

# A highly efficient heterogeneous montmorillonite K-10-supported palladium catalyst for Suzuki–Miyaura cross-coupling reaction in aqueous medium

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**A heterogeneous montmorillonite K-10-supported palladium triphenylphosphine catalyst is reported for the Suzuki–Miyaura cross-coupling reaction at room temperature. A library of electronically diverse aryl bromides and arylboronic acids underwent the cross-coupling reaction at very good rates in aqueous solvent. The reusability of the catalyst was also examined and it was found to be effective up to three catalytic cycles. Copyright © 2014 John Wiley & Sons, Ltd.**

**Keywords:** C–C coupling; Pd–mont-K-10; heterogeneous; reusability; Suzuki–Miyaura

## Introduction

In recent years transition metal-based heterogeneous catalyst systems have been found to be some of the most effective tools for cross-coupling reactions of various types. Among these, Pd-based catalyst systems have attracted wide attention owing to their excellent catalytic activity in Suzuki–Miyaura, Sonogashira, Heck and Tsuji–Trost reactions.<sup>[1–6]</sup> The Suzuki–Miyaura reaction is a commonly studied reaction where arylboronic acid couples with aryl halide to produce diverse biaryls which have been recognized as potential intermediates in agrochemicals, material science and some pharmaceutical products.<sup>[7–11]</sup> Due to easy availability of substrates with various functionalities and low toxicity associated with organoboron compounds, the Suzuki reaction ranks top among its competitors.<sup>[12]</sup> Initially these reactions were carried out with homogeneous Pd catalysts in the presence of amine-based,<sup>[13]</sup> phosphine-based<sup>[14,15]</sup> and oxime-based<sup>[16]</sup> ligands. In spite of the very high efficiency of homogeneous catalysts, Pd contamination of products is a major drawback of such systems.<sup>[17,18]</sup> Also, from the commercial point of view, lack of possibility of reuse of such costly homogeneous catalysts makes their widespread or industrial use less viable. Considering the above, the use of supported or impregnated heterogeneous Pd catalyst will obviously be a better alternative. Recently various reports have been published where Pd is embedded on various solid matrices such as zeolite,<sup>[19,20]</sup> microporous polymers,<sup>[21–24]</sup> mesoporous silica,<sup>[25–28]</sup> charcoal,<sup>[29–31]</sup> clay,<sup>[32]</sup> metal oxides,<sup>[33,34]</sup> etc. In spite of these developments, the main concern with these systems is the use of some additives with concomitant application of heat in the form of microwave or reflux for achieving optimum coupling.<sup>[35–38]</sup> Reports of additive-free heterogeneous Pd-catalysed Suzuki reaction in aqueous medium and at room temperature are very scarce.<sup>[39,40]</sup>

Montmorillonite K-10 (mont-K-10) is a hydrophilic clay generally used as a catalyst and support in various organic transformations.<sup>[41–43]</sup> It has a layered structure with high cation exchange capacity and

hence can be easily pillared with various metals and metal complexes of choice.<sup>[44–46]</sup> Modified mont-K-10 show excellent catalytic activity. Considering the above, we report herein the preparation of Pd–PPh<sub>3</sub> complex-loaded mont-K-10 clay and its application in the Suzuki–Miyaura reaction at room temperature in aqueous medium under aerobic conditions (Fig. 1).

## Experimental

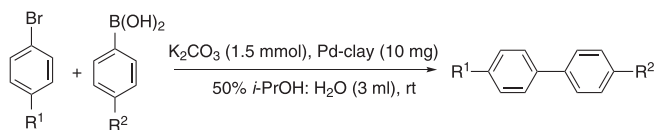
Unless otherwise noted, all chemicals were used as received. 4-Nitrobromobenzene, 4-bromoanisole, triphenylphosphine, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, NaOH, KOH, NaHCO<sub>3</sub>, Et<sub>3</sub>N, Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O, MeOH, DMF, CH<sub>3</sub>CN, THF, dichloromethane (DCM), EtOH and *i*-PrOH were purchased from EMERCK. 4-Chlorophenylboronic acid, 4-methoxyphenylboronic acid, 4-*t*-butylphenylboronic acid and phenylboronic acid were purchased from Spectrochem. 4-Bromotoluene and 4-acetylphenylboronic acid were purchased from Alfa Aesar. PdCl<sub>2</sub> was purchased from Spectrochem. Mont-K-10 clay was purchased from Sigma Aldrich.

