

Synthesis of Kenaf Cellulose Supported Highly Active Poly(amidoxime) Palladium Complex and Its Application as a Reusable Catalyst for Allylic Arylation reactions

Bablu Hira Mandal^{ab*}, Shaheen M. Sarkar^a, Md. Lutfor Rahman^a, Ab. Rahim, Mohd Hasbi^a

^aFaculty of Industrial Sciences and Technology

University Malaysia Pahang

Malaysia

^bDepartment of Chemistry

Jessore University of Science and Technology

Bangladesh

**Corresponding author*

bhiramandal@gmail.com;shaheen@ump.edu.my;lutfor73@gmail.com;mohdhasbi@ump.edu.my

Abstract—A highly active kenaf cellulose supported poly(amidoxime) palladium catalyst was synthesized and the catalyst (65 mol ppm to 6.5 mol ppm) was found to promote efficiently allylic arylation of allylic ester with sodium tetraarylborates and arylboronic acids in ethanol at 60 °C temperature. Outstanding yields of the corresponding products as well as significant reusability of the catalyst were obtained. The total turnover number(TON) and frequency(TOF) were 144615 and 9641 h⁻¹ respectively.

Keywords: Kenaf, cellulose, poly(amidoxime)Pd-complex, allylic arylation

1. Introduction

Cellulose is a biodegradable natural polymer and available in plenty worldwide. It is low density, cheap and renewable. It also has attractive mechanical properties which are comparable to glass fibers. These characteristics of cellulose have received a great compelling position as a solid support for catalysts [1-5]. Cellulose is also fascinating since it can be chemically modified and selective chelating moiety can be incorporated onto its backbone to coordinate with metal ions [6-8]. Several biopolymers, for example alginate, gelatine, starch and chitosan derivatives have been used as supports for catalytic applications [9-12]. Hence, we have attempted to apply cellulose as an anchoring materials for transition metal catalysts.

Allyl-aryl coupling reactions with boron derivatives in the presence of transition metals, have come out as convenient synthetic routes from the standpoint of their availability, stability and ease of handling [13, 14]. The Tsuji-Trost reaction, an allylic substitution has been accepted as a superior method in the synthesis of natural and pharmaceutical products [15-19]. A number of effective catalysts for the allylic arylation along with boron reagents have been emerged [20-28]. However, the reaction often suffers from the necessity of comparatively high temperature and high catalyst loading (1-10 mol %). A self-assembled poly(imidazole) palladium composite which efficiently forwarded allylic arylation reactions has reported recently though the complex was not stable in polar solvents like EtOH, DMF, DMSO etc. [29,30]. So, development of highly stable and active, cheap and environment friendly simple heterogeneous catalysts for allylic arylation still left over a major dispute. Consequently, it is highly likely to develop a general, simple and convenient catalytic process which could be applied to a number of substrates of different natures under mild and environment friendly conditions.

This report is a continuation of our studies on palladium complex chemistry. We have synthesised and characterized kenaf cellulose supported poly(amidoxime) palladium complex and applied this complex as heterogeneous catalyst efficiently (65 to 6.5 mol ppm) in the allylic arylation of aromatic and aliphatic allylic acetates with sodium tetraarylborates and boronic acids in ethanol at 60°C temperature.

2. Experimental

2.1 General Information

All manipulations were performed under atmospheric conditions otherwise noted. Reagents and solvents were obtained from commercial suppliers and used without further purification. Water was deionized with a Millipore system as a Milli-Q grade. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was purchased from Aldrich Chemical Industries, Ltd. ^1H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra were measured with a BRUKER-500 spectrometer, central laboratory, University Malaysia Pahang (UMP). The ^1H NMR chemical shifts were reported relative to tetramethylsilane (TMS, 0.0 ppm).

The ^{13}C NMR chemical shifts were reported relative to CDCl_3 (77.0 ppm). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on Shimadzu ICPS-8100 equipment by the central laboratory, UMP. FTIR spectra were measured with a Perkin Elmer 670 spectrometer equipped with an ATR device (ZnSe crystal), UMP. XPS spectra were measured with a Scanning X-ray Microprobe PHI Quantera II, MIMOS, Kuala Lumpur. FE-SEM was measured with JSM-7800F, central laboratory, UMP. TLC analysis was performed on Merck silica gel 60 F_{254} . Column chromatography was carried out on silica gel (Wakogel C-200).

