



Development of cellulose-supported Pd-nanocatalyst for the heck coupling and michael addition reactions

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ABSTRACT

The development of reusable, bio-resource based nanocatalysts with high turnover numbers (TONs) is essential for increased sustainability in the chemical sector. Herein, cellulose-supported bio-resourced poly(hydroxamic acid) is employed as a ligand in the synthesis of a palladium nanocomposite (**PdNc-PHA**) that exhibits higher TONs than previously reported similar systems for the Mizoroki-Heck and Michael addition reactions. The **PdNc-PHA** catalyst was characterised using Fourier transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectrometry (EDX), high-resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses. Results showed that the **PdNc-PHA** catalyst exhibits excellent durability and high catalytic activity in the Mizoroki-Heck and Michael addition reactions, leading to high yields of the desired corresponding products. The Mizoroki-Heck reaction of aryl/heteroaryl chlorides with olefins resulted in the production of cross-coupled products, while the Michael addition reaction of phenol/thiophenol and aliphatic cyclic/alicyclic amines with a variety of olefins synthesised the corresponding O-, S-, and N-alkylated products. The recycle and reusability of the catalyst were tested using 4-nitrochlorobenzene and butyl acrylate. The results demonstrated that the catalyst maintained its catalytic activity effectively for up to ten cycles without any noticeable loss in performance. This research represents a promising strategy for efficient catalysis based on bio-waste as a wealth material.

1. Introduction

The Mizoroki-Heck reaction, which has revolutionized organic synthesis, is a key method for the formation of carbon-carbon bonds. Tsutomu Mizoroki and Richard F. Heck discovered this reaction in the 1970s, and it has since become one of the most significant and widely researched cross-coupling reactions in contemporary organic chemistry (K. Zheng et al., 2020, Korch and Watson, 2019, Heck, 1979, Waldvogel et al., 2018, Trzeciak and Augustyniak, 2019). The reaction involves Pd-catalyzed coupling of aryl or vinyl halides with alkenes, resulting in the formation of an alkene-aryl or alkene-vinyl bond. This is a one-step reaction procedure that does not necessitate the isolation of

intermediate products and allows for high atom economy and selectivity in the production of a variety of aryl derivatives (Soni et al., 2023, Stini et al., 2023, Ghadiri et al., 2023, Ashraf et al., 2023, Tubio et al., 2023). Due to the high catalytic activity, palladium is widely recognised as the most suitable metal for cross-coupling reactions (Anchi et al., 2022). Palladium metal is particularly beneficial for the cross-coupling reactions since it can be used in extremely low doses, commonly referred to as "homeopathic" doses, while simultaneously achieving high turnover numbers (TONs) of up to 10^6 (Deraedt and Astruc, 2014). The Mizoroki-Heck reaction has a high selectivity and functional group tolerance, which are some of its most important advantages. It is a useful tool in complex synthesis because the reaction can be used to form a

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single product only when a variety of other functional groups are present (Delcamp et al., 2008). This reaction has found extensive use in industry, with numerous commercial applications in the multi-ton annual production of fine chemicals, such as those in the pharmaceutical, agrochemical, and materials science sectors (Céspedes et al., 2021, Buskes and Jesus Blanco, 2020, Roselló et al., 2014).

The direct addition of, α,β -unsaturated olefins to amines in the Michael addition reaction is an important synthetic tool for the generation of β -amino carbonyl compounds (Lin et al., 2020, Noordzij and Wilsens, 2019, Huang et al., 2014). These compounds are important pharmaceutical intermediates that can be easily transformed into various biologically active molecules, natural products, and functional materials, including β -amino, β -thiol, and β -oxy ketone derivatives (Busacca et al., 2011, Fabris et al., 2009). Typically, Michael addition reaction is catalyzed by a stoichiometric amount of a strong acid or base in organic solvent, which often leads to undesirable side reactions, and isn't compatible with green chemistry approaches (Sunaba et al., 2014, Lee et al., 2014). To overcome these constraints, a variety of Lewis acid metal catalysts including Cu(I)Cl (Kim et al., 2016), Fe(III)Cl₃·6H₂O (Choudhary et al., 2012), NaSnO₃ (Zhang et al., 2011), CeCl₃·7H₂O·NaI (Xu et al., 2004), boric acid (Chaudhuri et al., 2005), ionic liquids (Roy and Chakraborti, 2010), Pt(IV)Cl₄·5H₂O (Kobayashi et al., 2002), InCl₃/TMSCl (Yang et al., 2007), have been investigated.

Despite some success, the use of conventional homogeneous metal catalysis reaction has led to challenges associated with quantitative separation, subsequent regeneration of the catalyst and aggregation of metal species resulting in deactivation. In recent times, there has been increasing demand for straight forward synthetic protocols that utilize recoverable and reusable metallic catalysts. Metallic nanoparticles have been at the forefront of these developments due to their large surface area resulting in high catalytic efficiency and their small size providing effective utilization of expensive metals. In addition, a suitable supported metal nanoparticle catalyst offers high loading capabilities relative to conventional metal complexes.

Recently, there has been an increased interest in stabilizing and incorporating metal species on a solid support to generate active and efficient catalytic systems (Guo et al., 2022, Keypour et al., 2023, Zhang et al., 2023). For Heck reaction: supports have included clay (Aryanasab, 2022), carbon nanotubes and nanofibers (Guo et al., 2016, Luo et al., 2021, Mercadante et al., 2022), graphene (M. Niakan et al., 2021, Kalay, 2022), magnetic MCM-41 (Choghamarani et al., 2019), silica (Gnad et al., 2019, Sarkar et al., 2015, Beiranvand and Habibi, 2023, Volovych et al., 2014), zeolites (Wang et al., 2020, Portolés et al., 2021), polymers (Favier et al., 2020, Sato et al., 2015, Gan et al., 2020), dendrimers (Astruc, 2010), magnetic-materials (Polshettiwar et al., 2011, Hafizi et al., 2022), MOF-808 (Zhao et al., 2022), and Pd-chitosan (Güzel et al., 2022, X. Zheng et al., 2020). For Michael addition reactions: cellulose based Cu(0) (Islam et al., 2016, Sarkar et al., 2016), MOF-99 (Nguyen et al., 2012), DABCO-based ionic liquid (Ying et al., 2014), magnetic nanoparticles (Payra et al., 2016, Li et al., 2017), MCM-41 (Xie et al., 2013), and silica-Co(acac)₂ (Sodhi et al., 2015) have been investigated and demonstrated good catalytic activity. However, most procedures for the synthesis of heterogeneous metal catalysts are expensive, potentially toxic, and as such are neither economically viable nor compatible with industrial processes. As such the development of a general, highly active, and versatile heterogeneous catalyst for chemical bond formation reaction remains a challenge.

