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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.

**Keywords:** Mizoroki-Heck reaction; Palladium nano-particles; Solvent-free; Gelatin; Pectin.

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## 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 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 nano-particles 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. 1H and 13C 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 5h 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-nano-particles (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).

(Product 11a): $^{1}$H NMR ($CDCl_3$, 400 MHz): δ (ppm): 0.99 (t, 3H, J= 7.2 Hz), 1.46 (sex, 2H, J= 7.6 Hz), 1.72 (quint, 2H, J= 7.2 Hz), 4.25 (t, 2H, J= 6.8 Hz), 6.54 (d, 1H, J= 16 Hz), 7.37 (m, 1H), 7.69 (d, 1H, J= 16.4 Hz), 7.87 (d, 1H, J= 8 Hz), 8.63 (s, 1H), 8.78 (s, 1H); $^{13}$C NMR (CDCl3, 100 MHz): δ (ppm): 13.75, 19.19, 30.73, 64.74, 120.60, 123.83, 130.35, 134.32, 140.76, 149.58, 150.82, 166.40; MS (m/e): 205 [$M^+$]; FT-IR ν($cm^{-1}$): 1715 (C=O).

## 3. Results and discussion

palladium nano-particles supported on gelatin/pectin mixture were prepared by disposal of aqueous solution of $PdCl_2$ (100 mL, 1 mmol) to pectin and gelatin (0.5 g of each dissolved in 100 mL water) without using any extra reducing agent under reflux conditions for 5h (Fig. 2). This solution was refluxed giving a gray solution and by drying in vacuum gave a dark gray solid.

*<Fig. 1>*

The UV–Vis spectroscopy of the resulted Pd supported nano-particles to ascertain the conversion of Pd(II) to Pd(0) by the disappearance of the peak at around 450 nm (Fig. 3). This change showed the pectin and gelatin can form complexes with Pd(II) ions and reduce them to Pd(0). The process of reduction is performed by oxidation of carboxyl groups and liberation of $CO_2$ gas at the reflux conditions [24b].

*<Fig. 2>*

The energy dispersive X-ray analysis (EDX) showed the presence of palladium and its loading amount was measured to be 1.75% (w/w) in the $Pd_{np}$/gelatin/pectin catalyst. The EDX spectrum also shows signals of carbon, nitrogen and oxygen which are present in the gelatin and pectin (Fig. 4).

*<Fig. 3>*

The XRD of $Pd_{np}$/gelatin/pectin catalyst confirmed the formation of Pd nano-particles. The XRD showed the three characteristic peaks at (1 1 1), (2 0 0) and (3 1 1) can be clearly observed for Pd particles (Fig. 5). These characteristic peaks shows crystallographic planes of the Pd(0) nano-particles. Generally, Solid material can be classified as being either amorphous or crystalline. In crystalline materials the ions engross specific locations in a regular lattice. The simplest such lattice is a simple cube with ions on each of the corners of the cube. The most common simple structures are the face centered cubic (fcc) and the body centered cubic (bcc). The fcc structure consists of a cube of ions with six additional ions located at the centers of each

of the six faces of the cube [26]. According to crystallographic planes in the diffraction pattern of the spectrum the face centered cubic (fcc) crystalline structure was indicated for Pd(0).

*<Fig. 4>*

The TEM image of the catalyst showed that the Pd nano-particles with near spherical morphology were formed onto the surface of gelatin and pectin with relatively good monodispersity. The TEM image indicates that the size of the palladium particles to be in the range 2–5 nm (Fig. 6a).

*<Fig. 5>*

The FESEM image of the $Pd_{np}$/gelatin/pectin catalyst shows the size of the particles to be in the range 2–5 nm (Fig. 7).

*<Fig. 6>*

In order to optimize the reaction conditions, first we studied the effect of media upon the reaction. For this purpose, the coupling reaction of iodobenzene with n-butyl acrylate was used as a model reaction to investigate the catalytic performance of $Pd_{np}$/gelatin/pectin.The influence of bases, solvents and reaction temperature on the yield was investigated (Table 1). Employing DMSO and DMF as the solvent in the presence of n-$Pr_3N$ at 140 °C gave 100% conversion of the starting material after 13 min (Table 1, entries 1 and 2). The use of other organic solvents (Table 1, entries 3 and 6) or protic solvents (Table 1, entries 4 and 5) was not beneficial to the process. We have also studied the reaction in solvent-free condition and in the presence of DMSO and DMF as the solvent after 3 min. The desired product was obtained in 42, 39 and 98% yields, respectively at 140 °C. Comparison of the results clearly shows that the reaction in solvent-free

conditions (Table 1, entry 11) proceeded better than in solvents with an excellent yield and shorter reaction time.