2.2 Materials

Kenaf fibre was procured from local market at Kuantan city, Pahang, Malaysia. The kenaf was cut into small pieces (~1 cm) and 100 g sample was boiled with 10% NaOH (800 mL) for 4 h. The product was washed with distilled water and was boiled with glacial acetic acid (600 mL) for 1 h. Again washed with distilled water and the cellulose was bleached with hydrogen peroxide (300 mL) and 5% NaOH (500 mL), washed with distilled water (500 mL) for several times and oven dried at 50 °C. Methyl acrylate monomer purchased from Aldrich and monomer was passed through columns filled with chromatographic grade activated alumina to remove inhibitors. Other chemicals such as ceric ammonium nitrate (CAN) (Sigma-Aldrich), methanol (Merck), sulphuric acid (Lab Scan), metal salts and other analytical grade reagents were used without purification.

2.3 Synthesis of cellulose supported poly (acrylonitrile) I

Kenaf cellulose (3.0 g) was added into 300 mL distilled water. The reaction was performed in 500 mL three-neck round bottom flask fixed with stirrer and condenser in a thermostat water bath. The mixture was heated at 55 °C and 0.1 mL of sulphuric acid (50%) was added to the mixture. During the grafting reaction, N_2 gas was purged into the flask to remove oxygen. After 5 min, 0.90 g of CAN (10 mL solution) was added and stirred with N_2 flow. After 20 min, 14 mL of acrylonitrile monomer was added into the reaction and stirred for further 3 h with N_2 flow. Then, the mixture was cooled under running tap water and the grafting product was washed with aqueous methanol (methanol : water = 4:1) (**Scheme 1**). The product was finally oven dried at 50 °C to a constant weight [31]

2.4 Determination of grafting fractions

The grafting product was weighed and the homopolymer was extracted using Soxhlet purification with acetone for 12 h. The purified grafted copolymer was dried at 50°C to a constant weight (see Fig. S1c at ESI). The percentage of grafting (Gp) was determined using the following equation (1):

$$\text{Grafting percentage (Gp)} = \frac{W_2}{W_1} \times 100 \quad (1)$$

where, W_1 is the weight of parent polymer (cellulose) and W_2 is the weight of grafted polymer (polyacrylonitrile).

2.5 Synthesis of poly(amidoxime) ligand 2

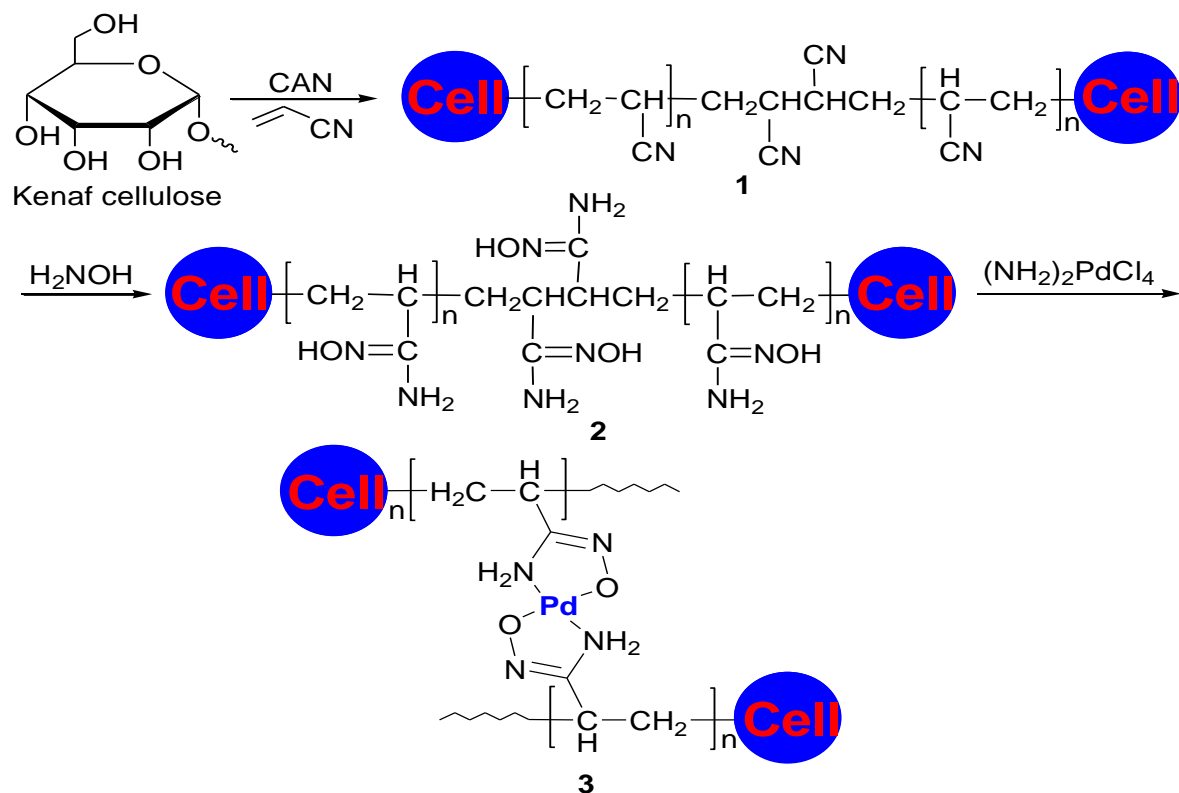
Hydroxylamine hydrochloride (NHOH·HCl) 20 g was dissolved in 500 mL of aqueous methanol (methanol/water, 4:1) and neutralized by NaOH solution and the resulting NaCl precipitate was removed by filtration. The pH of the reaction was adjusted to pH 11 by adding of NaOH solution. The ratio of methanol and water was maintained 2 as 4:1 (v/v). 10 g poly(acrylonitrile) grafted kenaf cellulose **1** was placed into a two-neck round bottom flask equipped with a stirrer, condenser and thermostat water bath. The hydroxylamine solution was then added to the flask and the reaction was started at 70 °C for 4 h. After completion of reaction, the chelating ligands were separated from the hydroxylamine solution by filtration followed by washed with aqueous methanol. The obtained cellulose based amidoxime ligand **2** was neutralized with 100 mL of methanolic 0.1 M HCl solution(**Scheme 1**). The ligand was filtered and washed several time with aqueous methanol and dried at 50 °C for 6 h [31, 32].

