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A green method for the synthesis of gelatin/pectin stabilized palladium nano-particles as efficient heterogeneous catalyst for solvent-free Mizoroki–Heck reaction

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ABSTRACT

A green method for the synthesis of gelatin/pectin stabilized palladium nano-particles has been described. These particles were prepared under green conditions without addition of any external reducing agent and ligand. All properties of the supported palladium particles on gelatin/pectin mixture were showed by UV–vis spectra and also by EDX, XRD, TEM and FESEM images. The synthesized palladium nanoparticles were studied in Mizoroki–Heck reaction between different aryl halides and *n*-butyl acrylate. The reaction was performed under solvent-free conditions and no complicated work up process was needed for the isolation of the nano-particles. Also the products were obtained in highly short reaction times with excellent yields.

1. Introduction

Lately, the application and development of green catalysts have possessed a large number of studies in academic and industrial groups to degrade or eliminate the use of dangerous substances [1,2]. Heterogenization of the catalysts to solid supports can provide opportunities for recycling of the catalysts from reaction environments. Heterogenization of the catalysts to solid supports by their immobilization on organic [3] or inorganic [4] polymers [5–7] is of great interest, because of having many benefits such as easy isolation, low extra production and the reduced cost.

In recent years, immobilization of the palladium nano-particles on solid supports to prepare active and stable catalytic systems is an interesting topic. Different supports have been used to stabilize the nano-particles [8–15]. Along this line, Pd/gellan [16], Pd/arabinogalactan [17], Pd/agarose [18], Pd/starch [19] and Pd/chitosan [20] have been prepared using polysaccharides as the bed. In order to develop the use of carbohydrate-based materials as the support for palladium nano-particles, we decided to introduce gelatin/pectin mixture as a suitable and naturally degradable support for stabilization of palladium nano-particles.

Gelatin is a colorless, fragile, translucent, nearly tasteless solid. It is a water soluble protein and is an irreversibly hydrolyzed form of collagen [21]. Gelatin contains free carboxyl groups on its backbone and has the potential for chelating and reducing transition metals [22].

Pectin is a family of complex polysaccharides that is found extensively in nature [23]. Unique properties of pectin, such as biodegradability, flexibility, non-toxicity, low price and carrying freely available hydroxyl groups make it suitable and ideal candidate for many practices in different areas of science.

Therefore, using gelatin/pectin mixture as a support for palladium species has two advantages; first it has the ability to reduces Pd(II) to Pd(0) via its available free carboxyl groups by liberation of CO_2 gas and the second is to act as a highly functionalized support, which stabilizes the reduced form of the palladium particles by ligation.

Palladium-catalyzed Mizoroki–Heck coupling reaction is one of the most powerful synthetic methods for the formation of carbon–carbon bonds, which allows the arylation, alkylation or vinylation of various alkenes through their reaction with aryl, vinyl, benzyl or allyl halides in the presence of palladium and a suitable base [7,24]. Total synthesis of complex organic molecules has benefited extraordinary from the Mizoroki–Heck reaction. The

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Mizoroki–Heck coupling products find good applications as intermediates in the preparation of materials, natural products, and bioactive compounds [25]. Herein, we report that palladium nanoparticles stabilized by gelatin/pectin mixture can be successfully used in the Mizoroki–Heck cross-coupling reaction between the activated and non-activated aryl halides and *n*-butyl acrylate under solvent-free conditions.

2. Experimental

2.1. General

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies and were used as purchased, without further purification. ^{1}H and ^{13}C NMR spectra were measured with Bruker Avance III-400 (at 400.2 and 100.6 MHz) spectrometer in pure CDCl3 solvent with tetramethylsilane (TMS) as the internal standard. Mass spectra were recorded on an Agilent Technologies (HP) 5973 mass spectrometer operating at an ionization potential of 70 eV. X-ray diffraction spectrum of the catalyst was obtained by XRD (Ital structures, APD 2000). The transmission electron micrographs (TEM) was obtained using TEM apparatus (100 kV Philips, EM208) for characterization of the nanoparticles. Field emission scanning electron micrographs (FE-SEM) were obtained by FE-SEM (Hitachi, Japan, S4160 at 20 kV). UV–vis spectra were recorded on Agilent, 8453, UV–vis spectrometer. The amount of palladium nanoparticles supported on gelatin/pectin was measured by SEM–EDX analyzer (Tescan Vega II, with a Rontec detector) and also by ICP analyzer (Varian, Vista-pro).

2.2. Synthesis of palladium nano-particles supported on gelatin/pectin mixture

Pectin (0.5 g) and gelatin (0.5 g) were dissolved in water (100 mL) at room temperature. To this solution was added a solution of $PdCl_2$ (100 mL, 1 mM) and diluted with water (100 mL). The reaction mixture was refluxed at 100 °C for 5 h to ensure the complete conversion of Pd(II) to Pd(0). The mixture was cooled down to room temperature and the solvent was evaporated. The obtained dark gray composite was dried by the flow of air over night and then under vacuum for 24 h.

