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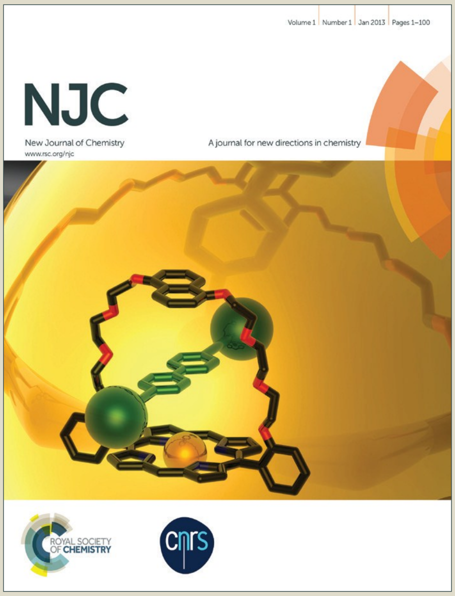

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Suzuki coupling reaction in the presence of polymer immobilized palladium nanoparticle: A heterogeneous catalytic pathway

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Abstract:

An *in-situ* method for the fabrication of metal-polymer composite architecture using the precursors of *1, 2*-diaminobenzene (DAB) and potassium tetrachloropalladate (K_2PdCl_4) has been reported in this manuscript where palladium nanoparticles were stabilized by the poly-(*1,2*-diaminobenzene), *p*DAB, matrix. During the reaction, DAB was oxidized, which produced *p*DAB, on the other hand the reduction of palladium salt formed palladium nanoparticles and were found to be uniformly dispersed throughout the macromolecule matrix. The composite material was characterized by means of different techniques, such as UV-visible and infra-red spectroscopy, which has contributed the information regarding the chemical structure of the polymer, whereas electron microscopy images yielded the information regarding the size and distribution of the metal particles in the polymer matrix. The composite material was successfully employed as a catalyst for the coupling of phenylboronic acid with aryl halides (Suzuki reaction) in the presence of an inorganic base under phosphine-free condition.

1. Introduction:

Nanostructured materials are attracting a great deal of attention because of their potential applications in areas of electronics, optics and catalysis.[1-4] The unique properties and the improved performances of nanomaterials are determined by their sizes and shapes. There are varieties of methods have been used for the synthesis of metal nanoparticles and also a wide variety of supports, ranging from polymers[5] and dendrimers[6] to solid materials, such as, metal oxides[7] and carbon based materials,[8] are reported for the stabilization of the metal nanoparticles. Combining the metal nanoparticles with a support of choice gives the enormous scope for the discovery of new and highly active catalysts for industrial importance. Among the various polymer, micro structured conjugated polymers have

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emerged as important support materials and biosensing platforms owing to their flexible nature, moderately wide electrochemical potential window and biocompatibility. Conjugated polymers, such as polyaniline and its derivatives, are the important conducting polymers and have been extensively studied because of its ease of fabrication, high conductivity, good biocompatibility and low cost.[9] Besides that the presence of an amine group on the polymer structure may lead to enhancement of biomolecular sensing[10] and also act as a good stabilizer for the metal nanoparticles through functionalization.[11]

Many investigations have been published regarding the incorporation of the metal nanoparticles into a polymer matrix and three different approaches have been utilized to make such a composite material. First one is the synthesis of the nanoparticles on the polymer matrix, which is achieved by the reduction of metal salts dissolved in the polymer matrix,[12] the second procedure is the polymerization of the monomer around the preformed nanoparticles[13] and the third method is an *in-situ* protocol for the synthesis of metal-polymer composite, where metal nanoparticles are made from their ionic precursor and the polymers are formed from its respective monomers and the process is called as *in-situ* polymerization and composite formation.[14] The latter method is likely to provide a high degree of synthetic control over both the size of the nanoparticles and the morphology of the polymer matrix, which in turn may be expected to exert a strong influence on the metal-polymer interaction.[15] Polymer stabilized metal nanoparticles have attracted much attention recently as a new research direction in catalysis.[16] The polymer matrices serve both as the support and stabilizer of the nanoparticles that provide the mechanism to prevent aggregation. Palladium based catalysts particularly nanoscale palladium particles have recently drawn enormous attention due to their versatile role in organic synthesis. Palladium nanoparticles on silicate and alumosilicate based solid support shows excellent catalytic performance for various carbon-carbon coupling reactions. It is also important to mention that Pd (II) species, supported on mesoporous silica, a novel design of heterogeneous catalyst, also shows excellent performance towards cross-coupling reaction under green solvent condition.[17] Supported palladium nanoparticles also show the electrocatalytic property of different analytes of interest[18,19] and neurotransmitter.[20] The use of palladium nanoparticles in catalysis is not only industrially important,[21,22] but also scientifically interesting as a result of the sensitive relationship between catalytic activity, nanoparticle size and shape as well as the nature of the surrounding media.[23]