Researchers are constantly looking for renewable, sustainable and low-cost, biodegradable resources and processes and such materials have additional potential in the field of catalysis. Isolation of natural cellulose from waste material would be highly advantageous as it can be employed as a low-cost solid support for heterogeneous metal catalysts. The numerous hydroxyl groups in cellulose can be easily modified by a variety of chemical processes, making it a flexible platform. These modifications allow cellulose to serve as a template or support for various chemical reactions, including the stabilization and

incorporation of metal nanoparticles in the catalytic system (Habibi, 2014, Isfahani et al., 2013). Recently, natural polymers such as cellulose, pectin, carrageenan, and alginate have emerged as promising candidates for efficient oral drug delivery systems for therapeutic agents, either alone or in conjunction with other polymers or components (Raghav et al., 2023, Raghav et al., 2021). Previously, our group has addressed employing bio-waste cellulose-supported polymeric ligands for wastewater treatment (M.L. Rahman et al., 2016, M.L. Rahman et al., 2016, Sarkar and Rahman, 2017) and metal catalyzed cross-coupling reactions (Sarkar et al., 2017). In this study, we describe the development and thorough characterization of a Pd-nanocomposite (PdNc-PHA) based on a poly(hydroxamic acid) ligand supported by waste corncob cellulose. The catalyst demonstrated effective catalytic activity in forming C-C and C-N, C-S, C-O bonds which are crucial for organic synthesis via Mizoroki-Heck and Michael addition reactions, respectively. Furthermore, the catalyst can be easily regenerated, reused and efficient use for a range of organic reactions. The waste corncob cellulose support also contributes to the bio-resourced nature of the catalyst, offering an alternative use for agricultural waste. Due to its promising preliminary testing outcomes, the PdNc-PHA catalyst has the potential for wide-ranging applications in the field of organic synthesis.

2. Experimental

2.1. General Information

The reagents and solvents were obtained from Sigma-Aldrich Chemical Industries Ltd. and used in accordance with the manufacturer's instructions. The ¹H NMR chemical shifts were measured with a BRUKER-500 spectrometer. Shimadzu ICPS-8100 and JSM-7800F were used for inductively coupled plasma atomic emission spectrometry (ICP-AES) and FE-SEM, respectively. The XPS spectra were captured using a PHI Quantera II Scanning X-ray Microprobe.

2.2. Material & Methods

The bio-waste corncobs were first cleaned with Milli-Q grade water, followed by a 12 h period of drying at 60 °C. The dried corncobs, weighing 300 g were then sliced into small pieces and subjected to treatment with 10% NaOH (350 mL) for 3 h under the reflux conditions. The cellulose was filtrated and washed with H₂O. To bleach the cellulosic material, it was further refluxed in CH₃CO₂H (350 mL) and H₂O₂ (225 mL) for 3 h respectively. A colourless cellulose fibre was produced after the crude cellulose was rinsed with water and dried for 5 h at 60 °C.

2.3. Copolymerization of cellulose

The co-polymerization reaction was conducted following the protocol described in our previous report. (Sarkar et al., 2017) A suspension of 5.0 g of cellulose in 350 mL of water was stirred continuously for 12 h at room temperature. The mixture that ultimately results was heated to 60 °C, and 1.12 mL of 50% H₂SO₄ and 1.2 g of (NH₄)₂Ce(NO₃)₆ (8 mL aqueous solution) were added under a nitrogen atmosphere. After 30 minutes of stirring, 10 mL of methyl acrylate was added to the reaction mixture and heated at 60 °C for another 4 h. The mixture was filtered and rinsed with aqueous MeOH (MeOH:H₂O; 4:1). The obtained polymer was dried for 5 h at 50 °C, yielding 7.2 g of poly(methyl acrylate) 1.

2.4. Synthesis of chelating ligand 2

The poly(hydroxamic acid) ligand 2 was prepared according to our previous report (Sarkar et al., 2017). To a 250 mL aqueous solution (MeOH:H₂O; 4:1) of hydroxylamine hydrochloride (NH₂OH.HCl, 10 g) was added ice-cold aqueous solution of NaOH and the pH of the solution was maintained to 11. The resulting solution was then transferred into a suspension of poly(methyl acrylate) 1 (4.25 g in 20 mL of H₂O) and the

mixture was stirred at 75 °C for 8 h. The methyl ester was converted into a hydroxamic acid chelating ligand **2** which was accumulated by filtering and rinsing with 0.15 M HCl in methanol and H₂O, respectively.

2.5. Synthesis of PdNc-PHA

Ammonium tetrachloropalladate(II) (180 mg) and poly(hydroxamic acid) chelating ligand **2** (1.5 g) were combined in 50 ml of water and stirred for an hour at room temperature. The colour of the chelating ligand **2** was changed to a light brown colour, indicating that the coordination between palladium species and the hydroxamic acid ligands was successful. To this suspension, 0.5 mL of hydrazine hydrate was incorporated and the resulting dark brown color mixture was stirred at 25 °C for another 2 h. The dark brown colour palladium nanocomposite PdNc-PHA was filtered and cleaned with 0.5% of ammonium chloride aqueous solution (3×5 mL) to remove the unreacted palladium species within the cellulose backbone. Finally, it was washed with water and methanol to give the cellulose supported bio-heterogeneous poly(hydroxamic acid) palladium nanocomposite PdNc-PHA. ICP-AES analysis indicated the loading amount of Pd-species onto the cellulose supported PdNc-PHA was 0.3 mmol/g.

2.6. Mizoroki-Heck reaction

To a 10 mL glass vial, 1 mg (0.03 mol%) of PdNc-PHA, aryl/heteroaryl chloride (1 mmol), olefine (1.5 mmol), and Et₃N (3 mmol) were combined in 2.5 ml of DMA and stirred at 130 °C for 12 h. TLC and GC analysis were used to monitor the progress of the cross-coupling reaction. After the aryl halide had been completely consumed, the reaction mixture was diluted with water and ethyl acetate. The reaction mixture was centrifuged, and the PdNc-PHA was recovered by decantation. The reaction product was extracted with ethyl acetate, dried over MgSO₄, and concentrated under reduced pressure. The raw mixture was then purified using silica gel column chromatography using ethyl acetate : hexane eluent (1:4).

2.7. Michael addition reaction

A combination of amine or phenol/thiophenol (1 mmol), olefins (1.1 mol equiv), and PdNc-PHA (1 mg) in 5 mL of EtOH was stirred at 25 °C for 6 h. As eventually as the reaction was completed, the reaction mixture was diluted with ethyl acetate, and PdNc-PHA was recovered using the decantation method. The organic layers were evaporated using a rotary evaporator, and the pure Michael addition product was obtained after the crude product was purified using silica gel column chromatography with an ethyl acetate:hexane eluent (1:6).