All reactions were performed at room temperature in a 50 ml oven-dried round-bottomed flask after cooling. Column chromatography was performed with EMERCK silica gel (60–120 mesh). TLC was carried out with EMERCK silica gel 60 F254 plates. Visualization of spots on TLC plates was accomplished with UV light. All products were characterized using <sup>1</sup>H NMR, <sup>13</sup>C NMR and EI mass spectroscopy. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at room temperature with a

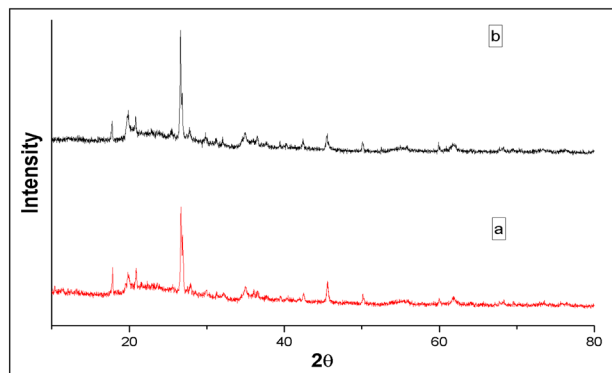
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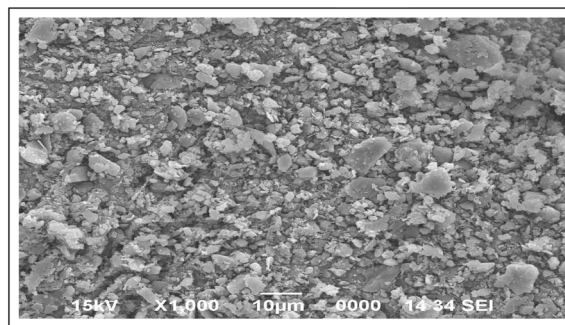


**Figure 1.** Suzuki–Miyaura cross-coupling reaction.



**Figure 2.** X-ray diffraction analysis of (a) mont-K-10 and (b) mont-K-10-supported Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.

Bruker Avance 300 MHz instrument. <sup>1</sup>H NMR chemical shifts were recorded in parts per million (ppm) downfield of tetramethylsilane (TMS). <sup>13</sup>C NMR chemical shifts were recorded in ppm downfield of TMS and were referenced to the carbon resonance of the solvent (CDCl<sub>3</sub>; δ = 77.2 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), integration and coupling constants in hertz. Gas chromatographic analysis coupled with mass spectrometry was performed using an Agilent Technologies GC system 7820A coupled with a 5975 mass detector and SHRXI-5MS column (15 m, 0.25 mm inner diameter, 0.25 μm film



**Figure 3.** Scanning electron micrograph of the mont-K-10-supported Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> catalyst.

thickness). The following temperature programme was used: 2 min at 80 °C, 10 °C min<sup>-1</sup> to 160 °C, 15 °C min<sup>-1</sup> to 250 °C, 7 min at 250 °C. Compounds described in the literature were characterized by comparing their <sup>1</sup>H NMR and <sup>13</sup>C NMR data to the previously reported data. The surface area of the catalyst was determined using Brunauer–Emmett–Teller (BET) surface area analysis with nitrogen gas adsorption method (Quantachrome Instruments, Boynton Beach, FL).

#### Procedure for Preparation of Catalyst

In a 250 ml round-bottomed flask, 200 mg of PdCl<sub>2</sub> was stirred with 500 mg of triphenylphosphine in MeOH solution under aerobic conditions for 30 min at room temperature. Pale yellow-coloured fine particles appeared in the solution. To this solution, 2 g of mont-K-10 clay was added and stirred for 6 days. After that the mixture was filtered and washed several times with MeOH followed by drying in air for 24 h.

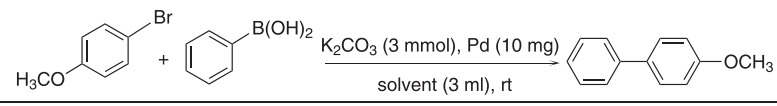
#### General Procedure for Suzuki–Miyaura Reaction

A 50 ml round-bottomed flask was charged with a mixture of aryl halide (0.5 mmol), arylboronic acid (0.6 mmol), base (1.5 mmol)