The well-known application of palladium nanoparticles as a catalyst in synthetic organic chemistry is in the reactions involving carbon–carbon bond formation which are commonly

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used for the synthesis of natural products, pharmaceutical products, fine chemicals and the manufacturing of long chain organic molecules for organo-electronics applications. Among the various carbon-carbon bond formation reactions the coupling reaction is one of the most important methods for the synthesis of biaryl products in a single step process.[24]

The present work report on the polymerization of 1, 2-diaminobenzene using K_2PdCl_4 as a polymerizing agent, which results for the formation of a metal-polymer, Pd nanoparticle-poly (1, 2-diaminobenzene), Pd(0)-*p*DAB, nano structured composite material. Palladium nanoparticles with an average size of 3 nm were found to be highly stabilized and evenly dispersed throughout the polymer matrix. We have paid special attention to characterizing the polymer product by optical spectroscopic and microscopic techniques. The nanocomposite material was used as a catalyst for Suzuki coupling reactions in the absence of phosphine ligand and was also recycled up to five times without significant loss of catalytic activity.

2. EXPERIMENTAL SECTION

2.1. Materials:

All the analytical grade chemicals were purchased and used as received without further purification for this study.

2.2. General procedure:

2.2.1. Preparation of Pd(0)-*p*DAB composite:

In a typical experiment, 20 mL of potassium tetrachloropalladate (K_2PdCl_4) solution (1.0×10^{-2}M) in water was added slowly, at room temperature (~25°C), to a 50mL conical flask containing 0.7g of 1, 2-diaminobenzene dissolved in methanol. A solid brown-yellow precipitation was formed at the bottom of the flask. The flask was kept under static condition for two hours and the colour of the precipitated material was changed to dark brown. Subsequently, the colloidal precipitation was taken from the bottom of the flask and pipetted onto lacey, carbon-coated copper grids for TEM and SEM analysis. A fraction of the colloidal material was also used for optical characterization using FTIR and UV-vis spectrophotometer. The rest of the solution was filtered, washed with distilled water and kept under vacuum. A small portion of the dried powder was used for XRD and XPS analysis. The remaining portion was used for the study of the catalytic property of the material.

2.2.2. Procedure for Suzuki coupling reactions catalyzed by the Pd(0)-*p*DAB:

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In a typical experiment, aryl halide (1.0 mmol), aryl boronic acid (1.5 mmol), K_2CO_3 (1.5 mmol) and the Pd(0)-*p*PD catalyst (5.0 mg, 0.14 mol% of Pd) were added to toluene (5 mL) in a small round-bottom flask with a magnetic stirring bar. The reaction mixture was placed on an oil bath at 90°C under stirring condition for 8 h and the reaction was monitored by thin-layer chromatography technique. At the end of the reaction, the material was cooled and then diluted with ethyl acetate. The reaction mixture was washed with water and brine and the combined extract was dried over $MgSO_4$. After the evaporation of the solvents, the residue was purified by using flash chromatography on silica gel.

2.3. Material characterization:

Infrared spectra, in the region between 4000-700 cm^{-1}, were obtained using a Shimadzu IRAffinity-1 FTIR spectrophotometer with a spectral resolution of 4 cm^{-1}. The sample was deposited in the form of thin film on a NaCl disk. Surface images were obtained by using a JEOL, JSM-840 scanning electron microscope (SEM) with an accelerated voltage of 20 kV. Transmission electron microscopy (TEM) studies of the nanocomposite were carried out at 197 kV using a Philips CM200 TEM equipped with a LaB6 source. An energy-dispersive X-ray analyser (EDX) attached to the TEM was used to determine the chemical composition of the samples. The X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-3A X-ray diffractometer operating at 20 kV using Cu-Ka line radiation (k = 0.1542 nm). The measurements were performed over a diffraction angle range of $2\theta = 30^o$ to 80^o. X-ray photoelectron spectra (XPS) were collected in an ultra-high vacuum chamber attached to a Physical Electronics 560 ESCA/SAM instrument.