2.6 Preparation of the poly(amidoxime)Paladium complex 3

An aqueous solution (NH₂)₂PdCl₄ was added into a stirred mixture of 1 g of poly(amidoxime) ligand **1** in 25 mL water at room temperature and the mixture was stirred for 2.5 h at room temperature. Brown color cellulose supported palladium complex was formed. The reaction mixture was filtrated and washed several times with excess amount of water, MeOH and dried at 60 °C for 1 h(**Scheme 1**). The ICP-AES analysis showed that cellulose supported palladium complex 3 contain Pd, 0.65 mmol/g [33]

2.7 General procedure for allylic arylation

In a typical experiment, a mixture allylic acetates with sodium tetraarylborates were used for the allylic arylation with cellulose supported poly(amidoxime) palladium complex 3(65 mol ppm) in EtOH was stirred at temperature 60 °C for 5 h. The reaction progress was monitored by GC analysis. After completion of the reaction, cellulose supported poly(amidoxime) palladium complex 3 was filtered, washed with MeOH (3 x 5 mL), dried, and reused in the next run under the same reaction conditions. The filtrate was concentrated to give the crude product, which was purified by column chromatography (hexane/ethyl acetate) to give the corresponding arylated products.



Scheme 1. Synthesis of cellulose-supported palladium complex 3

3. Results and discussion

Absorption bands at 3438, 2921 and 1638 cm^{-1} in the infrared (IR) spectrum of fresh kenaf cellulose are for O-H, C-H and C-C stretching, respectively (ESI, Fig. 1). A peak at 1426 cm^{-1} was due to CH_2 symmetric stretching and small peaks at 1376, 1160 and 1065 cm^{-1} are for C-O stretching [34]. The characteristic of α -glycosidic linkages between glucose in cellulose was confirmed by a small peak at 895 cm^{-1} which attributes to the glycosidic C_1 -H deformation with ring vibration contribution and OH bending [34]. The IR spectrum of acrylonitrile grafted cellulose 1 showed a new absorption band at 2244 cm^{-1} , which strongly indicated the successful introduction of CN function on to the cellulose backbone. Whereas, in the IR spectrum of hydroxylamine treated acrylonitrile grafted cellulose, CN band at 2244 cm^{-1} was disappeared and absorption bands for amidoxime group was appeared. The new absorption bands at 1680 and 1648 cm^{-1} for poly(amidoxime) chelating ligand 2 correspond to the C=N stretching and N-H bending modes respectively. Moreover, existence of a shoulder at 3304 cm^{-1} is for N-H and OH stretching bands and 1401 cm^{-1} for OH bending. The IR of 3 showed a broad peak at 3325 cm^{-1} and a peak at 1122 cm^{-1} , which demonstrated the absorption of palladium by amidoxime ligand [29, 30, 34,35].

