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FULL PAPER

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Methanol aided synthesis of PdNPs decorated on montmorillonite K 10 and its implication in Suzuki Miyaura type cross coupling reaction under base free condition

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An efficient catalyst PdNPs decorated on Montmorillonite K 10 is prepared by simply stirring $Pd(OAc)_2$ in methanol at room temperature without using any external reducing agent. The catalyst shows excellent activity for Suzuki Miyaura type cross coupling reaction between aryl diazonium salt and arylboronic acid under ligand and base free reaction conditions within short reaction time. The main advantage of this methodology is the easy synthesis of heterogeneous PdNPs @ Mont K 10 catalyst in a mild condition without using any reducing agent or additive and the catalyst is very efficient for biaryl synthesis. The catalyst is well characterized by SEM, EDX, TEM, BET, Powder XRD, TGA, DSC etc. The reaction pathway is greener with aqueous reaction medium, base free reaction condition, room temperature and reusable heterogeneous catalyst.

KEYWORDS

cross coupling, methanol, palladium NPs, room temperature

1 | INTRODUCTION

For centuries, the pursuit of designing green protocol in chemistry for the synthesis of efficient nano catalyst has become an utmost goal in research community as the chemistry of nano materials has gained much interest because of their higher efficiency compared to bulk materials. They have high surface area[1] and found wide applications in diverse areas such as catalysis, electronics, biochemical sensor[2] etc. Consequently, nano materials have emerged as sustainable alternative to conventional catalyst for different chemical transformations such as C-C and C-heteroatom bond forming reactions, C-H activation reaction etc. Among the metal nanoparticles (NPs), PdNPs find widespread applications as catalyst in aforementioned bond forming areas. Although, PdNPs exhibit excellent catalytic activity, but in most of the cases their synthetic route require high temperature,[3] ultra sonication,[4] active reducing agent[5] etc. As a result, there is growing interest for the development of green and eco-friendly route for the synthesis of PdNPs in a single step with minimum use of chemicals or by using environmentally acceptable solvents. Biological resources such as plant extracts,[6] microorganisms[7] etc. can be used for the synthesis of NPs as they have the reduction potential suitable for NPs synthesis. Additionally, considerable efforts have been made to prepare and stabilize PdNPs by using environmentally benign, robust, cheap and available support/stabilizer.[8,9] Reports have been found on the synthesis of PdNPs by using bio-reducing agents like leaf extract of *colocasia esculanta*,[9] tea and coffee extract,[10] soyabean leaf extract,[6] starch[11] etc. but, in most of the cases, temperature is an important parameter for synthesizing metal NPs which is against the prospect of 'green chemistry'. So, considering the above factors, synthesis of PdNPs at room temperature without using any external reducing agent is a very fascinating development in the area of nano catalysis. Alcoholic solvent has reducing properties itself and can be engaged for the synthesis of metal NPs which is considered as green synthetic process.[12a,b] Currently, a variety of

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reports have been published where PdNPs are embedded on various metal solid supports such as zeolite,[13] micro porous polymer,[14a,b] mesoporous silica,[15a,b,c] aluminium hydroxide,[16] agarose,[17] $BaCO_3$,[18] charcoal,[19a,b,c] clay,[20] metal oxides[21a–c] etc. and they show excellent catalytic activity.

In this manuscript, we wish to report a mild methodology for synthesizing PdNPs decorated on Montmorillonite (K 10) by simple stirring at room temperature using methanol as solvent without using any external reducing agent. We have chosen Mont. K 10 because the same is considered as one of the most demanding catalytic materials in heterogeneous catalysis due to its low cost and eco-friendliness. It also possesses high surface area and swelling property.[22] This clay is mainly comprised of aluminosilicate layers, where one octahedral alumina sheet is sandwiched between twice of the tetrahedral silica sheets. Again, in the layers of aluminosilicates, the partial isomorphous substitution of Si^{4+} ions by trivalent metal cations and Al^{3+} ions by divalent metal cations origins a charge deficiency. To balance this charge deficiency, hydrated alkali and alkaline earth metal cations reside in the interlayer spaces of montmorillonite. On the other hand these cations in the interlayers are found to be highly exchangeable, as a result, making montmorillonite able to immobilize various guest molecules like metal nanoparticles or metal complexes in its interlayers.[23] To note, the immobilization of metal NPs in this type support like in mont. K 10 prevents agglomeration by maintaining them in smaller sizes. These type of supports act like small molecular containers which modify the characteristics of free catalysts by escalating the steric constraints and enhancing the local concentration of reagents near the surface where the reaction takes place This type of heterogeneous catalytic system is able to overcome the drawbacks of homogeneous catalysts in case of recoverability issue.[24a,b]