3. Result and discussion:

Characterization of the composite material:

We have first examined the spectroscopic behaviour of the dried material by FTIR analysis. IR analysis of the fingerprint region is particularly useful for examining the resonance modes of the benzenoid and quinoid units, and the individual bonds, such as, out-of-plane C–H and C-N of the substituted polyaniline compound. In the IR spectrum (Figure 1), the characteristic band at 1560 cm^{-1} can be assigned to the C=C stretching of the quinoid rings while the peak at 1495 cm^{-1} is the characteristic bands of the C=C stretching vibration mode for benzenoid rings. The band at 1410 along with the low intensity peaks in the range of 1150-1020 cm^{-1} corresponds to the aromatic C–H in-plane bending vibration. The peak at

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1270 cm^{-1} can be assigned to the C–N stretching mode of the polaronic units. The bands at 730 and 680 cm^{-1}are due to an aromatic out-of-plane C–H deformation vibration and related to the substituted benzene ring. The bands in the range of 2800-3000 cm^{-1} correspond to the C–H stretching vibration, whereas, aromatic primary amine shows N–H stretching in the range of 3300-3400 cm^{-1}.

Figure: 1

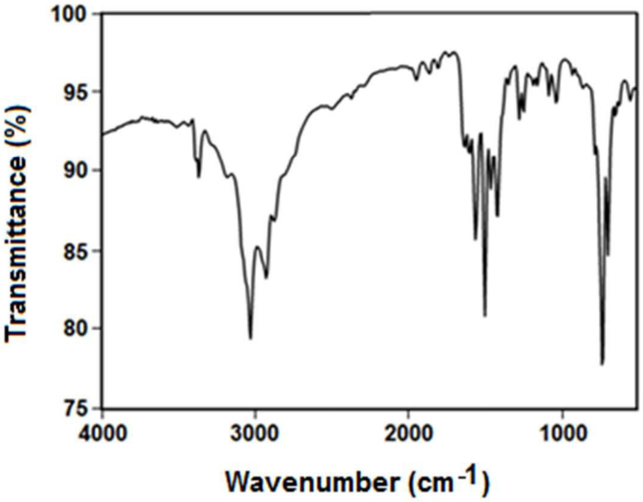

Figure 1: In the IR spectrum, the band at1560 cm^{-1}can be assigned for the quinoid rings while the peak at 1495 cm^{-1}is the characteristic bands for benzenoid rings.

The above spectral data indicates the formation of the poly-(*1, 2*-diaminobenzene) with the presence of both benzenoid and quinoid structure in the polymer backbone. The SEM image, Figure 2A, reveals that the product was composed of fiber-like morphology and the diameter of the fibers is in the range of 50-100 nm. The TEM image, Figure 2, B and C, shows the polymeric material at various magnifications. Figure 2B is a low-magnification image illustrating the general morphology of the product.

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Figure: 2

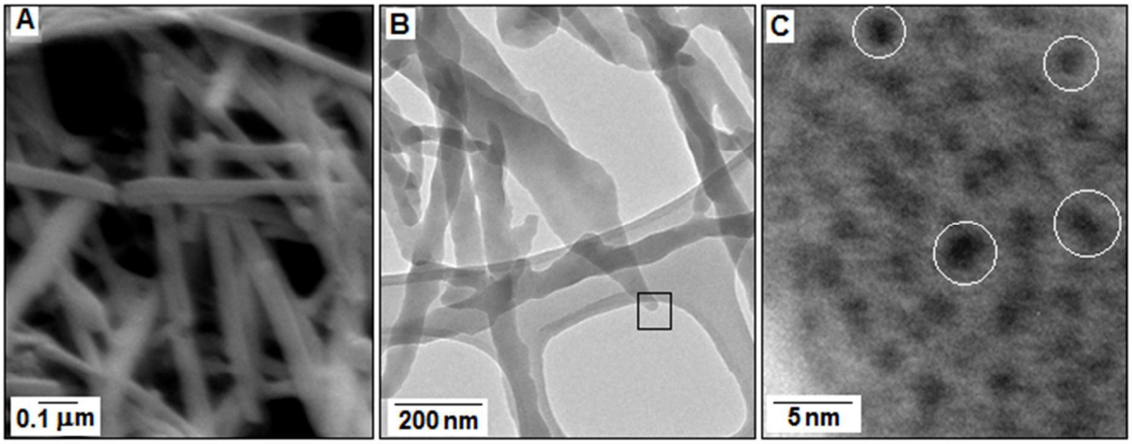

Figure 2: The SEM image (A) reveals fiber-like morphology of the product and the diameter of the fibers is in the range of 50-100 nm. The TEM image (B) illustrates the general morphology of the product, whereas, the high-magnification TEM image (C) shows the palladium nanoparticles (dark spots, some of them are marked within the circles) within the size range of 2-4 nm.

In the high-magnification TEM image (Figure 2C), captured from the demarked boxed portion of Figure 2B, dark spots are the palladium nanoparticles within the size range of 2-4 nm and some of them are marked within the circles. A typical energy-dispersive X-ray spectroscopy analysis (Figure 3A), obtained from the electron beam being focused onto a dark spot in the polymer, confirms that these spots are palladium particles.

