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In-situ synthesis of a palladium-polyaniline hybrid catalyst for a Suzuki coupling reaction

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ABSTRACT

Palladium-catalyzed cross-coupling reactions are one of the most frequently used synthetic tools for the construction of new carbon–carbon bonds in organic synthesis. The present study describes the use of palladium-polyaniline composite material as a catalyst for the Suzuki coupling of aryl halides. Palladium-polyaniline nanocomposite material was synthesized using an *in-situ* technique in which palladium acetate and aniline hydrochloride were used as the precursors of the composite. Electron microscopy imaging showed that the palladium particles were well-dispersed within the polymer matrix and were typically 3–5 nm in diameter. The metal-polymer composite material was used as a catalyst for the coupling of phenylboronic acid with aryl halides in the presence of an inorganic base and showed excellent yield with high TOF values.

1. Introduction

Palladium based catalysts particularly nanoscale palladium particles have recently drawn enormous attention due to their versatile role in organic synthesis [1–3]. The use of palladium nanoparticles in catalysis is not only industrially important [4–6], 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 [7]. Unfortunately, aggregation of bare nanoparticles often prohibits the tailoring of particle size [8]. To overcome this problem, catalytic nanoparticles have been immobilized on solid supports, such as carbon [9], titania [10], zeolites [11], alumina [12], silica spheres [13] and polymers [14]. Over recent years, especially following the rapid development of combinatorial chemistry, the use of polymeric supports in organic synthesis has become common practice in constructing small organic molecules [15,16]. One of the well-known applications of palladium nanoparticles as catalysts for the coupling of carbon–carbon molecules is the Suzuki-Miyaura reaction [17,18]. The Suzuki–Miyaura coupling reaction is one of the most useful methods for selective C–C bond formation during the construction of biaryl-skeletons, which are often used in pharmaceuticals, natural products and functional materials. The classical conditions for performing the Suzuki–Miyaura coupling reaction involve the use of a palladium complex or palladium salt and a phosphine ligand [19]. Palladium-catalyzed reactions under phosphine-free conditions are a topic of considerable interest as a result of economic and environmental reasons.

We describe here the fabrication of a metal-polymer hybrid material in which palladium nanoparticles are stabilized in a macromolecular matrix and its application in Suzuki coupling reactions. The coupling of arylboronic acids with aryl halides, the Suzuki reaction, is perhaps the most powerful and versatile method for the formation of new biaryls. Our approach is to use an '*In situ* polymerization and composite formation (IPCF)' [20] method for the synthesis of palladium-polyaniline hybrid material and to use that composite as a catalyst for Suzuki coupling reaction. We found that the hybrid material was very active as a catalyst for the Suzuki reaction and that the reaction could be carried out in the absence of a phosphine ligand.

2. Experimental

2.1. Materials

Reagent grade aniline hydrochloride was purchased from Merck. Pd-acetate from Next *Chimica* was dissolved in toluene

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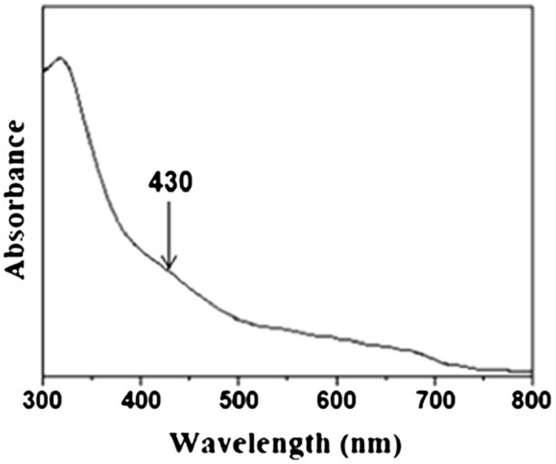


Fig. 1. UV–visible spectrum of the polyaniline compound. A shoulder-like appearance at 430 nm (indicated by an arrow) is due to the polaron/bipolaron transition.

(Merck). All other chemicals were purchased from Aldrich and used as received.

