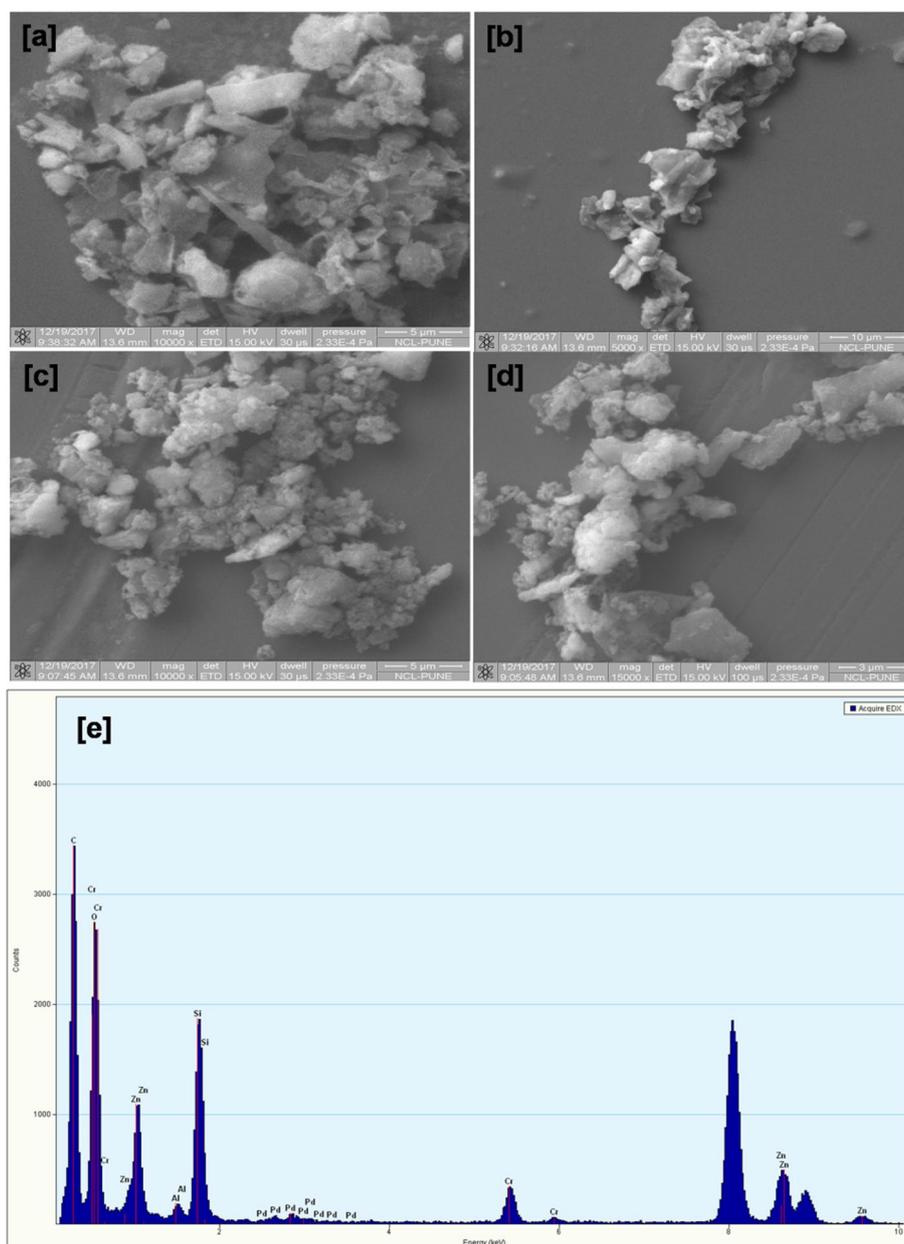
### TGA-DTA

The thermal behavior of the PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 catalyst was studied by TGA-DTA analysis (Fig. 6). The TGA analysis showed three weight losses. The first is 3.5% weight loss due to the desorption of physically adsorbed water molecules up to 120 °C temperature. The second weight loss of 25.59% observed at 150 to 600 °C is due to the decomposition of grafted alkylamine (Rao et al. 2018) as well as the loss of water via condensation of Si–OH groups (Chen et al. 1993). The weight of APTES started at 150 °C and reached the maximum at approximately 600 °C. The final loss (around 15%) in the region last (> 600 °C) is due to the dehydroxylation of the support structure (Bérend et al. 1995).