The reaction was also studied at various temperatures under non-solvent conditions. The results demonstrated that the temperature plays a significant role in the reaction rate. The activity of the catalyst was increased in high temperatures (Table 1, entries 7–11) with the activity being very high at 140 °C. During our optimization studies, various bases were examined and it was found that the catalyst was very active and selective for the reaction in the presence of n-$Pr_3N$ (Table 1, entry 11) as a liquid organic base, while the reaction rate was very slow when inorganic bases were used (Table 1, entries 12–14). Remarkably, the reactions were carried out in air indicating that the $Pd_{np}$/gelatin/ pectin catalyst was highly stable and insensitive to oxygen.

*<Table 1>*

In order to show the ability of synthesized Pd nano-particles and their application in organic synthesis, we applied $Pd_{np}$/gelatin/pectin as the catalysts in the Mizoroki–Heck reaction. Employing the optimized reaction conditions (Table 1, entry 11) a range of aryl iodides and bromides with various substituent groups were examined in the Mizoroki–Heck reaction (Table 2).

*<Table 2>*

The reaction was carried out in the presence of aryl halide (1mmol), alkene (1.5 mmol), n-$Pr_3N$ (1.5mmol) and Pd- nano-particles supported on gelatin and pectin (0.05 g, containing 0.002 mmol of Pd).

In the Mizoroki–Heck reaction, various substituents on aryl halides can influence on the rate of reaction. Therefore, electron-withdrawing substituents (such as $NO_2$, $CH_3CO$ and F) on aryl halides increase the reaction rate and electron-donating substituents (such as Me, OMe and $NH_2$) on aryl halides decrease the reaction rate [27].

According to results, high reaction rates and yields were obtained with both activated and non-activated aryl iodides (Table 2, entries 1–6). Aryl iodides without any substituent and activated aryl iodides with electron-withdrawing substituents are reactive substrates in Mizoroki–Heck reaction and the related reactions were completed in shorter times. As an example, the reaction of iodobenzene with n-butyl acrylate was completed within 3 min giving the desired product in 98% isolated yield (Table 2, entry 1). Non-activated aryl iodides with electrondonating substituents (such as Me and OMe) on the aromatic ring are not reactive substrates in Mizoroki–Heck reaction and the related reactions were completed in longer reaction times (Table 2, entries 2–4).

The observed longer reaction time for the reaction of 4-iodoanisole in compare with 4-iodotoluen is due to electrondonating ability of substituents on aromatic rings (Table 2, entries 3 and 4). As shown in Table 2, the coupling reaction of butyl acrylate with o-substituted in compare with p-substituted aryl iodides performed in longer reaction times (Table 2, entries 2 and 3).

The synthesized $Pd_{np}$/gelatin/pectin catalytic system was also applied for the substituted aryl bromides and hetero aryl bromide giving the desired products in moderate to high yields (Table 2, entries 7–11).

There are many reports in the applying palladium nano-particles for the Mizoroki–Heck reaction. To show the catalytic activity of $Pd_{np}$/gelatin/pectin system, we compare the previously

reported systems with this system in Mizoroki–Heck reaction. Bhaumik et al. reported the application of $Pd_{np}$ tethered into mesoporous polymer MPTA1 in the Mizoroki–Heck reaction of iodobenzene with n-butyl acrylate in the presence of $K_2CO_3$ as a base in $H_2O$ at reflux. Under these conditions, the reaction was completed within 5 h [28]. While for the similar reaction with our catalytic system gave the desired product within 3 min in 98% yield (Table 2, entry 1). Also the synthesis of poly(N-vinyl imidazole) grafted silica-containing palladium nano-particles has been applied as a catalyst in Mizoroki–Heck reaction of 4-iodoanisole with n-butyl acrylate using DMF as solvent in the presence of $K_2CO_3$ under phosphine free conditions and the reaction was completed within 1 h [29]. While for the similar reaction, using the $Pd_{np}$/gelatin/pectin the reaction was completed after 18 min (Table 2, entry 4). In another report, palladium supported on super para magnetic nano-particles was used as a catalyst for Mizoroki–Heck reaction of iodobenzene with n-butyl acrylate. The reaction was completed within 5 h in the presence of $K_2CO_3$ in NMP as the solvent at 130 °C [30], whereas, the similar reaction, as mentioned above, went to completion within 3 min. Wang and coworkers reported the application of Pd nano-particles supported on functionalized mesoporous silica in the Mizoroki–Heck reaction of iodobenzene with n-butyl acrylate in the presence of $Et_3N$ as a base in DMF at 120 °C. Under these conditions, the reaction was completed within 1 h [31]. Similar reaction under our conditions gave the desired product within only 3 min in 98% yield (Table 2, entry 1).