2.2. *In-situ synthesis of palladium-polymer composite*

In a typical experiment, aniline hydrochloride (0.442 g) was dissolved in methanol under continuous stirring conditions. Pd-acetate (0.4×10^{-2} moldm^{-3}) was added drop by drop to aniline hydrochloride in methanol solution. The solution turned a light green colour and the precipitation occurred after the addition of all of the Pd-acetate. TEM specimens were prepared by pipetting 2 μL of the colloid solution onto lacey carbon coated copper grids. Subsequently after viewing, the TEM grids were sputter coated with a 10 nm thick conducting layer of Au-Pd and viewed in a SEM. A small portion of the colloidal sample was used for optical characterization. The rest of the solution was filtered and the solid mass was dried under vacuum at 60 °C. The solid sample was used as a catalyst for Suzuki coupling reaction. The amount of Pd present in the catalyst was quantified by ICPMS technique, which revealed the Pd loading in the sample to be 1.7 wt %.

2.3. *Procedure for the Suzuki coupling reactions catalyzed by palladium-polymer composite*

In typical experiment aryl halide (1.0 mmol), phenylboronic acid (1.5 mol), K_2CO_3 (1.5 mmol) and the catalyst (0.036 mol% 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 80–90 °C and stirred for 6–8 h depending on the aryl halides used. The reaction was monitored by a thin layer chromatography (TLC) technique. Subsequently, the mixture was extracted with ethyl acetate three times. Subsequently, the reaction mixture was cooled, diluted with Et_2O, filtered through a pad of silica gel with copious washings and purified by flash chromatography on silica gel.

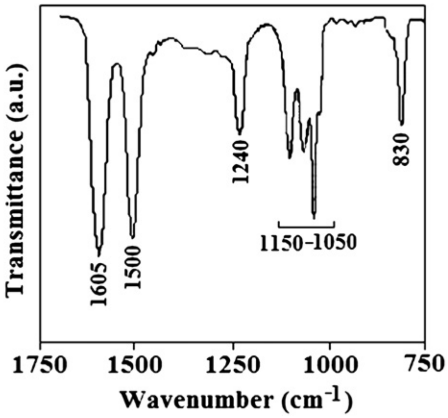


Fig. 3. IR spectra obtained from the composite material. The main peaks at 1510 and 1600 cm^{-1} correspond respectively to the stretching deformation of the quinine and the benzene rings.

2.4. *Characterization techniques*

For UV–vis spectra analysis, a small portion of the solid sample was dissolved in methanol and scanned within the range 300–800 nm using a Varian, CARY, 1E, digital spectrophotometer. Raman spectra were acquired using the green (514.5 nm) line of an argon ion laser as the excitation source. Light dispersion was undertaken via the single spectrograph stage of a Jobin-Yvon T64000 Raman spectrometer. Power at the sample was kept low (0.73 mW), while the laser beam diameter at the sample was ~1 μm. A Perkin–Elmer 2000 FT-IR spectrometer, operating within the range 800–1700 cm^{-1}, with a resolution 4 cm^{-1}, was used for the infrared spectra analyses. For this study, the sample was deposited in the form of a thin film on a KBr disk. Transmission electron microscopy studies of the composite were carried out at an accelerating voltage of 197 kV using a Gatan GIF Tridiem on a Philips CM200 TEM equipped with a LaB_6 source. SEM studies were undertaken in a FEI Quanta 400F ESEM at 2 kV. The X-ray

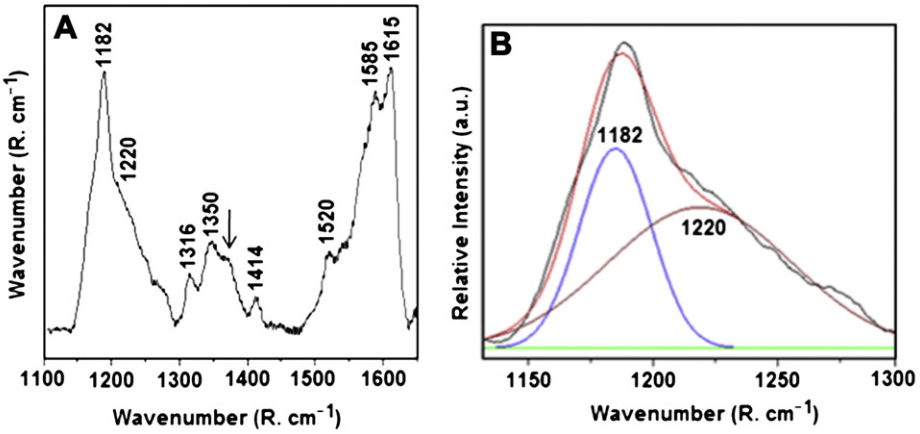


Fig. 2. Raman spectra recorded for the green precipitate. The characteristic bands from 1100 to 1700 cm^{-1} indicate the formation of polyaniline. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