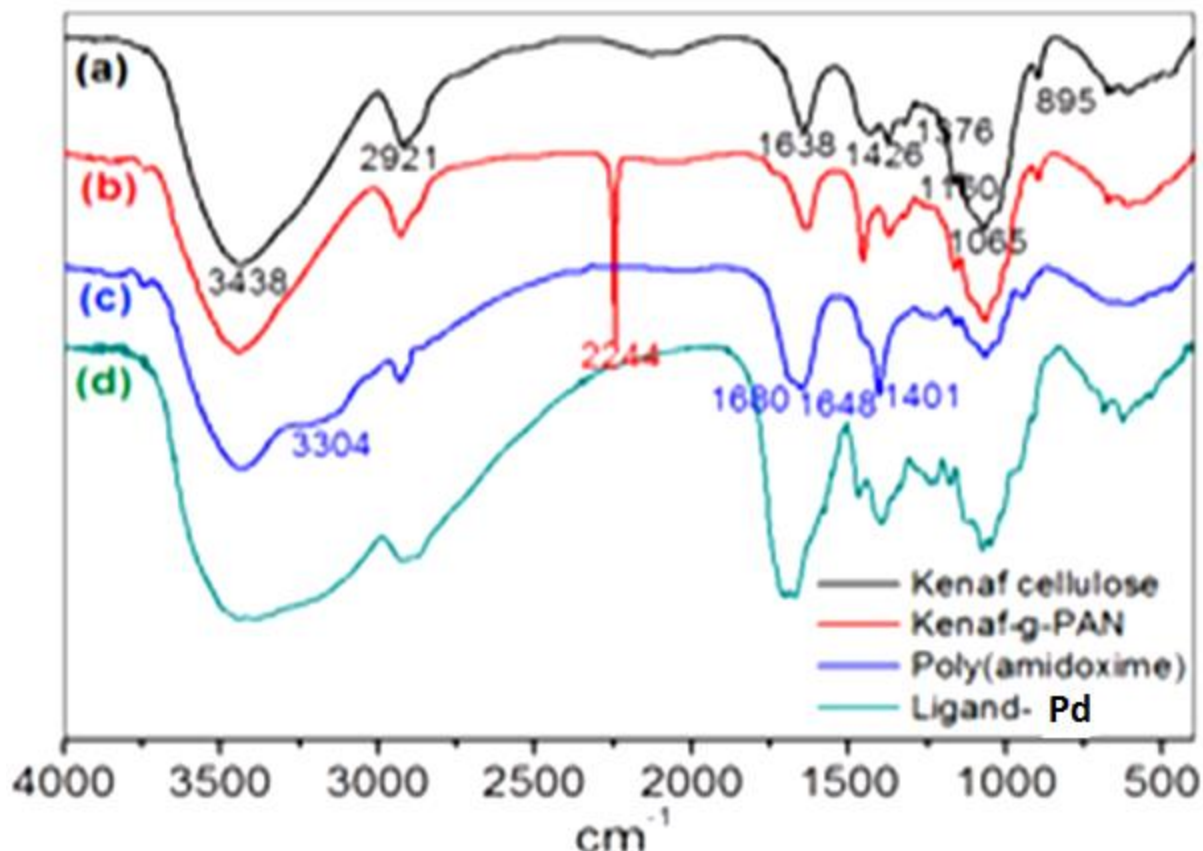


Figure 1. IR Spectrum of (a) kenaf cellulose, (b) poly(acrylonitrile) 1, (c) poly(amidoxime) 2, (d) poly(amidoxime) palladium catalyst 3

The scanning electron microscopy (SEM) of fresh kenaf cellulose displayed unsmooth morphologies including fine crystalline surface (Fig. 2a) whereas poly(acrylonitrile) grafted cellulose 1 showed a distinguished spherical shape beads structure (Fig. 2b) from fresh kenaf cellulose fine crystalline structure. The poly(amidoxime) chelating ligand 2 exhibited clear morphologies with variable size of spherical bead on the surface (Fig. 2c). The SEM image of 3 revealed a globular-aggregated, self-assembled structure. The globules ranged from 250 to 560 nm in diameter, and aggregated to construct a mesoporous suprastructure (Fig. 2d). X-ray photoelectron spectroscopy (XPS) showed a major peak at 337 eV which were assigned as Pd(II) in the complex (Fig.2e). The UV-Vis absorption spectrum of cellulose supported 2 and 3 were also analysed (Fig. 2f). No UV signal was found for the pure poly(amidoxime) sample whereas UV signals were well overlaid for 3. These results suggested that the poly(amidoxime) ligand 2 was coordinated with palladium to give polymeric cellulose supported poly(amidoxime) palladium complex 3 [29,30].

