Metal-Polymer Hybrid Material: A Unique Coordination for Carbon-Carbon Coupling Reactions

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ABSTRACT

A method for making poly-aminophenol based hybrid material by in-situ polymerization of aminophenol using palladium acetate as the oxidant is described. 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. This hybrid nanocomposite material showed excellent catalytic efficiency with respect to Heck, Suzuki-Miyaura and Sonogoshira coupling reactions.

Keywords: carbon-carbon coupling reaction, palladium nanoparticle, TEM, EELS, metal-polymer composite

1 INTRODUCTION

With the advancement of nanotechnology, many fields in science and engineering have achieved great stimulus in both research and development. Since materials scientists are always looking for new materials with improved behavior and superior performance, nanomaterials have yielded a new thrust. This is true for catalysis, an area in which the application of nanoparticles has undergone tremendous growth during the past few years [1-5].

Palladium nanoparticles have drawn considerable attention due to their catalytic properties. The use of palladium nanoparticles in catalysis is not only industrially important, but also scientifically interesting due to the sensitive relationship between the catalytic activity, nanoparticle size and shape as well as the nature of the surrounding media. The 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 such as 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 a broad industrial application. In addition, a homogeneous palladium catalyst usually precipitates from the solution while recycling or the recovery of the expensive catalyst is difficult. To overcome the latter drawback, polymer-supported palladium complexes [8], palladium on carbon [9] and palladium on different metal oxides [10] have been used by several groups for the carbon-carbon bond formation reaction.

Metal-polymer nanocomposite materials have the unique combination of metallic nanoparticles and functional polymers which yield a benefit from both components such as good stability, exceptional optical property and high conductivity from the metal as well as from the polymer its light weight and ease of processing. In a previous report, we have shown that such a composite material can be used 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 the 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. Raman, IR, and UV-vis spectrophotometry were utilized to determine the chemical structure and oxidation states of the polymer. TEM was employed for the investigation of both the morphology of the composite material and the size of the nanoparticles while XPS was used to determine the chemical state of the palladium. The catalytic activity of the palladium based composite material was investigated for Heck, Suzuki and Sonogoshira coupling reactions.

2 EXPERIMENTAL

2.1 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 \(10^{-2}\) mol dm\(^{-3}\) in toluene. All the other chemicals are obtained from commercial sources (Aldrich...
2.2 Characterization Techniques

The sample was characterized by scanning electron microscopy in a JEOL JSM-840 and by transmission electron microscopy using a Philips CM200 equipped with a LaB₆ source. Infrared spectroscopy was undertaken using a Perkin-Elmer 2000 in the region 4000–700 cm⁻¹, while Raman spectra were acquired employing a Jobin-Yvon T64000 Raman spectrometer using the green (514.5 nm) line of an argon ion laser as the excitation source. The X-ray photoelectron spectra (XPS) were collected in a UHV chamber attached to a Physical Electronics 560 ESCA/SAM instrument.

2.3 Synthesis of the Metal-Polymer Nanocomposite

In a typical experiment, 1.07 g of o-aminophenol was dissolved in 30 mL of toluene under continuous stirring conditions. 17 mL of a previously prepared stock solution of palladium acetate in toluene was added drop by drop to the first solution. A slow precipitation occurred and the solution turned brown in colour. Samples were collected onto lacey carbon coated copper grids for TEM analysis. Subsequently after viewing, the TEM grids were sputter coated with a conducting layer a few nm 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 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 reactions.

3 RESULTS AND DISCUSSION

The spectroscopic behavior of the synthesized material was examined by IR analysis within the spectral region between 4000 to 700 cm⁻¹ (Fig. 1).

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 –OH substituted polyaniline compound. 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 benzenoid rings. The peak at 1390 cm⁻¹ can be attributed to the C-OH deformation vibration that indicates the formation of a –OH substituted polyaniline type compound. The presence of a C-N stretching vibration was confirmed from 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. For polyaniline or substituted polyaniline type compounds, the band at ~1150 cm⁻¹ has been explained as a vibrational band of nitrogen quinone [12]. The 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 in 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 electronic absorption spectra (Fig. 2) of the resultant material shows three characteristic absorption bands at 315 nm, 420 nm and 610 nm.