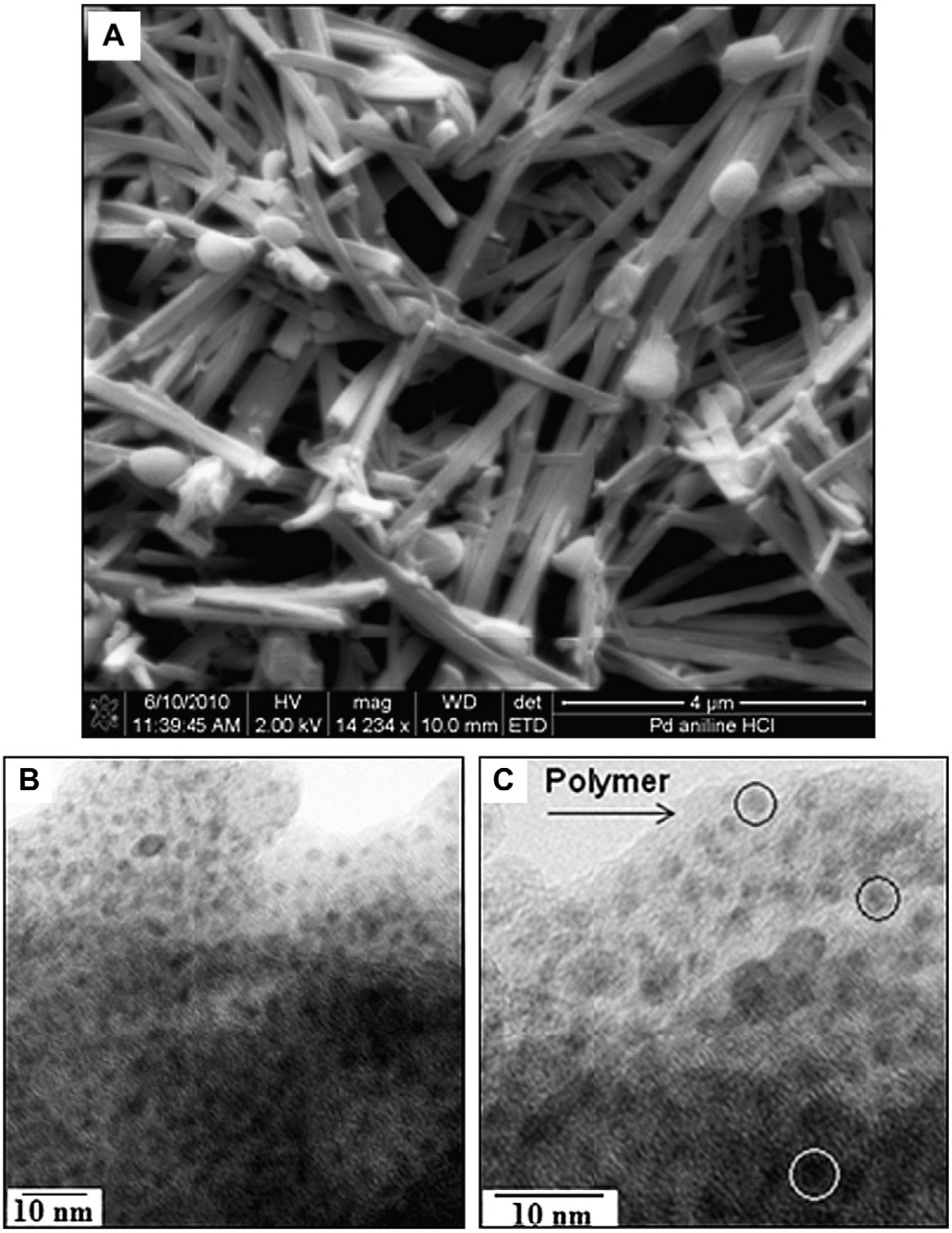


Fig. 4. SEM image of polyaniline nanofibers with a three dimensional morphology (A). TEM images of the polyaniline (B and C). The high-density distribution of dark spots on the polymer corresponds to the palladium nanoparticles (B). The higher magnification TEM image (C) clearly indicates the 2–4 nm diameter palladium nanoparticles encapsulated and dispersed within the polyaniline matrix (some of them are within the circle).

photoelectron spectra (XPS) were collected in a UHV chamber attached to a Physical Electronics 560 ESCA/SAM instrument.

