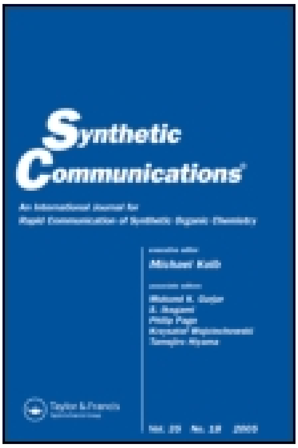

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METAL–POLYMER HYBRID MATERIAL AS A CATALYST FOR THE HECK COUPLING REACTION UNDER PHOSPHINE-FREE CONDITIONS

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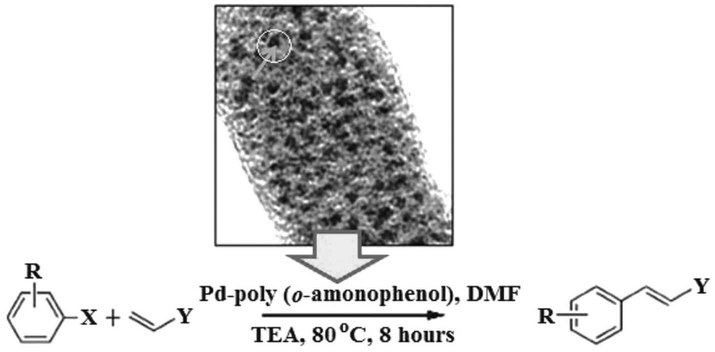
[4]*Advanced Materials Division, Mintek, Randburg, South Africa*

GRAPHICAL ABSTRACT



Abstract *A method is described for making a poly-aminophenol-based hybrid material by in situ polymerization of aminophenol using palladium acetate as the oxidant. The oxidative polymerization of aminophenol leads to the formation of poly-aminophenol, while the reduction of palladium acetate results in the formation of palladium nanoparticles. The palladium nanoparticles were found to be highly dispersed and stabilized throughout the polymer matrix. The hybrid nanocomposite material showed excellent catalytic efficiency with respect to a Heck coupling reaction at a relatively low temperature and under flexible conditions.*

Keywords Carbon–carbon coupling reaction; IPCF; metal–polymer composite; palladium nanoparticle; TEM

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INTRODUCTION

With the advancement of nanotechnology research, almost all the fields in science and engineering have achieved great momentum in both research and development. There has been great enthusiasm by scientists in the area of nanotechnology with regard to finding new materials with improved behavior and superior performance. Nanoparticles are of considerable interest in catalysis, and this subject has undergone tremendous growth during the past few years.[1–5] Palladium nanoparticles have drawn considerable attention because of their catalytic properties. The use of palladium nanoparticles in catalysis is not only industrially important but also scientifically interesting, as a result of the sensitive relationship between catalytic activity and the nanoparticle size and shape as well as the nature of the surrounding media.

Palladium-catalyzed carbon–carbon bond-formation chemistry occupies a special place in fundamental academic research as well as in industrial research and development. The C–C bond-forming reactions are very promising for the synthesis of fine chemicals, agrochemicals, and many complex pharmaceutical intermediates. This chemistry has been stimulated by the discovery of a new generation of catalysts, for example, palladacycles and palladium–carbene complexes.[6,7] Nevertheless, several factors, such as the use of toxic, easily oxidable phosphines and volatile organic solvents, have hampered broad industrial application. In addition, a homogeneous palladium catalyst is usually precipitated from a solution and thus recycling or recovery of the expensive catalyst can be difficult. To overcome this drawback, polymer-supported palladium,[8] palladium on carbon,[9] and palladium on different metal oxides[10] have been utilized by several groups for the carbon–carbon bond-formation reaction. Metal–polymer nanocomposite materials have the unique combination of good stability, easy processing ability, and light weight. We have shown previously that such a composite material can be used successfully as a catalyst for a gas-phase hydrogenation reaction.[11]

In the present study, we have synthesized a metal–polymer composite material in which the palladium metal nanoparticles have been immobilized in a poly-aminophenol matrix. We have paid particular attention to both the polymer and the metal nanoparticles, which have been characterized by optical and microscopic techniques. Optical characterization techniques have been used to determine the chemical structure and oxidation states of the polymer. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques were used to explore both the morphology of the composite material and the size of the nanoparticles while x-ray photoelectron spectroscopy (XPS) was utilized to determine the ionic state of the palladium. The catalytic activity of the polymer-based composite material was investigated for a Heck coupling reaction with different aryl halides and substituted alkenes under phosphene-free conditions.