3. Results and Discussion

3.1. Synthesis of palladium catalyst

The isolation and characterization of disposal corncob cellulose, as well as the synthesis of poly(methyl acrylate) **1** and poly(hydroxamic acid) chelating ligand **2**, were carried out in accordance with previously published work (M.L. Rahman et al., 2016, Mandal et al., 2017). To form the PdNc-PHA catalyst, an aqueous solution of ammonium tetrachloropalladate(II) [(NH₄)₂PdCl₄] was added into a stirred suspension of poly(hydroxamic acid) chelating ligand **2**. The reaction mixture turned into a light brown color suspension which confirmed the formation of the Pd(II) coordination bond between the hydroxamic acid ligands and palladium species. The suspension was then treated with an aqueous solution of hydrazine hydrate, and the resulting dark brown color suspension indicated that the Pd(II) complex was reduced to deliver the Pd (0) nanocomposite in the presence of hydrazine (Sreedhar et al., 2011). The solid materials were then filtrated off and rinsed with ammonium chloride solution, water and methanol respectively to give PdNc-PHA as

a dark color solid (Scheme 1).

3.2. FTIR analysis

The incorporated Pd-species were examined using inductively coupled plasma-atomic emission spectrometry (ICP-AES), and it was revealed that 0.3 mmol/g of palladium was incorporated onto the PdNc-PHA. The IR spectrum of bio-waste corncob cellulose demonstrated adsorption frequency band at 3428 cm⁻¹, 2915 cm⁻¹, and 1630 cm⁻¹, which were associated with the O-H, C-H stretching, and O-H bending modes, respectively (Fig. 1a) (Chuan et al., 2006). The cellulosic pyranose ring C-O-C vibration band was detected at 1064 cm⁻¹, and at 892 cm⁻¹ a tiny sharp peak correlated with the glycosidic C₁-H deformation of ring vibration participation and OH bending. Stretching of C=O and C-H resulted in an IR absorption band at 1734 cm⁻¹ and 2974 cm⁻¹ in the poly(methyl acrylate) **1** respectively (Fig. 1b). The poly(hydroxamic acid) ligand **2** displayed two new absorption bands at 1678 cm⁻¹ and 1647 cm⁻¹ respectively, which were associated with the stretching of the amide NC=O and NC-O (resonance structures). A broad band was also noticed at 3178 cm⁻¹ for N-H stretching and 1398 cm⁻¹ for OH bending mode (Fig. 1c). The IR peak of C=O for poly(methyl acrylate) **1** and poly(hydroxamic acid) ligand **2** were observed at 1734 cm⁻¹ and 1678 cm⁻¹ respectively. The shifting of the C=O peak indicates that poly(hydroxamic acid) ligand **2** was successfully synthesized within the polymer chain. Furthermore, the C=O stretching band in PdNc-PHA was shifted toward the lower wave number at 1660 cm⁻¹ due to the formation of a coordination bond between poly(hydroxamic acid) ligand **2** and palladium species, indicating the successful formation of PdNc-PHA.

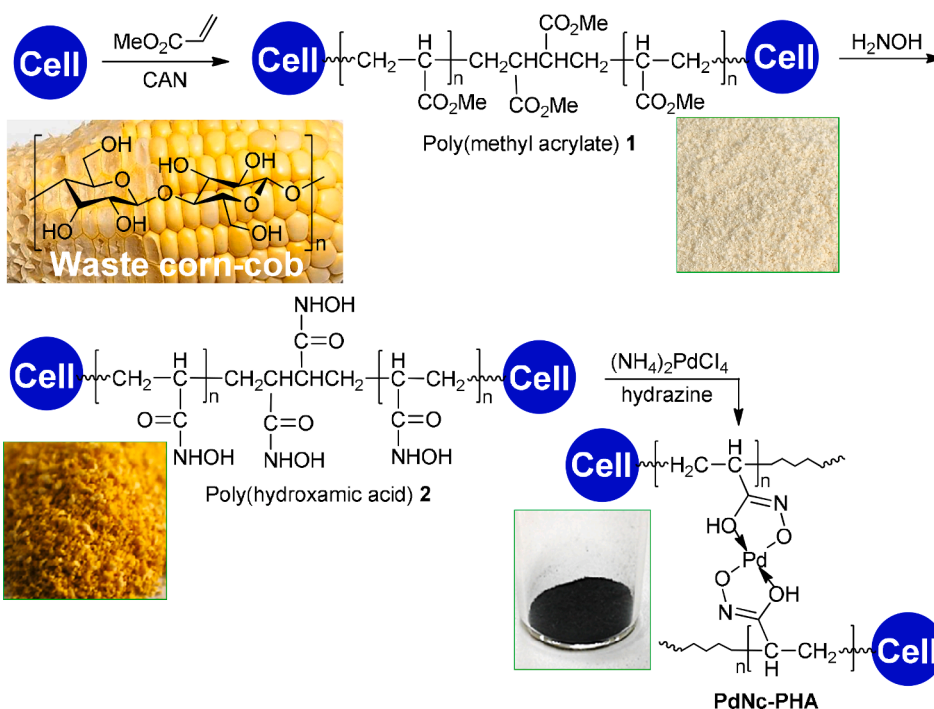
3.3. FE-SEM, EDX and TEM analysis

The FE-SEM images provide visual evidence of the successful synthesis of PdNc-PHA and support the results obtained from other characterization techniques. The FE-SEM images of fresh corncob cellulose showed a smooth surface morphology, as represented in Fig. 2a. However, after co-polymerization, small spherical shapes of poly(methyl acrylate) **1** was observed (Fig. 2b), indicating that the co-polymerization reaction was successful on the cellulose surface.

The next step involved treating poly(methyl acrylate) **1** with hydroxylamine to obtain chelating ligand **2** (Fig. 2c), which displayed a relatively bigger spherical morphology than **1**. Upon complexation of ligand **2** with (NH₄)₂PdCl₄, the FE-SEM image of PdNc-PHA showed aggregated, compact globular structures across the polymeric cellulose (Fig. 2d). These observations suggest that the chelating ligand **2** was able to bind to the palladium, forming compact structures across the polymeric cellulose backbone. This finding is consistent with the successful synthesis of PdNc-PHA, as the chelating ligand **2** plays an important role in facilitating the incorporation of palladium onto the cellulose surface.

The energy-dispersive X-ray (EDX) spectrum in Fig. 3 provided confirmation that palladium was successfully incorporated onto the polymeric cellulose backbone. This technique works by measuring the characteristic X-ray energy emitted by the sample, which can be used to determine the elemental composition of the material. In this study the EDX spectrum showed the presence of palladium in the PdNc-PHA. The ICP-AES analysis provided further quantitative information, indicating that the PdNc-PHA contained 0.3 mmol/g of palladium.

The HR-TEM image of PdNc-PHA (Fig. 4) revealed that the palladium composite were scattered throughout the polymeric cellulose backbone, indicating that the coordination of poly(hydroxamic acid) with the palladium species was successful. The size and distribution of the palladium complexes are important factors that can influence the catalytic properties of the material. To obtain information on the size and distribution of the palladium particle, we analysed about 190 palladium composite and found that the average diameter was 6.5 ± 0.2



Scheme 1. Detailed synthesis process of the catalyst PdNc-PHA.