The notable properties of $Pd_{np}$/gelatin/pectin system are in situ generation of nano-particles without addition of any external reducing agents, stability toward air and humidity, easy handling and recycle ability. It is worth noting, some of the reactions proceeded in the presence of $Pd_{np}$/gelatin/pectin system under solvent-free conditions, are among the fastest ever reported.

The importance of using heterogeneous catalyst is due to their application in industry and the reusability of catalyst is the major area of interest. The reusability of the catalyst was checked upon the reaction of iodobenzene with n-butyl acrylate as the substrates in the presence of the catalyst and n-Pr3N at 140 °C. After completion of the reaction in the first time, the organic compounds were separated from the reaction mixture by a simple extraction and the resulting solid mass was reused for the six times. At the first time, the reaction was completed within 3 min in 98% yield. The $Pd_{np}$/gelatin/pectin has been recovered for six times with some decrease in the catalytic activity of the catalyst. At the sixth time, the reaction was completed within 20 min in 82% yield (Fig. 7).

*<Fig. 7>*

It is interesting that among the recycling process the shape and size of the nano-catalyst does not change notably. The TEM picture of the recovered nanocatalyst after sixth run showed that the morphology and the size of the particles were not disturbed notably in comparison with the TEM picture of the fresh catalyst (Fig. 6a and 6b).

In order to get more information about the leaching of palladium in reaction, the reaction of iodobenzene with n-butyl acrylate as a model reaction was studied. After completion of the reaction and the workup for the first run, the amount of leaching was determined by ICP analysis to be <2.5%. The amount of Pd leaching after the 6th run was also determined by ICP analysis to be only 14%.

## 4. Conclusion

$Pd_{np}$/gelatin/pectin as a new category of nano-composite was obtained easily by the in situ reduction of $PdCl_2$ under green conditions without addition of any external reducing agents.

The $Pd_{np}$/gelatin/pectin system showed a high activity toward the Mizoroki–Heck cross-coupling reaction of various aryl halides (I and Br) under solvent-free conditions. The catalyst was very stable and could be easily separated from the products and reused for six times.

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## Table captions

**Table 1.** Optimization studies for the reaction of iodobenzene with n-butyl acrylate in the presence of $Pd_{np}$/gelatin/ pectin.[a]

**Table 2**. Reaction of aryl halides with n-butyl acrylate catalyzed by $Pd_{np}$/gelatin/pectin.

## Figure captions

**Fig. 1.** Preparation of $Pd_{np}$/gelatin/ pectin.

**Fig. 2.** UV–Vis spectroscopy of (a) Pd(II) before reduction and (b) Pd(0) after reduction with gelatin and pectin.

**Fig. 3.** The EDX spectrum of $Pd_{np}$/gelatin/pectin.

**Fig. 4.** The XRD spectrum of $Pd_{np}$/gelatin/pectin.

**Fig. 5.** TEM image of the fresh $Pd_{np}$/gelatin/pectin catalyst that shows the morphology of Pd nano-particles on the surface (a), TEM image of the $Pd_{np}$/gelatin/pectin catalyst after the 6th run of recycling of the catalyst (b).