RESULTS AND DISCUSSION

Optical Characterization

We first examined the spectroscopic behavior of the synthesized material by infrared (IR) analysis (Fig. 1). In the IR spectra (Fig. 1), the bands at 1590 and 1496 cm^{-1} can be assigned to the C=C stretching vibration of the quinoid and

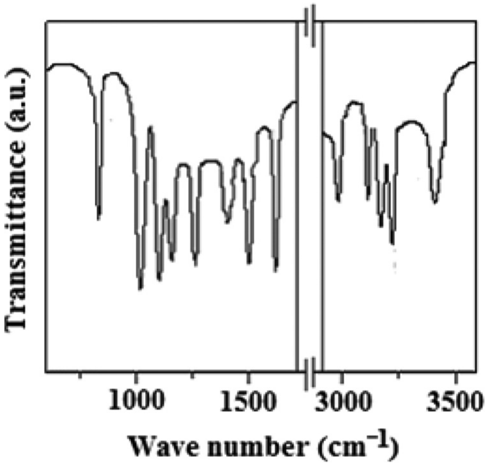


Figure 1. IR spectrum of the polymeric compound. The bands at 1572 and 1499 cm^{-1} indicate that the polymer is composed of quinoid and benzenoid units.

benzenoid rings respectively. The peak at 1390 cm^{-1} can be attributed to the –C–OH deformation vibration. The presence of a C-N stretching vibration can be confirmed through the presence of the band at 1250 cm^{-1}. The peaks at 1150, 1100, and 1015 cm^{-1} correspond to the aromatic C-H in-plane bending vibration. The band at ~1150 cm^{-1} has been explained as a vibrational band of nitrogen quinine.[12] A high-intensity band at 830 cm^{-1} is due to an aromatic out-of-plane C-H deformation vibration and is related to the 1,2,4-trisubstituted benzene ring. The bands at the higher wavenumber region correspond to the N–H stretching (3500–3200 cm^{-1}) and the aromatic C–H stretching vibration (3000–2850 cm^{-1}).

The Raman spectrum (Fig. 2B) reveals the C–C deformation bands of benzenoid ring at 1612 and 1589 cm^{-1}, which are characteristic of the semiquinone rings.[13,14] The band at 1521 cm^{-1} corresponds to the N–H bending deformation structure. An overlapping feature of bands observed between 1300 and 1400 cm^{-1}, with peak positions at 1316 and 1347 cm^{-1} as well as a shoulder at 1367 cm^{-1},

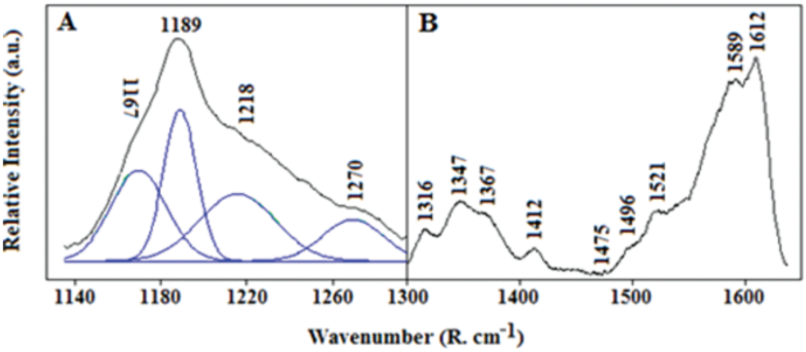


Figure 2. Raman spectrum of the resultant material revealing the presence of both quinoid and benzenoid units in the polymer backbone. (Figure is provided in color online.)