**Table 1.** Effect of base on Suzuki–Miyaura reaction<sup>a</sup>

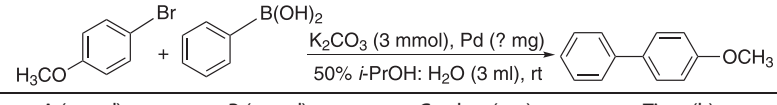
Entry	Base	Time (h)	Yield (%) <sup>b</sup>
1	K <sub>2</sub> CO <sub>3</sub>	6	96
2	Na <sub>2</sub> CO <sub>3</sub>	18	80
3	Cs <sub>2</sub> CO <sub>3</sub>	08	92
4 <sup>c</sup>	NaHCO <sub>3</sub>	24	75
5	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	7	86
6 <sup>c</sup>	NaOH	24	41
7 <sup>c</sup>	KOH	24	32
8 <sup>c</sup>	Et <sub>3</sub> N	24	58
9 <sup>d</sup>	K <sub>2</sub> CO <sub>3</sub>	7	96
10 <sup>c,e</sup>	K <sub>2</sub> CO <sub>3</sub>	24	75

<sup>a</sup>Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.6 mmol), base (1.5 mmol), Pd-clay (10 mg), i-PrOH–H<sub>2</sub>O (1:1, 3 ml), ca 28 °C unless otherwise noted.  
<sup>b</sup>Yields are of isolated product.  
<sup>c</sup>Reaction did not complete.  
<sup>d</sup>4 equiv. of K<sub>2</sub>CO<sub>3</sub> was used.  
<sup>e</sup>2 equiv. of K<sub>2</sub>CO<sub>3</sub> was used.

**Table 2.** Effect of solvent on Suzuki–Miyaura reaction<sup>a</sup>


Entry	Solvent	Time (h)	Yield (%) <sup>b</sup>
1	MeOH	10	85
2	i-PrOH	7	89
3	EtOH	6	88
4 <sup>c</sup>	i-PrOH–H <sub>2</sub> O	6	96
5 <sup>d</sup>	EtOH–H <sub>2</sub> O	9	90
6 <sup>e</sup>	H <sub>2</sub> O	24	76
7	DMF	18	81
8 <sup>e</sup>	CH <sub>3</sub> CN	24	60
9 <sup>e</sup>	THF	24	64
10 <sup>e</sup>	DCM	24	56

<sup>a</sup>Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.6 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), Pd–clay (10 mg), solvent (3 ml), ca 28 °C.  
<sup>b</sup>Yields are of isolated product.  
<sup>c</sup>50% aqueous isopropanol was used.  
<sup>d</sup>50% aqueous ethanol was used.  
<sup>e</sup>Reaction did not complete.

**Table 3.** Optimization for effective amount of catalyst and substrate


Entry	A (mmol)	B (mmol)	Catalyst (mg)	Time (h)	Yield (%) <sup>a</sup>
1	0.5	0.75	10	6	96
2 <sup>b</sup>	0.5	0.75	5	24	63
3	0.5	0.75	15	6	96
4	0.5	0.6	10	6	96
5 <sup>b</sup>	0.5	0.5	10	24	80

<sup>a</sup>Yields are of isolated product.  
<sup>b</sup>Reaction did not complete.

and Pd–clay (10 mg) and the mixture was stirred in solvent (3 ml) at room temperature for the required time. After completion, the reaction mixture was diluted with water (20 ml) and extracted with ether (3 × 20 ml). The combined extract was washed with brine (2 × 20 ml) and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, ethyl acetate–hexane) to obtain the desired products.

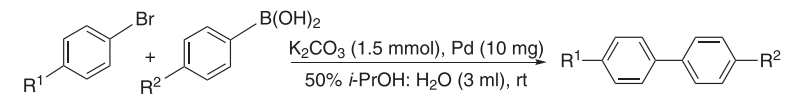
## Results and Discussion

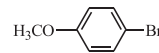
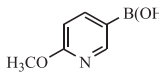

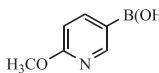

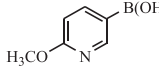

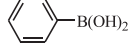
### Characterization of Catalyst

The prepared catalyst was characterized using BET surface area measurements, energy-dispersive X-ray analysis (EDX) and scanning electron microscopy. The BET surface areas of the mont-K-10 clay and catalyst are found to be 209 and 167 m<sup>2</sup> g<sup>-1</sup>, respectively. The decrease in surface area of the catalyst can be attributed to the incorporation of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> into the clay. Further, the EDX data of the

mont-K-10-supported Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> clearly indicate the presence of Pd in the clay at 0.06 wt%.