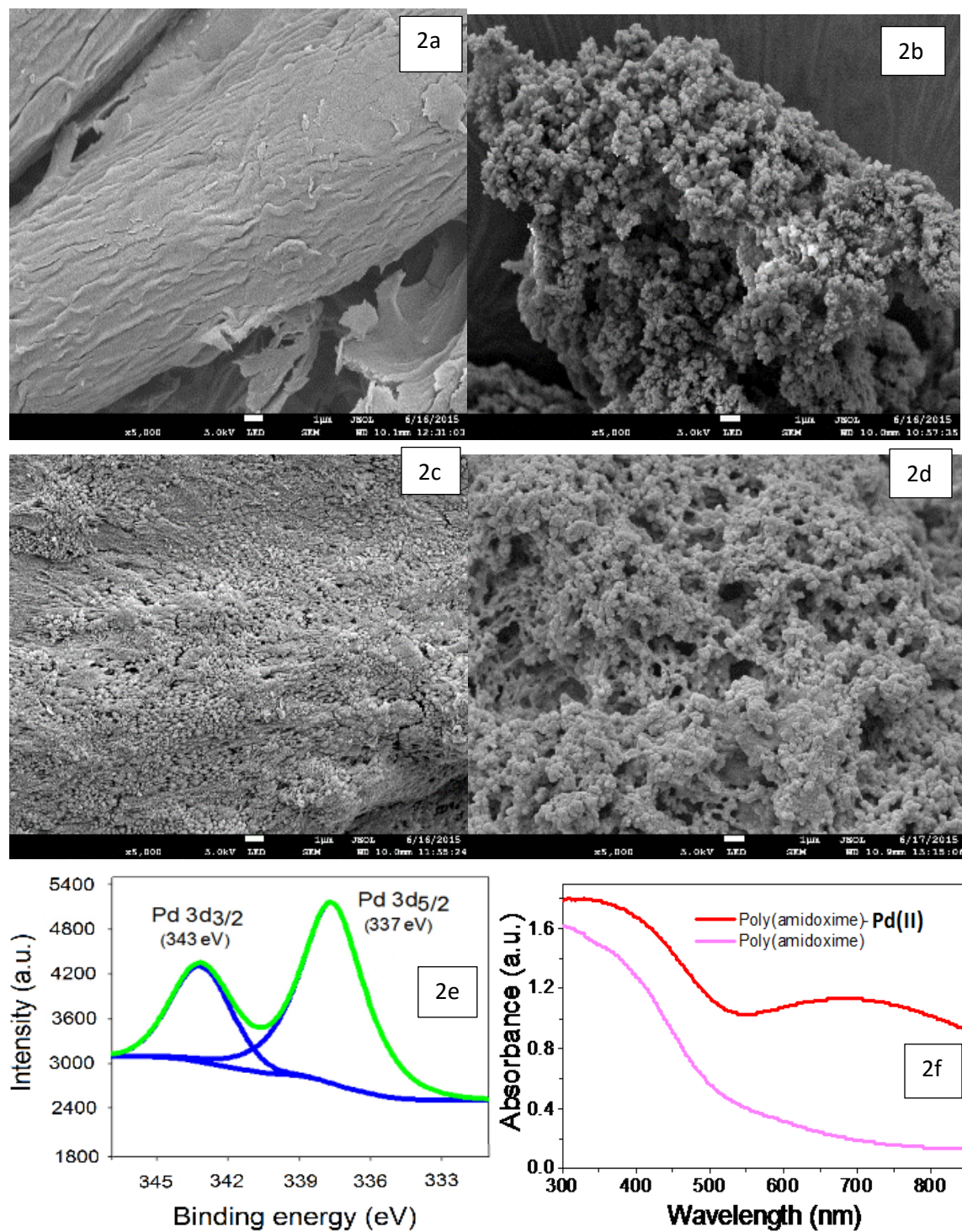


Figure 2. a) fresh kenaf cellulose; b) poly(acrylonitrile) grafted cellulose 1; c) poly(amidoxime) chelating ligand 2; d) poly(amidoxime)Pd complex 3; e) (XPS of 3; f) UV of poly(amidoxime) & poly(amidoxime)Pd complex 3