Over the last few decades, Palladium catalyzed Suzuki-Miyaura cross-coupling reaction of aryl halide and organoboron derivatives has become one of the most widely used methods for construction of C-C bond which have made an enormous contribution to research as their cross-coupled products present as subunits of many marketed drugs[25a,b] and agrochemicals.[26] The reaction has main advantage of having organoboron starting materials which are air stable, easily available, large functional group tolerance and moisture compatible.[27a,b] Aryl bromide and aryl iodides are the common coupling partners in Suzuki-Miyaura reaction. However, it is a challenging task to perform Suzuki-Miyaura reaction using aryl chlorides as coupling partner under mild condition as they react sluggishly and are considered as pollutants. Furthermore, aryl bromides and iodides are found to be costly, so it is distinctively an endeavour to find readily available, non-toxic and inexpensive alternatives for aryl halides as a coupling partner for concerned coupling reaction. In last few decades, aryl diazonium salts come out to be an extremely productive coupling partner for Suzuki-Miyaura cross-coupling reaction[28a,b] as they can be easily prepared from anilines which are more economical than aryl halides. The other advantages of diazonium salts are that they are more reactive than corresponding halides; so, reaction takes place within short reaction time and is feasible under mild and aqueous condition as diazonium salts are better electrophile[29] than the aryl halides. Eventually, the chemistry of a ‘base free’ synthetic route for Suzuki-Miyaura reaction is also highly appreciable because racemization of optically active compounds takes place in presence of base. Moreover, according to green chemistry prospect, lesser the chemical used in the reactant side higher will be the atom economy and atom efficiency and so more greener the reaction pathway as both are the chief parameters of green chemistry.

So, as a part of our ongoing programme to develop simplistic protocol for Suzuki Miyaura type cross coupling C-C bond forming reaction herein, we wish to report PdNPs@K 10 as an efficient heterogeneous catalyst for base free Suzuki Miyaura type cross-coupling reaction in aqueous medium at room temperature.

2 | EXPERIMENTAL

2.1 | Preparation of the catalyst

In a round bottom flask containing methanol as solvent, 0.075 g of Palladium acetate and 0.750 g of K 10 (Montmorillonite) were taken and the solution was stirred for two days at room temperature. The colour of the reaction mixture turned to black from brown. It was filtered by suction funnel and washed with MeOH for several times, the residue was collected and dried. The collecting residue was kept under a flow of air overnight and under vacuum for 24 h which gave a black powder of heterogeneous K 10 supported palladium catalyst.

2.2 | General Experimental procedure for Suzuki Miyaura type cross coupling reaction

A 50 ml round-bottom flask was charged with a mixture of 10 wt % PdNPs @K 10 catalyst, 1.2 mmol of arylboronic acid and 1 mmol of aryldiazonium salt and stirred at room temperature in 3 ml distilled water for the required time. The reaction was monitored by TLC and after completion of the reaction the solution was extracted three times with ethylacetate (3 × 10 ml). The products were purified by column chromatography and confirmed by ^{1}H, ^{13}C NMR spectroscopy (Supporting Information) and mass spectrometry.

2.3 | Characterizations of the catalyst:

The catalyst was characterised by BET surface area measurement, Energy Dispersive X-Ray analysis (EDX), Powder XRD, Thermo Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) etc.

2.3.1 | BET surface area

Figure 1 depicts the N_2 adsorption–desorption isotherm and pore size distribution of the prepared catalyst under study. It can be predicted from the figure that the compounds are mesoporous material with highly uniform pore size distribution (Type IV isotherm). The BET surface area of the clay and the catalyst was found to be 209 and 154 m^2 g^{-1}, respectively. The decrease in the value for the catalyst indicates the incorporation of the metal to the clay. Furthermore, from ICP-OES analysis it was found that 0.056 g of Pd was loaded on montmorillonite i.e., 0.33 mg/g.

