

Biomacromolecule supported N-heterocyclic carbene-palladium(II) as a novel catalyst for Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions

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Abstract

The field of catalysis is ever flourishing to meet the challenges faced in our day-to-day needs keeping in mind the environmental concerns. In line with this quest, a new *N*-heterocyclic carbene-palladium(II) complex grafted on cellulose, a naturally available biomacromolecule from agriculture waste sugarcane bagasse (Cellu@NHC-Pd) was synthesized as a heterogeneous catalyst. The facile multistep synthesis was achieved using low-cost chemicals and mild reaction conditions. The characterization of the Cellu@NHC-Pd heterogeneous catalyst by various analytical techniques such as FT-IR, FE-SEM, EDS, HR-TEM, TG/DTA, ICP-OES and *p*-XRD confirmed its structure, morphology, thermal stability and chemical composition. The Cellu@NHC-Pd heterogeneous catalyst was successfully investigated for its catalytic ability in Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions under green reaction medium at ambient temperature. The heterogeneous catalyst was examined for its catalytic effectiveness in the cross-coupling reactions for various parameters like solvent, base, temperature, time and catalyst loading. Additionally, the developed heterogeneous catalyst showed very good tolerance to a variety of functional groups. Being heterogeneous, the catalyst could be easily recovered by simple filtration. The Cellu@NHC-Pd heterogeneous catalyst can be additionally probed for its catalytic excellence in other applications.

1. Introduction

Catalysts, being the backbone of most reactions, play a vital role by decreasing the energy of activation thereby the reaction time, and providing good yields by increasing the conversion rate (Rafieian et al. 2019). Of the different types of catalysts; heterogeneous and homogeneous, though having their own advantages and disadvantages, have shown flourishing developments in profitable ways for industries (Polshettiwar et al. 2011; Singh and Tandon 2014). Although homogeneous catalysts have advantages like good activity due to high catalytic surface, the separation and reusability of the catalyst is a major issue (Ghiaci et al. 2014; Wang et al. 2014). On the other hand, in heterogeneous catalysis as the phases are different, the efficiency for reaction though hampered, the recovery of the catalyst after reaction is easy (Polshettiwar et al. 2011; Vishal et al. 2017). Therefore, great efforts have been made to develop economical and efficient semi-heterogeneous catalysts, with the pros of both homogeneous and heterogeneous nature, for industrial purposes (Ghiaci et al. 2014; Kandathil et al. 2017; Khazaei et al. 2013).

In this new era of research, the development in cross-coupling reactions has led to new pathways in research approach. An important organic transformation in synthetic organic chemistry is the cross-coupling reactions for the formation of new C-C/C-N bond formation (Ghiaci et al. 2014). One of the most frequently used cross-coupling reactions is the Suzuki-Miyaura cross-coupling reaction (Rajabi et al. 2015). The cross-coupling reaction has gained great attention for its excellent ability and features, for instance easy availability of starting materials (aryl halides and arylboronic acids), resistance to air and moisture, high tolerance to various functional groups, mild reaction conditions and formation of non-toxic by-products (D'Alterio et al. 2021; Gujral et al. 2012; Kandathil et al. 2018). The Suzuki-Miyaura cross-coupling reaction is widely used in the synthesis of pharmaceutical drugs, compounds of biochemical

and agrochemical importance, supramolecular chemistry, engineering materials, conducting polymers, molecular wires, to name a few (Dong et al. 2020; Hooshmand et al. 2019; Kempasiddaiah et al. 2021).

In addition to Suzuki-Miyaura cross-coupling reaction, Mizoroki-Heck cross-coupling reaction has also gained a lot of importance due to its remarkable effectiveness and ease in carrying out the reaction (Heck and Nolley Jr 1972; Mirza-Aghayan et al. 2020). The Mizoroki-Heck cross-coupling reaction is appealing due to its gentle reaction conditions, nominal toxicity and affordable reagents (Köhler et al. 2007; Kumar et al. 2012). The reaction leads to the formation of higher functionalized olefinic cross-coupled products in multistep industrial synthesis of bioactive natural products, drugs and functional materials (Kandathil et al. 2017).