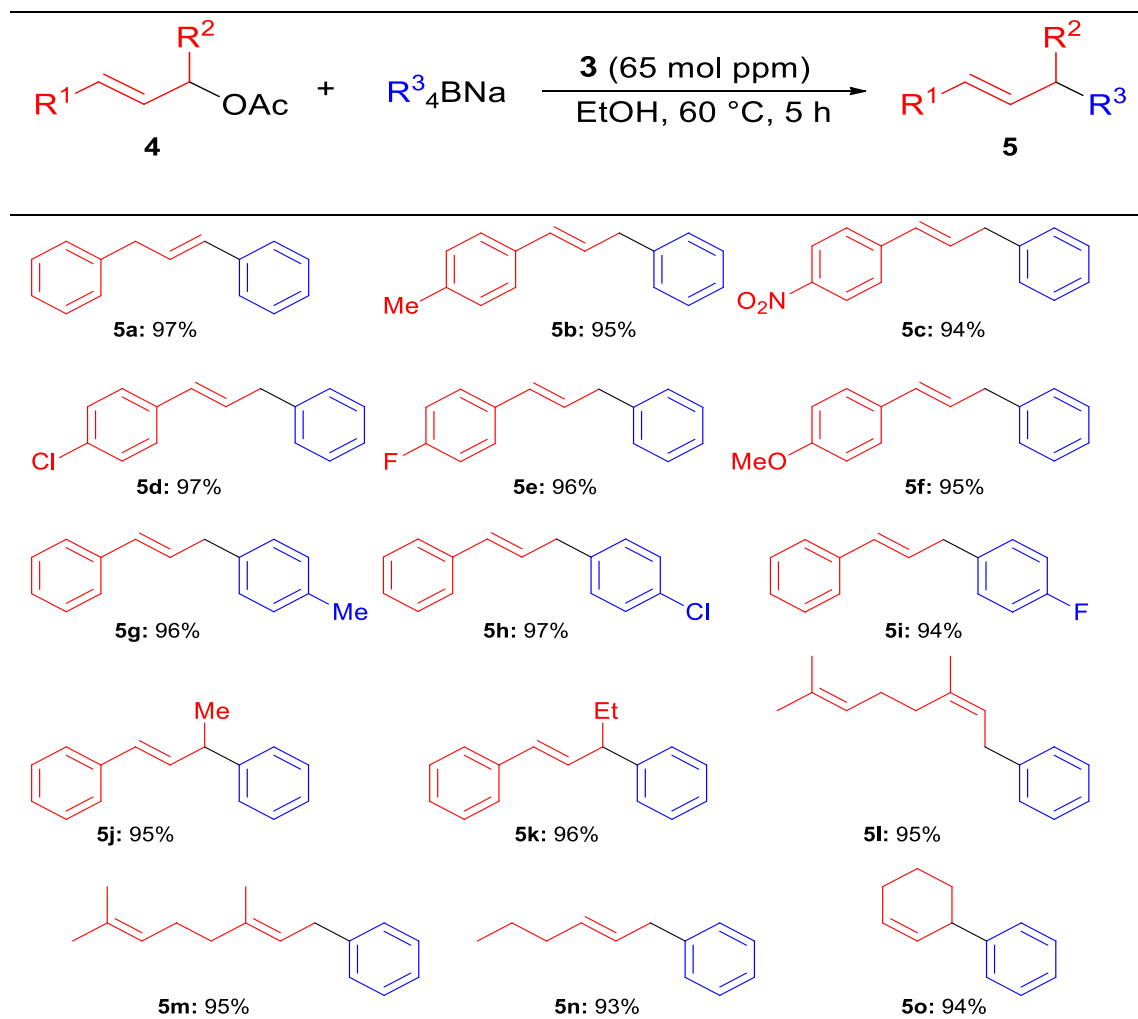
The cellulose supported poly(amidoxime) palladium complex 3 was then used as catalyst in allylic arylation of allylic esters with tetraarylborates to investigate its catalytic activity and reusability. To find optimization conditions the allylic arylation of cinnamyl acetate 4a and sodium tetraphenylborate was chosen as standard examination of catalytic activity. The reaction proceeded efficiently to give 1, 3-diphenylpropene 5a quantitatively when 4a and sodium tetraphenylborate was carried out in EtOH with 65 mol ppm of 3 as catalytic dose at temperature 60 °C for 5 h. As the catalytic activity was found acceptable, different allylic acetates with sodium tetraarylborates were used for the allylic arylation with 65 mol ppm of 3 (Table 1). Cinnamyl esters substituted with electron donating and withdrawing group (4b–f) tetraaryl/substitute tetraarylborates were efficiently promoted to their corresponding products (5b–i) with yields of 94–97%.