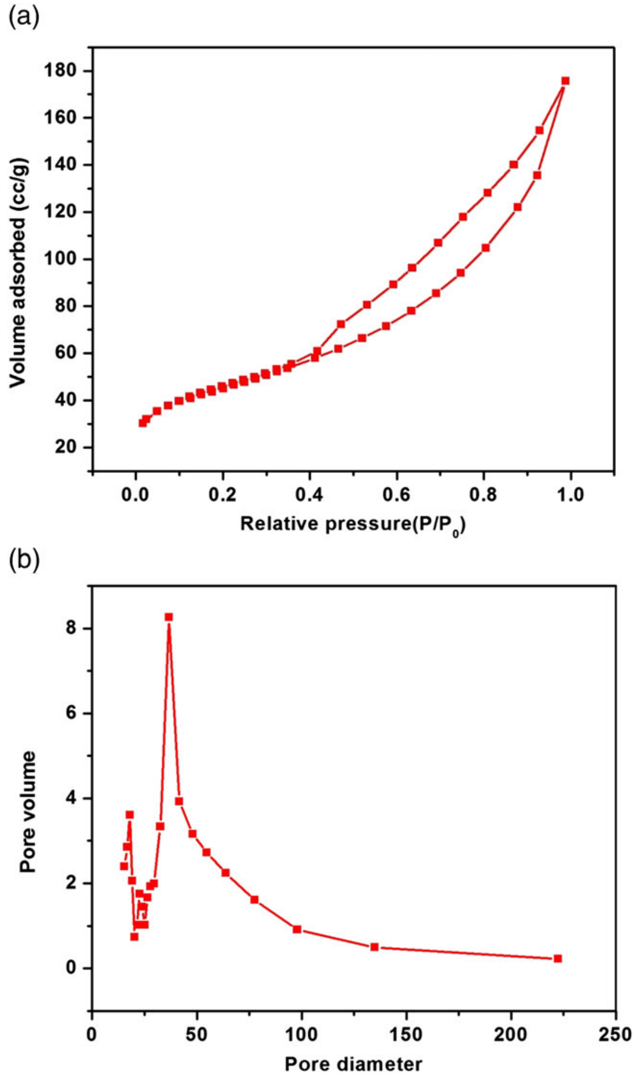


FIGURE 1 (a) N_2 adsorption–desorption isotherm (b) pore size distribution curve of the catalyst

2.3.2 | SEM and EDX:

EDX analysis of the catalyst clearly depicts the presence of Pd in the catalyst (Figure 2b). EDX spectrum also shows the presence of metal Si, Fe, K, Mg, Cl, O etc which are the basic constituents of the clay Montmorillonite. The scanning electron microscopic image for catalyst shows the surface morphology of the catalyst (Figure 2a)

2.3.3 | TEM

The particle size and surface morphology of the synthesized catalyst is studied by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). The TEM image (Figure 3) of the NPs clearly shows that uniformly dispersed Pd(0)NPs on the surface of montmorillonite and most of the particles are spherical in nature. The crystal lattice of PdNPs is clearly resolved in the HRTEM image (Figure 3f) and it is found to be