### Suzuki–Miyaura cross-coupling reactions

The synthesized PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 catalyst was applied to Suzuki–Miyaura cross-coupling reaction. To check the efficiency of the catalyst, the 4-bromoacetophenone (1 mmol) and phenylboronic acid (1 mmol) were selected as model reaction partners under different reaction conditions. Initially, the effect of solvent on the Suzuki–Miyaura coupling reaction was studied and

**Fig. 3** SEM images of (a) Al-MCM-41, (b) Al-MCM-41-LDH, (c) NH<sub>2</sub>-LDH-Al-MCM-41, (d) PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41, and (e) EDS map of PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41



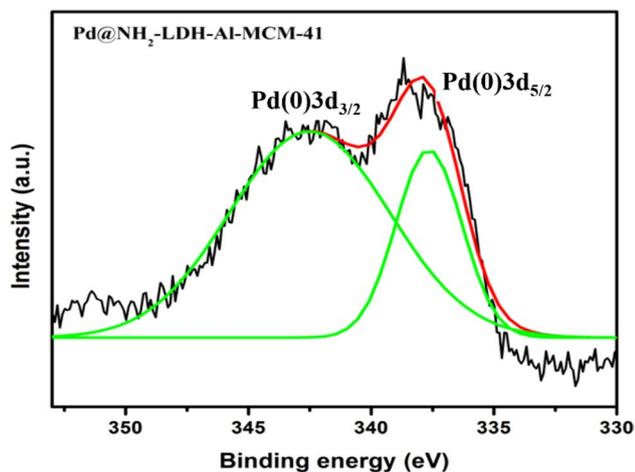
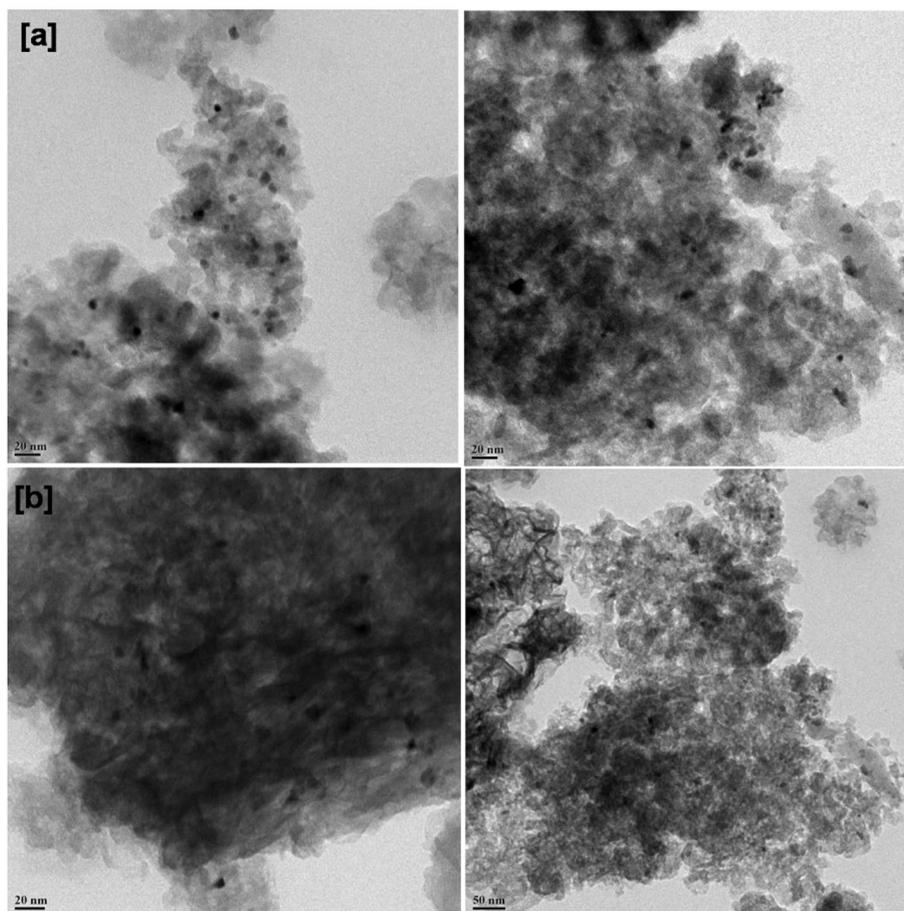
the results are depicted in Table 2. When 4-bromoacetophenone and phenylboronic acid reacts in the presence of 2 mol% catalysts (0.116 g) and K<sub>2</sub>CO<sub>3</sub> (2 mmol) in 95% EtOH (5 mL) under stirring at 80 °C. The desired coupling product was obtained with 92% yield, TON = 45.86, and TOF = 22.93 h<sup>-1</sup>. (Table 2, entry 7). However, using organic solvents like MeCN, THF, and toluene, the reaction under identical conditions gave poor to moderate yields within 12 h (Table 2, entries 1–6).