In transition metal catalysis, complexes of the noble metal palladium have been extensively used as catalysts in various organic transformations (Baran et al. 2018; Dong et al. 2020). Palladium, being expensive, increases the cost of production of the cross-coupled products on a commercial scale (Antony et al. 2021). This can be overcome by effective and quantitative recovery and reuse of the catalyst (Selander and Szabó 2011). However, the nature of ligands presents in the metal complexes influence their catalytic activity and stability. Currently, *N*-heterocyclic carbenes (NHCs) are widely explored due to its significantly better functionality than phosphine as suitable ligands (Ranganath et al. 2013). These NHCs have benefits like ease of synthesis, higher dissociation energy, less toxicity, high thermal and moisture stability, minimal metal leaching and have σ -donor and π -acceptor ability as good as phosphine ligand (Cruden and Allen 2004; Ranganath et al. 2013; Wang et al. 2014). A wide range of NHC-Pd based catalysts have been widely employed as catalytic system for Suzuki-Miyaura and Mizoroki- Heck cross-coupling reactions (Nahra and Cazin 2021; Peh et al. 2009). The NHC-Pd based catalysts have been recognized due to its exceptional tuneable properties and ligand flexibility increasing its employability as catalytic system (Nahra and Cazin 2021). Both homogeneous and heterogeneous Pd-NHC complex as catalysts have been used as catalytic system cross-coupling reactions. The major drawback of the homogeneous Pd-NHC complex as catalyst is the residual palladium by-product and inconvenience in recyclability (Fortman and Nolan 2011; Rajabi et al. 2015). In contrast, heterogeneous catalysts can be easily separated and reused, hence shows the ability for commercialization and industrial scale application (D'Alterio et al. 2021; Hooshmand et al. 2019). One of the methods for heterogenization of a catalyst is by attaching the homogeneous catalytically active site onto an inert heterogeneous support material. Various materials have been used as supports like, silica, metal oxides, carbon nanotubes (CNTs), 2D materials such as carbon nitride and boron nitride (Antony et al. 2021), polymers etc (Wang et al. 2014). One such support is cellulose, a polymer of glucose units, which can be a potential alternative material for catalyst support (Xie et al. 2016). Compared to other support materials, cellulose being naturally and abundantly available biomaterial, is biodegradable and therefore environmental friendly (Dong et al. 2020; Kandathil et al. 2018). The presence of hydroxyl groups makes it an excellent choice for functionalization and can be easily modified to one's need (Kale et al. 2017). The NHC-palladium complex can be immobilized onto the modified cellulose support making it feasible for separation and therefore an excellent heterogeneous catalyst for various organic transformations (Kale et al. 2017; Rahmatpour 2011).

Herein, we report the synthesis of cellulose tethered *N*-heterocyclic carbene-palladium(II) complex as heterogeneous catalyst carried out through a facile sustainable approach. The synthesized heterogeneous catalyst was investigated for its catalytic efficiency in Suzuki-Miyaura cross-coupling reaction and Mizoroki-Heck cross-coupling reaction where it demonstrated high catalytic performance in green solvent medium and ambient reaction conditions. Also, the influence of various parameters and recyclability were also investigated.

2. Experimental Section

2.1. Materials

All solvents were purified per standard methods prior to use. Unless otherwise stated, all reactions were performed under aerobic conditions in oven-dried glassware with magnetic stirring. The sugarcane bagasse was obtained from local juice shop in Bengaluru, India. Benzimidazole, isopentyl bromide, (3-chloropropyl)triethoxysilane, palladium(II) acetate, aryl halides, arylboronic acids, bases and solvents were purchased from Avra and Sigma-Aldrich chemical companies and were used without further purification. Heating was accomplished by either a heating mantle or silicone oil bath. Column chromatography was conducted on silica gel 60–120 mesh (Merck) and thin layer chromatography was carried out using 0.25 mm Merck TLC Silica gel plates with UV light as a visualizing agent. Yields refer to chromatography pure material. Concentration *in vacuo* refers to the removal of volatile solvent using a rotary evaporator attached to a dry diaphragm (10–15 mm Hg) followed by pumping to a constant weight with an oil pump (300 mTorr). All the organic products were known and identified by comparison of their spectral data with those of authentic samples.

2.2. Instrumentation and analysis

Fourier transform infrared spectra (FT-IR) were recorded with a PerkinElmer spectrum two spectrometer. Field-emission scanning electron microscopy (FE-SEM) along with energy-dispersive X-ray spectroscopy (EDS) to observe morphology and determine elemental distributions, respectively, were conducted with a JEOL model JSM7100F. The elemental palladium content of the nanocatalyst was determined with a Perkin Elmer Optima 5300 DV inductively coupled plasma optical emission spectrometer (ICP-OES). High resolution transmission electron microscopy (HR-TEM) images were obtained using a Jeol/JEM 2100 microscope. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was carried out with a PerkinElmer Diamond TG/DTA with a heating rate of 10.0°C min⁻¹. Powder X-ray diffraction (*p*-XRD) patterns were obtained using Rigaku X-ray diffraction Ultima-IV.