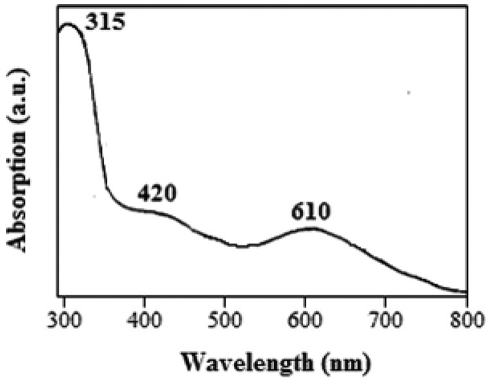


Figure 3. A typical UV-vis spectrum of the composite material, which shows three characteristic absorption bands at 315, 420, and 610 nm. The absorption peak at 315 nm is due to the π-π* transition of the benzenoid rings. The high intensity peak at 420 nm results from the polaron/bipolaron transition. A broad band with an absorption maximum at ~610 nm corresponds to the benzenoid to quinoid excitonic transition.

correspond to C–N stretching modes. Using the Gaussian fit from the 1140 to 1300 cm^{-1} region (Fig. 2A), four peaks at 1167, 1182, 1218, and 1270 cm^{-1} are clearly visible. The band at 1270 cm^{-1} can be assigned to the C–N stretching mode of the polaronic units. The band at 1218 cm^{-1} corresponds to the C–N stretching mode of a single bond. The positions of the C–H benzene deformation modes fall at 1167 cm^{-1} and 1189 cm^{-1}, indicating the presence of the quinoid rings.

Both the IR and the Raman analyses suggest the formation of poly-(*o*-aminophenol) with both benzenoid and quinoid segments in the polymer backbone.

The electronic absorption spectrum (Fig. 3) of the resultant material shows three characteristic absorption bands at 315, 420, and 610 nm. The absorption peak at 315 nm is due to the π-π* transition of the benzenoid rings, while the high intensity peak at 420 nm results from the polaron/bipolaron transition. A broad band with an absorption maximum at ~610 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.[15]

Mechanism of Formation Pd–Poly-(*o*-Aminophenol) Composite

The formation of the *o*-aminophenol polymer suggests the operation of the following mechanism. The presence of an electron-donating group (-OH) in aminophenol makes the amino group electron rich and forms an electrostatic bond with Pd^{2+} cations, and the aminophenol, under acidic condition undergoes polymerization, an oxidation process. Each step of the polymerization is associated with the release of one electron, which is then used in the reduction of palladium ions to form palladium atoms. These atoms subsequently coalesce and form clusters, which are stabilized within the growing polymer.

Microscopic Characterization

The TEM image in Fig. 4 illustrates the formation of polymer. The chain length of the polymer was found to be about 1 μm while the diameter was between

100 and 150 nm. TEM images (Figs. 5A and 5B) show the surface morphology and internal structure of the polymer. From such images, it is clear that the surface is not smooth. Both on the rough surfaces and in the interior of the polymer as shown by these and stereo images, there are seen to be highly distributed dark regions within and throughout the polymer; these regions have a diameter of about 2–3 nm. A typical energy dispersive X-ray analysis (EDX) (Fig. 5C) obtained from the electron beam being focused onto a dark spot in the polymer confirms that these spots are palladium particles. Focusing the beam between the dark spots near the edge of the nanocomposite yielded no palladium x-ray peaks. Thus, we can envisage that the polymer acts as a cage, and the palladium nanoparticles are encapsulated and highly dispersed inside that cage.

X-Ray Photoelectron Spectroscopy (XPS) Analysis

XPS analysis was undertaken to determine the chemical state of the palladium in the composite material. The Pd 3*d* core lines of the XPS spectrums are seen in Fig. 6, which reveals the presence of Pd $3d_{5/2}$ and $3d_{3/2}$ peaks at binding energies of 335.5 and 341.0 eV respectively. These binding energy values are in accordance with those reported for metallic palladium.[16]

Catalytic Application of the Synthesized Pd–Polymer Nanocomposite

The palladium-based polymer composite material was used as a catalyst for the Heck coupling reaction of an unsaturated halide with an alkene in the presence of a strong base to form a substituted alkene (Scheme 1).

