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In situ synthesis of a Pd–poly (1,8-diaminonaphthalene) nanocomposite: An efficient catalyst for Heck reactions under phosphine-free conditions

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ABSTRACT

Polymerization of 1,8-diaminonaphthalene was performed using palladium acetate as an oxidizing agent. During the oxidative polymerization process the electrons liberated reduced the palladium (II) ions with the formation Pd nanoparticles, these colloidal particles being stabilized within the poly (1,8-diaminonaphthalene) matrix. Electron microscope images revealed that the palladium particles were well dispersed in the polymer matrix and had an average diameter of 2.5 nm. The metal–polymer composite material was initially tested for the coupling of iodobenzene with alkene (methyl acrylate) in the presence of a base. The yield of the substituted alkene derivative was found to be excellent. A series of iodo- and bromobenzene derivatives were tested for the coupling reaction with different alkenes. A coupled product was produced with high TOF values proving the efficiency of the composite material as an efficient catalyst for the Heck reaction under phosphine-free conditions.

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1. Introduction

Nanotechnology is a rapidly growing area of material science because of its numerous applications in various fields such as catalysis [1–4], sensors [5,6], electronics [7] and optics [8,9] as well as in the medical sciences [10,11]. The unique properties of metal nanoparticles are directly related to their size and are significantly different from those of the corresponding bulk materials [12,13]. Besides precise control over the size and shape, the stability of nanoparticles is an extremely important issue. Surfactants [14], polymers [15] and thiol molecules [16] have been employed to promote the stabilization of the nanoparticles. The advantage of polymers as a stabilizer is due to its robust nature which could give the metal particles additional stability [17].

Palladium nanoparticle based catalysts are often used in organic syntheses. We have previously successfully used polymer stabilized palladium nanoparticles as a heterogeneous catalyst for a model hydrogenation reaction [2]. Organophilic Pd-montmorillonite catalyst has shown efficient activity in alkyne hydrogenation [18] while Cinchonidine-modified 5% Pd–Al₂O₃ catalyst has been utilized for the hydrogenation of α , β -unsaturated carboxylic acids [19]. Many palladium complexes have been used as homogeneous systems, such systems exhibit better activity and selectivity than their heterogeneous equivalents. Palladium is probably the most versatile metal in promoting or catalyzing reactions, particularly for those involving C–C bond formation. Palladium-catalyzed Heck reactions [20,21] between aryl halides and alkenes continue to attract attention because of the versatility of the reaction and the uses of the products formed [22,23]. Recently, there has been increasing interest in the many uses of a 'ligand-free' catalyst for the Heck reaction, either using palladium salts, metallic palladium, or palladium nanoclusters immobilized on supports [20]. Palladacycle complexes [24] and ionic liquid [25] supported Pd nanoparticles also show the good catalytic efficiency for Heck reactions. Polymer is a good support for the metal nanoparticles. Polymer stabilized palladium nanoparticles have also been used in the C–C bond formation type of reaction [26].

In the present report, a phosphine-free condition has been employed in which a palladium–poly (1,8-diaminonaphthalene) composite has been utilized as a catalyst for the Heck coupling reactions in the presence of a base. A palladium–polymer composite material was synthesized using an 'in situ polymerization and composite formation' (IPCF) approach in which a single-step polymerization of 1,8diaminonaphthalene (DAN) was undertaken using palladium acetate as the oxidizing agent. This resulted in the formation of a Pd–poly-DAN composite material which was employed as the catalyst. IPCF types of reactions for the synthesis of 'metal–polymer composite materials' [27], have potential advantage in the area of 'synthetic material science' since both the polymer and the nanoparticles are produced simultaneously facilitating an intimate contact between the particles and the polymer through functionalisation [28]. In addition, the

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polymer acts as an effective stabilizer of the nanoparticles. Palladium nanoparticles with an average size of 2.5 nm were found to be highly stabilized and evenly dispersed throughout the poly-DAN matrix. We have paid equal attention to characterizing the polymer product by using UV-vis, Raman spectra analysis. SEM and TEM techniques were used to visualize the morphology of the polymer, and to determine the size and distribution of the metal nanoparticles stabilized in the polymer matrix.