The base plays a vital role in the activation of phenylboronic acid (Braga et al. 2005), hence the effect of nature and the amount of organic and inorganic bases were studied in ethanol at 80 °C (Table 3). Though, organic bases like pyrrolidine, dimethylamine, and piperidine are commonly

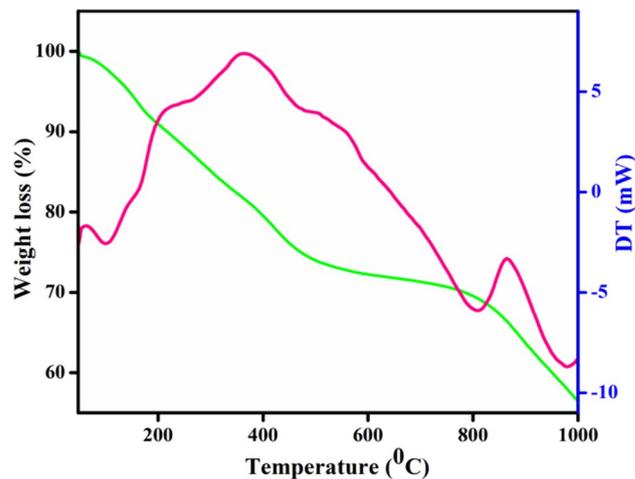
used in the Suzuki–Miyaura coupling reactions. These bases were proved to be less effective (Table 3, entries 3–5). The carbonate base, K<sub>2</sub>CO<sub>3</sub> gave an excellent yield of the desired product (Table 3, entries 2–4), while K<sub>3</sub>PO<sub>4</sub> and NaOH were highly inactive (Table 3, entries 5 and 6). It is noteworthy to mention that decreasing the quantity of K<sub>2</sub>CO<sub>3</sub> from 2.0 equivalent to 1.0 equivalent considerably decreased the yield of the coupling product (Table 3, entries 11–14), representing that the 2 equivalent of the base was the optimal amount for the effective coupling. Thus 2 mol % catalyst was highly efficient as it attained the highest TON = 45.86 and TOF = 22.93 h<sup>-1</sup>.

The effect of the amount of catalyst loading was also examined. A maximum yield of 92% was obtained for a

**Fig. 4** TEM images of (a) PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 catalyst and (b) recycled catalyst



**Fig. 5** XPS spectra of PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 catalyst

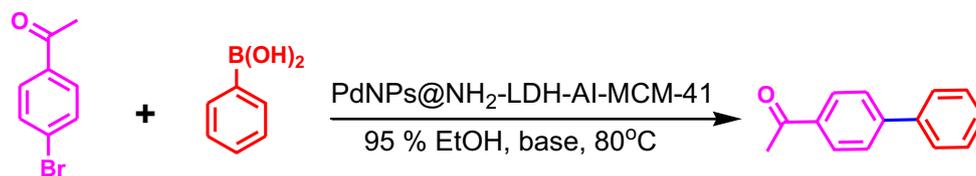


**Fig. 6** TGA-DTA analysis of PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 catalyst

2.0 mol% catalyst. Decreasing the amount of the catalyst resulted in a slightly lower yield even after a long reaction time (Table 3, entry 12). Moreover, increasing the quantity of catalyst did not have much significant effect on the yield

of the product as well as reaction time (Table 3, entries 13 and 14).