Figure: 3

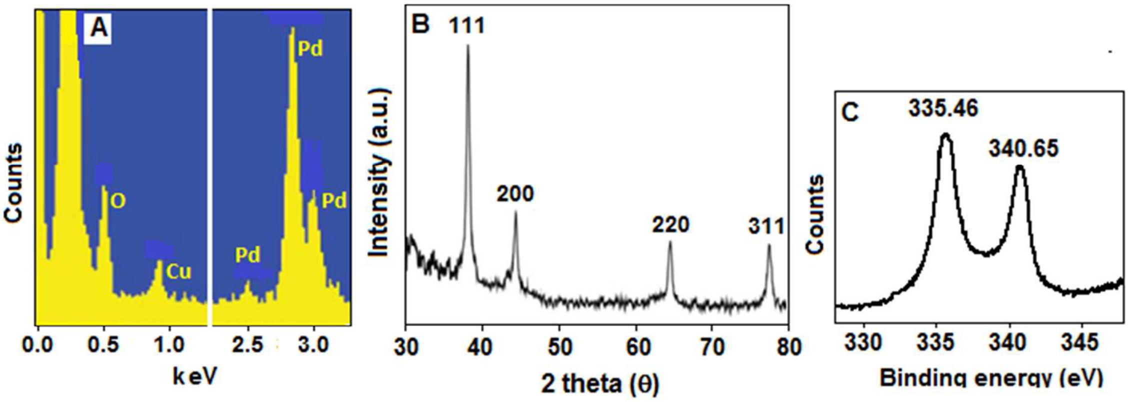

Figure 3: The energy dispersive spectroscopy **(**EDS**)** analysis (A) shows the palladium peaks those are derived from the nanoparticles, whereas the copper peak comes from the TEM copper mesh support grid. (B) Strong (111) Bragg reflection, indicating that the palladium particles possess a highly oriented crystalline character. X-ray photoelectron spectroscopy (XPS) spectrum (C) of the Pd3d region: Pd3d$_{5/2}$ and 3d$_{3/2}$spin-orbit couplings give rise to the

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peaks positioned at 335.46 and 340.65 eV, respectively, and confirm the metallic character of the palladium.

The XRD pattern (Figure 3B) shows that the palladium nanoparticles in the metal-polymer composite material were highly face-selective toward strong {111} Bragg reflection which indicates that the metal particles possess a highly oriented crystalline character. To identify the chemical state of the polymer-stabilised Pd particles, X-ray photoelectron spectroscopy (XPS) measurements were performed. The Pd3d region of the XPS spectrum of the synthesized material is illustrated in Figure 3C, which reveals the presence of Pd3d$_{5/2}$ and 3d$_{3/2}$ peaks at binding energies of 335.46 and 340.65 eV, respectively. These binding energy values are in accord with those reported for metallic palladium.[25]

Performance of Pd(0)-*p*DAB as a catalyst: The synthesized metal-polymer composite was investigated as a catalyst for a carbon-carbon bond formation reaction and the Suzuki cross-coupling reaction was chosen as it is one of the important reactions from a standpoint of its versatile applicability. For an effective coupling a basic reaction condition is very important. In this study, a series of various bases (K_2CO_3, Na_2CO_3, Cs_2CO_3, Na^{t}OBu and K^{t}OBu) have been utilized to determine the optimum condition of the reactions. Among them, K_2CO_3 was found to be highly efficient for the present Suzuki coupling reaction in the presence of Pd(0)-*p*DAB composite catalyst and toluene was used as a solvent at an optimized temperature of 90 ^{o}C (Table 1).

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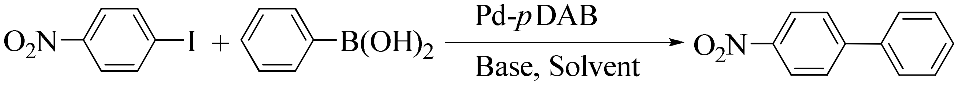
Table 1. Optimization of Suzuki coupling reaction between 4-nitroiodobenzene and phenylboronic acid[a]



Entry	Solvent[b]	Base	T (°C)	Conversion (%)[c]
1	Water	K_2CO_3	80	15
2	Water-toluene (1:1)	K_2CO_3	80	36
3	Toluene	K_2CO_3	RT	-
4	Toluene	K_2CO_3	80	82
5	Water-EtOH (1:1)	K_2CO_3	90	90
6	**Toluene**	$\mathbf{K_2CO_3}$	**90**	**98**
7	Toluene	Na_2CO_3	90	76
8	Toluene	Cs_2CO_3	90	52
9	Toluene	^tBuOK	90	25
10	Toluene	^tBuOK	90	32
11	1,4-Dioxane	K_2CO_3	90	21

[a] 4-Nitroiodobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), Base (1.5 mmol), Catalyst (0.14 mol% Pd) and solvent (5 ml)