2. Experimental

2.1. Materials

1,8-diaminonaphthalene was purchased from Alfa Aesar GmbH & Co. KG. Pd acetate obtained from *Next Chimica* was used to prepare a stock solution having a concentration of 10^{-3} mol dm⁻³ in toluene (Merck). All other chemicals were purchased from Aldrich and used as received.

2.2. Synthesis of palladium-polymer composite

In a typical experiment, 0.910 g of 1,8-diaminonaphthalene was dissolved in 15 ml of toluene under continuous stirring conditions. 10 ml of a previously prepared stock solution of Pd acetate in toluene was added drop by drop to the first solution. Precipitation occurred, the solution turning a deep brown colour. TEM specimens were prepared by pipetting 2 μ l of the colloid solution onto lacey carbon coated copper grids. Subsequently after viewing, the TEM grids were sputter coated with a few nm thick conducting layer of Au–Pd and viewed in the SEM. The rest of the solution was immediately filtered after the preparation of the TEM grids, the deposit being collected for IR and Raman analyses. An ICPMS study indicated the palladium loading in the catalyst to be 1.16 wt.%.

2.3. General procedure for the Heck coupling reactions catalyzed by poly (1,8-diaminonaphthalene) supported Pd nanoparticles

The catalyst (4 mg), aryl halide (1.0 mmol), alkenes (1.5 mmol), triethyl amine (1.5 mmol), and DMF (5 ml) were placed in a round bottom flask containing a small stirring bar. The reaction mixture was placed on an oil bath at 80 °C under stirring conditions. The reaction was monitored by TLC and after completion of the reaction, the mixture was extracted with ethyl acetate three times. Subsequently the ethyl acetate layer was washed with water (2×25 ml) and brine (25 ml). The combined extract was dried over MgSO₄. After the evaporation of the solvents under reduced pressure, the crude product was purified by flash chromatography over silica gel to afford the product.

2.4. Characterization techniques

Transmission electron microscopy studies of the composite were carried out at an accelerating voltage of 197 kV using a Gatan GIF Tridiem and an Oxford INCA energy dispersive X-ray analysis system (EDX) attached to a Philips CM200 TEM equipped with a LaB₆ source. Scanning electron microscopy studies were undertaken in a FEI Nova 600 FEG Nanolab at 5 kV. The X-ray photoelectron spectra (XPS) were collected in a UHV chamber attached to a Physical Electronics 560 ESCA/SAM instrument. 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 very low (0.73 mW), while the laser beam diameter at the sample was ~1 μ m. 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 infra-red spectra analyses. For this study, the sample



Fig. 1. The UV-visible spectrum of the resultant polymer material shows three characteristic absorption bands for π - π * transition, polaron/bipolaron transition and benzenoid to quinoid excitonic transition at 325, 485 and 800 nm respectively.

was deposited in the form of a thin film on a NaCl disk. For UV-vis spectra analysis, a small portion of the solid sample was dissolved in methanol and scanned within the range 300–1000 nm using a Varian, CARY, 1E, digital spectrophotometer.

3. Results and discussion

Polyaniline derivatives have attracted growing scientific attention due to their chemical properties being similar to polyaniline and the fact that they are more easily processed than the parent polymer [29]. A wide variety of methods have been applied to the preparation of polyaniline and substituted polyaniline-type compounds by the oxidative polymerization of their monomer [30]. According to the most widely accepted mechanism, the first step during the polymerization of the aniline or the substituted aniline involves the formation of a radical cation accompanied by the release of an electron. This step is the initiation process of the polymerization reaction. In the present work, during the addition of the palladium acetate, the pH of the solution dropped. Spectroscopic analysis confirmed that the aniline oxidation product only had a head-to-tail (-N-Ph-N-Ph-)-like arrangement rather than a head-to-head (-Ph-N=N-Ph-) type. The N-N characteristics arise from the head-to-head coupling only under neutral or basic pH conditions. On the other hand, aniline oxidation products obtained in an acid medium have a predominantly head-to-



Fig. 2. Raman spectrum of the composite material recorded within the range of 1700 and 1000 cm⁻¹ indicating the presence of both quinoid and benzenoid structures in the polymer.