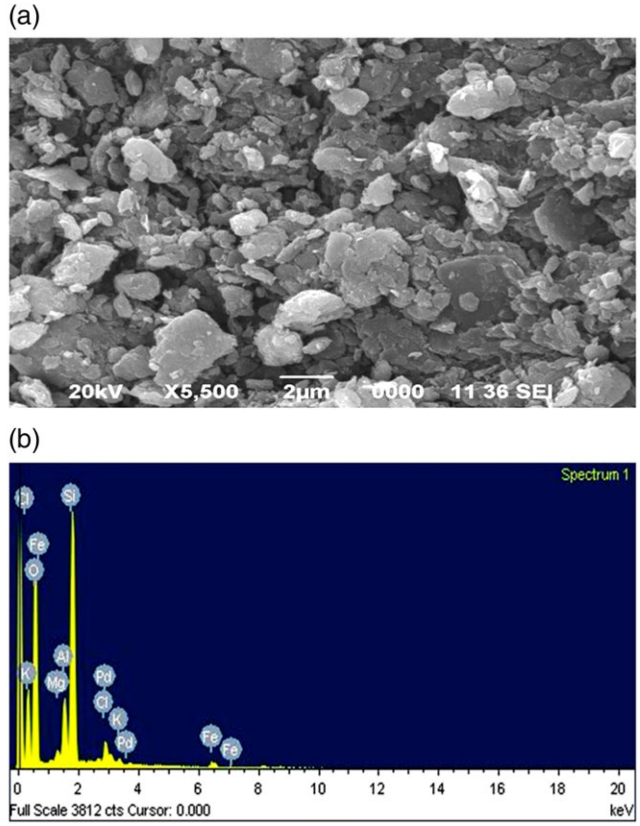


FIGURE 2 SEM and EDX analysis spectra of the catalyst

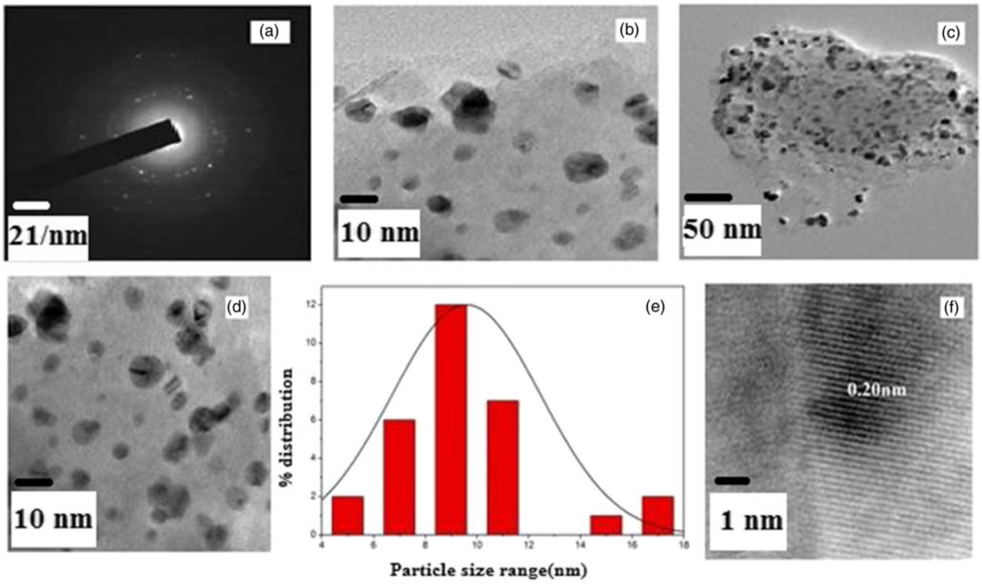


FIGURE 3 TEM images of PdNPs@K 10 before reaction (a) SAED pattern of PdNPs, (b-e) TEM images along with particle size distribution, (f) HRTEM image along with fring spacing

0.20 nm. The size of the NPs is found to be around in a range of 10-15 nm. The bright spot in the SAED pattern [Figure 3 (a)] depicts the crystalline state of the NPs.

We have investigated also the surface morphology and size of the PdNPs after performing reaction by characterizing the catalyst by TEM analysis after reaction. For that, we have chosen the recovered catalyst after 4th cycle of the reaction. TEM images of the catalyst after 4th cycle shows (Figure 4) that the immobilized PdNPs on montmorillonite also have particle size in the range of approx. 10-15 nm which is also found in the TEM image of the catalyst before the reaction. Therefore, from the above results, it

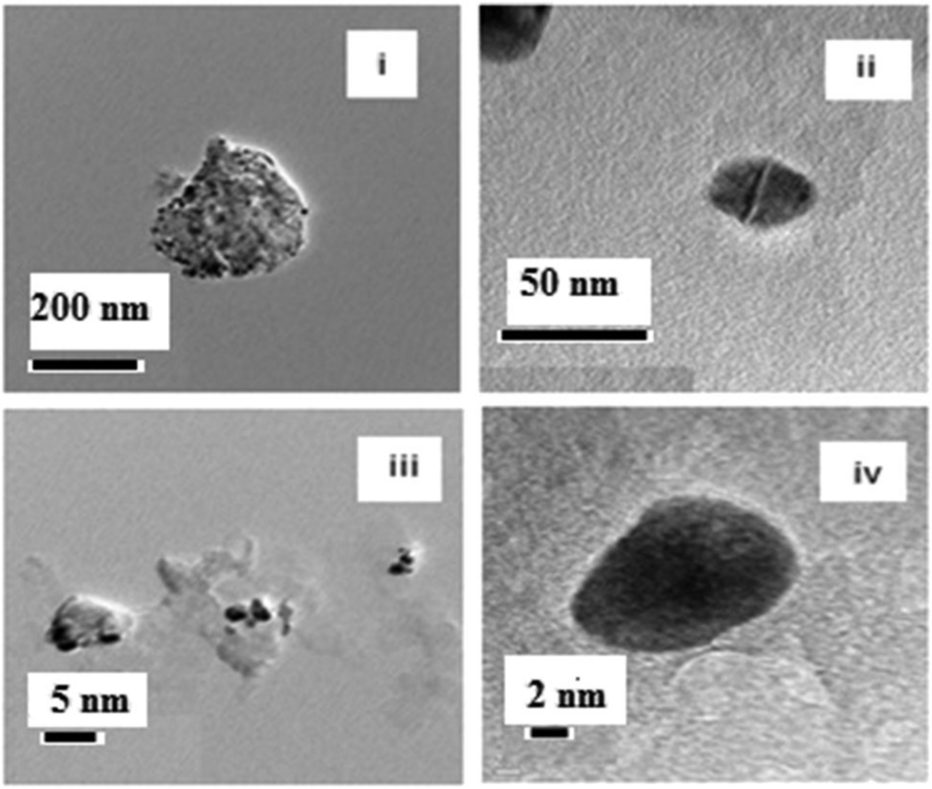


FIGURE 4 TEM images (i-iv) of the recovered catalyst after 4th cycle

is evident that the catalyst does not undergo any change in size as well as morphology, which in turn does not show any significant decrease in the catalytic activity.