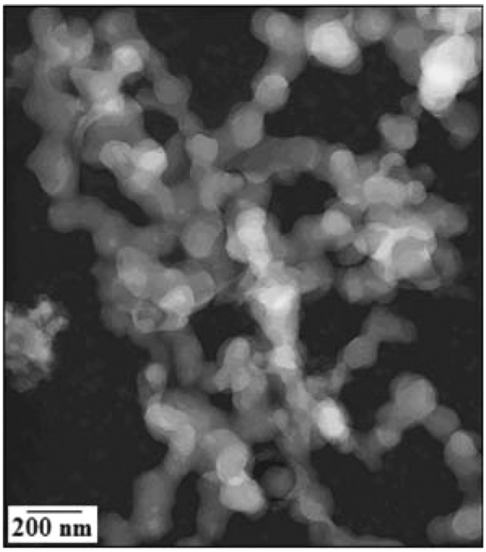


Figure 4. SEM image of the composite material synthesized during the reaction between Pd-acetate and *ortho*-aminophenol.

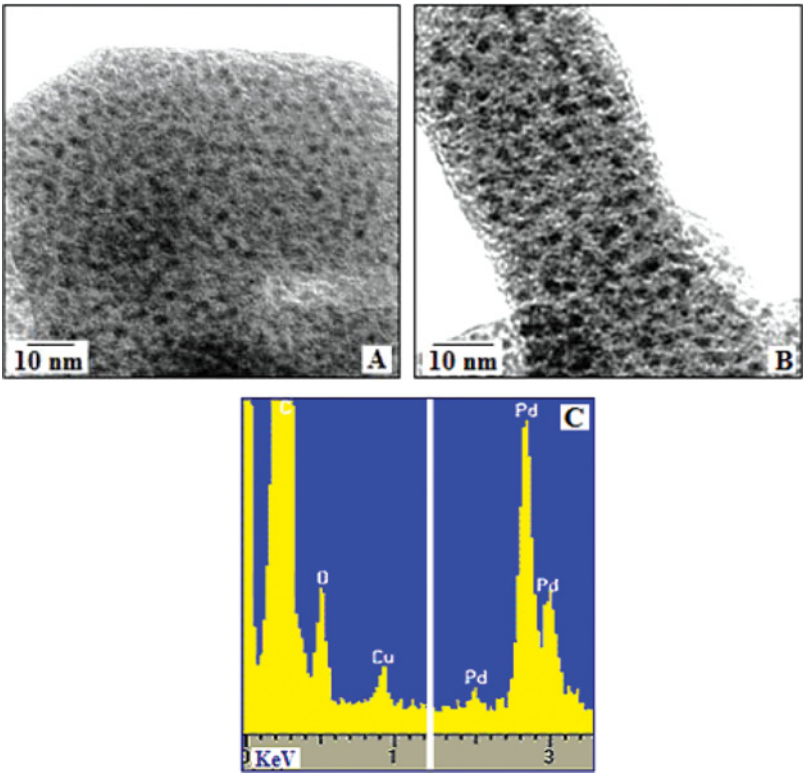


Figure 5. TEM micrograph of the palladium-(poly-aminophenol) composite. (A) and (B) show the surface morphology and internal microstructure of the composite. The ~2 nm sized dark spots are the palladium nanoparticles, which showed a high dispersion throughout the polymer. An EDX spectrum (C) derived from placing the focused electron beam onto a single dark spot in Figure 3B clearly shows the presence of palladium. The copper signal results from electron scattering onto the sample support grid. (Figure is provided in color online.)

Heck reaction of aryl iodide with olefin. We utilized the poly-(*o*-aminophenol)-palladium composite as a catalyst for the Heck reaction of iodobenzene and *n*-butyl acrylate in dimethylformamide (DMF) as solvent for the test reaction. The reaction mixture was heated at 80 °C for about 8 h, and the reaction was monitored by thin-layer chromatography (TLC) from time to time. The reaction showed an excellent yield with the formation of the coupled product (Table 1, entry 1). The other aryl iodides were also coupled with different olefins, producing very good yields under the same reaction conditions (see Table 1).