In addition, the existence of the Pd–PPh<sub>3</sub> complex was confirmed using IR spectroscopy. In the IR spectrum of mont-K-10-supported Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, the appearance of peaks at 426 cm<sup>-1</sup> for ν<sub>Pd–P</sub> and 337 cm<sup>-1</sup> for ν<sub>Pd–Cl</sub> confirms that Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> is embedded in the mont-K-10 clay.<sup>[47]</sup> Furthermore, a sharp peak of the mont-K-10 clay-supported catalyst is observed at 1436 cm<sup>-1</sup> due to ν<sub>C–C</sub> of phenyl rings present in Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. The powder X-ray diffraction pattern (Fig. 2) of the parent mont-K-10 exhibits a diffraction peak at 2θ = 19.86°, which upon Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> incorporation slightly shifts to 2θ = 19.82°, and there is also a corresponding decrease in its intensity. Further, the interplanar spacing value (*d*) increases from 4.466 Å to 4.475 Å. All these observations can be attributed to the incorporation of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> into the mont-K-10 clay, which also correlates with the results obtained from IR spectra of mont-K-10 and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>-loaded mont-K-10 clay. A typical scanning electron micrograph showing the microstructure of the catalyst is

**Table 4.** Pd-catalysed Suzuki reaction with various aryl bromides and arylboronic acids<sup>a</sup>


Entry	R <sup>1</sup>	R <sup>2</sup>	Time (h)	Yield(%) <sup>b</sup>
1	OCH <sub>3</sub>	<i>t</i> -Butyl	12	94
2	OCH <sub>3</sub>	Cl	3	95
3	OCH <sub>3</sub>	OCH <sub>3</sub>	10	99
4	NO <sub>2</sub>	OCH <sub>3</sub>	5	94
5	NO <sub>2</sub>	Cl	8	95
6	NO <sub>2</sub>	<i>t</i> -Butyl	5	94
7	CH <sub>3</sub>	OCH <sub>3</sub>	1	95
8	CH <sub>3</sub>	Cl	0.5	93
9	CH <sub>3</sub>	<i>t</i> -Butyl	1	96
10	OCH <sub>3</sub>	H	6	96
11	CH <sub>3</sub>	H	0.5	97
12	NO <sub>2</sub>	H	13	98
13	CHO	H	11	94
14			15	97
15			12	93
16			18	90
17			10	92

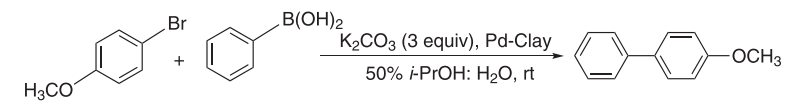
<sup>a</sup>Reaction conditions: aryl bromide (0.5 mmol), arylboronic acid (0.6 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), Pd-clay (10 mg), *i*-PrOH–H<sub>2</sub>O (1:1, 3 ml), *ca* 28 °C.  
<sup>b</sup>Yields are of isolated product.

depicted in Fig. 3. An ordered morphology is observed with homogeneous particle distribution. The prepared complex was then applied in the Suzuki–Miyaura cross-coupling reaction.

#### Application of Prepared Catalyst in Suzuki–Miyaura Reaction

Our first step was optimization of the reaction conditions for the Suzuki coupling reaction. It is well known that base plays

a significant role in the Suzuki reaction. Hence it was decided to investigate the effectiveness of various bases in the cross-coupling reaction. For that purpose phenylboronic acid (0.6 mmol) and 4-bromoanisole (0.5 mmol) were chosen as a model substrate. The reaction was carried out in a water–isopropanol (1:1, 3 ml) solvent system with 10 mg of Pd-clay catalyst at room temperature under aerobic conditions.

**Table 5.** Reusability test


Run	A (mmol)	B (mmol)	Catalyst (mg)	Time (h)	Yield (%) <sup>a</sup>
1	2	2.4	40	06	96
2	1.6	1.92	32	08	95
3	1.25	1.5	25	17	89
4 <sup>b</sup>	1	1.2	20	24	59

<sup>a</sup>Yields are of isolated product.  
<sup>b</sup>Reaction did not complete.

It is clear from Table 1 that carbonate bases, namely  $K_2CO_3$ ,  $Na_2CO_3$  and  $Ca_2CO_3$ , give comparable yields (Table 1, entries 1–3), and  $K_2CO_3$  is considered for further optimization of reaction conditions. In contrast, the reaction does not go to completion with the relatively weak base  $NaHCO_3$  (Table 1, entry 4). We also tested some hydroxide bases (NaOH and KOH), but the yield is very poor (Table 1, entries 6 and 7). An organic base also does not improve the yield to any great extent (Table 1, entry 8). Further screening with different amounts of  $K_2CO_3$  confirms that 3 equiv. is the optimum for efficient coupling (Table 1, entries 9 and 10). Based on these observations we consider  $K_2CO_3$  for further optimization.