2.3.4 | Powder XRD

Powder XRD analysis for the parent montmorillonite and the fresh catalyst has been done before performing the reaction. In the [Figure 5 (a)] three peaks are observed for the catalyst at 2θ=39.57°, 46.17° and 67.90° corresponding to the reflections of (111), (200), and (220) planes of PdNPs, (JCPDS no. 88-2335) respectively. The broadening of the peaks is a sign of formation of nano particles. Again we have done powder XRD analysis for the recovered catalyst after 4th cycle of the reaction. The XRD pattern [Figure 5 (b)] shows the prominent peaks at 2θ values of about 39.94, 45.96, 67.43 are assigned to the (111), (200), (220) crystallographic planes of PdNPs which clearly confirms that PdNPs remain in zero oxidation state as before performing the reaction.

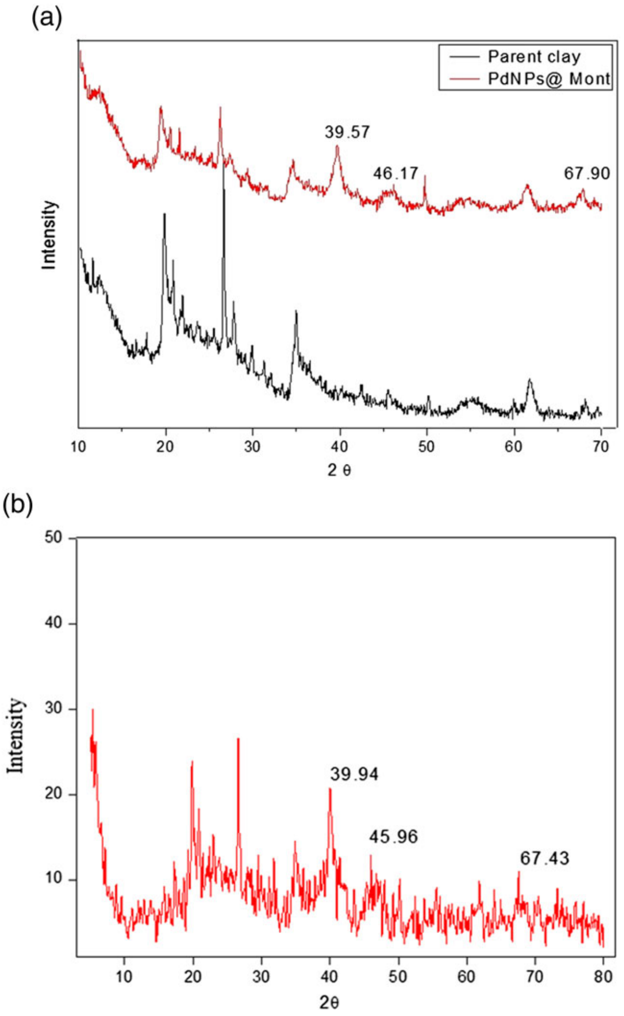


FIGURE 5 **(a)** Powder XRD pattern of the catalyst and the parent clay, (b) powder XRD pattern of the recovered catalyst after 4th cycle

2.3.5 | TGA and DSC:

To know the thermal stability of the catalyst it is characterized by TGA analysis. The analysis shows [Figure 6 (a)] that the catalyst is stable up to 600°C. The weight loss at temperature range 250-300°C is due to the evaporation of the physically absorbed water molecules. Like that DSC analysis [Figure 6 (b)] is also performed for the catalyst. From the curve it can be concluded that there are two endothermic peaks within 80-100°C regions due to the volatilization of water and low molecular weight compounds.

3 | RESULT AND DISCUSSION

3.1 | Optimization of reaction condition

To explore the catalytic activity of the newly synthesized catalyst for Suzuki Miyaura type cross coupling reaction,