3. Results and discussion

The electronic absorption spectrum of the polyaniline salt has been documented in the literature [21]. The polyaniline salt shows three absorption peaks at 310-360, 400-440 and 700–825 nm. In the present study, the UV–visible spectrum of the resultant material, Fig. 1, shows one sharp and prominent absorption band with its peak at 325 nm, which corresponds to the π-π^* transition of the benzenoid rings. A shoulder-like appearance at 430 nm (indicated by an arrow) is due to the polaron/bipolaron transition. A broad absorption band starting from 500 to 750 nm is also seen which results from the benzenoid-to-quinoid excitonic transition. In our previous work [22,23] when the starting material was aniline and no protonic acid was used as a doping agent, the benzenoid–quinoid excitonic transition showed the absorption peak to be at 620 nm. In that case, the polyaniline was formed under either neutral or basic conditions resulting in the absorption peak for the benzenoid–quinoid excitonic transition appearing at a lower wavelength. The position of the excitonic peak can shift from 800 to 560 nm depending on various factors such as nature of the counter ions, the type of solvent, the pH value and the chemical structure of the polymer [24].

In the Raman spectrum (Fig. 2A), the characteristic bands from 1100 to 1700 cm^{-1} are sensitive to the oxidation state of the polyaniline. The Raman spectrum of polyaniline obtained during the reaction between palladium acetate and aniline hydrochloride

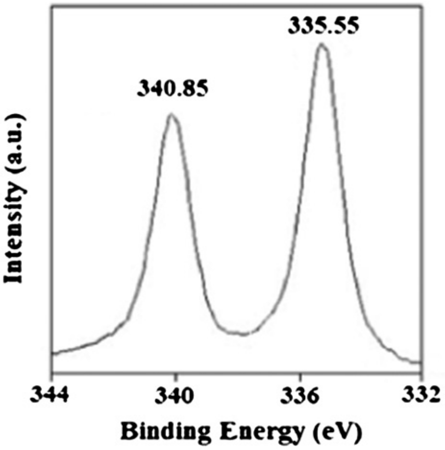
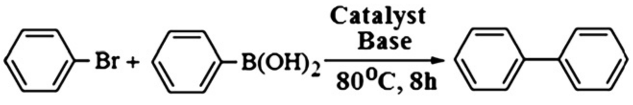


Fig. 5. Palladium 3d XPS spectrum of the palladium-polyaniline composite. The peaks at binding energies at 335.55 eV for $3d_{5/2}$ and 340.85 eV for $3d_{3/2}$ are the indicative of metallic palladium.

reveals C—C deformation bands of the benzenoid ring at 1615 and 1585 cm^{-1}, which are characteristic for semiquinone rings [25,26]. The band at 1520 cm^{-1} corresponds to the N—H bending deformation. Intense overlapping features between 1300 and 1400 cm^{-1} with two prominent bands at 1316 and 1350 cm^{-1} along with a clearly visible shoulder at 1370 cm^{-1} (indicated with an arrow) correspond to semiquinone radical structures. The band at 1414 cm^{-1} is due to the C—C stretching vibration of the quinoid units. Applying a Gaussian fit to the 1100—1300 cm^{-1} region (Fig. 2B), two peaks at 1182 and 1220 cm^{-1} are clearly visible. The position of the benzene C—H bending deformation band at 1182 cm^{-1} is characteristic of the reduced and semiquinone structures while the 1220 cm^{-1} band corresponds to the C—N stretching mode of single bonds.

The IR spectroscopic technique was used to further investigate the optical behaviour of the solid sample. The IR spectrum of the resultant compound is presented in Fig. 3. The bands at 1605 and 1500 cm^{-1} can be assigned to the C = C stretching vibration of the quinoid (N = Q = N, Q represents the quinoid ring) and benzenoid (N—B—N, B represents the benzenoid ring) rings respectively [27,28]. The material shows a band at 1240 cm^{-1}, which corresponds to the C—N stretching vibration [29]. The high intensity peaks in the region 1150—1050 cm^{-1} correspond to the aromatic C—H in-plane bending vibration [30]. Aromatic out-of-plane C—H deformation vibration corresponds to the band at 830 cm^{-1}. This band is characteristic of the presence of 1—4 substituted benzene rings [30]. The Raman and IR spectrum indicate the formation of the polymeric product of aniline hydrochloride with quinoid and benzenoid type of ring structure in the polyaniline chain.