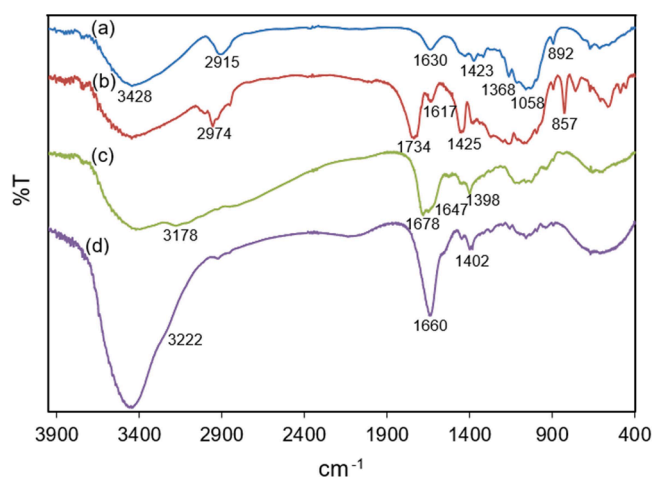


Fig. 1. FTIR spectra of (a) fresh corncob cellulose, (b) poly(methyl acrylate) **1**, (c) chelating ligand **2**, and (d) PdNc-PHA.

nm (Fig. 5).

3.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is an analytical technique that provides information about the chemical composition and electronic states of materials. It is a surface-sensitive technique that is particularly useful for studying thin films and surfaces. In the present study, XPS was used to investigate the chemical potential of the palladium species in PdNc-PHA. The wide scan XPS spectra of the poly(hydroxamic) ligand **2** and PdNc-PHA showed three peaks at 284.2 eV, 399.1 eV, and 531.3 eV, which correspond to the C 1s, N 1s, and O 1s spectra, respectively. The presence of these peaks in both materials indicated that the hydroxamic ligand **2** was present in PdNc-PHA (Fig. 6). However, two additional peaks were observed at 343.2 and 337.5 eV in the PdNc-PHA but not in the ligand **2**. These peaks were

indicative of the presence of the palladium species in the PdNc-PHA. The absence of these peaks in the ligand **2** suggested that the coordination of the poly(hydroxamic acid) ligands with the palladium species was responsible for the observed peaks.

To obtain more detailed information about the palladium species, we also studied the narrow scan profile XPS for palladium species (Fig. 7). This technique provided higher resolution and allowed the peaks to be assigned to specific palladium species. The two additional peaks observed in the PdNc-PHA were assigned to the Pd⁰ species Pd3d_{3/2} and Pd3d_{5/2}, respectively (Mandegani et al., 2015, Smith et al., 2005). These peaks provided valuable information on the chemical potential of the palladium species in PdNc-PHA. Fig. 7 showed the narrow scan spectrum of PdNc-PHA, which exhibited two signals at 340.5 eV and 335.2 eV corresponding to Pd3d_{3/2} and Pd3d_{5/2}, respectively. Smith et al (Smith et al., 2005) studied that the profile of Pd 3d photoemission can be monitored for the reduction of Pd²⁺ to Pd⁰ in the presence of 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid. During the 90 min analysis, the XPS spectrum showed decreased amount of Pd²⁺ available corresponding increase in the amount of Pd⁰. The almost complete reduction of Pd²⁺ (Pd3d_{3/2} and Pd3d_{5/2} corresponded to 342.7 and 337.5 eV, respectively) to Pd⁰ (Pd3d_{3/2} and Pd3d_{5/2} corresponded to 340.5 eV and 335.2 eV, respectively) is shown in Fig. 7.

3.5. Application of catalyst

Following characterization of the PdNc-PHA, the catalytic performance was investigated for the Mizoroki-Heck reaction. The Heck reaction between aryl chlorides and olefins is a favourable synthetic strategy for industrial applications due to the wide availability of low-cost aryl chlorides. To evaluate the efficacy of PdNc-PHA in the Heck reaction, we conducted a screening experiment where we varied the solvent and bases while keeping the catalyst dosage, temperature, and reaction time constant. The results of the screening experiment can be found in Table 1 of the supplementary information. Through several iterations, we determined that the optimal conditions for achieving a high yield in the cross-coupling reaction were using 0.03 mol% of PdNc-PHA as the catalyst, DMA as the solvent, and triethylamine as the base. Results demonstrate the importance of optimization of reaction