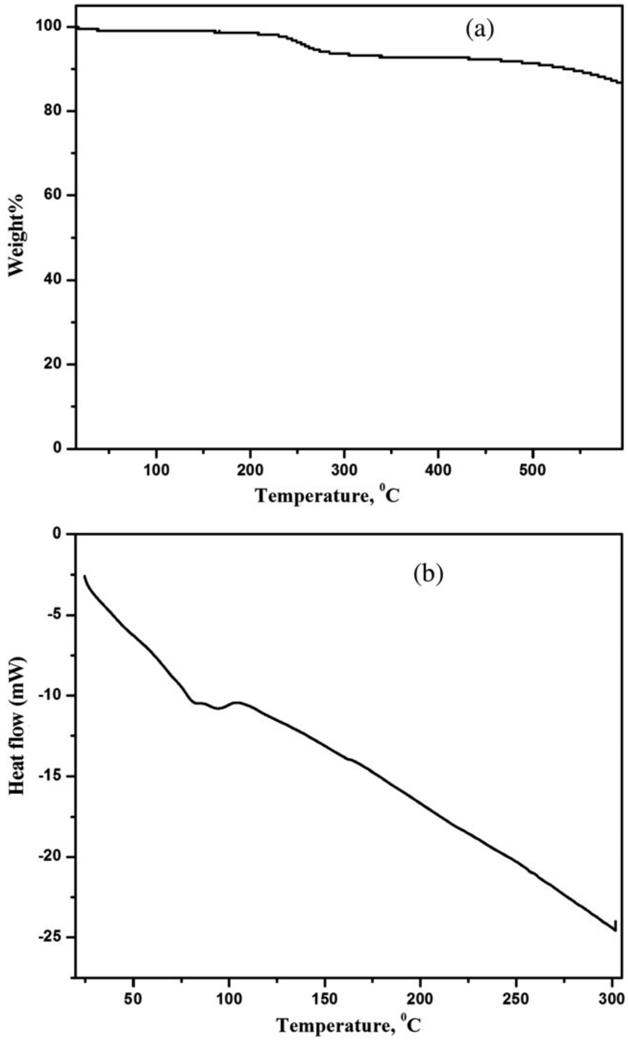
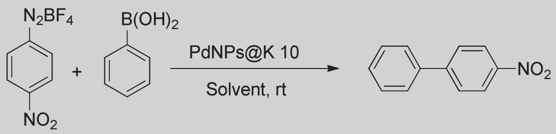


FIGURE 6 (a) TGA curve for the catalyst and (b) DSC curve for the catalyst

a model reaction between 1.2 mmol of phenylboronic acid and 1 mmol of 4-nitrobenzenediazonium tetrafluroborate was investigated in presence of 10 wt% of the catalyst under open air condition using methanol at room temperature (Table 1, entry 1). It has been observed that no base is required when aryl diazonium tetraflouroborate salt has used as a substrate for Suzuki Miyaura type cross-coupling reaction. It may be due to the *in-situ* generation of conjugate base BF_4^- ion in the system which can activate the boronic acid moiety. We first checked the reaction in methanol as it was reported as most apposite solvent for this coupling reaction.[28] Encouraging us, the reaction was found to be completed with excellent yield of desired product within 45 min (Table 1, entry 1). Though various reports are found on base free Suzuki Miyaura type cross coupling reaction with benzene diazonium tetraflouroborate, but still literature reveals only a few methodologies for the concerned reaction which have been performed at room temperature. In the next experiment checked the reaction with 5 wt% of the catalyst which also showed an almost good yield of 90% of the coupling product (Table 1 entry 2).

To advance the progress of the aforementioned reaction, we optimized the effect of different solvents like ethanol, iso-propanol, isopropanol: water (1:1) and water in both 10 wt% and 5 wt% of the catalyst (Table 1, entries 3-10). From the experiments it was found the reaction deliver slight lesser yield and need almost double times for its completion when performed with 5 wt% of the catalyst than with 10 wt% of the same in all of the solvents mentioned. But, interestingly, the reaction showed excellent progress in water with 93% isolated yield with 10 wt% of the catalyst (Table 1, entry 9). Though benzene diazomium tetraflouroborate salt is sparingly soluble in water, but here, in this case we believe that the heterogeneous catalyst provides a better surface for smooth advancement of the reaction and it seems to progress through ‘on water’ reaction route. The reaction under aqueous system completed within the comparable time as the alcoholic reaction system. For the next assessment, an attempt was made with 15 wt% of catalyst loading keeping other reaction conditions same using water as reaction medium. Interestingly, we found no significant variation in yield and time for 15 wt% of the catalyst (Table 1, entry 11). The reaction was also performed in non-polar solvents like DCM and toluene, reaction in both of the solvents showed excellent results as it was completed in shorter reaction time with excellent yield