[b] All reactions were carried out for 8 h

[c] Isolated yields

We have investigated the Suzuki reaction for the coupling between different aryl halides with phenylboronic acid in the presence of various activating and deactivating substituents (Table 2). High catalytic activity of composite for both the deactivated and activated aryl iodides was observed with the formation of the corresponding biphenyl compounds with excellent yields (Table 2, entries 1-10). When methyl and methoxy derivatized aryl iodide coupled with phenylboronic acid, the formation of 4-methylbiphenyl and 4-methoxybiphenyl with the

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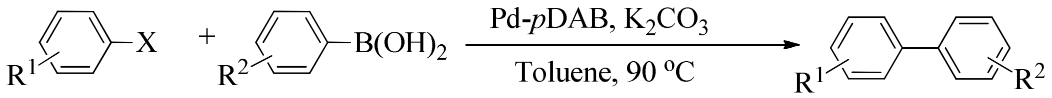
Table 2. Suzuki coupling reaction between aryl halides and substituted /unsubstituted phenyl boronic acids[a]



Entry	X[b]	R^1	R^2	Yield (%)[c]
1	I	H	H	90
2	I	4-Me	H	92
3	I	4-OMe	H	89
4	I	4-NO_2	H	98
5	I	H	4-OMe	95
6	I	4-OMe	4-OMe	96
7	I	4-NO_2	4-OMe	99
8	I	H	4-Ph	91
9	I	4-OMe	4-Ph	88
10	I	4-NO_2	4-Ph	95
11	Br	H	H	80
12	Br	4-Me	H	78
13	Br	4-OMe	H	76
14	Br	4-NO_2	H	82
15	Cl	H	H	43
16	Cl	4-NO_2	H	55

[a] Aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), K_2CO_3 (1.5 mmol), toluene (5 ml) and catalyst concentration 0.14 mol% Pd. Entries 11-14: catalyst concentration 0.28 mol% Pd. Entries 15-16: catalyst concentration 0.56 mol% Pd

[b] All reactions were carried out at 90 °C for 8 h

[c] Isolated yields

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yield of 92 and 89% has been achieved, entries 2 and 3, respectively. In 4-nitroiodobenzene, the deactivated nitro group facilitate the coupling reaction with phenylboronic acid with the formation of *4*-nitrobiphenyl with a yield of 98% (entry 4). When both R^1 and R^2 is equivalent with *–H,* a yield of 90% of the coupled product has been achieved (entry 1), whereas, activated group ($R^2 = –OCH_3$) substituted phenylboronic acid has a positive impact, with a yield of 95%, on the coupling reaction (entry 5). A similar kind of trend has also been observed when both R^1 and R^2 is equivalent with $–OCH_3$ (entry 6). According to the results of our study, the most favoured coupling is possible when R^1 and R^2 are equivalent with $–NO_2$ and $–OCH_3$ respectively. We have also followed the reactions for $–C_6H_5$ substituted phenylboronic acid with aryl iodide (entry 8), $–OCH_3$ (entry 9) and $–NO_2$ (entry 10) substituted aryl iodide and found the highest coupled product has been achieved when $–NO_2$ group was involved with aryl iodide system. Almost identical trend on the coupling reaction has been observed for aryl bromides (entries: 11-14) but obviously a lower yield has been obtained compared with aryl iodide system. For a typical example, when 4-nitrobromobenzene coupled with phenylboronic acid, 82% of 4-nitrobiphenyl has been formed as a Suzuki coupled product (entry 14) using Pd(0)-*p*DAB composite as a catalyst. Similarly, as expected, aryl chlorides showed the least reactivity towards the coupling reaction (entries: 15, 16) as the bond strength of *C–Cl* is high due to the stronger *2s–3p* interaction. Aryl bromides and iodides, are the large molecules with bromine (*4p-orbital*) and iodine (*5p-orbital*) atoms, when interact with carbon (*2s-orbital*) a comparatively poor orbital overlapping process involved that causes aryl iodide and aryl bromides showed the high performance for coupling reaction than aryl chlorides (order of bond strength: *C–Cl* > *C–Br* > *C–I*).

Recyclability, scaling-up and metal leaching study: There is always an effort in industries to reduce the chemical waste and improve the selectivity as well as efficiency of synthetic processes. The need to implement the green chemistry principles is a driving force towards the development of recoverable and recyclable catalysts. The design and synthesis of recoverable catalysts is highly challenging. In this current report, the recyclability study was performed for the coupling of 4-nitroiodobenzene with phenylboronic acid using Pd(0)-*p*DAB catalyst. For the convenience of the study, we have increased the amounts of both the catalyst and the reactants by a factor of ten and performed the experiment under the similar reaction conditions as mentioned in the section of general procedure. After the first run, the

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product (*4*-nitrobiphenyl), with a yield of 97%, was extracted from the reaction mixture and the recovered catalyst was further used for another five cycles under the same reaction conditions. At the end of the sixth cycle, we have obtained a yield of 68% of the coupled product (Figure 4A).