**Fig. 6.** FESEM image of the $Pd_{np}$/gelatin/pectin catalyst that shows the morphology of $Pd_{np}$ on the surface.

**Fig. 7.** Recoverability of $Pd_{np}$/gelatin/ pectin

## Table section:

**Table 1.** Optimization studies for the reaction of iodobenzene with n-butyl acrylate in the presence of $Pd_{np}$/gelatin/ pectin.[a]

| Entry | Base | Solvent | T(°C) | Time | Yield(%)[b,c] |
|---|---|---|---|---|---|
| **1** | n-$Pr_3N$ | DMSO | 140 | 13 min | 94 (100) |
| **2** | n-$Pr_3N$ | DMF | 140 | 13 min | 90 (100) |
| **3** | n-$Pr_3N$ | Toluene | Reflux | 12 h | 12 (24) |
| **4** | n-$Pr_3N$ | EtOH | Reflux | 12 h | 31 (37) |
| **5** | n-$Pr_3N$ | $H_2O$ | Reflux | 12 h | 48(53) |
| **6** | n-$Pr_3N$ | THF | Reflux | 12 h | 8 (12) |
| **7** | n-$Pr_3N$ | None | 80 | 6 h | 12 (18) |
| **8** | n-$Pr_3N$ | None | 100 | 5 h | 82 (87) |
| **9** | n-$Pr_3N$ | None | 120 | 85 min | 90 (100) |
| **10** | n-$Pr_3N$ | None | 130 | 30 min | 92 (100) |
| **11** | **n-$Pr_3N$** | **None** | **140** | **3 min** | **98 (100)** |
| **12** | NaOH | None | 140 | 14 h | 70 (75) |
| **13** | KOAc | None | 140 | 14 h | 80 (84) |
| **14** | $K_2CO_3$ | None | 140 | 15 h | 91 (93) |
| **15** | DABCO | None | 140 | 1 h | 94 (100) |

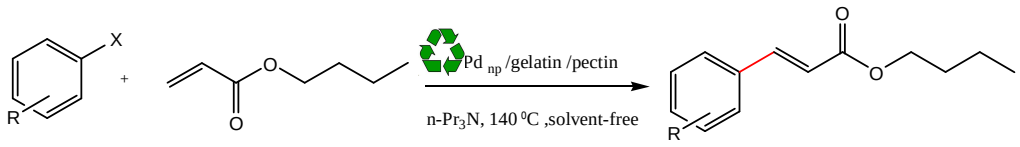
The bold values (entry 11) show our selected conditions for Mizoroki-Heck reaction.

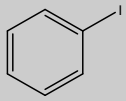
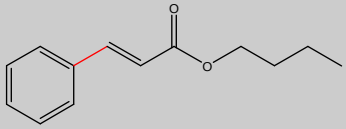
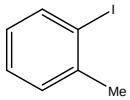
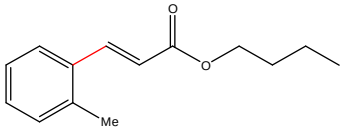
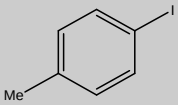
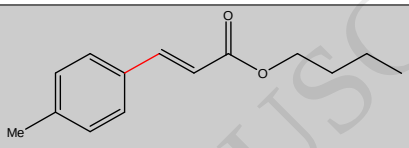
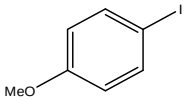
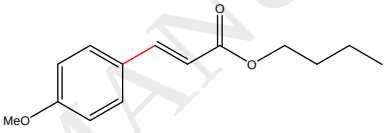
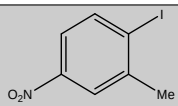
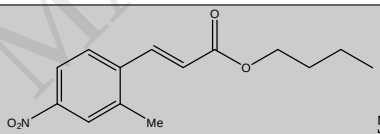
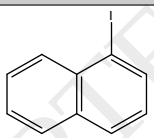
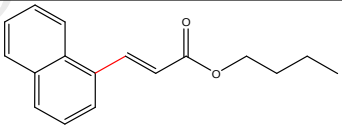
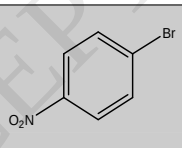
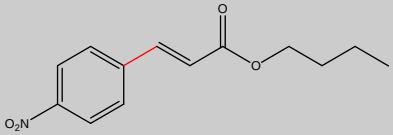
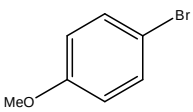
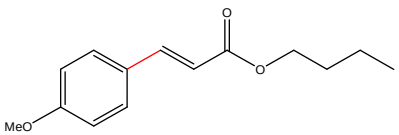
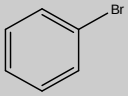
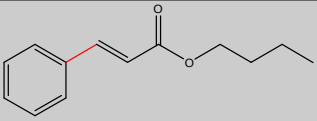
[a] Reactions were carried out using 1 mmol of idobenzene, 1.5 mmol of n-butyl acrylate and 1.5 mmol of base.