TABLE 1 Optimization of reaction condition for catalyst, base, solvent



Entry	Catalyst	Solvent (3 ml)	Time(min)	Yield (%)
1	10 wt%	Methanol	45	93
2	5 wt%	Methanol	45	90
3	10 wt%	Ethanol	45	92
4	5 wt%	Ethanol	90	88
5	10 wt%	Iso-propanol	45	92
6	5 wt%	Iso-propanol	90	86
7	10 wt%	Iso-propanol:Water	45	92
8	5 wt%	Iso-propanol:Water	90	88
9	10 wt%	Water	45	93
10	5 wt%	Water	90	86
11	15 wt%	Water	90	93
12	10 wt%	DCM	30 min	95
13	10 wt%	Toluene	35 min	92
14[a]	1 mol%	Water	120	Not completed
15[b]	10 wt%	Water	120	Not completed

Reaction condition: Phenylboronic acid (1.2 mmol), 4-nitrobenzediazoniumtetrafluroborate (1 mmol)

[a] homogeneous $Pd(OAc)_2$ was used

[b] heterogeneous Pd(0)/C was used.

than in water or other polar solvents (Table 1, entries 12 and 13). Although results were better in non-polar solvent, yet we preferred the optimized reaction condition taking water as solvent because a reaction in aqueous solvent and at room temperature is highly appreciable as it refers to an exciting area of research from green chemistry point of view and has good application in both academia and industries due to availability, cost and environmental acceptability of water. Therefore, we fixed the reaction condition with 10 wt% of the catalyst in water (Table 1, entry 9). We also investigated the activity of homogeneous $Pd(OAc)_2$ and heterogeneous Pd(0)/C catalysts towards the coupling reaction (Table 1, entries 14 and 15). Both of the catalysts failed to show better result than PdNPs@K 10. The reactions catalysed by homogeneous $Pd(OAc)_2$ and heterogeneous Pd(0)/C were not fully converted towards the desired product till 2 hours. The higher reactivity of PdNPs@K 10 may be due to the presence of hydroxyl groups of aluminium, silica etc. on montmorillonite surface which might activate the arylboronic acid moiety as shown in Figure 7.

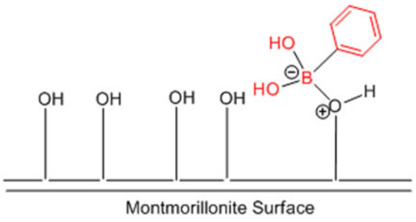


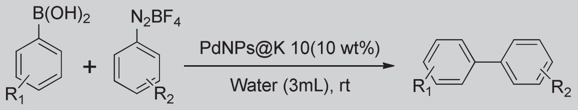
FIGURE 7 Activation of the boronic acid moiety by the hydroxyl groups of montmorillonite

Moreover, such an enhancement and increase in activity of the PdNPs@ K 10 catalyst may be due to the formation of Pd-O interaction at the particle/support interface between PdNPs and metal oxides present in the montmorillonite.[30]

3.2 | Generalization of reaction condition

Being inspired by the above studies, next, we focused on the substrate scope of the reaction with different electron donating and withdrawing arylboronic acids and aryl diazonium salts and found satisfactory result with excellent yield in most of the cases within 3 hours. Only the reaction with heteroarylboronic acid, 6-methoxy pyridine 3-yl boronic acid needed a longer time of 8 h for its completion (Table 2, entry 14). We found no effect of electron donating and withdrawing groups on the rate of the reaction as illustrated in Table 2:

TABLE 2 Cross-coupling of aryl diazonium salt and arylboronic acid



Entry	Arylboronic acid (R_1)	Aryl diazonium salt(R_2)	Time	Yield[a] (%)
1	-H	4-OMe	1.5 h	92
2	4-OMe	4-OMe	55 min	98
3	4-F	4-NO_2	1 h	89
4	4-Cl	4-NO_2	1.5 h	95
5	4-CHO	4-OMe	50 min	95
6	-H	4-NO_2	45 min	93
7	4-F	4-OMe	75 min	87
8	4-CH_3	4-OMe	1.5 h	88
9	3-Me	4-OMe	2.5 h	92
10	4-OMe	4-NO_2	45 min	96
11	2-Me	4-OMe	1 h	89
12	4-tertbutyl	4-NO_2	2 h	95
13	4-tertbutyl	4-OMe	2 h	92
14	6-methoxy 3 pyridine yl	4-NO_2	8 h	81
15	-H	3-me	3 h	84

Reaction condition: Phenylboronic acid (1.2 mmol), 4-bromonitro benzene (1 mmol), PdNPs@ K 10 (10 wt%), water (3 ml) at room temperature

[a] isolated yield

3.3 | Mechanism study

A plausible mechanism is designed and schematic mechanistic pathway (Figure 8) is discussed below based on the literature report.[31]

In this mechanism, the palladium catalyst first inserts into the C-N_2 bond to form an intermediate II. In the next step, a fluoride from tetraflouroborate counter ion displaces the diazonium and an intermediate III is formed then the Palladium-flouride complex III undergoes transmetallation with arylboronic acid through the formation of a strong fluorine boron bond. Finally, step IV undergoes reductive elimination to form the biaryls.