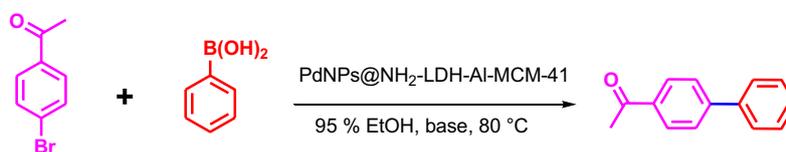
Through the optimization studies, the outcome of temperature and reaction time was also examined using a 2 mol

**Table 2** The effect of solvent on the Suzuki–Miyaura cross-coupling reaction

Entry	Solvent	Time (h)	Yield (%) <sup>a</sup>	TON	TOF (h <sup>-1</sup> )
1	EtOH	2	88	43.82	21.91
2	CH <sub>3</sub> CN	12	10	4.84	0.40
3	DMF	12	70	34.90	2.90
4	THF	12	50	24.96	2.08
5	Toluene	12	57	28.28	2.35
6	MeOH	12	73	36.43	3.03
7	95% EtOH	2	92	45.86	22.93
8	H <sub>2</sub> O	12	15	7.38	0.61

Reaction conditions: 4-bromoacetophenone (1 mmol), phenylboronic acid (1 mmol), catalyst (2 mol %), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), solvent (5.0 mL), at 80 °C in air

<sup>a</sup>Isolated yields

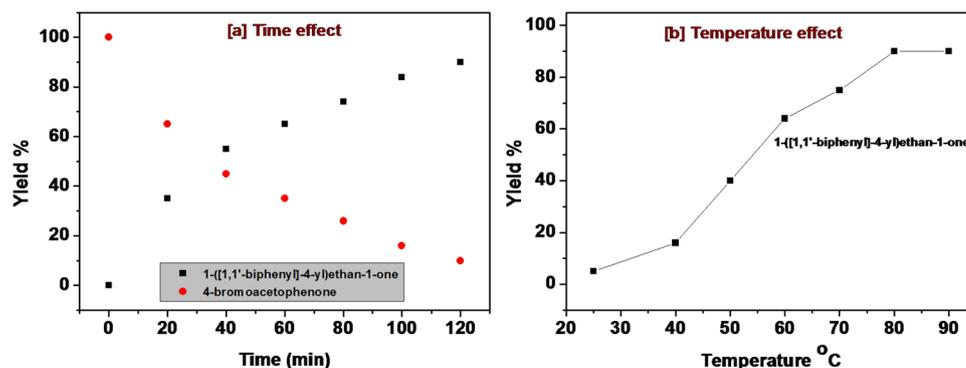
**Table 3** The effect of base and catalysts loading on the Suzuki–Miyaura cross-coupling reaction

Entry	Base (mmol)	Catalyst (mol %)	Time (h)	Yield (%) <sup>a</sup>	TON	TOF (h <sup>-1</sup> )
<i>Optimization of base</i>						
1	K <sub>3</sub> PO <sub>4</sub> (2 mmol)	2.0	12	20	9.93	0.82
2	NaOH (2 mmol)	2.0	12	10	4.84	0.40
3	Et <sub>3</sub> N (2 mmol)	2.0	12	26	12.73	1.06
4	Me <sub>2</sub> NH (2 mmol)	2.0	12	60	30.82	2.56
5	Pipridine (2 mmol)	2.0	12	25	12.42	1.04
6	Pyrrolidine (2 mmol)	2.0	12	30	14.77	1.23
7	K <sub>2</sub> CO <sub>3</sub> (2 mmol)	2.0	2.0	92	45.86	22.93
<i>Optimization of amount of base</i>						
8	K <sub>2</sub> CO <sub>3</sub> (1 mmol)	2.0	12	55	27.26	2.27
9	K <sub>2</sub> CO <sub>3</sub> (1.5 mmol)	2.0	12	80	39.74	3.31
10	K <sub>2</sub> CO <sub>3</sub> (2.5 mmol)	2.0	2.0	92	45.86	22.93
11	K <sub>2</sub> CO <sub>3</sub> (3 mmol)	2.0	2.0	92	45.86	22.93
<i>Optimization of catalyst loading</i>						
12	K <sub>2</sub> CO <sub>3</sub> (2 mmol)	1.0	4.0	85	84.59	21.14
13	K <sub>2</sub> CO <sub>3</sub> (2 mmol)	1.5	3.0	90	59.79	19.93
14	K <sub>2</sub> CO <sub>3</sub> (2 mmol)	2.5	2.0	92	36.68	18.34
15	K <sub>2</sub> CO <sub>3</sub> (2 mmol)	3.0	2.0	92	30.57	15.28
16	K <sub>2</sub> CO <sub>3</sub> (2 mmol)	5.0	2.0	92	18.34	9.17