[b] Yields are given for isolated products.

[c] The data presented in the parenthesis refer to the conversion of iodobenzene.

**Table 2**. Reaction of aryl halides with n-butyl acrylate catalyzed by $Pd_{np}$/gelatin/pectin.




| Entry | Aryl halide | Product | Time | Yield(%) |
|---|---|---|---|---|
| 1 |  |  1a | 3 min | **98** |
| 2 |  |  2a | 25 min | **92** |
| 3 |  |  3a | 14 min | **95** |
| 4 |  |  4a | 18 min | **93** |
| 5 |  |  5a | 23 min | **93** |
| 6 |  |  6a | 30 min | **90** |
| 7 |  |  7a | 70 min | **93** |
| 8 |  |  8a | 16 h | **72** |
| 9 |  |  9a | 14 h | **84** |

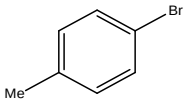
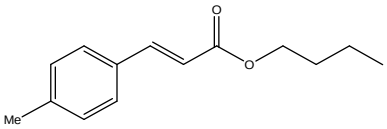
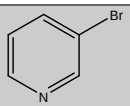
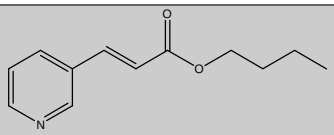
| | | | | |
|---|---|---|---|---|
| 10 |  |  10a | 16 h | **75** |
| 11 |  |  11a | 7.5 h | **80** |