Fig. 3. The IR spectrum of the composite material reveals the presence of the quinoid and the benzenoid rings in the polymer backbone. The intensity of the peak indicates that the presence of the quinoid ring structure is predominant in the polymer chain.

tail arrangement [30]. The mechanism of formation of the palladium nanoparticles and the poly-DAN is as follows. During the addition of palladium acetate to DAN, the palladium salt acts as an oxidizing agent that can oxidize DAN to form poly-DAN. During polymerization, each step involves the release of an electron [30] and that free electron is then used to reduce the Pd²⁺ ion to form palladium atoms. The coalescence of these palladium atoms ultimately forms Pd nanoparticles, which are encapsulated by the polymer. The following optical and microscopic analysis confirmed the above mechanism of the formation of metal–polymer nanocomposite material.

The electronic absorption spectrum (Fig. 1) of the resultant material shows three characteristic absorption bands at 325, 485 and 800 nm. The absorption peak at 325 nm is due to the π - π * transition of the benzenoid rings. The peak at 485 nm results from the polaron/bipolaron transition. The absorption peak at 800 nm corresponds to the transition from a localized benzenoid highest occupied molecular orbital to a quinonoid lowest unoccupied molecular orbital, that is, a benzenoid to quinoid excitonic transition. In polyaniline, the position of excitonic peak shifts from 630 to 560 nm and is sensitive to the nature of the counter ions, the solvent and to the chemical

structure of the polymer [31–33]. The excitonic peak may shift towards a higher wavelength region when polyaniline is doped with protonic acid [34]. In the present scenario, the absorption peak due to a benzenoid to quinoid excitonic transition shifts towards the higher wavelength region due to the longer conjugation length in the diaminonaphthalene group in comparison with that in aniline.

Fig. 2 shows a typical Raman spectrum recorded from the polymer composite material. In the 1700 and 1000 cm^{-1} range the bands derived from Raman spectra analysis involve the poly-DAN oxidation state. The spectrum of polymer reveals C–C stretching deformation bands of benzene ring at 1610, 1590, 1570 and 1542 cm^{-1} , which are characteristic of the semiguinone structure [35]. A shoulder-like appearance at 1505 cm⁻¹ corresponds to the N–H bending deformation band as a result of the interaction of the palladium particles with nitrogen. Intense overlapping features between 1300 and 1420 cm⁻¹ correspond to the C–N•⁺ stretching modes, the intensity of the peaks confirming the high concentration of these species present in the polymer. The broad and intense band at 1247 cm^{-1} can be assigned to C-N stretching modes. The position of the benzene C-H bending deformation band at 1165 cm⁻¹ is again characteristic of the reduced and semiguinone structures. Another broad band with peak position at 1450 cm^{-1} corresponds to the C=N stretching mode of the quinoid units while the band at 1221 cm⁻¹ corresponds to the C-N stretching mode of the single bonds. These latter two bands also indicate the presence of both quinoid and benzenoid structures in poly-DAN.

The IR spectrum, Fig. 3 reveals the presence of the different species, which are present in the polymer composite material. The peaks at 1600 and 1510 cm⁻¹ are respectively due to the stretching deformation of the quinoid and the benzenoid rings. The band at 1300 cm⁻¹ is assigned to C–N stretching in a secondary aromatic amine, whereas the peaks at 1145 and 1080 cm⁻¹ represent the aromatic C–H inplane bending modes. The out-of-plane deformation of C–H in the substituted benzene ring is located at 840 cm⁻¹. Both the Raman and IR spectra indicate that the polymer contains both benzenoid and quinoid rings in the chain.