Figure: 4

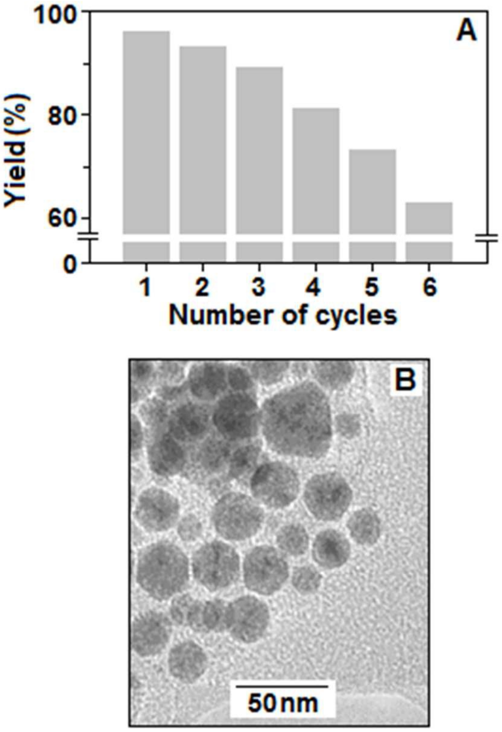

Figure 4: The histogram (A), generated from the recyclability study of the Pd(0)-*p*DAB catalytic system, shows that the used material was active as a catalyst without a significant loss of catalytic performance. At the end of the sixth cycle, a yield of 68% of the coupled product (4-nitrobiphenyl) has been achieved. The TEM image (B) of the used catalyst at the end of the recyclability experiment and found the enlargement of the palladium particles, with different sizes and shapes.

It is also important to mention that almost identical amount of yield has been achieved for the same reaction during the checking the versatility of the catalyst (Table 2, entry 4) and also for the scaling up of the reaction which was done to find out the recyclability of the catalyst (for the first cycle). The above results indicate that the Suzuki coupling reaction using palladium-polymer composite catalyst is a heterogeneous catalysis reaction with the recyclability performance of the catalyst.

Metal leaching is an unavoidable phenomenon for palladium based catalyst for carbon-carbon bond formation reactions.[26] In this current study, to check the leaching of metallic palladium

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from the polymer matrix the composite material was kept in hot water (90 ^{o}C) for an hour and removed by filtration and the filtrate was monitored for catalytic activity for the title reaction. Within the timeframe of 8h, there was no indication of formation of any coupled product which indicates that no catalytically active Pd remained in the filtrate. But when the above study was conducted for the real reaction, the leaching of palladium was noticed during the recovery process of the catalyst with the aid of inductively coupled plasma mass spectrometry (ICP-MS) technique. To determine the degree of metal leaching, we have collected 2 mL of filtrate, during the separation process of the product from the recyclability experiment, each from the first and the sixth cycle of the reactions and found that the concentration of leached palladium in the filtrate solution were 4.5 and 26.5 ppm, respectively. The increase of metal leaching with number of cycles can be explained as follows. In the first cycle, the metal-polymer binding energy was strong for the virgin catalyst and for that the amount of leached metal was low whereas in the sixth cycle due to the repeated exposure of the composite catalyst to the harsh environment (temperature as well as organic solvent and reactants) decreases of binding energy between metal and polymer that causes the higher amount of palladium release from the support.

The gradual decrease of the yield with increasing the number of recycling experiments (Figure 4A) was due to the combined effect of (a) leaching of catalyst particle and (b) loss of composite material (catalyst and support) during the recovery process of the product. For each of the subsequent cycles, the fresh reaction mixture had a lower amount of catalyst affected the yield. We have also performed the microscopic characterization study of the used catalyst at the end of the recyclability experiment and found the enlargement of the palladium particles, with different sizes and shapes, in the range of 15-60 nm (Figure 4B), which was due to the subsequent dissolution of palladium nanoparticle in the form of Pd(II) in the first half of the reaction (oxidative addition) and regeneration of metallic particles in the other half of the reaction (reductive elimination) of the total catalytic cycle, scheme 1.[27]

Kinetic study: The kinetics of the Suzuki reaction in the presence of the catalyst was further studied (Figure 5) using the reactions between *4*-halo *(–I, –Br* and *–Cl*) nitrobenzene with phenylboronic acid (Table 2 entries 4, 14 and 16, respectively). In order to achieve the maximum yield of biaryl products, all three above mentioned coupling reactions were performed at 90 ^{0}C for the duration of 9 hours using the composite catalyst (0.56 mol% Pd). The coupling reaction between 4-nitroiodobenzene and phenylboronic acid (A) showed a steady conversion of 98% within the time duration of 6h. A similar trend has also observed for the reaction between 4-nitrobromobenzene and phenylboronic acid (B), where 82% coupled product was obtained within 7h. For the reaction between 4-nitrochlorobenzene and phenylboronic acid (C), a <5% of the coupled product has been formed within 2h from the beginning of the reaction and about 55% coupled product has been formed within 8h; indicates a very slow reaction rate as compared with other two (A and B).