Heck reaction of aryl bromide with olefin. Application of the same catalyst for the coupling between activated and deactivated aryl bromides with acrylic acid was also found to be effective, producing substituted olefins in very good yields (Table 2). Activated aryl bromides afforded the product in slightly greater conversions rather than deactivated ones, which displayed a lower reaction rate. A comparative study of different aryl halides (iodo, bromo, and chloro) with acrylic acid

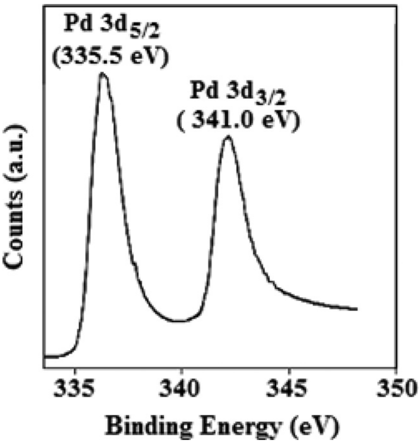
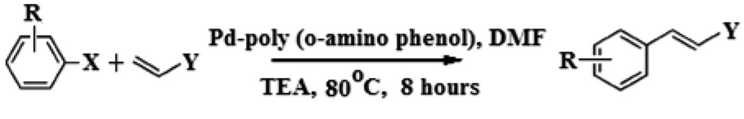


Figure 6. The Pd 3d core line XPS spectrum of palladium-(poly-aminophenol) composite. The binding energy values obtained from the peaks identify the presence of metallic palladium in the composite.

were carried out under the same reaction conditions, and the yields of the C-C coupling products were determined. Aryl iodide produced a better yield (95%) than the aryl bromide (82%), while aryl chloride afforded only a very low conversion (8%) to the coupled product.

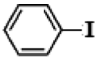
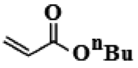
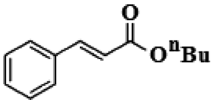
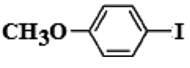
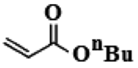
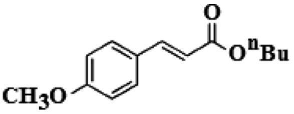
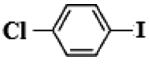
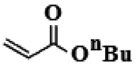
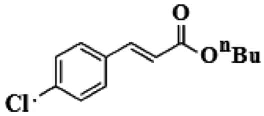
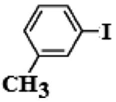
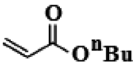
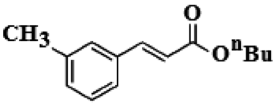
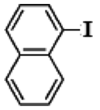
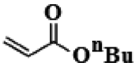
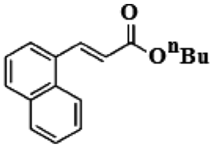
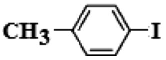
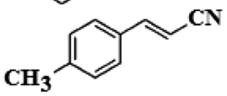
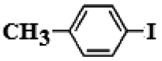
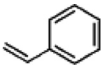
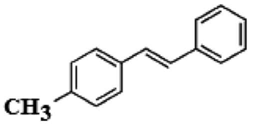
We also carried out a comparative kinetic study between two coupling reactions: 1 aryl iodide with *n*-butyl acrylate (Table 1, entry 1) and 2 3-substituted aryl iodide with *n*-butyl acrylate (Table 1, entry 4) in the presence of the same amount of catalyst (0.006 mol% Pd). The experimental progress was monitored by gas chromatographic (GC) analyses, and to minimize experimental errors, we repeated both the experimental procedures twice. From Fig. 7, it can be seen that for reaction 1, 96% of the conversion was achieved after 7 h, and after that no further improvement in conversion was detected. For reaction 2, 91% conversion was achieved after 8 h. For reaction 1, a small conversion (~9%) was measured after 1 h, whereas, for reaction 2, an almost comparable level of conversion was achieved only after 2 h.

Because of the increasing aryl-halogen bond strengths of the different halides, the reactivity of aryl halides decreases in the order I > Br > Cl. Accordingly, activation of aryl iodides and aryl bromides is feasible in the presence of almost any kind of palladium catalyst. In contrast, activation of aryl chlorides remains a major challenge, requiring a highly active catalyst system. A comparative study (Table 3) was undertaken to show the efficiency of the Pd–poly-(*o*-aminophenol) composite catalyst in comparison with some of the active Pd-based catalysts toward the Heck coupling of aryl bromides and terminal olefins from the literature.[17–21] Some of the



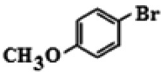
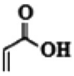
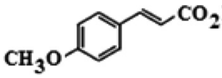
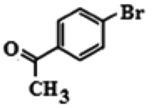
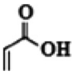
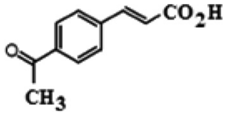
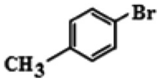
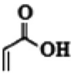
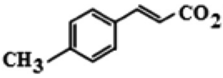
Scheme 1. Heck coupling reaction of an unsaturated halide with an alkene.