TEM images at different magnifications (Fig. 4) show the nanostructure morphology of the resultant material. The average diameter of the polymer chain is less than 100 nm while the length of the chain is ~1 μ m. Fig. 4B shows the formation of a branching structure of the polymer that indicates that the polymerization process initiated from both of the amino groups of the monomer. In the TEM image (Fig. 5A) the uneven surface and uniformly distributed



Fig. 4. TEM images at different magnifications showing the nanostructure morphology of the polymer and that the average diameter of the macromolecule chain was less than 100 nm.



Fig. 5. (A) TEM image of the composite material revealing uniformly distributed dark spots within the polymer; (B) an EDX analysis confirming that the dark spots were palladium particles; (C) is a higher magnification TEM image showing that the palladium nanoparticles are stabilized on the polymer matrix, a few nanoparticles being highlighted as examples within the white circles.

dark spots within the polymer can be seen. Stereo images (not included here due to the need for a 3D viewer) have shown that all the palladium particles were homogeneously distributed within and throughout the polymer matrix. A typical EDX analysis (Fig. 5B) obtained from the electron beam being focused onto a dark spot in the polymer yielded palladium X-ray peaks while focusing the electron beam between the dark spots near the thin edge of the fiber yielded no palladium X-ray peaks confirming that these spots are palladium particles. Fig. 5C is a higher magnification TEM image which indicates that the palladium nanoparticles are stabilized in the polymer matrix with no agglomerations. A few of the more prominent nanoparticles are shown, for example, within the white circles. The average size of the nanoparticles was 2.5 nm. Selected area diffraction (SAD) showed the nanoparticles to have an amorphous structure. To gain further insight into the ionic state of the nanoparticles, XPS measurements were performed. A high-resolution Pd 3d X-ray photoelectron spectrum of the palladium nanoparticles is shown in Fig. 6. The spectrum was characterized by peaks with binding energies of 335.20 eV for $3d_{5/2}$ and 340.35 eV for $3d_{3/2}$, both these peaks being distinctive for metallic palladium [36]. XPS analyses revealed that



Fig. 6. Palladium 3d XPS spectrum of the palladium–polymer composite. The peaks at binding energies of 335.10 eV for $3d_{5/2}$ and 340.35 eV for $3d_{3/2}$ are indicative of metallic palladium.

the concentration of the palladium at the surface of the catalyst varied from 1.3 to 1.5%.

The catalytic activity of the palladium nanoparticles has been successfully combined with different polymers to form a hybrid material, which has been used successfully in hydrogenation reactions [2]. It is well established that palladium nanoparticles are efficient catalysts for various carbon–carbon coupling reactions [37]. One of the most important examples of carbon–carbon bond coupling type of reactions is the Mizoroki–Heck reaction [37,38], such as the arylation or vinylation of olefins by aryl or vinyl halides. The reaction has been applied to many areas, including natural products [39] and fine chemical syntheses [40].

Heck's original recommendation for the catalyst cocktail involved the combination of palladium acetate, a triaryl phosphine ligand and a tertiary amine as the scavenger base. It is commonly believed that one role of the phosphine ligand is the reduction of Pd(II) to a catalytically active Pd(0) species for which a stabilizing ligand is required to prevent the formation of palladium black [18]. The base Et_3N has also been implicated as a reducing agent for the generation of the Pd (0) species [41].

In the present report, the palladium–poly-(1,8-diaminonaphthalene) nanocomposite has been employed as a catalyst for the Heck reaction of substituted iodo- and bromobenzene with different types of alkenes in DMF. When iodobenzene was treated with methyl acrylate in the presence of a base, triethyl amine (TEA), at 80 °C for 8 h substituted alkene derivatives were obtained with very good yields. Phosphinefree Heck coupling reactions with the other aryl iodides for the generalization of the activity of the catalyst were also undertaken. The catalyst was found to be efficient giving C–C coupled products in the range very good to excellent yields (Table 1). Aryl bromides with different styrene derivatives and olefins were also found to be effective for the Heck coupling reaction when the reaction was carried out at mild conditions in DMF. When para-bromo toluene was treated with styrene at 80°C in the presence of triethyl amine (TEA) and DMF for 12 h, the coupled product was produced with good yields (Table 2). Different aryl halides with different alkenes formed the coupled products as expected. Aryl halides with an ortho- substituent (due to the steric hindrance) or an electron donating substituent were found to considerably lower the reaction rate resulting in lower yields of the coupled products than for the para- substituted arenes. The melting temperature of the polymer is 135 °C. For the present study, our reaction temperature was restricted to 80 °C and thus the melting

Table 1

Heck coupling reactions of aryl iodides with different olefins.