2.3. Extraction of cellulose from agriculture waste sugarcane bagasse (Cellu) (1)

Cellulose was extracted from waste sugarcane bagasse obtained after extraction of sugar by alkaline treatment as reported in our previous work (Kandathil et al. 2019). In short, the sugarcane bagasse was sun-dried, cut into small pieces and treated with 5% NaOH solution at 85°C for 6 h with stirring. The pulp

obtained was separated by centrifugation, washed with water thoroughly till neutral pH was attained and dried overnight at 50°C to yield cellulose (1).

2.4. Synthesis of silyl chloride functionalized cellulose (Cellu@SC) (3)

Silyl functionalization of the cellulose support was carried out as reported by Rafeian *et al* with some modification (Rafeian et al. 2019). Into a round bottom flask with distilled water (20 mL), (3-chloropropyl)triethoxysilane (2 mL) (2) was added and the pH was adjusted to ~ 4 using glacial acetic acid. To the above mixture plant-based cellulose was dispersed by sonication. The reaction mass was magnetically stirred for 2 h at 120°C. This pale-yellow silyl chloride functionalized cellulose (Cellu@SC) (3) was centrifuged, washed with water (1 x 20 mL), methanol (2 x 20 mL) and water (1 x 20 mL), and dried at 50°C for 24 h.

2.5. Synthesis of 1-isopentyl-1H-benzo[d]imidazole (6)

Benzimidazole (2 g, 16.92 mmol) (4) was dissolved in DMSO (40 mL). Potassium hydroxide (1.42 g, 25.39 mmol) was added and heated at 100°C till it dissolved. The temperature was then reduced to 40°C and isopentyl bromide (2.56 g, 16.92 mmol) (5) was added in one portion and stirred at same temperature for 2 h (monitored by TLC). On completion, the reaction mixture was cooled and transferred to ice cold water (20 mL). The separated oily layer was extracted with DCM, washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to obtain 1-isopentyl-1H-benzo[d]imidazole (6). Yield: 96%. ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.87 (s, 1H), 7.83–7.77 (m, 1H), 7.40–7.36 (m, 1H), 7.30–7.24 (m, 2H), 4.15–4.12 (m, 2H), 1.75 (dd, *J* = 14.9, 7.1 Hz, 2H), 1.58 (m, *J* = 13.4, 6.7 Hz, 1H), 0.96 (d, *J* = 6.7 Hz, 6H). FT-IR (KBr method) (cm⁻¹): 3058 (aromatic C-H str), 2957 & 2930 (aliphatic C-H str), 2872 (C-H str), 1615, 1496, 1460 (C = C str & C-H ben) 1286 (C-N str), 890 (C = C ben), 734 (C-H ben). Mass data (m/z, GC-MS): 188(C₁₂H₁₆N₂), 131 base peak C₈H₇N₂), 77(C₆H₅) (Fig. S1-S3).

2.6. Synthesis of 1-isopentyl-1H-benzo[d]imidazole incorporated cellulose (Cellu@NHC) (7)

Into toluene (80 mL), Cellu@SC (2 g) (3) and 1-isopentyl-1H-benzo[d]imidazole (1 g) (6) were dispersed and heated at 100°C for 48 h. The product was filtered, washed with methanol (2 x 20 mL) and water (2 x 20 mL), and the obtained 1-isopentyl-1H-benzo[d]imidazole incorporated cellulose (Cellu@NHC) (7) was dried 50°C for 24 h.

2.7. Synthesis of cellulose tethered N-heterocyclic carbene-palladium(II) complex as heterogeneous catalyst (Cellu@NHC-Pd) (8)

Cellu@NHC (1.8 g) (7) and Pd(OAc)₂ (0.36 g) were dispersed in DMF (36 mL) by sonication and stirred at 60°C for 24 h. The desired cellulose tethered N-heterocyclic carbene-palladium(II) complex (Cellu@NHC-

Pd) (8) was obtained as blackish brown fibrous product. The Cellu@NHC-Pd heterogeneous catalyst was filtered, washed with methanol (2 x 20 mL) and water (2 x 20 mL), and dried 50°C for 24 h.