Table 1. Heck coupling reaction of aryl iodides with different olefins

Entry	Aryl iodide	Olefin	Product	Yield (%)
1				96
2				89
3				83
4				91
5				93
6				85
7				81

Notes. 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-(*o*-aminophenol)] (4 mg), for 8 h at 80 °C.

Table 2. Heck coupling reaction of aryl bromides with acrylic acid

Entry	Aryl halide	Olefin	Product	Yield (%)
1				78
2				81
3				75

Notes. Reagents and reaction conditions: Aryl bromides (1.0 mmol), alkenes (1.5 mmol), triethyl amine (1.5 mmol), DMF (5 ml), and catalyst [Pd–poly-(*o*-aminophenol)] (4 mg), for 8 h at 80 °C.

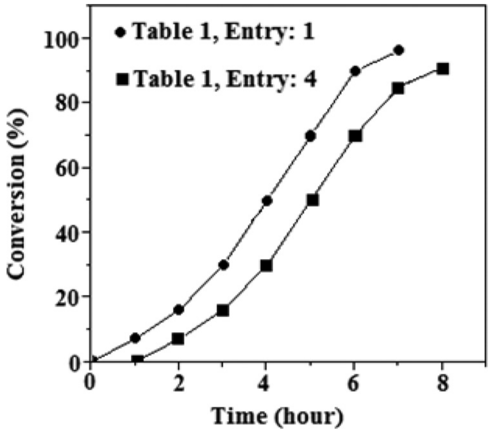
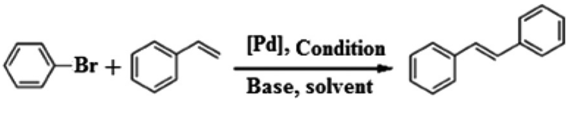


Figure 7. A comparative kinetic study between two coupling reactions: (I) aryl iodide with *n*-butyl acrylate (entry: 1) and (II) 3-substituted aryl iodide with *n*-butyl acrylate (entry: 4) in the presence of the same amount of catalyst (0.006 mol% Pd).

catalysts (entry 2 and 4) show higher turnover number (TON) when the reaction took place for longer time period and at higher temperature than the Pd-poly(*o*-aminophenol) composite catalyst, but our composite catalyst shows greater turnover frequency (TOF) value than others mentioned in Table 3.

The recyclability of the palladium–(poly-aminophenol) catalyst was also investigated (Table 1, entry 1). The recovery of the catalyst required a tedious filtration technique because of the minute quantity of the material used for the reaction. The results indicated that the used material was active without significant loss of catalytic performance, the yield loss being within 5% of the original after three cycles. At the end of the third cycle, a slight enlargement of the particles was observed, which was found to be due to interparticle agglomeration within the catalyst. All the products were purified by chromatography and identified from their

Table 3. Catalytic performance of the Pd–poly-(*o*-aminophenol) composite catalyst as compared to some other Pd-based catalysts reported for the Heck coupling reaction of aryl bromides and styrene



Entry	[Pd] (mol%)	Base	Solvent	Condition	Yield (%)	TON	TOF (h^{-1})	Reference
1	0.006	TEA	DMF	80 °C, 8 h	72	12,000	1500	This work
2	0.00247	K_3PO_4	DMA	140 °C, 44 h	95	38,500	875	17
3	1.5	NaOAc	NMP	150 °C, 30 h	70	47	—	18
4	0.002	NaOAc	DMA	140 °C, 28 h	56	28,000	1000	19
5	0.1	NaOAc	DMA	150 °C, 24 h	76	760	—	20
6	0.1	NaOAc	DMA	140 °C, 26 h	77	770	—	21

Notes. Dimethylformamide (DMF), dimethylacetamide (DMA), and N-methylpyrrolidone (NMP).

spectroscopic data. These recovered compounds were found to be identical with the reported ones. For the Heck cross-coupling reactions, Pd(0) is the catalytic species, and the possible mechanism is the interaction of aryl halide (R^1X) and Pd(0) to form the aryl–palladium halide complex [R1(Pd^{2+})X], which then couples with aryl (R^2) alkenes in the presence of a base to produce the [R^1–(Pd^{2+})–R^2] intermediate, which finally produces the biaryl product (R^1–R^2) via the reductive elimination of Pd^{2+} to Pd(0).