Interestingly, methyl- and ethyl- carbinol esters underwent palladium-catalyzed allyl–aryl coupling with tetraarylborate to the corresponding coupling products 5j, 5k in quantitative yields. The reaction of alkyl vinyl carbinol esters must proceed via the corresponding π -allylpalladium intermediate bearing the β -sp³-hydride, which often suffers from β -hydride elimination under palladium-catalyzed conditions to give undesirable 1, 3-dienes. However, no trace of 1, 3-dienes was observed in the reactions [29, 30]. Besides, neryl acetate 4i, geranyl acetate 4j, 2-hexenyl acetate 4k, and cyclohexyl acetate were efficiently converted to their corresponding phenylated compounds 5l–o at the yield of range 93–95%. No isomeric products were found in any reactions.

The kenaf cellulose supported poly(amidoxime) palladium catalyst 3 (65 mol ppm) was also utilized in the allylic substitution with aryl boronic acids which are versatile as well as readily available boron reagents and the catalyst was observed to aid the allylic arylation effectively efficiently. Therefore, the reaction of 4a with phenylboronic acid was carried out to find the optimum reaction conditions and was found to yield 5a quantitatively in ethanolic KF at 60 °C (Table 2). The substituted arylboronic acids also promptly underwent carbon–carbon bond formation reaction under similar conditions to produce 5h, 5p, and 5q with a yield in the range of 93–94%. The alkyl vinyl carbinol esters 4k, and neryl acetate 4l were transformed into the corresponding alkenes 5k, and 5l, with 95% yields.

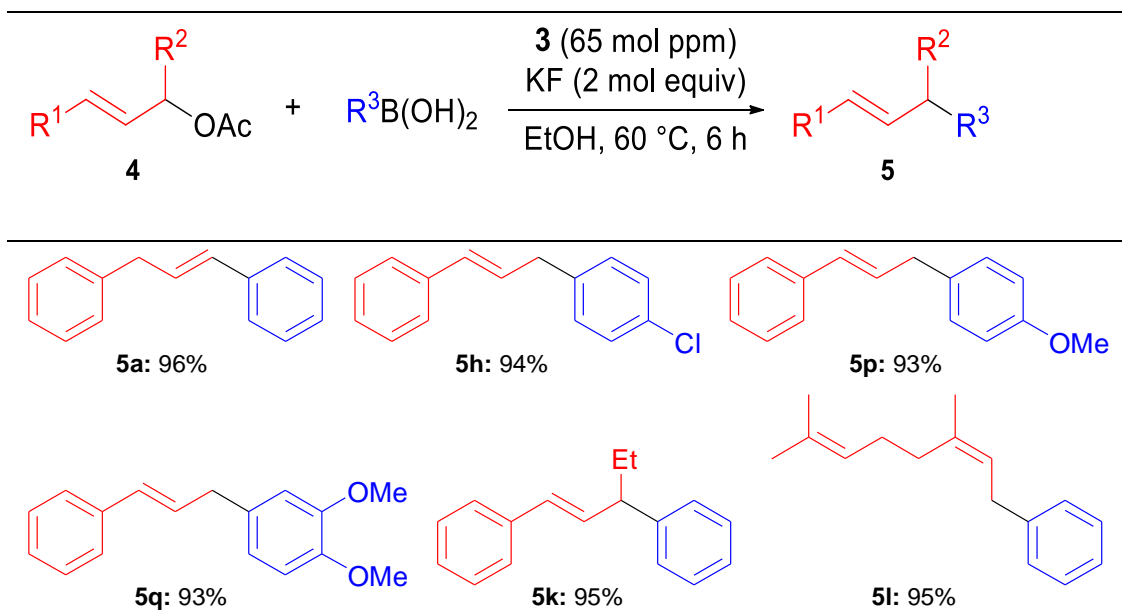
A hot filtration test was carried out to verify the heterogeneity of the catalyst using the reaction of 4a with sodium tetraphenylborate during the progress of the reaction (Figure 3). The reaction was studied under identical conditions as provided in Table 1. The catalyst 3 was separated through membrane filtration ($\phi = 0.45 \mu\text{m}$) at 60 °C after 3 h, and the filtrate was stirred at 60 °C for another 2 h. As depicted in Figure 2, GC analysis showed the yield of 5a after the filtration. According to the results, the reaction progressed under heterogeneous conditions. Furthermore, as described in Figure 3, ICP-AES analysis also indicated no leaching of Pd in the reaction mixture (detection limit 5 ppb Pd; >99.5% of Pd was retained in 3). So, cellulose supported poly(amidoxime) palladium catalyst 3 stimulated the reaction under heterogeneous conditions without leaching of Pd metal.