Reaction conditions: 4-bromoacetophenone (1 mmol), phenylboronic acid (1 mmol); catalyst (1–3 mol %); base (1.0–3.0 mmol); 95% EtOH (5.0 mL), at 80 °C in air

<sup>a</sup>Isolated yields

**Fig. 7** Effect of temperature and reaction time on the yield of the coupling reaction



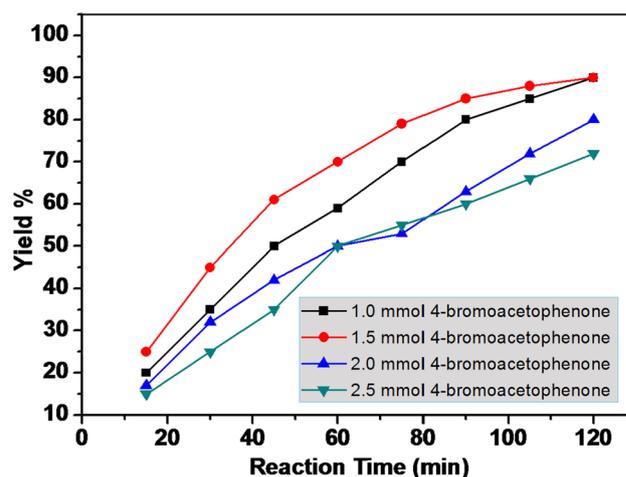
% catalyst in the presence of  $K_2CO_3$  as a base in 95% EtOH at different temperatures (Fig. 7). With decreasing the reaction temperature significant decreases in the yield of product with increased reaction time was observed.

The effect of the amount (mmol) of aryl bromide on the yield of the product was also scrutinized under optimized reaction conditions and the results are summarized in Fig. 8. In each of the experiments, a constant ratio of 4-bromoacetophenone was coupled with phenylboronic acid. The results indicated that the nice activity was testified for 1.5 mmol of aryl bromide. Though the 1.0 mmol works less efficiently initially, as compared to other scales, it showed similar reactivity as to 1.5 mmol of 4-bromoacetophenone. It was also shown that half of the reaction was completed within 1 h.

Next, we further explored the activity of the catalyst for coupling various aryl bromides with different arylboronic acids under optimized reaction protocol, and results are précised in Table 4. It was observed that excellent catalytic activity was observed for the Suzuki–Miyaura coupling reaction with differently substituted phenylboronic acids. Similarly, sterically hindered 1-naphtyllboronic acid was easily coupled with 4-florobromobenzene in excellent yields in 3–6 h. The catalyst attained TON up to 47.34 and TOF  $\sim 47.34 h^{-1}$ .

To further extend the scope of this methodology, we carried out reactions of 4-bromobenzophenone with various substituted arylboronic acids. The results depicted in Table 5 showed that there was no appreciable change in reactivity in most of the cases. The maximum TON of 47.42 and TOF of  $23.741 h^{-1}$  were obtained for compound 1 under optimized reaction conditions.

It is noteworthy that the reactions of bromo-biphenyl coupled with electron-withdrawing groups donating groups, such as chloro, bromo, and methyl functional groups of arylboronic acids, were all converted to the corresponding coupling products with high yield (Table 6). The best TON



**Fig. 8** The effect of concentration of 4-bromoacetophenone on coupling with phenylboronic acid

(46.89) and TOF ( $7.81 h^{-1}$ ) were obtained for the reaction of 4-bromobiphenyl and phenylboronic acid.