2.3. General method for the Mizoroki–Heck reaction using the nano-catalyst

To a flask, a mixture of gelatin/pectin supported Pd-nanoparticles (0.05 g of the composite, contains 0.002 mmol of palladium), aryl halide (1 mmol), *n*-butyl acrylate (1.5 mmol, 0.21 mL) and *n*-Pr_3N (1.5 mmol, 0.29 mL) were added under solvent-free conditions. The mixture was stirred at 140 °C in the air. After completion of the reaction (monitored by TLC), ethylacetate (10 mL) was added to the flask. The catalyst was separated by simple filtration. Water (3 × 15 mL) was added to the ethylacetate phase and decanted. The organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography.

2.4. Spectral data for products

(Product 1a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 0.99 (*t*, 3H, *J* = 7.2 Hz), 1.47 (sex, 2H, *J* = 7.6 Hz), 1.72 (quint, 2H, *J* = 6.8 Hz), 4.24 (*t*, 2H, *J* = 6.4 Hz), 6.51 (*d*, 1H, *J* = 16 Hz), 7.39 (*t*, 3H, *J* = 4 Hz), 7.54 (*m*, 2H), 7.71 (*d*, 1H, *J* = 16 Hz); ^{13}C NMR (CDCl3, 100 MHz): δ (ppm): 13.78, 19.23, 30.81, 64.42, 118.31, 128.06, 128.88, 130.22, 134.50, 144.55, 167.08; MS (m/e): 204 [M$^+$]; FT-IR ν(cm^{-1}): 1715 (C=O).

(Product 2a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 1.00 (*t*, 3H, *J* = 7.2 Hz), 1.48 (sex, 2H, *J* = 7.2 Hz), 1.73 (quint, 2H, *J* = 6.8 Hz), 2.46 (*s*, 3H), 4.25 (*t*, 2H, *J* = 6.8 Hz), 6.40 (*d*, 1H, *J* = 16 Hz), 7.23 (*t*, 2H, *J* = 7.2 Hz), 7.11 (*m*, 1H), 7.58 (*d*, 1H, *J* = 7.2 Hz), 8.01 (*d*, 1H, *J* = 16 Hz); ^{13}C NMR (CDCl3, 100 MHz): δ (ppm): 13.79, 19.25, 19.79, 30.82, 64.42, 119.32, 126.34, 126.41, 129.97, 130.79, 133.46, 137.62, 142.26, 167.17; MS (m/e): 218 [M$^+$]; FT-IR ν(cm^{-1}): 1715 (C=O).

(Product 3a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 1.00 (*t*, 3H, *J* = 7.6 Hz), 1.47 (sex, 2H, *J* = 7.2 Hz), 1.72 (quint, 2H, *J* = 6.4 Hz), 2.39 (*s*, 3H), 4.23 (*t*, 2H, *J* = 6.4 Hz), 6.42 (*d*, 1H, *J* = 15.6 Hz), 7.21 (*d*, 2H, *J* = 8 Hz), 7.45 (*d*, 2H, *J* = 8 Hz), 7.69 (*d*, 1H, *J* = 16 Hz); ^{13}C NMR (CDCl3, 100 MHz): δ (ppm): 13.79, 19.24, 21.47, 30.83, 64.35, 117.20, 128.07, 129.62, 131.77, 140.61, 144.57, 167.31; MS (m/e): 218 [M$^+$]; FT-IR ν(cm^{-1}): 1715 (C=O).

(Product 4a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 0.97 (*t*, 3H, *J* = 7.2 Hz), 1.45 (sex, 2H, *J* = 7.6 Hz), 1.69 (quint, 2H, *J* = 6.8 Hz), 3.83 (*s*, 3H), 4.21 (*t*, 2H, *J* = 6.8 Hz), 6.32 (*d*, 1H, *J* = 16 Hz), 6.90 (*d*, 2H, *J* = 8.8 Hz), 7.48 (*d*, 2H, *J* = 8.8 Hz), 7.65 (*d*, 1H, *J* = 16 Hz); ^{13}C NMR (CDCl3, 100 MHz): δ (ppm): 13.77, 19.23, 30.84, 55.32, 64.24, 114.30, 115.76, 127.20, 129.68, 144.20, 161.34, 167.40; MS (m/e): 234 [M$^+$]; FT-IR ν(cm^{-1}): 1713 (C=O).

(Product 5a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 0.98 (*t*, 3H, *J* = 7.2 Hz), 1.46 (sex, 2H, *J* = 7.6 Hz), 1.72 (quint, 2H, *J* = 7.2 Hz), 2.54 (*s*, 3H), 4.25 (*t*, 2H, *J* = 6.8 Hz), 6.48 (*d*, 1H, *J* = 16 Hz), 7.68 (*d*, 1H, *J* = 8.4 Hz), 7.93 (*d*, 1H, *J* = 16 Hz), 8.08 (m, 2H); ^{13}C NMR (CDCl3, 100 MHz): δ (ppm): 13.74, 19.19, 19.93, 30.70, 64.88, 121.41, 123.34, 125.49, 127.30, 138.98, 139.77, 139.87, 148.16, 166.22; MS (m/e): 263 [M$^+$]; FT-IR ν(cm^{-1}): 1715 (C=O).