The SEM image (Fig. 4A) shows that the product consists of regular straight nanofibers up to 20 μm in length and of rectangular cross section 0.4—1.7 μm by about 0.08 μm thick. The fibers were almost identical in morphology and very straight suggesting a high level of rigidity. Fig. 4B displays TEM images of the composite. The high-density distribution of dark spots on the polymer corresponds to the location of the palladium nanoparticles. Fig. 4C is a higher magnification image and this and stereo images (not shown) clearly indicate that the 2—4 nm diameter nanoparticles are encapsulated and dispersed within the polymer matrix (some of them are within the circle). Selected area diffraction (SAD) patterns indicated that the Pd nanoparticles were amorphous. To identify the chemical state of the polymer stabilized palladium particles, X-ray photoelectron spectroscopy (XPS) measurements were carried out. The Pd 3d region of the XPS spectrum of the Pd-polyaniline composite is illustrated in Fig. 5, which reveals the presence of Pd $3d_{5/2}$ and $3d_{3/2}$ peaks at binding energies of 335.5 and 340.85 eV respectively. These binding energy values are in accordance with those reported for metallic palladium [31].



Scheme 1. Suzuki coupling of benzene bromide and phenylboronic acid.

Table 1
Suzuki reaction of benzene bromide and phenylboronic acid with different bases.

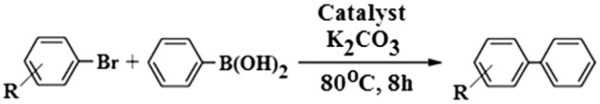
Base	K_2CO_3	Na_2CO_3	K_3PO4	Cs_2CO_3	K_F
Yield(%)	93	85	91	87	73

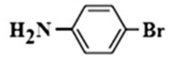
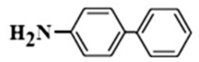
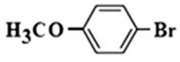
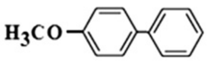
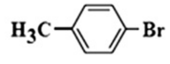
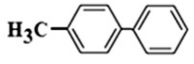
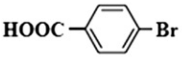
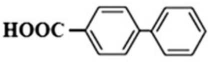
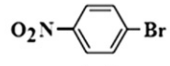
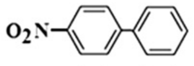
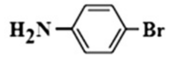
Reaction condition: Benzene bromide (1.0 mmol), phenylboronic acid (1.5 mmol), base (1.5 mmol), toluene (5 ml) and catalyst (polymer supported Pd 0.02 mol%), 80 °C, 8 h.

A wide variety of methods have been applied to the preparation of polyaniline or substituted polyaniline-type compounds by the oxidative polymerization of their respective monomers [32]. According to the most widely accepted mechanism, the first step during the polymerization involves the formation of a radical cation accompanied by the release of an electron. This step is the initiation process of the polymerization reaction. The released electron [32] is then used to reduce the Pd^{2+} ions to form palladium atoms. The coalescence of these palladium atoms ultimately forms palladium nanoparticles, which are encapsulated by the polyaniline.

The polyaniline-supported palladium nanoparticle based catalyst was used in the Suzuki coupling reaction, which is a versatile method for carbon—carbon bond formation, especially when applied to the synthesis of biaryls in organic synthesis. Initially, a solvent-base optimization study was performed for the coupling of phenylboronic acid with bromobenzene using toluene and 1, 4-dioxane as solvents and K_2CO_3, Na_2CO_3, K_3PO_4, Cs_2CO_3 and KF as bases. Among them, K_2CO_3 and K_3PO_4 in combination with toluene

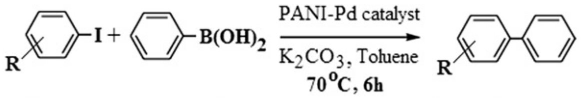
Table 2
Suzuki reaction between derivatives of benzene bromide and phenylboronic acid.

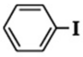
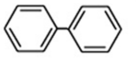
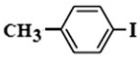
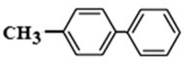
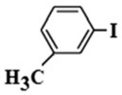
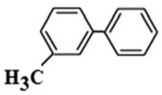
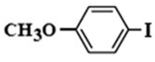
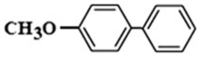
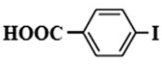
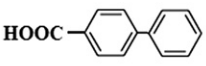
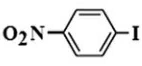
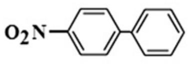


Entry	Aryl Bromide	Product	Yield (%)	TOF (h^{-1})
1			63	1125
2			87	1553
3			88	1571
4			94	1678
5			97	1732
6			85	758

Reaction conditions: Derivatives of benzene bromide (1.0 mmol)(1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (1.5 mmol), toluene (5 ml) and catalyst (polymer supported Pd 0.02 mol%), 80 °C, 8 h. Entry 6, 0.07 mol % Pd as catalyst was used at 80 °C, 10 h to achieve a higher yield.