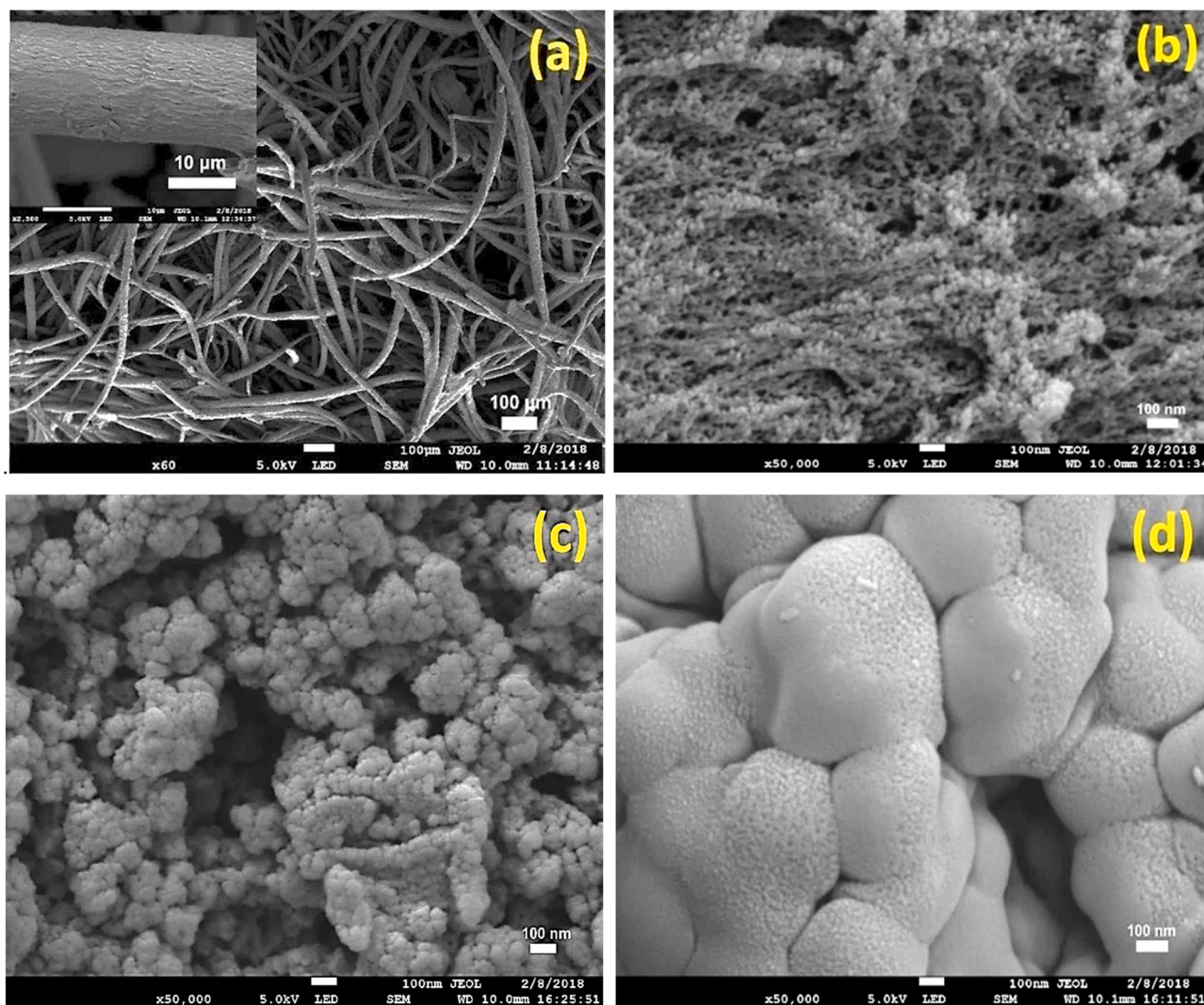


Fig. 2. FE-SEM images of (a) corncob cellulose, (b) poly(methyl acrylate) 1, (c) chelating ligand 2, (d) PdNc-PHA.

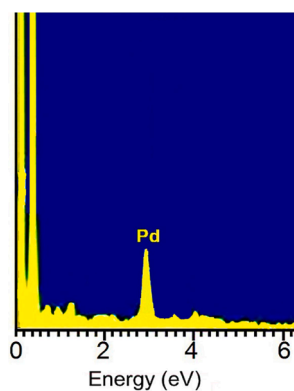


Fig. 3. EDX-spectra of PdNc-PHA.

conditions to maximize the efficiency of the Heck reaction when using PdNc-PHA as the catalyst. Under the optimized reaction conditions, we conducted the Mizoroki-Heck reaction with various olefins and aryl chlorides at 130 °C for 12 hours using 0.03 mol% PdNc-PHA and three mole equivalents of triethylamine, as outlined in Table 1. This allowed us to explore the versatility of this catalyst system in a range of reactions, which is crucial for its potential application in the synthesis of

substituted alkenes. By conducting reactions under optimized conditions, high yields of the desired products were obtained. Furthermore, the successful coupling of various aryl chlorides with olefins provides valuable insights into the scope and limitations of this catalyst system.

The PdNc-PHA demonstrated excellent catalytic performance in the coupling of substituted activated and deactivated aryl chlorides with methyl acrylate, yielding up to 93% of the corresponding coupling products 3a-f. Aryl chlorides bearing an electron withdrawing nitro group provided higher yields of the corresponding coupling product 3c. The 4-chlorobenzyl alcohol bearing a free hydroxyl group in 3d was not affected during the cross-coupling reaction. Aryl chlorides were investigated with butyl acrylate and *N*-isopropyl acrylamide to produce the associated coupling products 3g-l in 86–94% yields respectively. Studies showed that the amide bond was not affected under the reaction conditions. A bulky and relatively less reactive styrene was coupled with 4-cyano and 4-methoxy chlorobenzene to afford the products 3m and 3n with 90% and 88% yield respectively. Heterocyclic organic compounds have important medicinal and biological applications, and several of their respective derivatives can be easily synthesised by metal catalysed reactions (Gilchrist, 2001, Collins, 2002). As such, the chloro-substituted thiophene, pyridine, quinolone and pyrimidine were reacted with methyl, butyl and *N*-isopropylacrylamide to give 3o-v with 87–94% yield thereby highlighting the potential of PdNc-PHA in the synthesis of medicinal and pharmaceutical compounds.

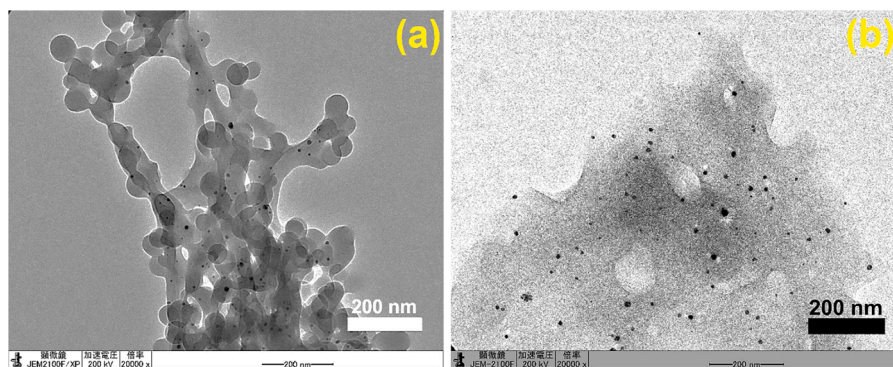


Fig. 4. HR-TEM image of (a) fresh PdNc-PHA, (b) 3rd reused of PdNc-PHA.

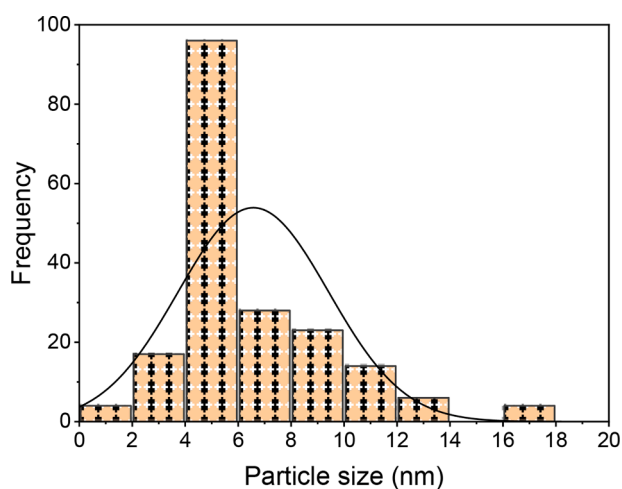


Fig. 5. Palladium nanoparticles size distribution of PdNc-PHA.

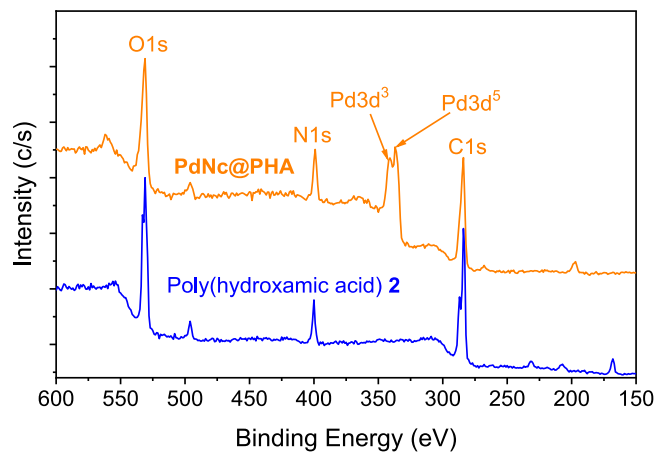


Fig. 6. Full scan XPS of poly(hydroxamic acid) 2 and PdNc-PHA.