3.4 | Reusability study

From the green chemistry perspective, the reusability of catalysts makes them more attractive. For the investigation of the reusability of our catalyst, a reaction taking 2.4 mmol of phenylboronic acid and 2 mmol of 4-nitrodiazonium salt as model substrates, 20 wt% of PdNPs@ K 10 catalyst and 6 ml of water at room temperature was carried out. For easy recovery issue we have taken two times scale of model reaction. As indicated in the Figure 9 the catalyst is reusable up to 6th run without significant loss of the yield.

3.5 | Sheldon test

To check the heterogeneous nature of the catalyst, hot filtration test was done. To do this, the reaction was carried out at different time intervals taking the model reaction condition and after half completion of the reaction, i.e., after 15 minutes the catalyst PdNPs@K10 was filtered off from the reaction mixture. After removal of the catalyst, the reaction was monitored for an additional 6 h and found no further product formation (Figure 10). This proves the heterogeneous nature of the catalyst

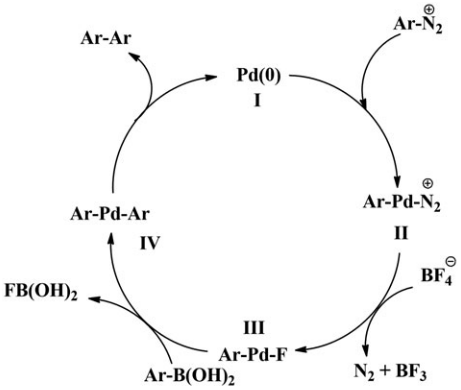


FIGURE 8 Mechanistic route for the reaction over the heterogeneous catalyst

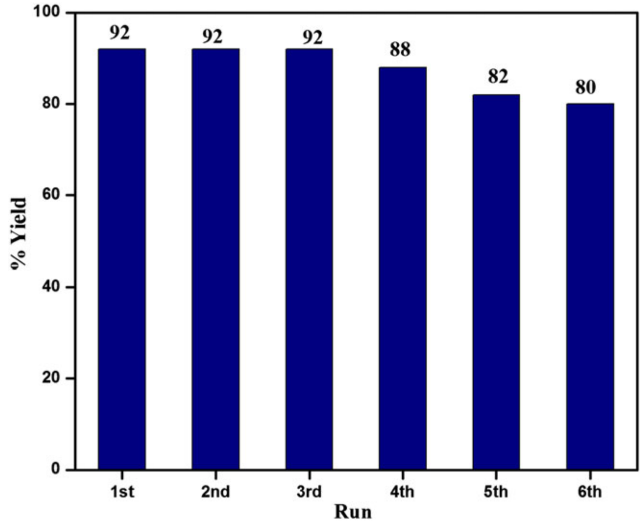


FIGURE 9 Reusability plot of the catalyst

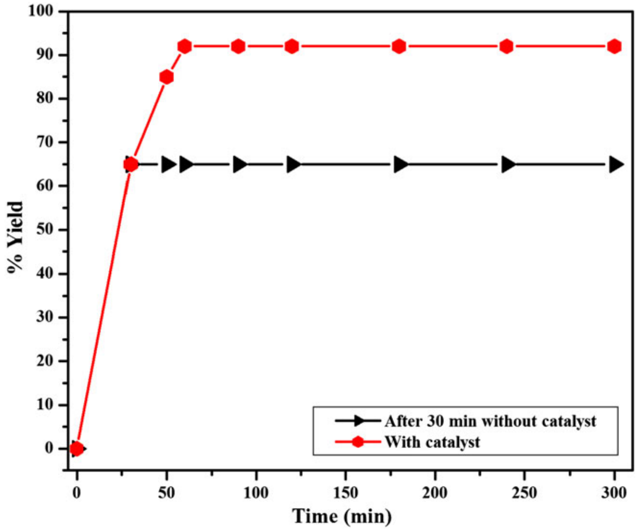


FIGURE 10 Hot filtration test

4 | CONCLUSION

In conclusion, a highly efficient heterogeneous catalyst PdNPs@K 10 has been developed for the cross-coupling reaction between aryl diazonium salt and arylboronic acids with a wide range of both of the reactants in base free condition. The reaction proceeds in easily available green solvent water and at room temperature. The catalyst we have synthesized showed excellent catalytic activity and reused up to six times with slight decrease of the yield of the reaction. We have done all essential characterization in support of the catalyst.

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