Figure 2: A typical UV-vis spectrum of the composite material showing 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 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 [13]. The position of excitonic peak shifts from 630 to 560 nm and it is sensitive to the nature of the counter ions [14], solvent [15] and the chemical structure of the polymer [16]. The excitonic peak shifts towards the higher wavelength region when doped with protonic acid [17]. The optical properties of the resultant material confirm the formation of a polyaniline-like compound.

The TEM images in Figure 3 illustrate the structure of the polymer composite. Figures 3A and B reveal images both of the surface morphology and internal microstructure of the polymer.
Figure 3: TEM micrograph of the palladium-(polyaminophenol) 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 show a high dispersion throughout the polymer.

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 highly distributed dark regions of diameter about 2-3 nm in size. A typical EDX analysis (Fig. 4) 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 yielded no palladium x-ray peaks. Stereo images have shown that the palladium particles are homogeneously distributed within and throughout the polymer. 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 was undertaken in order to determine the chemical state of the palladium in the composite material. The Pd 3d region of the XPS spectrum is illustrated in Figure 5 and reveals the presence of Pd 3d5/2 and 3d3/2 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 [18].

Figure 4: An EDX spectrum 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 5: The Pd 3d region of XPS spectrum of palladium-(poly-aminophenol) composite.

The palladium-poly (aminophenol) composite has been employed as a catalyst for the Heck reaction of iodobenzene and styrene in DMF as the solvent for this test reaction. The reaction showed an excellent yield with the formation of the coupled product, (E)-1, 2-diphenylethene (Table: 1a).

The above success with the Heck reaction utilizing this metal-polymer composite catalyst prompted us to explore its applicability for similar kinds of C-C coupling reactions such as Suzuki and Sonogashira reactions. When phenylboronic acid was treated with different aromatic halides using the same catalyst in the presence of K2CO3 in toluene at 85 °C, biaryls products were formed with excellent yields (Table: 1b). The Sonogashira reaction is a coupling between terminal alkynes with aryl or vinyl halides in the presence of a palladium catalyst, a copper (I) co-catalyst, and an amine base. In our case, we used the same polymer supported palladium nanoparticle based catalyst for the Sonogashira type of coupling reaction. We have successfully carried out Cu free Sonogashira coupling reactions between different aryl halides with terminal alkynes in DMF with triethyl amine as a base at about 90 °C for 4-6h and obtained alkyne derivatives with excellent yields (Table: 1c).

The recyclability of the palladium-(poly-aminophenol) catalyst was also investigated (Table: 1a, entry 1). The recovery of the catalyst was a tedious filtration technique due to 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 (yield loss within 2 % after three cycles). At the end of the third cycle, TEM images (Fig. 6) of the used catalyst indicated some particle agglomeration within the catalyst.
Figure 6: TEM image of the used catalyst.

Table 1:

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<tr>
<th>Entry</th>
<th>Aryl halide</th>
<th>Alkenes</th>
<th>Product</th>
<th>Yield(%)</th>
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<tr>
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<td>HCO-C6H4-Br</td>
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b Suzuki coupling reaction

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<tr>
<td>2</td>
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<td>C</td>
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c Sonogashira coupling reaction

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<td>HCO-C6H4</td>
<td>Ph</td>
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</table>

a Aryl halide (1.0 mmol), alkenes (1.5 mmol), triethyl amine (1.5 mmol), DMF (5 ml) and catalyst (palladium-poly-aminophenol, 4mg) were placed in a round bottom flask and refluxed at 85 °C for 5h.

b Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K2CO3 (1.5 mmol), toluene (5 ml) and catalyst (4mg) were placed in a round bottom flask and refluxed at 85 °C for 3h.

c Aryl halide (1.0 mmol), different acetylenes (1.5 mmol), triethyl amine (1.5 mmol), toluene (5 ml) and catalyst (4mg) were placed in a round bottom flask and refluxed at 90 °C for 6h.

4 CONCLUSIONS

We have successfully synthesized a metal-polymer composite material in which palladium nanoparticles were stabilized by a poly-aminophenol matrix. The composite showed an excellent and versatile activity with regards to various carbon-carbon bond formation reactions. For a Suzuki reaction, the catalyst revealed good activity under phosphine-free conditions which is an area of considerable interest resulting from economic and environmental reasons. The catalyst showed a similar activity for the Sonogashira reaction in absence of copper (I), the latter acting as a co-catalyst in the original protocol. Other advantages such as high yields, reusability and a wide range of application makes this material a promising candidate in the area of synthetic organic chemistry.

REFERENCES