2.8. General procedure for the Cellu@NHC-Pd catalysed Suzuki-Miyaura cross-coupling reaction

The catalytic activity of the synthesized Cellu@NHC-Pd heterogeneous catalyst was investigated in Suzuki-Miyaura cross-coupling reaction. Aryl halide (1 equiv.), aryl boronic acid (1.1 equiv.), potassium carbonate (2.5 equiv.) and Cellu@NHC-Pd heterogeneous catalyst (2.22 mol% Pd) were taken in EtOH:H₂O mixture (1:1, 6 mL) and sonicated for 5 min. The reaction mass was then stirred at room temperature for the required period of time. The progress of the reaction was monitored by TLC periodically. On completion of the reaction, the catalyst was separated by simple filtration and the residual reaction mass was extracted using DCM (2 x 20 mL). The organic layer was washed with water (1 x 10 mL) and brine solution (1 x 10 mL), and dried over anhydrous Na₂SO₄. The product obtained by concentrating the organic layer *in vacuo* was purified through column chromatography using hexane and ethyl acetate as eluents and analysed by ¹H NMR spectroscopy.

1. *4-Methoxybiphenyl* (Table 2, entries 1 and 2): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.46 (dd, *J* = 10.2, 8.8 Hz, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H).
2. *4-Chloro-4'-methoxybiphenyl* (Table 2, entry 3): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.39 (t, *J* = 8.1 Hz, 4H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 3.76 (s, 3H).
3. *4'-Methoxybiphenyl-4-carboxylic acid* (Table 2, entry 4): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 9.87 (s, 1H), 8.06 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 2H), 3.80 (s, 3H).
4. *4-Hydroxybiphenyl* (Table 2, entries 5, 6 and 7): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.47 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.81 (s, 1H).
5. *4-Chloro-4'-hydroxybiphenyl* (Table 2, entry 8): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.35 (t, *J* = 8.3 Hz, 4H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 2H), 5.04 (s, 1H).
6. *4'-Hydroxybiphenyl-4-carboxylic acid* (Table 2, entry 9): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 9.83 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H).
7. *4-Methylbiphenyl* (Table 2, entry 10): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.61 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.31–7.27 (*m*, 2H), 2.43 (s, 3H).
8. *Biphenyl* (Table 2, entries 11, 12 and 13): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.52 (d, *J* = 7.5 Hz, 4H), 7.37 (t, *J* = 7.6 Hz, 4H), 7.27 (t, *J* = 7.3 Hz, 2H).
9. *4-Chlorobiphenyl* (Table 2, entry 14): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.47 (d, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H).
10. *4-Biphenylcarboxylic acid* (Table 2, entries 15, 22 and 23): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 8.02 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* =

7.3 Hz, 1H).

11. *4-Nitrobiphenyl* (Table 2, entries 16 and 17): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 8.22 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 7.3 Hz, 2H), 7.46–7.32 (m, 4H).
12. *4-Acetylbiphenyl* (Table 2, entry 18): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 7.95 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 7.3 Hz, 1H), 2.55 (s, 3H).
13. *4-Biphenylaldehyde* (Table 2, entry 19): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 9.95 (s, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.32 (d, J = 7.2 Hz, 1H).
14. *2-Biphenylaldehyde* (Table 2, entry 20): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 9.91 (s, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.44–7.40 (m, 2H), 7.35 (dd, J = 33.5, 7.7 Hz, 5H).
15. *2-Biphenylcarboxylic acid* (Table 2, entry 21): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 8.18 (d, J = 7.3 Hz, 1H), 7.97 (dd, J = 21.6, 7.8 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.3 Hz, 2H), 7.40–7.32 (m, 2H), 7.13 (t, J = 7.6 Hz, 1H).

2.9. General procedure for the Cellu@NHC-Pd catalysed Mizoroki-Heck cross-coupling reaction

Inspired by the outstanding findings obtained from Suzuki-Miyaura cross-coupling reaction, we further explored the catalytic activity of the Cellu@NHC-Pd heterogeneous catalyst in Mizoroki-Heck cross-coupling reaction. To EtOH:H₂O (1:1 v/v, 5 mL) mixture, aryl halide (1 equiv.) *tert*-butylacrylate (1.2 equiv.), K₂CO₃ (2.5 equiv.) and Cellu@NHC-Pd heterogeneous catalyst (2.22 mol% Pd) were taken and sonicated for 5 min. The reaction mass was then stirred at 60°C for the requisite amount of time. TLC was used to check the progress of the reaction on a regular basis. Following the conclusion of the reaction, the catalyst was removed by simple filtering, and the leftover reaction mass was extracted using DCM (2 x 20 mL). The organic layer was washed with water (1 x 10 mL) and brine solution (1 x 10 mL) before being dried over anhydrous Na₂SO₄. The product produced by condensing the organic layer *in vacuo* was purified using column chromatography with hexane and ethyl acetate as eluents and evaluated using $^1\text{H NMR}$ spectroscopy.