Table 3
Suzuki reaction between derivatives of benzene iodide and phenylboronic acid.



Entry	Aryl Iodides	Product	Yield (%)	TON (h^{-1})
1			85	2023
2			87	2071
3			90	2142
4			94	2238
5			97	2309
6			91	2166

Reaction conditions: Derivatives of benzene iodide (1.0 mmol)(1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (1.5 mmol), toluene (5 ml) and catalyst (polymer supported Pd 0.02 mol%), 70 °C, 6 h.

as a solvent turned out to be highly efficient under the given conditions (Scheme 1 and Table 1). The reaction conditions were systematically optimized and, based upon the results, a series of different bromobenzene based derivatives were tested in the presence of the Pd-polymer composite and the toluene-K_2CO_3 combination under the reaction conditions at 80 °C for 8 h (Table 2).

In order to investigate the potential of aryl halides in coupling with phenylboronic acid, different aryl bromides were employed in the reaction. Electron-rich and electron-deficient aryl bromides were readily coupled in the presence of the metal-polymer hybrid material. However, aryl bromides with an electron donating group (entries 1-3) showed a slight drop of reactivity in comparison with the aryl bromides with an electron withdrawing group (entries 4 and 5). In the case of 4-bromoaniline a higher palladium loading (0.07 mol %) was required to obtain a good yield of the desired biaryl product (Table 2, entries 1 and 6). This may be due to the fact that the amine functionality in the 4-bromoaniline could coordinate to the support source from the catalyst used in the reaction.

Furthermore, the polyaniline-supported palladium nanoparticles can also be applied as a very active catalyst for the synthesis of biaryls starting from aryl iodides and phenylboronic acid under comparatively mild conditions and shorter reaction times (Table 3, entry 1–6) than for aryl bromide. The reaction between chlorobenzene and phenylboronic acid necessitated a higher temperature, higher catalyst concentration (0.35 mol% Pd) and longer reaction time to afford a biphenyl coupling product. A moderate yield of 37% was achieved at 120 °C for 16 h for the coupled product. The metal-polymer composite catalyst was found to be very stable, insensitive to air and showed no performance loss even after one year of manufacture.

For the Suzuki reaction Pd(0) is the catalytic species and the possible mechanism, Scheme 2, is the interaction of aryl halide (R^1X) and Pd(0) to form the aryl-palladium halide complex [$R^1Pd(II)X$], which then couples with arylboronic acid, $R^2B(OH)_2$, in the presence of a base to produce the [R^1-(Pd^{2+})-R^2] intermediate, finally providing the biaryl product (R^1-R^2) via the reductive elimination of Pd^{2+} to Pd(0) as outlined in Scheme 1. It was also found that the reaction did not occur in the absence of Pd nanoparticles [33]. The recovery of the catalyst for the recyclability study was practically not feasible in this study due to the nature of the support and minute amount of the material used for the reaction as a catalyst.Please note that scheme 2 was not cited in the text.

$$\mathrm{Pd(0)} \xrightarrow{R^1X} \underset{[1]}{R^1\mathrm{Pd(II)}X} \xrightarrow[R^2B(OH)_2]{\text{Base}} \underset{[2]}{R^1\mathrm{Pd(II)}R^2} \longrightarrow R^1\text{-}R^2 + \mathrm{Pd(0)}$$

Scheme 2. Possible mechanism of Suzuki coupling reaction.

4. Conclusions

The metal-polymer composite material in which the palladium nanoparticles are stabilized in the polyaniline matrix showed excellent activity towards a Suzuki coupling reaction. Such high catalytic activities presumably result from the small size and narrow size distribution of the palladium nanoparticles. When aniline was used as a precursor no composite formation was observed, but when utilizing aniline hydrochloride an instant reaction took place with Pd-acetate resulting in the formation of the metal-polymer hybrid material. This hybrid material acts as a catalyst and shows good performance for the Suzuki coupling reaction under phosphine-free conditions which is a topic of considerable interest from both economic and environmental reasons. The combination of easy synthesis route, resistance to air, and a long expiry period could make the hybrid material very attractive for industrial applications.

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