The next goal was to find a suitable solvent in which the reaction can proceed at a good rate. A wide range of organic and aqueous solvents were investigated and the results obtained are listed in Table 2. Alcoholic solvents MeOH, EtOH and i-PrOH are found to be very effective for the catalytic system under investigation (Table 2, entries 1–3). We also examined 50% aqueous composition of the alcoholic solvents and, to our surprise, excellent yields of the isolated cross-coupling product are observed in almost all cases. But considering the time factor, we take 50% aqueous isopropanol to be superior (Table 2, entries 4 and 5). Interestingly, when water is used alone as solvent the reaction does not complete even after 24 h and only 75% of the coupled product can be isolated (Table 2, entry 6). The use of other organic solvents (DMF,  $CH_3CN$ , THF and DCM) is found to be less effective in our protocol (Table 2, entries 7–10).

In order to optimize the amount of catalyst and substrate, a series of reactions were performed with 4-bromoanisole and phenylboronic acid. The observations are listed in Table 3. It is found that 10 mg of Pd–clay catalyst is enough for the complete conversion of 0.5 mmol of 4-bromoanisole (Table 3, entries 1–3). Further increasing the amount of catalyst has no effect on the reaction system in terms of yield and time (Table 3, entry 3), while decreasing its amount to 5 mg leads to lower yield of isolated product (Table 3, entry 2). We also optimized the effective amount of phenylboronic acid required for the complete conversion of 4-bromoanisole. Maximum yield is observed with 1.2 equiv. of phenylboronic acid (Table 3, entries 4 and 5).

With the optimized reaction conditions we next explore the scope with various electronically diverse aryl bromide and arylboronic acids. The results clearly indicate that aryl bromide and arylboronic acids having both electron-withdrawing and electron-donating groups ( $OCH_3$ ,  $NO_2$ ,  $CH_3$  and  $COCH_3$ ) couple successfully to give good to excellent yield of isolated cross-coupling product (Table 4, entries 1–13). To check the compatibility of our protocol for heterocyclic boronic acids and heterocyclic bromides, 2-methoxypyridine-5-boronic acid was stirred with 4-bromoanisole and to our delight isolated cross-coupled product is obtained in 97% yield (Table 4, entry 14). Similar results are also obtained with 5-bromopyrimidine and 3-bromothiophene (Table 4, entries 15 and 16). Excellent yield of the product is also obtained for the coupling of 3-bromothiophene with phenylboronic acid (Table 4, entry 17).

It is worth noting that the system is effective for gram-scale reaction of aryl bromide and arylboronic acids. When 1000 mg of 4-bromoanisole (5.35 mmol), 783.24 mg of phenylboronic acid (6.42 mmol), 2215 mg of  $K_2CO_3$  (16.05 mmol) and 100 mg of Pd–mont-K-10 in 30 ml of i-PrOH– $H_2O$  (1:1) are stirred using our optimized conditions, the reaction completes in 8 h with an isolated yield of 96%. Further, the catalyst can be recovered and applied successfully for another cycle.

## Reusability Test

From a green chemistry perspective, the reusability of catalysts makes them more attractive. We also investigated the reuse of our catalyst. The reuse test was performed with 4-bromoanisole and phenylboronic acid as substrate and we find that the catalyst is reusable up to three cycles without any significant loss of catalytic activity (Table 5, entries 1–3). However, after the third cycle the yield is decreased (Table 5, entry 4). This may be due to the deactivation of the catalyst during the course of the reaction and recovery process. Although in the literature few reports are available of similar recycling activity, the requirement of high reaction temperature and harmful organic solvents detract from their applicability.<sup>[48–50]</sup>

To check the heterogeneity of the catalyst, we performed a hot filtration test with 4-bromoanisole (0.5 mmol) and phenylboronic acid (0.6 mmol). After 3 h of reaction the solid catalyst was separated from the reaction mixture (65% conversion determined using GC-MS). The filtrate was further stirred for 6 h. As expected no further increase in the yield was detected (indicated by GC-MS). Inductively coupled plasma atomic emission spectroscopic analysis of the filtrate collected by filtration confirmed that Pd was absent from the reaction mixture.

## Conclusions

We have developed a mild and efficient protocol for the Suzuki–Miyaura cross-coupling reaction at room temperature under aerobic conditions using a palladium triphenylphosphine–mont-K-10 catalyst. The catalyst system was found to be effective for a wide array of functionalized aryl bromides and arylboronic acids. The application of aqueous solvent in our protocol and the reusability of the catalyst are significant advantages compared to other existing catalyst systems for the Suzuki reaction.

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