1. *Tert-butyl-4-(methoxyphenyl)acrylate* (Table 4, entries 1 and 2): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 7.47 (d, J = 15.9 Hz, 1H), 7.38 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 6.17 (d, J = 15.9 Hz, 1H), 3.75 (s, 3H), 1.45 (s, 9H).
2. *Tert-butyl phenylacrylate* (Table 4, entry 3): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 7.51 (d, J = 16.0 Hz, 1H), 7.43 (d, J = 4.3 Hz, 2H), 7.29 (d, J = 4.3 Hz, 3H), 6.30 (d, J = 16.0 Hz, 1H), 1.46 (s, 9H).
3. *Tert-butyl-4-(hydroxyphenyl)acrylate* (Table 4, entry 5): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 7.45 (d, J = 15.9 Hz, 1H), 7.29 (d, J = 8.3 Hz, 2H), 6.78 (d, J = 8.2 Hz, 2H), 6.14 (d, J = 15.9 Hz, 1H), 1.46 (s, 9H).

4. *Tert-butyl-2-(methoxyphenyl)acrylate* (Table 4, entry 7): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 7.84 (d, J = 16.1 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 6.92–6.79 (m, 2H), 6.37 (d, J = 16.1 Hz, 1H), 3.80 (s, 3H), 1.46 (s, 9H).
5. *Tert-butyl-4-(methylphenyl)acrylate* (Table 4, entry 8): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 7.49 (d, J = 16.0 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.10 (d, J = 7.7 Hz, 2H), 6.25 (d, J = 16.0 Hz, 1H), 2.29 (s, 3H), 1.46 (s, 9H).
6. *Tert-butyl-2-(fluorophenyl)acrylate* (Table 4, entry 9): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 7.65 (d, J = 16.2 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.26 (dd, J = 13.4, 6.4 Hz, 1H), 7.04 (dt, J = 19.0, 8.3 Hz, 2H), 6.39 (d, J = 16.2 Hz, 1H), 1.47 (s, 9H).

2.10. Procedure for recovery and recycling of Cellu@NHC-Pd heterogeneous catalyst

The catalyst was subjected to recyclability study using the model reactions for Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions respectively, under the optimized reaction conditions. In both the cases, on completion of the reaction, the Cellu@NHC-Pd heterogeneous catalyst was separated by simple filtration, washed with EtOH (2 x 10mL) and distilled H_2O (2 x 10mL), and dried at 50°C for 12 h. The dried Cellu@NHC-Pd heterogeneous catalyst was as such used for the next catalytic cycle.

3. Results And Discussion

3.1. Synthesis of Cellu@NHC-Pd heterogeneous catalyst

Keeping green chemistry aspects in mind we carried out the synthesis of the heterogeneous catalyst supported on cellulose obtained from biogenic sugarcane bagasse as depicted in Scheme 1. A waste material formed in sugar industries, bagasse is obtained following the extraction of sugar from sugarcane. The cost-effective alkaline hydrolysis of sun-dried small-sized pieces of the sugarcane bagasse assists in the eradication of hemicellulose and lignin as by-products. Following delignification, the obtained residual pulp was washed until neutral pH and dried to get the cellulose fibres (**1**) (Scheme 1a). The cellulose fibres was treated with (3-chloropropyl)triethoxysilane (**2**) in water, and to adjust the pH, glacial acetic acid was used. The mixture was stirred for 2 h at 120°C to functionalize the cellulose to form silyl chloride functionalized cellulose (Cellu@SC) (**3**). Simultaneously, the NHC precursor was prepared by treatment of benzimidazole (**4**) with isopentyl bromide (**5**) in presence of KOH as base and DMSO as solvent to get 1-isopentyl-1*H*-benzo[*d*]imidazole (**6**). Additionally, the structure of 1-isopentyl-1*H*-benzo[*d*]imidazole was confirmed by $^1\text{H NMR}$, FT-IR and GC-MS. The prepared NHC-precursor (**6**) was then treated with Cellu@SC (**3**) in toluene at 100°C for 48 h. The 1-isopentyl-1*H*-benzo[*d*]imidazole incorporated cellulose (Cellu@NHC) (**7**) further on treatment with $\text{Pd}(\text{OAc})_2$ in DMF at 60°C for 48 h gave the desired heterogeneous catalyst cellulose tethered *N*-heterocyclic carbene-palladium(II) complex (Cellu@NHC-Pd) (**8**) as a dark grey fibres (Scheme 1b). The σ bonding and π back-bonding interactions between the NHC and palladium makes it stable system in the heterogeneous catalyst.