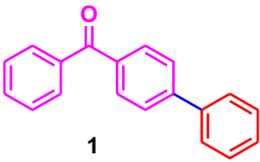
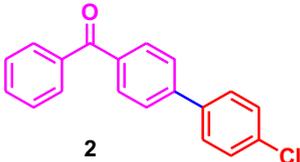
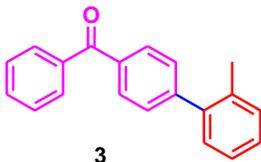
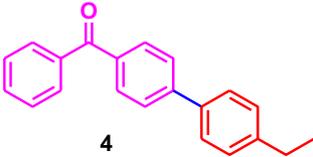
Suzuki–Miyaura cross-coupling is the facile route to form C–C bonds for the construction of biaryl compounds which are used for the synthesis of bioactive compounds. Therefore, we focus to prepare a variety of biaryl compounds. The catalytic activity of PdNPs@ $NH_2$ -LDH-Al-MCM-41 was extended to a couple of 4-bromo-biphenyl with various arylboronic acids. The results in Table 7 showed that the conversion of 4-bromo-biphenyl into the desired products was 85–93% yields in 2 h (Table 7, entries 1–6). A good catalytic performance was observed for all the phenylboronic acids containing both electron-donating and withdrawing groups.

Leaching of the Pd metal during the reaction is one of the problems for PdNPs supported catalysts. LDH can largely avoid the leaching of the active species through the protective function. This was ascertained based on the hot filtration

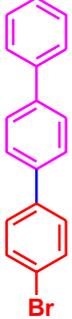
**Table 4** The generality of the reaction protocol of coupling aryl bromides with arylboronic acids

<p><b>1</b> Yield= 95 % Time= 1h TON= 47.34 TOF= 47.34 h<sup>-1</sup></p>	<p><b>2</b> Yield= 88 % Time= 3h TON= 43.96 TOF= 14.65 h<sup>-1</sup></p>	<p><b>3</b> Yield= 85 % Time= 4h TON= 42.33 TOF= 10.58 h<sup>-1</sup></p>	<p><b>4</b> Yield= 88 % Time= 3h TON= 43.90 TOF= 14.63 h<sup>-1</sup></p>	<p><b>5</b> Yield= 86 % Time= 5h TON= 43.00 TOF= 8.6 h<sup>-1</sup></p>
<p><b>6</b> Yield= 87 % Time= 6h TON= 43.37 TOF= 7.22 h<sup>-1</sup></p>	<p><b>7</b> Yield= 88 % Time= 4h TON= 44.00 TOF= 11.0 h<sup>-1</sup></p>	<p><b>8</b> Yield= 95 % Time= 4h TON= 47.17 TOF= 11.79 h<sup>-1</sup></p>	<p><b>9</b> Yield= 85 % Time= 6h TON= 42.18 TOF= 7.03 h<sup>-1</sup></p>	<p><b>10</b> Yield= 86 % Time= 6h TON= 42.68 TOF= 7.11 h<sup>-1</sup></p>
<p><b>11</b> Yield= 84 % Time= 6h TON= 41.69 TOF= 6.94 h<sup>-1</sup></p>	<p><b>12</b> Yield= 90 % Time= 3h TON= 44.71 TOF= 14.90 h<sup>-1</sup></p>	<p><b>13</b> Yield= 86% Time= 6h TON= 42.82 TOF= 7.13 h<sup>-1</sup></p>	<p><b>14</b> Yield= 85% Time= 6h TON= 42.29 TOF= 7.04 h<sup>-1</sup></p>	<p><b>15</b> Yield= 88% Time= 5h TON= 43.69 TOF= 8.73 h<sup>-1</sup></p>
<sup>a</sup> Reaction conditions: arylbromides (1 mmol), arylboronic acids (1 mmol), PdNPs@NH <sub>2</sub> -LDH-Al-MCM-41 (2 mol %), K <sub>2</sub> CO <sub>3</sub> (2 mmol), 95 % EtOH (5.0 mL), at 80 °C in air. Isolated yields.				