Table 1. Allylic arylation of allylic acetates with sodium tetra-*a*-arylbates^a



^aReaction conditions: **4** (1 mmol), sodium tetraphenylborate (1.5 mmol), **3** (0.065 mol%), EtOH (2 mL), 60 °C, 5 h.

Table 2: Allylic arylation of allylic acetates with arylboronic .^[a]



^aReaction conditions: **4** (1 mmol), boronic acids (1.5 mmol), **3** (0.065 mol%), KF (2 mmol), EtOH (2 mL), 60 °C, 5 h.

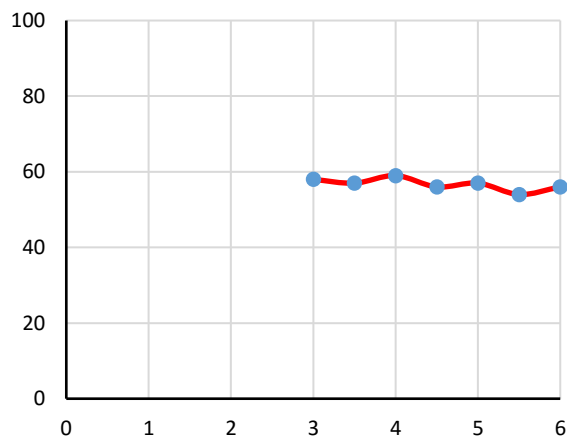


Figure. 3 Hot filtration test of **3** in allylic arylation of **4a**.

Considering the importance of recycling of heterogeneous catalysts in real applications, we concentrated to the recycling and reusability of the synthesized catalyst **3**. To investigate the reusability, we accomplished the reaction of cinnamyl acetate (**4a**) in the presence of 0.1 mole of Pd-catalyst **3**. When the reaction completed, it was diluted with ETOAc and the catalyst was separated from the reaction mixture by simple filtration and washed with ETOAc. It was then again reapplied for the next run under the identical reaction conditions. Outstanding catalytic activity was observed over six cycles of reaction (fig.4).

As poly(amidoxime) palladium complex **3** assisted allylic arylations efficiently, 6.5 ppm of **3** was applied for the reaction of **4a** and sodium tetraphenylborate to evaluate TON and TOF under similar reaction conditions (Scheme 2). It is interesting to note that the expected product **5a** was achieved quantitatively and TON 144615 & TOF 9641 h⁻¹ were obtained. So far as we know, this is the highest TON and TOF obtained for allylic arylation using kenaf cellulose supported poly(amidoxime) palladium complex **3**.

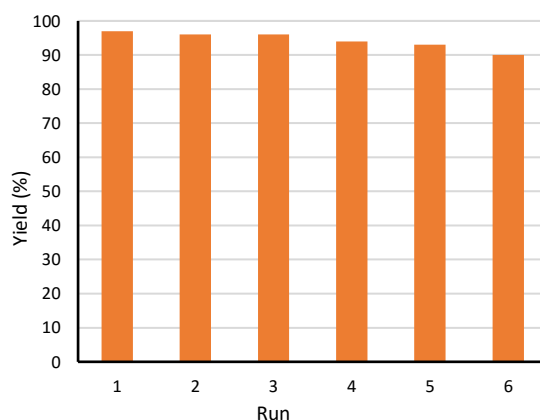
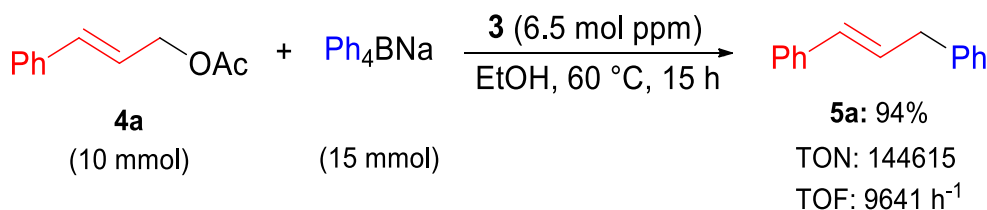


Figure.4 Recycling of the catalyst **3** in allylic arylation of **4a**



Scheme 2: Allylic arylation of **4a** with sodium tetraphenylborate catalyzed by 6.5 ppm of **3**.

4. Conclusion

We conclude that a novel highly active kenaf cellulose supported poly(amidoxime) Pd complex was synthesized and characterized. It has been successfully used for the allylic arylation reaction and was observed to promote the reactions effectively (6.5 ppm Pd) in alcohol media under mild reaction conditions. The catalyst showed highest TON and TOF values with simple recycling and excellent reusable performance for allylic arylation for several cycles.

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