(Product 6a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 1.04 (*t*, 3H, *J* = 7.2 Hz), 1.52 (sex, 2H, *J* = 7.6 Hz), 1.78 (quint, 2H, *J* = 6.8 Hz), 4.31 (*t*, 2H, *J* = 6.8 Hz), 6.58 (*d*, 1H, *J* = 15.6 Hz), 7.49–7.62 (*m*, 3H), 7.78 (*d*, 1H, *J* = 7.2 Hz) 7.91 (*t*, 2H, *J* = 6 Hz) 8.23 (*d*, 1H, *J* = 8.4 Hz), 8.57 (*d*, 1H, *J* = 15.6 Hz); ^{13}C NMR (CDCl3, 100 MHz): δ (ppm): 13.84, 19.30, 30.87, 64.57, 120.97, 123.42, 125.02, 125.48, 126.24, 126.87, 128.76, 130.49, 131.44, 131.85, 133.71, 141.61, 167.02; MS (m/e): 254 [M$^+$]; FT-IR ν(cm^{-1}): 1714 (C=O).

(Product 7a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 0.98 (*t*, 3H, *J* = 7.2 Hz), 1.45 (sex, 2H, *J* = 7.6 Hz), 1.71 (quint, 2H, *J* = 6.8 Hz), 4.24 (*t*, 2H, *J* = 6.4 Hz), 6.57 (*d*, 1H, *J* = 16 Hz), 7.67 (*m*, 3H), 8.25 (*d*, 2H, *J* = 8.4 Hz); ^{13}C NMR (CDCl3, 100 MHz): δ (ppm):13.73, 19.17, 30.67, 64.90, 122.61, 124.16, 128.63, 140.61, 141.57, 148.46, 166.11; MS (m/e): 249 [M$^+$]; FT-IR ν(cm^{-1}): 1709 (C=O).

(Product 8a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 0.97 (*t*, 3H, *J* = 7.2 Hz), 1.45 (sex, 2H, *J* = 7.6 Hz), 1.69 (quint, 2H, *J* = 6.8 Hz), 3.83 (*s*, 3H), 4.21 (*t*, 2H, *J* = 6.8 Hz), 6.32 (*d*, 1H, *J* = 16 Hz), 6.90 (*d*, 2H, *J* = 8.8 Hz), 7.48 (*d*, 2H, *J* = 8.8 Hz), 7.65 (*d*, 1H, *J* = 16 Hz); ^{13}C NMR (CDCl3, 100 MHz): δ (ppm): 13.77, 19.23, 30.84, 55.32, 64.24, 114.30, 115.76, 127.20, 129.68, 144.20, 161.34, 167.40; MS (m/e): 234 [M$^+$]; FT-IR ν(cm^{-1}): 1713 (C=O).

(Product 9a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 0.99 (*t*, 3H, *J* = 7.2 Hz), 1.47 (sex, 2H, *J* = 7.6 Hz), 1.72 (quint, 2H, *J* = 6.8 Hz), 4.24 (*t*, 2H, *J* = 6.4 Hz), 6.51 (*d*, 1H, *J* = 16 Hz), 7.39 (*t*, 3H, *J* = 4 Hz), 7.54 (*m*, 2H), 7.71 (*d*, 1H, *J* = 16 Hz); ^{13}C NMR (CDCl3, 100 MHz): δ (ppm): 13.78, 19.23, 30.81, 64.42, 118.31, 128.06, 128.88, 130.22, 134.50, 144.55, 167.08; MS (m/e): 204 [M$^+$]; FT-IR ν(cm^{-1}): 1715 (C=O).

(Product 10a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 1.00 (*t*, 3H, *J* = 7.6 Hz), 1.47 (sex, 2H, *J* = 7.2 Hz), 1.72 (quint, 2H, *J* = 6.4 Hz), 2.39 (*s*, 3H), 4.23 (*t*, 2H, *J* = 6.4 Hz), 6.42 (*d*, 1H, *J* = 15.6 Hz), 7.21 (*d*, 2H, *J* = 8 Hz), 7.45 (*d*, 2H, *J* = 8 Hz), 7.69 (*d*, 1H, *J* = 16 Hz); ^{13}C NMR (CDCl3, 100 MHz): δ (ppm): 13.79, 19.24, 21.47, 30.83, 64.35, 117.20, 128.07, 129.62, 131.77, 140.61, 144.57, 167.31; MS (m/e): 218 [M$^+$]; FT-IR ν(cm^{-1}): 1715 (C=O).