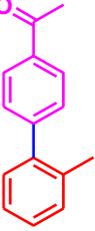
**Table 5** The generality of the reaction protocol of coupling 4-bromobenzophenone with different arylboronic acids

 <p><b>1</b> Yield= 95 % Time= 2h TON= 47.42 TOF= 23.71 h<sup>-1</sup></p>	 <p><b>2</b> Yield= 90 % Time= 4h TON= 44.78 TOF= 11.19 h<sup>-1</sup></p>	 <p><b>3</b> Yield= 87 % Time= 6h TON= 43.38 TOF= 7.23 h<sup>-1</sup></p>	
 <p><b>4</b> Yield= 88 % Time= 4h TON= 43.88 TOF= 10.97 h<sup>-1</sup></p>			
<p>Reaction conditions: 4-bromobenzophenone (1 mmol), arylboronic acids (1 mmol), PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 (2 mol %), K<sub>2</sub>CO<sub>3</sub> (2 mmol), 95 % EtOH (5.0 mL), at 80 °C in air. Isolated yields.</p>			

**Table 6** The generality of the reaction protocol of coupling 4-bromobiphenyl with different arylboronic acids

 <p><b>1</b> Yield= 94 % Time= 6h TON= 46.89 TOF= 7.81 h<sup>-1</sup></p>	 <p><b>2</b> Yield= 90 % Time= 6h TON= 44.95 TOF= 7.49 h<sup>-1</sup></p>	 <p><b>3</b> Yield= 87 % Time= 6h TON= 43.24 TOF= 7.20 h<sup>-1</sup></p>	 <p><b>4</b> Yield= 93 % Time= 6h TON= 46.24 TOF= 7.70 h<sup>-1</sup></p>
<p><sup>a</sup>Reaction conditions: 4-bromobiphenyl (1 mmol), arylboronic acids (1 mmol), PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 (2 mol %), K<sub>2</sub>CO<sub>3</sub> (2 mmol), 95 % EtOH (5.0 mL), at 80 °C in air. Isolated yields.</p>			

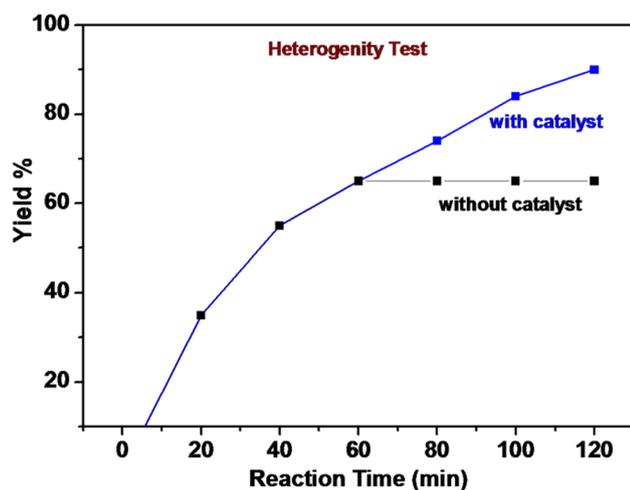
**Table 7** The generality of the reaction protocol of coupling 4-bromoacetophenone with different arylboronic acids

 <p><b>1</b> Yield= 92 % Time= 2h TON= 45.86 TOF= 22.93 h<sup>-1</sup></p>	 <p><b>2</b> Yield= 93 % Time= 6h TON= 46.16 TOF= 7.69 h<sup>-1</sup></p>	 <p><b>3</b> Yield= 88 % Time= 5h TON= 43.97 TOF= 8.79 h<sup>-1</sup></p>
 <p><b>4</b> Yield= 91% Time= 4h TON= 45.41 TOF= 11.35 h<sup>-1</sup></p>	 <p><b>5</b> Yield= 90% Time= 4h TON= 44.94 TOF= 11.23 h<sup>-1</sup></p>	 <p><b>6</b> Yield= 85% Time= 6h TON= 42.35 TOF= 7.05 h<sup>-1</sup></p>
<p><sup>a</sup>Reaction conditions: 4-bromoacetophenone (1 mmol), arylboronic acids (1 mmol), PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 (2 mol %), K<sub>2</sub>CO<sub>3</sub> (2 mmol), 95 % EtOH (5.0 mL), at 80 °C in air. Isolated yields.</p>		

and leaching tests (Sheldon et al. 1998). This study was carried out by coupling 4-bromoacetophenone and phenylboronic acid under optimized reaction conditions. After 65% conversion of the 4-bromoacetophenone (analyzed by GC), the catalyst was separated at 80 °C and the reaction was continued by stirring the reaction mixture for an additional 2 h at 80 °C. There was no more increase in the product yield, indicating that the catalyst was truly heterogeneous in nature (Fig. 9). The Pd leaching in the reaction was also tested by

investigating Pd concentration in the reaction mixture by ICP-AES. The ICP-AES results showed that there was no Pd leaching.