3.2. Spectroscopic and microscopic analysis of Cellu@NHC-Pd heterogeneous catalyst

3.2.1. FT-IR analysis

FT-IR spectroscopic analysis was carried out to study the characteristic peaks for the confirmation of the intermediates and final product at each step (Fig. 1). Cellulose showed the presence of broad strong peak at 3282 cm^{-1} corresponds to O-H stretching vibration, while at 1648 cm^{-1} indicates O-H overtone vibrations due to the strong cellulose water interaction. (Thiangtham et al. 2020). The sharp peaks observed at 2890 cm^{-1} and in the region of $1427\text{-}1319\text{ cm}^{-1}$ can be attributed to due to C-H stretching, CH_2 symmetric bending and C-H bending vibrations respectively. The characteristic C-O-C skeletal vibrations of pyranose ring can be observed at 1057 cm^{-1} (Baruah et al. 2015) and the bending and stretching vibrations of C-O-C, C-C-O and C-C-H at 895 cm^{-1} (Fig. 1a) (Kandathil et al. 2019; Mandal and Chakrabarty 2011). On functionalization, the characteristic peaks of cellulose are still observed, with slight shifts in the vibrational frequencies, confirming the retention of the structure of cellulose (Fig. 1b-d). In the silylated intermediate Cellu@SC, the peaks at 2942 cm^{-1} and 996 cm^{-1} can be ascribed to stretching vibrations of the C-H and Si-O bonds of the (3-chloropropyl)triethoxysilane moiety (Fig. 1b) (Antony et al. 2021). The absorption peaks owing to the NHC precursor in Cellu@NHC are not observed as they could be hidden in the strong broad absorption peaks of cellulose (Fig. 1c). The final catalyst Cellu@NHC-Pd heterogeneous catalyst showed no new peaks but a small shift in the peak values, which might be denotes the bonding between palladium(II) and the functionalized cellulose support (Fig. 1d). The FT-IR spectrum of three times recycled Cellu@NHC-Pd heterogeneous catalyst used for Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions were compared with the fresh Cellu@NHC-Pd heterogeneous catalyst. The characteristic absorption peaks of the heterogeneous catalyst were retained with merging of the peaks which may be due to the reaction conditions (Fig. 2a-c), signifying the heterogeneous nature of the Cellu@NHC-Pd heterogeneous catalyst.

3.2.2. FE-SEM analysis

The morphologies of cellulose isolated from sugarcane-based bagasse and Cellu@NHC-Pd heterogeneous catalyst were investigated *via* FE-SEM. The examined FE-SEM images of cellulose showed fibrous nature with rough surface as shown in (Fig. 3a). The morphology was unaffected on functionalization with the silyl group and NHC precursor (Fig. 3b), and on tethering of the palladium to form the Cellu@NHC-Pd heterogeneous catalyst (Fig. 3c) preserving the fibrous nature. The thickness of catalytic system was observed to be $\sim 9\text{-}22\text{ }\mu\text{m}$. In the FE-SEM image of the three times recycled Cellu@NHC-Pd heterogeneous catalyst, it can be observed that the fibrous nature was retained as that of the fresh Cellu@NHC-Pd heterogeneous catalyst (Fig. 3d & e).

3.2.3. EDS analysis

The chemical composition of Cellu@NHC-Pd heterogeneous catalyst was confirmed by EDS. In the EDS spectrum, the synthesized Cellu@NHC-Pd heterogeneous catalyst showed the characteristic peaks of

carbon, nitrogen, oxygen, silicon, chlorine and palladium, indicating the successful grafting of palladium on the NHC precursor incorporated cellulose (Fig. 4a). Likewise, the elemental mapping exhibited the uniform distribution of these elements (Fig. 4b).