CONCLUSIONS

A metal–polymer composite material has been synthesized in which palladium nanoparticles were stabilized by the poly-(*o*-aminophenol) matrix. The composite material showed excellent activity towards the Heck coupling reaction under phosphine-free conditions. This is quite advantageous from both economic and environmental points of view. Other advantages such as good yield and reusability make this material potentially useful in synthetic organic chemistry as well as for industrial applications.

EXPERIMENTAL

Materials

Ortho-aminophenol was purchased from BDH (London). Toluene was obtained from Merck. Palladium acetate from Next Chimica was used to prepare a stock solution having a concentration of 10^{-3} mol dm^{-3} in toluene. All other chemicals were obtained from commercial sources (Aldrich or Alfa-Aesar) and were used as received without further purification.

Synthesis of the Metal–Polymer Nanocomposite

In a typical experiment, 1.005 g of *o*-aminophenol was dissolved in 30 mL of toluene under continuous stirring conditions. A previously prepared stock solution of palladium acetate in toluene (15 mL) was added drop by drop to the first solution. A slow precipitation occurred, during which time the solution turned brown in color. Samples were collected onto lacy carbon-coated copper grids for TEM analysis. After viewing, the TEM grids were sputter coated with a conducting layer a few nanometers thick of Au-Pd and viewed in the SEM. The rest of the solution was immediately filtered and dried under vacuum. A small portion of the dried sample was used for ultraviolet–visible (UV-vis), IR, and Raman analyses. The remaining portion of the sample was dried in an oven at 80 °C and used as the catalyst for the Heck coupling reaction.

General Procedure for the Heck Coupling Reactions

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 in an 80 °C oil bath and stirred for 8 h. The reaction was monitored by TLC, and after completion of the reaction, the mixture was extracted three times with ethyl acetate. Subsequently, the ethyl acetate layer was washed with water (2 × 25 mL) and brine (25 mL). The extract was dried over $MgSO_4$. After the evaporation of the solvents under reduced pressure, the residue was purified by flash chromatography over silica gel to obtain the product.

Characterization of Materials

The samples were characterized using a FEI FEG Nova 600 Nanolab SEM at 5 kV and a Philips CM200 TEM operating at 197 kV equipped with a Gatan Tridiem GIF. IR spectra were collected in the region 4000–700 cm^{-1} with a Perkin-Elmer 2000, while Raman spectra were acquired using the green (514.5 nm) line of an argon ion laser as the excitation source using a Jobin-Yvon T64000 Raman spectrometer. UV-vis spectral analyses were obtained within the range 300–700 nm using a Varian Cary 1E digital spectrophotometer. XPS were collected in a ultra-high vacuum (UHV) chamber attached to a Physical Electronics 560 ESCA/SAM instrument.