Figure: 5

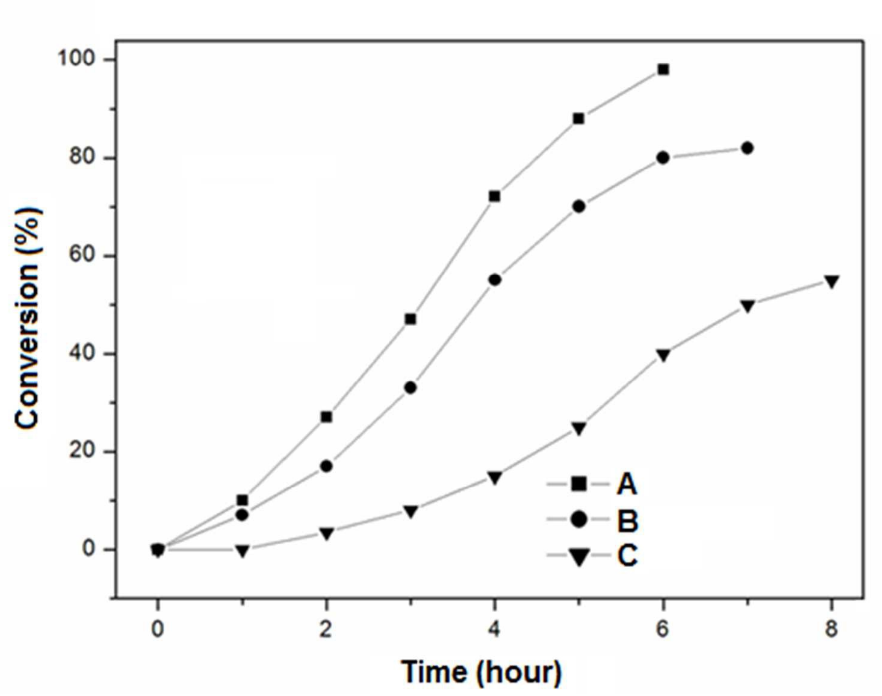

Figure 5: Comparative kinetic study of the Suzuki coupling reactions for (A) 4-iodo nitrobenzene (Table 2, entry 4), (B) 4-bromo nitrobenzene (Table 2, entry 14) and (C) 4-chloro nitrobenzene (Table 2, entry 16) with phenylboronic acid. All the reactions were carried out in the presence of Pd(0)-*p*DAB catalyst (0.56 mol% Pd) at 90 ^{0}C for 9 hours.

For all of the above reactions it was observed that with increasing the reaction time no further improvement of 'yield' has been achieved but the concentration of the catalyst has a positive impact on the 'duration of the reaction' and consequently on the 'yield' of the product. A comparison of efficiency of the current catalyst with other catalysts, previously reported, for the reaction between 4-nitrohelobenzene and phenylboronic acid is examined in table: 3.[28]

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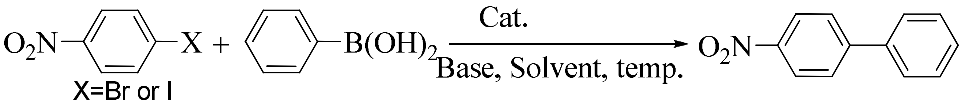
Table 3: Comparative literature survey of the Suzuki reaction between 4-nitrohelobenzene and phenylboronic acid by different catalysts.