3.2.4. HR-TEM Analysis

HR-TEM analysis was carried out to further confirm the morphology of the Cellu@NHC-Pd heterogeneous catalyst. The HR-TEM images of cellulose revealed the fibre-like structure with smooth surface of cellulose as shown in (Fig. 5a & b). Likewise, in the HR-TEM images of Cellu@NHC-Pd heterogeneous catalyst (Fig. 5c & d), the fibrous nature of cellulose was intact along with the presence of small quantities of palladium nanoparticles distributed over the cellulose support which may have formed during the synthesis of catalyst (Kandathil et al. 2019; Wang et al. 2014).

3.2.5. Thermogravimetric Analysis

The thermal stability of cellulose and Cellu@NHC-Pd heterogeneous catalyst was investigated and compared by TGA analysis for moisture content, presence of volatile moieties, purity and thermal stability of cellulose and Cellu@NHC-Pd heterogeneous catalyst (Kandathil et al. 2019). The TG curve of cellulose (Fig. 6a) showed negligible weight loss of 6% below 100 °C which can be attributed to the removal of chemisorbed and physisorbed water. The complete degradation by the cleavage of glycoside bonds of the cellulose skeletal structure was observed above 250 °C. From the DTA curve, the temperature was found to be 248 °C. Thus in experimental conditions, cellulose showed high stability as a catalyst support under aerial conditions (Wang et al. 2014). As of the TG curve of Cellu@NHC-Pd heterogeneous catalyst (Fig. 6b), 6% weight loss due to moisture was seen below 100 °C. The first sharp weight loss occurred above 275 °C trailed by the second up to 450 °C which can be ascribed to the decomposition of the organic moieties grafted on cellulose followed by the cellulose support itself (Wang et al. 2014). The DTA curve of Cellu@NHC-Pd heterogeneous catalyst demonstrated major weight loss of 55% at 310 °C, clearly indicating the higher thermal stability of the Cellu@NHC-Pd heterogeneous catalyst which can be used for chemical transformations up to 300 °C (Doke et al. 2019).

3.2.6. ICP-OES Analysis

The ICP-OES technique was employed to evaluate the exact amount of palladium loading in the Cellu@NHC-Pd heterogeneous catalyst. The palladium loading of 11.84 % (w/w) on the catalyst was observed.

3.2.7. *p*-XRD analysis

To investigate the crystal structure of cellulose and Cellu@NHC-Pd heterogeneous catalyst, *p*-XRD was carried out. The *p*-XRD pattern of cellulose demonstrated the presence of both crystalline and amorphous regions (Fig. 7a). The diffraction peaks at 2θ of 15.9°, 22.3° and 34.7° of cellulose represents the crystallographic planes (110) (200) and (004) respectively (Thiangtham et al. 2020). However, in the Cellu@NHC-Pd heterogeneous catalyst along with the diffraction peaks of cellulose, peaks at 2θ value

40.0°, 46.6°, 68.1° corresponding to (111), (200), (220) planes indicate the presence of palladium nanoparticles formed in small quantities in confirmation to the TEM images (Fig. 7b). The crystallinity index (CrI) was calculated from Segal's equation from X-ray patterns by equation 1.

$$\text{CrI (\%)} = \left(\frac{I_{200} - I_{\text{am}}}{I_{200}} \right) \times 100 \text{ ----- (1)}$$

For cellulose CrI was found to be 59.69%, while for the Cellu@NHC-Pd heterogeneous catalyst it was 62.20%. The slight increase in crystalline nature of cellulose in the Cellu@NHC-Pd heterogeneous catalyst may be due to the removal of the amorphous parts and cleavage of glycosidic linkages releasing crystallites (Thiangtham et al. 2020).