REFERENCES

1. Astruc, D. Palladium nanoparticles as efficient green homogeneous and heterogeneous carbon–carbon coupling precatalysts: A unifying view. *Inorg. Chem.* **2007**, *46*, 1884.
2. Zhong, L. S.; Hu, J. S.; Cui, Z. M.; Wan, L. J.; Song, W. G. In situ loading of noble metal nanoparticles on hydroxyl-group-rich titania precursor and their catalytic applications. *Chem. Mater.* **2007**, *19*, 4557.
3. Astruc, D.; Lu, F.; Aranzaes, J. R. Nanoparticles as recyclable catalysts: The frontier between homogeneous and heterogeneous catalysis. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852.
4. Moreno-Manas, E.; Pleixats, R. Formation of carbon–carbon bonds under catalysis by transition-metal manoparticles. *Acc. Chem. Res.* **2003**, *36*, 638.
5. Li, Y.; Boone, E.; El-Sayed, M. A. Size effects of PVP–Pd nanoparticles on the catalytic Suzuki reactions in aqueous solution. *Langmuir* **2002**, *18*, 4921.
6. Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C. P.; Priermeier, T.; Beller, M.; Fisher, H. Palladacycles as structurally defined catalysts for the Heck olefination of chloro- and bromoarenes. *Angew. Chem., Int. Ed.* **1995**, *34*, 1844.
7. Selvakumar, K.; Zapf, A.; Beller, M. New palladium carbene catalysts for the Heck reaction of aryl chlorides in ionic liquids. *Org. Lett.* **2002**, *4*, 3031.
8. Andersson, C. M.; Hallberg, A. Synthesis of β-arylvinyl ethers by palladium-catalyzed reaction of aroyl chlorides with vinyl ethers. *J. Org. Chem.* **1988**, *53*, 235.
9. Köhler, K.; Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, J. Highly active palladium-activated carbon catalysts for Heck reactions: Correlation of activity, catalyst properties, and Pd leaching. *Chem. Eur. J.* **2002**, *8*, 622.
10. Yang, H.; Zhang, G.; Hong, X.; Zhu, Y. Dicyano-functionalized MCM-41 anchored-palladium complexes as recoverable catalysts for Heck reaction. *J. Mol. Catal. A: Chem.* **2004**, *210*, 143.
11. Scalzullo, S.; Mondal, K.; Witcomb, M.; Deshmukh, A.; Scurrell, M.; Mallick, K. Polymer-encapsulated metal nanoparticles: Optical, structural, micro-analytical and hydrogenation studies of a composite material. *Nanotechnology* **2008**, *19*, 075708.
12. Palaniappan, S.; Nivasu, V. Emulsion polymerization pathway for preparation of organically soluble polyaniline sulfate. *New J. Chem.* **2002**, *26*, 1490.

13. Louarn, G.; Łapkowski, M.; Quillard, S.; Proń, A.; Buisson, J. P.; Lefrant, S. Vibrational properties of polyaniline-isotope effects. *J. Phys. Chem.* **1996**, *100*, 6998.
14. Łapkowski, M.; Berrada, K.; Quillard, S.; Louarn, G.; Lefrant, S.; Proń, A. Electrochemical oxidation of polyaniline in nonaqueous electrolytes: *In situ* Raman spectroscopic studies. *Macromolecules* **1995**, *28*, 1233.
15. Mallick, K.; Witcomb, M.; Erasmus, R.; Strydom, A. Electrical and optical properties of polyaniline with a web-like morphology. *J. Appl. Poly. Sci.* **2010**, *116*, 1587.
16. Bera, D.; Kuiry, S. C.; McCutchen, M.; Kruize, A.; Heinrich, H.; Meyyappan, M.; Seal, S. In-situ synthesis of palladium nanoparticles-filled carbon nanotubes using arc-discharge in solution. *Chem. Phys. Lett.* **2004**, *386*, 364.
17. Yao, Q.; Kinney, E. P.; Yang, Z. Ligand-free Heck reaction: $Pd(OAc)_2$ as an active catalyst revisited. *J. Org. Chem.* **2003**, *68*, 7528–7531.
18. Reetz, M. T.; Westermann, E.; Lohmer, R.; Lohmer, G. A highly active phosphine-free catalyst system for Heck reactions of aryl bromides. *Tetrahedron Lett.* **1998**, *39*, 8449–8452.
19. Gruber, A. S.; Zim, D. Z.; Ebeling, G.; Monteriro, A. L.; Dupont, J. Sulfur-containing palladacycles as catalyst precursors for the Heck reaction. *Org. Lett.* **2000**, *2*, 1287–1290.
20. Gruber, A. S.; Pozebon, D.; Monteriro, A. L.; Dupont, J. On the use of phosphine-free $PdCl_2(SEt_2)_2$ complex as catalyst precursor for the Heck reaction. *Tetrahedron Lett.* **2001**, *42*, 7345–7348.
21. Herrmann, W. A.; Brossmer, C.; Reisinger, C. P.; Priermeier, T. H.; Öfele, K.; Beller, M. Palladacycles: Efficient new catalysts for the Heck vinylation of aryl halides. *Chem. Eur. J.* **1997**, *3*, 1357–1364.