**Figure section:**

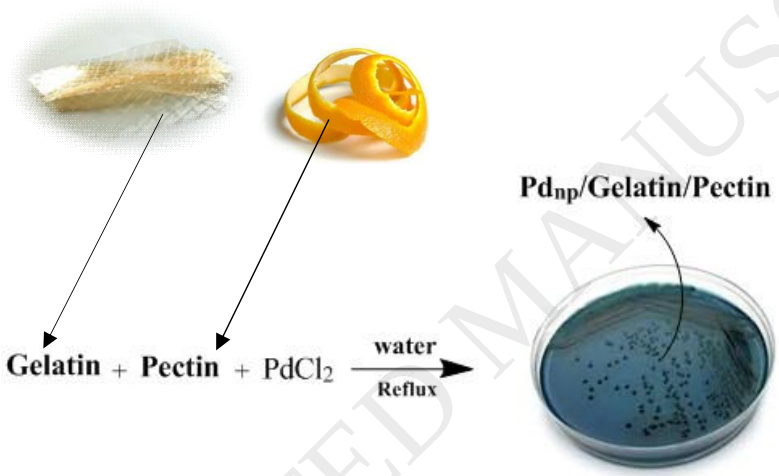



**Fig. 1.** Preparation of $Pd_{np}$/gelatin/ pectin.

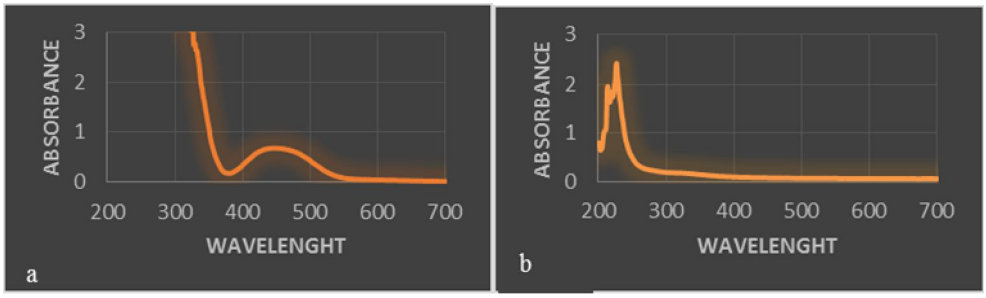



**Fig. 2.** UV–Vis spectroscopy of (a) Pd(II) before reduction and (b) Pd(0) after reduction with gelatin and pectin.

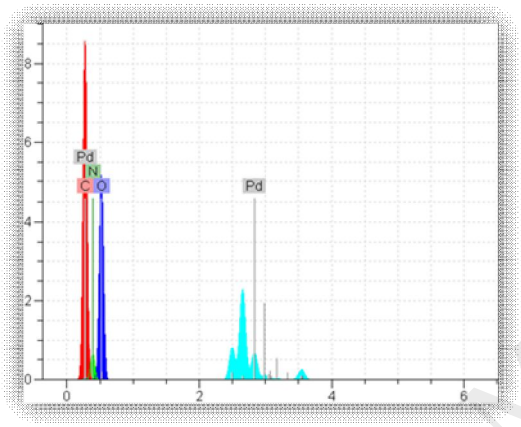



**Fig. 3.** The EDX spectrum of $Pd_{np}$/gelatin/pectin.

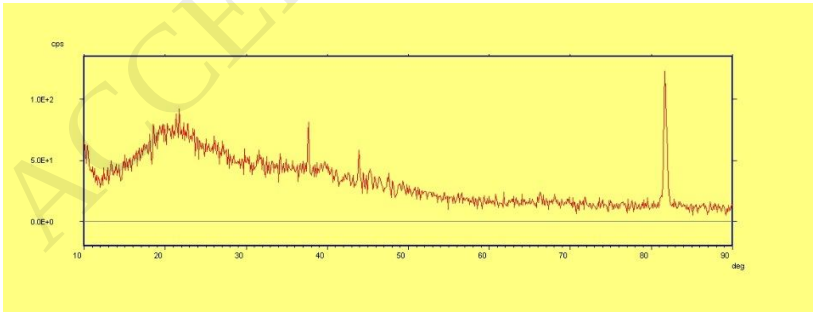



**Fig. 4.** The XRD spectrum of $Pd_{np}$/gelatin/pectin.

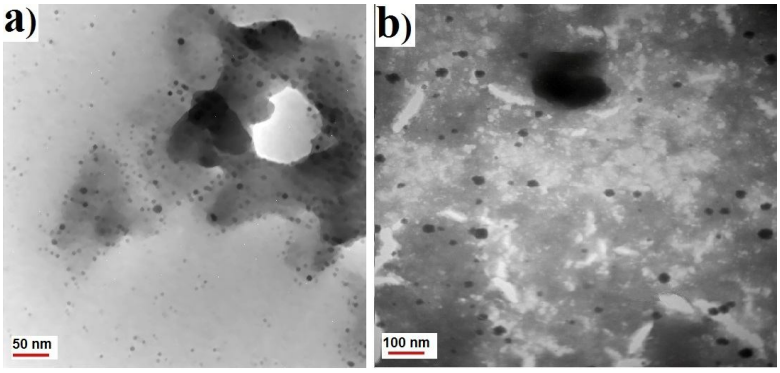



**Fig. 5.** TEM image of the fresh $Pd_{np}$/gelatin/pectin catalyst that shows the size and morphology of Pd nano-particles on the surface (a), TEM image of the $Pd_{np}$/gelatin/pectin catalyst after the 6th run of recycling of the catalyst (b).

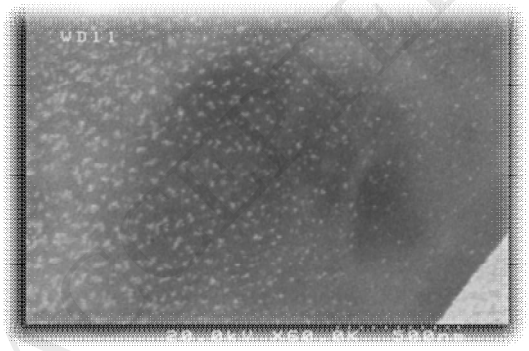


**Fig. 6.** FESEM image of the $Pd_{np}$/gelatin/pectin catalyst that shows the morphology of $Pd_{np}$ on the surface.

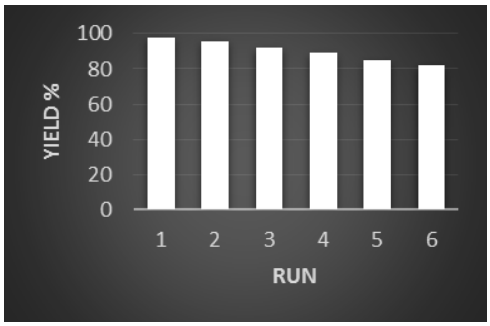



**Fig. 7.** Recoverability of $Pd_{np}$/gelatin/pectin