The efficiency of PdNc-PHA was then investigated for applicability to di-substituted aryl chlorides. The PdNc-PHA (0.05 mol%) promoted Heck reaction of di-substituted aryl chlorides in presence of three mol equivalent of olefins and six mol equivalent of Et₃N under the same reaction conditions. Thiophene, pyridine and pyrimidine are known as π -electron deficient heterocyclic aromatic compounds (Berthiol et al., 2002). Interestingly, all heterocyclic aryl chlorides produced the desired corresponding coupling products with high yield. The 1,4-dichlorobenzene, 4,4'-dichloro-1,1'-biphenyl, 9,10-dichloroanthracene were smoothly proceeded Heck reaction with methyl and butyl acrylate to

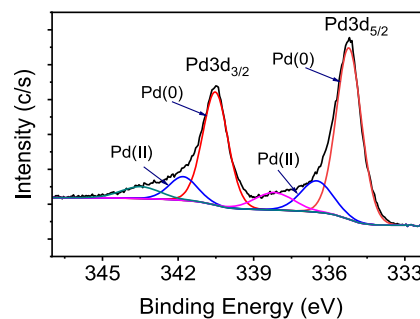
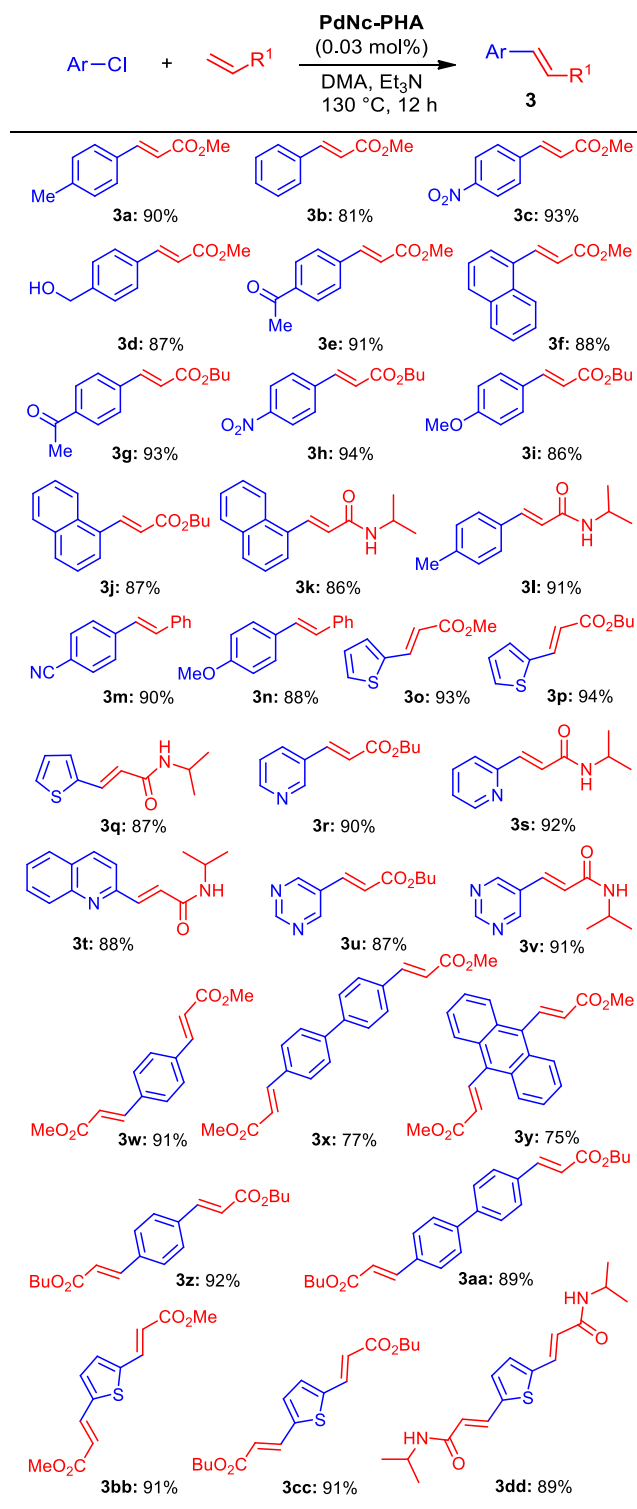


Fig. 7. Narrow-scan XPS of PdNc-PHA.

provide the respective cross-coupling products **3w-aa** with a 75–92% yield. The 4,4'-dichloro-1,1'-biphenyl and 9,10-dichloroanthracene were displayed lower yields of the coupling products due to their low reactivity and solubility in the DMA solvent. The associated cross-coupling products **3bb-3dd** with up to 91% yield were delivered by smoothly coupling of 2,5-dichlorothiophene with the methyl, butyl, and *N*-isopropylacrylamide. Based on the obtained results, it can be concluded that the PdNc-PHA catalyst exhibited outstanding catalytic activity for the Heck reaction involving both activated and inactivated aryl chlorides, as well as heterocyclic aryl chlorides.

The development of heterogeneous and efficient catalysts for organic transformations is an ongoing effort in the field of chemical synthesis. The present study aims to provide a systematic comparison of some existing heterogeneous Heck coupling protocols with the newly developed PdNc-PHA catalyst. Table 2 summarizes the results obtained from comparing the reaction time, loading of palladium species, and product yields for the reaction of chlorobenzene and 4-chloronitrobenzene using PdNc-PHA and other previously reported catalysts (M. Niakan et al., 2021, Ashiri and Mehdipour, 2018, Lv and Zhang, 2017, Calò et al., 2004, Firouzabadi et al., 2012, Khazaei et al., 2013, Nezhad and Panahi, 2011, Parouch et al., 2021). The results clearly indicate that PdNc-PHA has outstanding catalytic activity and shows significant advantages over the reported methods. The use of waste corn cob cellulose as a starting material for the synthesis of PdNc-PHA not only offers a utilization of bioresource approach but also demonstrates the concept of waste-to-wealth in chemical synthesis. The use of a small amount of PdNc-PHA (0.03 mol% of Pd) compared to other catalysts is another notable advantage of the present protocol. This feature not only contributes to the cost-effectiveness of the reaction but also reduces the amount of waste generated during the process. The excellent activity of PdNc-PHA suggests its potential for use in other organic transformation reactions that require palladium catalysts.

The fabrications of C-S, C-O, and C-N bonds through the Michael addition reaction is a major impetus for establishing an effective method for the fabrication of novel essential materials. Michael addition

Table 1Heck reaction of aryl chloride and aryl dichlorides^a.