From an economic and industrial point of view, the lifetime of the catalyst and its reusability is very important. In this connection, the recyclability of the catalyst was investigated for the reactions of 4-bromoacetophenone with phenylboronic acid. After the completion of the reaction, the catalyst was separated by centrifugation and washed with

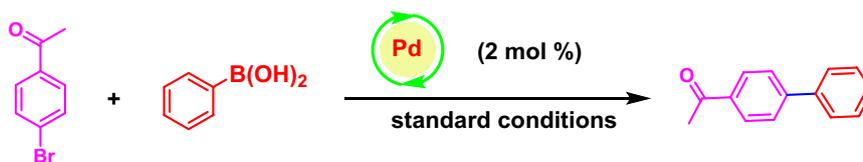


**Fig. 9** Hot filtration test of catalyst in Suzuki–Miyaura coupling reaction

water and organic solvent several times. This catalyst was then reused for the next cycle under the same reaction conditions with freshly charged reactants. The catalyst exhibited moderate activity, with an 80% yield of the desired coupling product after five cycles (Fig. 10). The moderate catalytic performance can be attributed to the protection of PdNPs, which prevents it from leaching into the solution and the catalyst showed 10 to 12% decrease of yield after five catalytic cycles, confirming that the crystalline structure and integrity of the well retained during the reaction as analyzed by TEM analysis (Fig. 4) (Molnár and Papp 2017).

The present reaction protocol was confirmed with those similar catalysts reported for Heck coupling reactions (Table 8). It was observed that the present method is more efficient as compared to some heterogeneous Pd amine-based catalysts. It required comparatively less time.

**Fig. 10** Recyclability of the catalyst in the Suzuki–Miyaura coupling reaction



Cycle	Time (h)	Yield %
Fresh	2	92
1	4	90
2	6	85
3	6	82
4	6	80

**Table 8** Comparison of the present method with heterogeneous Pd amine-based catalysts

Catalyst (mol%)	Solvent	T (°C)	Time (h)	Yield (%)	Reuse	Ref
Pd-APGO (2)	H <sub>2</sub> O;EtOH	80	6	45–96	5	Saptal et al. (2019)
MCNTs-(A-V)-Silica-Pd (1.5)	EtOH	Reflux	1.5–24	71–95	7	Khalili et al. (2017)
Pd(4)en(2)HMS (4)	Aq. DMF	80	6	80–99	3	Das et al. (2019)
Pd-CS-SiO <sub>2</sub> (2)	EtOH	80	1–10	60–95	5	Jadhav et al. (2015a, b)
BnPd–DnPd (0.05)	Toluene	100	0.5–3.0	21–100	5	Fukaya et al. (2011)
LDH-Pd(0)	Dioxane–water	80	10	64–94	–	Singh et al. (2011)
Iminatophosphanyl-Pd-SiO <sub>2</sub>	H <sub>2</sub> O/TBAB	60	4–10	80–94	6	Lee et al. (2010)
Pd-Al <sub>2</sub> O <sub>3</sub> -CELL (1)	DMF: H <sub>2</sub> O	80	20 min-9 h	40–97	5	Kumbhar et al. (2013a, b)
PdNPs-NH <sub>2</sub> -LDH-Al-MCM-41(2)	EtOH	80	1–6	84–95	6	Present work

## Conclusion

This work reports the amine-functionalized PdNPs@NH<sub>2</sub>-LDH-Al-MCM-41 catalyst was developed using a simple protocol that can be adapted for the synthesis of C–C coupling compounds. After synthesis and characterization of the catalyst, we checked its applicability as the catalyst for Suzuki–Miyaura cross-coupling reactions of various aryl bromides and arylboronic acids containing different functional groups. The catalyst showed good to excellent yields of the desired cross-coupling products (84–95%) without the formation of homocoupling products, which is one of the problems associated with other catalysts. Only a few catalysts were applied for the synthesis of 1–4 arylbenzenes. The prepared catalyst showed excellent yields of 1–4 biarylbenzenes. The prepared catalyst showed excellent recyclability and thermal stability with coupling yields maintained over six catalytic cycles. Unfortunately, the catalyst failed to couple aryl chlorides.

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## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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