Sr. No.	Ref.	Reaction time (h)	Yield (%)	Reaction Condition [solvent, base, temperature (^{0}C)]	Support material used for Pd
1	17(d)	12	97	20% EtOH/H_2O, K_2CO_3, 80	Modified MCM-41
2	17(e)	12	99	20% EtOH/H_2O, Na_2CO_3, 60	Organic modification of MCM-41 with (3-aminopropyl)-triethoxysilane
3	17(f)	0.5	91	20% EtOH/H_2O, K_2CO_3, 50	Triazine amine-functionalized SBA-15
4	28(a)	0.5	99	Dioxane: H_2O (1:1), K_2CO_3, 60	Commercially available Poly(N-isopropylacrylamide)
5	28(b)	2	97	EtOH-H_2O, Na_2CO_3, 80	Graphene oxide (GO)
6	28(c)	15	80	DMF, K_2CO_3, 110	$(C_6H_5)(2\text{-}HOC_6H_4)CHNH(CH_2)_3SePh$
7	28(d)	3	95	DMF, K_2CO_3, 120	EDTA modified SAB-15
8	28(e)	24	99	20 MPa pressure of CO_2, $K_3PO_4.3H_2O$, 90	SBA-15 modified with $(MeO)_3SiPh$ and a phosphine ligand, $(MeO)_3SiCH_2CH_2CH_2SCH_2C_6H_4PPh_3$

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9	28(f)	12	97	Toluene, Cs_2CO_3, 80	$^tBu_2PN{=}P(^iBuNCH_2CH_2)_3N$: (4-chloronitrobenzene was used as coupling partner)
10	28(g)	24	87	MeOH, NaOAc, 70	Hollow graphitized nanofibers
11	28(h)	3.5	95	DMF, KF, 100	Functionalization of 2D-hexagonally ordered MCM-41 with 3-aminopropyltriethoxysilane followed by the grafting with 2,6-diacetylpyridine
12	28(i)	8	98	Toluene, K_2CO_3, 80	Poly (1, 2-diaminobenzene)

The original recommendation for the Suzuki reaction involved a phosphine-based palladium catalyst and it is believed that the phosphine ligand is responsible for the formation of catalytically active metallic palladium species. Recently, there has been considerable interest in the development of new catalysts that are environmentally benign and efficient. The coupling reaction under phosphine-free conditions is a topic of interest resulting from both economic and environmental considerations. For the Suzuki cross-coupling reactions metallic palladium is the catalyst species and the possible mechanism is the interaction of aryl halide and palladium nanoparticle to form the aryl-palladium halide complex (Scheme 1), which couples with phenylboronic acid in the presence of a base to produce an intermediate complex and finally forms the biaryl product via the reductive elimination of metallic palladium.

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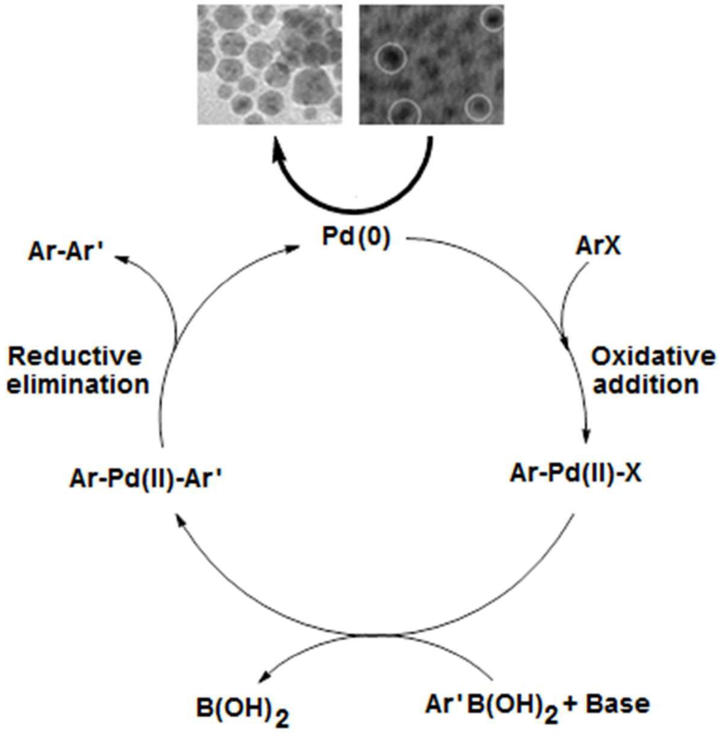
Scheme: 1



Scheme 1: Mechanistic pathway for the coupling between aryl halide and phenylboronic acid in the presence of palladium catalyst.

In this current experiment, the polymer (*p*DAB) plays the dual role, such as, (a) a stabilizer (support matrix) of the palladium nanoparticles and (b) an alternative ligand that can replace phosphine without altering the reaction route.

Conclusion:

We have reported here a simple one step method for the synthesis of a heterogeneous metal-polymer composite material. On the basis of spectroscopic and microscopic characterization results we have concluded that the palladium nanoparticles, within size range of 2-4 nm, are dispersed and stabilized in the poly-(*1, 2*-diaminobenzene) matrix. The metal-polymer composite material is robust and performed as an excellent catalyst towards the activity and recyclability for Suzuki coupling reaction under phosphine free condition with a moderately less metal leaching property. The catalyst also showed the reactivity with a less venerable aryl chloride system for the coupling reaction.

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