^a All reactions were performed using mono/dichlorobenzene (1.0 mmol), acrylate (1.5/3.0 mmol), 0.03/0.05 mol% of PdNc-PHA and 3.0/6.0 mmol of Et₃N in 2.5 mL of DMA for 12 h.

reaction has recognized itself as the most efficient and widely used method for the preparation of heteroatomic compounds. These chemical bonds formation have drawn greater attention because they have numerous uses in the synthesis of biologically active natural products,

pesticides, antimicrobials, food ingredients, detergents, pharmaceuticals, polymers, and other nitrogen, oxygen, and sulfur-containing biomolecules that are extremely important in daily life (Dunbar et al., 2017, Yang and Chen, 2009, Acton, 2012, Backvall, 2002, Kondo and Mitsudo,

Table 2

Comparison of PdNc-PHA with previous Pd-based heterogeneous catalysts for the Heck coupling of aryl halides and olefins (M. Niakan et al., 2021, Ashiri and Mehdipour, 2018, Lv and Zhang, 2017, Calò et al., 2004, Firouzabadi et al., 2012, Khazaei et al., 2013, Nezhad and Panahi, 2011, Parouch et al., 2021).

Entry	Catalyst (Pd mol%)	Aryl chloride	Olefin	Reaction conditions	Yield % and TON	Ref
1	GO-Fe ₃ O ₄ -cellulose-Pd (0.75)	Chlorobenzene	Methyl acrylate	DMAC: Gly (1:2), K ₂ CO ₃ , 100 °C, 20 h	92 123	(M. Niakan et al., 2021)
2	GO/CS-NPs -cellulose nanowhiskers-Pd-hydrogel (0.25)	Chlorobenzene	Methyl acrylate	EtOH/H ₂ O, K ₂ CO ₃ (1.5 equiv.) 85 °C, 30 min	81 324	(Ashiri and Mehdipour, 2018)
4	Pd-(OCMCS) (2)	4-chloronitrobenzene	<i>tert</i> -Butyl acrylate	DMF, Et ₃ N (1.5 equiv.), 140 °C, 12 h	51 26	(Lv and Zhang, 2017)
5	Pd-NPs/Chitosan (0.35)	4-chloronitrobenzene	<i>tert</i> -Butyl acrylate	TBAA, TBAB (2.0 equiv.) 130 °C, 15 min	90 257	(Calò et al., 2004)
6	Agarose/Pd nano (0.52)	Chlorobenzene	Butyl acrylate	PEG 400, Et ₃ N (2.0 equiv.) 120 °C, 24 h	65 125	(Firouzabadi et al., 2012)
7	Pd-nano/Pectin (0.28)	Chlorobenzene	Butyl acrylate	Solvent free, n-Pr ₃ N (1.5 equiv.) 140 °C, 18 h	70 250	(Khazaei et al., 2013)
8	Pd nano-PNP-SSS (1.2)	4-chloronitrobenzene	Ethyl acrylate	H ₂ O, K ₂ CO ₃ (2.0 equiv.), 100 °C, 2 h	87 73	(Nezhad and Panahi, 2011)
9	Fe ₃ O ₄ @fbroin-Pd (0.15)	Chlorobenzene	Methyl acrylate	DMF, Et ₃ N (1.0 equiv.) 100 °C, 35 min	45 300	(Parouch et al., 2021)
10	PdNc-PHA (0.03)	4-chloronitrobenzene	Methyl acrylate	DMA, Et ₃ N (3.0 equiv.), 130 °C for 12 h	93 3100	Present work
11	PdNc-PHA (0.03)	chloronitrobenzene	Methyl acrylate	DMA, Et ₃ N (3.0 equiv.), 130 °C for 12 h	81 2700	Present work

TON = No of mole of Product/No of mole of Catalyst

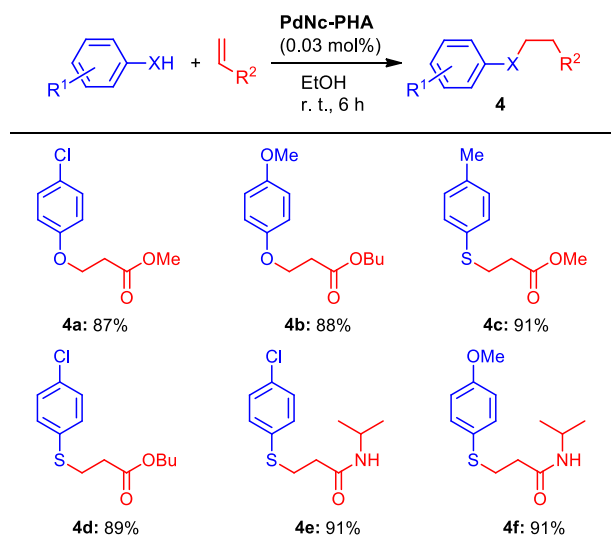
2000, Alt et al., 2013). The applicability of the PdNc-PHA to *thia*- and *oxa*-Michael addition reaction with conjugated alkenes was then investigated. The addition reactions were carried out using 0.03 mol% PdNc-PHA at room temperature in ethanol for 6 h. The 4-chloro and 4-methoxyphenols were combined with methyl and butyl acrylates to produce the corresponding *O*-alkylated products **4a** and **4b** with yields of 87% and 88%, respectively (Table 3). The 4-methyl and 4-chloro substituted thiophenols were also investigated with Michael addition reactions using methyl and butyl acrylates, yielding *S*-alkylated products **4c** and **4d** with 91% and 89% yields respectively. *N*-isopropylacrylamide was the reacted with 4-chloro and 4-methoxy thiophenol to produce the corresponding *S*-alkylated products **4e** and **4f** with 91% yield. S. Banerjee et al (Payra et al., 2016) previously developed a magnetic NiFe₂O₄ nanoparticle capable of catalysing Michael additions of aromatic/aliphatic amines, alcohols, and thiols to

conjugated alkenes at room temperature. To achieve the high yield in the Michael addition product 4 mol% of NiFe₂O₄ was employed. This is more than one hundred times higher loading than the catalyst developed herein.

We further expanded our investigations into the aza-Michael addition reactions of aliphatic cyclic and alicyclic amines as presented in Table 4. These results demonstrate the potential for this catalyst to be utilized in the synthesis of a variety of functionalized cyclic and alicyclic compounds, with implications for drug development and other areas of chemical research. The aza-Michael addition reactions were conducted in accordance with Table 3. When dibutyl, dibenzyl, and piperidine were investigated via addition reaction with methyl acrylate, *N*-alkylated products **5a-c** with high yields of up to 94% (entries 1–3) were obtained. Furthermore, the addition reaction of a piperidine derivative containing a tertiary alcohol group with butyl acrylate provided the

Table 3

Michael addition reaction of phenol and thiophenol^a.



^a All reactions were performed using 1.0 mmol of phenol/thiophenol, 1.1 mol equiv. of olefin, 0.03 ml% of PdNc-PHA in 5.0 mL of EtOH at room temperature.

Table 4
Michael addition reaction of amine^a.