Pd-polymer composite $DMF \xrightarrow{R}$					
$Ar-1 + K \longrightarrow Ar \sim TEA, 80 °C, 8h$					
Entry	Aryl iodide	Alkene	Product	Yield (%)	TOF (h ⁻¹)
1		CO ₂ CH ₃	CO ₂ CH ₃	95	3298
2		– COOH	COOH	93	3229
3		\bigtriangledown	$\sim \sim$	89	3090
4	CH3O	CO ₂ CH ₃	сн ₃ о - СО ₂ СН ₃	87	3020
5		− CO ₂ CH ₃	NO ₂	81	2812
6		сн ₃ 0-		85	2951

Reagents and reaction conditions: aryl iodides (1.0 mmol), alkenes (1.5 mmol), triethyl amine (1.5 mmol), DMF (5 ml) and catalyst [Pd-poly-(1,8-diaminonaphthalene)] (4 mg), 80 °C, 8 h.

temperature did not affect the reaction. Before reaching the melting temperature the polymer would undergo a phase transition process, polymer softening at about 95 °C and physical and chemical cross linking at around 110 °C. As a result of cross linking the active site of the catalyst could reorient and thus this would be expected to affect the reaction. For the Heck cross-coupling reactions Pd(0) is the catalytic species and the possible mechanism is the interaction of aryl halide (R¹X) and Pd(0) to form the aryl-palladium halide complex [R1 $(Pd^{2+})X$], which then couples with aryl (R^2) alkenes in presence of a base to produce the $[R^1-(Pd^{2+})-R^2]$ intermediate and finally the biaryl product (R^1-R^2) is produced via the reductive elimination of Pd^{2+} to Pd(0).

Table 2

Heck coupling reactions of aryl bromides with different alkenes.



Reagents and reaction conditions: Aryl iodides (1.0 mmol), alkenes (1.5 mmol), triethyl amine (1.5 mmol), DMF (5 ml) and catalyst [Pd-poly-(1,8-diaminonaphthalene)] (4 mg), 80 °C, 8 h.

We also tested the coupling reaction between aryl chlorides with different alkenes, but no formation of a coupled product could be detected. The products were purified by chromatography and identified from their spectroscopic data. These compounds were found to be identical with those reported by others. The TOF value indicates that the polymer nanocomposite is a potential candidate for this kind of reaction, TOF being defined as the mol product/(mol catalyst. hour) and this was calculated from the isolated yield, the amount of palladium used and the reaction time. The recyclability of the catalyst was practically not feasible due to the minute quantity of the material used for the reaction and as a consequence of the nature of the support which was soluble in organic solvent and thus is not recoverable from the system. An ICPMS study indicated that the Pd loading in the coupled organic products was less than 0.4 wt.% while an XPS study of the same sample failed to reveal any signal for Pd which indicates an absence of Pd at the surface or near surface region.

4. Conclusions

The present paper reports a synthesis route for the preparation of a metal-polymer composite material that successfully served as an efficient catalyst for a Heck coupling reaction under phosphine-free conditions. The process of the formation of the C-C bond by our catalyst without the use of a phosphine ligand, is eco-friendly, easy to handle especially since the poly-(1,8-diaminonaphthalene) supported palladium catalyst is air-stable, all our reactions having been conducted in air. Such a phosphine-free production process thus has potential importance in industry as well as in small scale laboratories from both an environmental and economic point of view. All these merits indicate that the composite material has potential as a promising catalyst in Heck reactions. Furthermore, we also believe that this polymer based composite catalyst is a very promising candidate for developing other kinds of carbon-carbon coupling reactions.

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