PdNc-PHA
(0.03 mol%)
EtOH
r.t., 6 h

Entry	Amine	Olefin	Product
1	Bu ₂ NH		 5a : 90%
2			 5b : 94%
3			 5c : 92%
4			 5d : 88%
5			 5e : 91%
6			 5f : 90%
7			 5g : 87%
8			 5h : 89%
9 ^b			 5i : 86%

^a Reaction conditions: 1.0 mmol of amine, 1.1 mol equiv of olefin (for **5i**, 2.2 mol equiv), 0.03 mol% of **PdNc-PHA** in 5.0 mL of EtOH at room temperature. ^bMethyl acrylate was used 2.2 mol equiv. and **PdNc-PHA** 0.06 mol%.

corresponding product **5d** with 88% yield (entry 4).

The addition reaction of morpholine and dibenzyl amine with butyl acrylate synthesised the respective *N*-alkylated products **5e** and **5f** with 91% and 90% yield respectively (entries 5, 6). Similarly, when piperidine and dibenzyl amine were treated with acrylonitrile, the corresponding products **5g** and **5h** were also produced with 87% and 89% yields respectively (entries 7, 8). Furthermore, a primary cyclic amine i. e. cyclohexyl amine, reacted with 2.2 mol equivalent of methyl acrylate in presence of 0.06 mol% of **PdNc-PHA** to provide the corresponding dialkyl product **5i** with 86% yield (entry 9).

3.6. Reusability study

The reusability of heterogeneous catalysts has significant advantages in terms of industrial applicability, as it reduces waste and resource

consumption by allowing the same catalyst to be used for multiple catalytic cycles. This approach can also be cost-effective, as it saves cost on catalyst production, purification, and disposal. Additionally, the use of heterogeneous catalysts can be more environmentally friendly than homogeneous catalysts because they can be separated more easily from the reaction mixture, preventing contamination of the products and reducing the amount of waste generation. Fig. 8 shows the recyclability of the **PdNc-PHA** catalyst for the Heck reaction. The recycle reaction was carried out using 4-nitrochlorobenzene and butyl acrylate according to Table 1. After the initial run of reaction, the reaction mixture was diluted with ethyl acetate, and the reaction vessel was centrifuged. The next step involved a decantation procedure to separate the ethyl acetate layer. The **PdNc-PHA** remained into the vessel and it was dried at 60 °C for 2 h. The **PdNc-PHA**-containing reaction vial was then filled with aryl chloride, butyl acrylate, Et₃N, DMA and heated under the same reaction

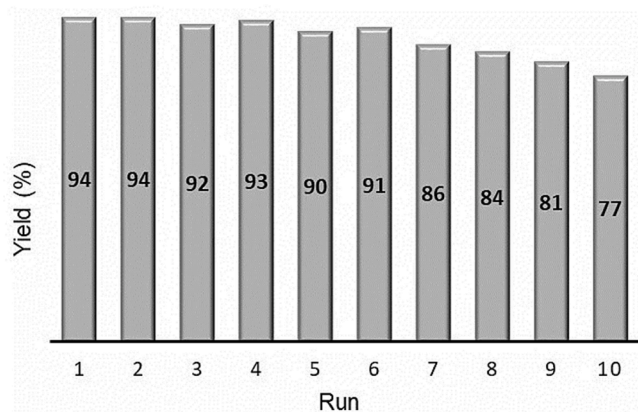


Fig. 8. Recycle of the PdNc-PHA in the Heck reaction.

conditions (Table 1, 3 h). The PdNc-PHA was reused ten times consecutively with only a minor reduction in catalytic activity being observed due to the loss of PdNc-PHA during the decantation process.

The spent catalyst was then characterised using HR-TEM. HR-TEM analysis (Fig. 4b) of the third reuse of PdNc-PHA revealed that the palladium complexes were of similar size and remained unaggregated, indicating the stability of the catalyst and potential to maintain high catalytic performance even after multiple uses. Therefore, the cellulose-supported bio-heterogeneous PdNc-PHA is believed to be a practical approach for organic syntheses.

To assess the heterogeneity of PdNc-PHA, a hot filtration investigation (Fig. 9) was conducted on the Heck reaction using 4-chloroacetophenone and butyl acrylate under standard reaction conditions. After allowing the reaction to proceed for three hours, the mixture was filtered under hot conditions, and the resulting filtrate was returned to the reaction vial and heated under identical conditions. GC analysis was used to monitor the post-reaction progress, and it was observed that the reaction did not progress further after the catalyst was removed. Additionally, ICP-AES analysis of the filtrate further confirmed that no palladium was lost during the hot filtration process. This evidence supports the assumption that the Heck reaction occurs under a heterogeneous reaction medium, suggesting the PdNc-PHA catalyst maintains its heterogeneity during the reaction.

4. Conclusion

In conclusion, we have successfully synthesized and characterized a highly active recyclable heterogeneous cellulose-supported biopolymeric PdNc-PHA catalyst. The PdNc-PHA catalyst demonstrated remarkable catalytic efficiency in the Mizoroki-Heck coupling reaction of aryl/heteroaryl chlorides with a broad range of olefins, resulting in the desired coupling products with excellent yields. Furthermore, we conducted the Michael addition reaction of amines, phenols, and thiophenols with olefins using PdNc-PHA and observed the respective addition products with high yields. We rinsed the supported PdNc-PHA catalyst with solvent and activated it by drying while it was still inside the reaction vial. The catalyst was robust, allowing for recycling and reuse up to ten times without any noticeable loss of catalytic activity.

CRedit authorship contribution statement

Shaheen M. Sarkar: Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Conceptualization. **Md Lutfur Rahman:** Writing – review & editing, Writing – original draft, Resources, Methodology, Conceptualization. **Kamrul Hasan:** Writing – review & editing, Writing – original draft, Visualization. **Md. Maksudur Rahman Khan:** Writing – review & editing, Writing – original draft, Visualization. **Emmet J. O'Reilly:** Writing – review & editing, Writing –

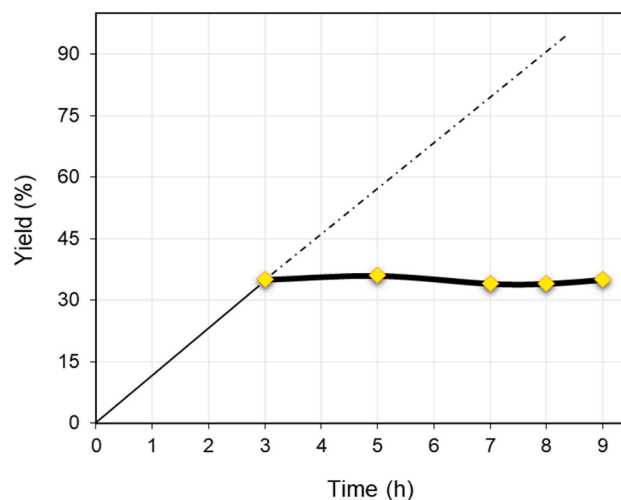


Fig. 9. Heterogeneity test of PdNc-PHA.

original draft, Visualization, Validation. **Mohd Hasbi Ab. Rahim:** Writing – review & editing, Writing – original draft, Visualization.

Declaration of competing interest

The authors declare no competing financial interests.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.carpta.2024.100578](https://doi.org/10.1016/j.carpta.2024.100578).

Data availability

Data will be made available on request.

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