3.3. Catalytic activity of Cellu@NHC-Pd heterogeneous catalyst in Suzuki-Miyaura cross-coupling reaction

The Cellu@NHC-Pd heterogeneous catalyst, subsequent to characterization, was explored for its catalytic activity in Suzuki-Miyaura cross-coupling reaction for the synthesis of biaryl derivatives from aryl halides and arylboronic acids. Presently, huge emphasis is placed on designing facile, cost-efficient and greener synthetic methodologies, to avoid tedious procedures and curb environmental pollution. In line with this, the optimization and thereby substrate scope for the Cellu@NHC-Pd heterogeneous catalyst in Suzuki-Miyaura cross-coupling reaction was studied (Table 1). The reaction condition was optimized using the cross-coupling reaction between 4-iodoanisole (1.0 equiv.) and phenylboronic acid (1.1 equiv.) as the model reaction. The best result for the model reaction was obtained in 30 min with K_2CO_3 as base in presence of 2.2 mol% of palladium of Cellu@NHC-Pd heterogeneous catalyst with respect to aryl halide in EtOH:H₂O (1:1) solvent medium at room temperature affording an excellent yield of 95% (Table 1, entry 17). The performance of Suzuki-Miyaura cross-coupling reaction is governed by several factors such as base, solvent, temperature, time and catalyst loading, and these factors were inspected to understand and evaluate the catalytic performance of Cellu@NHC-Pd heterogeneous catalyst for Suzuki-Miyaura cross-coupling reaction for the model reaction (Table 1).

3.3.1. Effect of base on Suzuki-Miyaura cross-coupling reaction

The performance of Cellu@NHC-Pd of heterogeneous catalyst was studied using different bases like, NaOH, KOH, Cs_2CO_3 , K_2CO_3 , Na_2CO_3 , KF and $\text{Na}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$, and are tabulated in (Table 1, entry 1-6). Most of the bases other than KF showed good to excellent yield (Table 1, entries 5). Among these K_2CO_3 showed the best conversion of 95% towards Suzuki-Miyaura cross-coupling reaction (Table 1, entry 17).

3.3.2. Effect of solvent on Suzuki-Miyaura cross-coupling reaction

The activity of Cellu@NHC-Pd of heterogeneous catalyst was checked for its efficiency in various polar and non-polar solvents such as H₂O, EtOH, DMF, acetonitrile, toluene, 1,4-dioxane, THF, and EtOH:H₂O (1:1) and tabulated in Table 1 (entries 7-13). From the results obtained, the Cellu@NHC-Pd heterogeneous catalyst worked well with water and EtOH:H₂O (1:1) mixture, while others did not provide any considerable product. This could be due to the low solubility product of the K₂CO₃ in the other solvents in comparison to water. Also, cross-coupling reaction carried out in EtOH:H₂O (1:1) gave the best yield of 95 % (Table 1, entry 17).

3.3.3. Effect of temperature on Suzuki-Miyaura cross coupling reactions

The activity of the Cellu@NHC-Pd heterogeneous catalyst towards Suzuki-Miyaura cross coupling reactions was checked at various temperatures. The model reaction was carried out at varying temperatures as shown in (Table 1, entries 14 and 15). The heterogeneous catalyst provided excellent catalytic activity at room temperature itself (Table 1, entry 17). Enhancement of yield was unobserved on increasing the temperature. Hence room temperature was taken as the optimized temperature for the Suzuki-Miyaura cross-coupling reaction.

3.3.4. Effect of time on Suzuki-Miyaura cross coupling reactions

To understand the progress/rate of the reaction with respect to time, the Suzuki-Miyaura cross-coupling reaction was conducted at different time intervals as tabulated in Table 1 (entries 16-18). The catalytic activity was seen to be increased with the increase in time up to 30 min. further increase in time did not increase the yield. Hence 30 min was considered to be the optimized time for further cross-coupling reactions (Table 1, entry 17).

3.3.5. Effect of catalyst ratio on Suzuki-Miyaura cross-coupling reaction

Catalyst ratio plays an important role in Suzuki-Miyaura cross-coupling reaction. To determine the effective quantity of Cellu@NHC-Pd heterogeneous catalyst required for the reaction, different catalyst ratio ranging from 1.67 to 2.78 mol% of palladium with respect to aryl halide was employed in the model reaction. The results are tabulated in Table 1 (entries 19-21). Increase in the yield was observed corresponding with the increase in catalyst loading up to 2.22 mol% Pd from 90 to 95 % yield (Table 1, entry 17). Further use of higher quantities did not improve the conversion. This shows that 2.22 mol% of Pd was sufficient for the reaction to progress well.

3.3.6. Suzuki-Miyaura cross-coupling reactions of different aryl halides

The Cellu@NHC-Pd heterogeneous catalyst, under the optimized conditions was probed for its consistency in Suzuki-Miyaura cross-coupling reaction between various substituted aryl halides (iodides, bromides & chlorides) and arylboronic acids (phenyl boronic acid, 4-chloro boronic acid & 4-carboxy boronic acids). The results of the substrate scope are tabulated in Table 2. The effect of electron donating and electron withdrawing groups present on aryl halides either at positions 2 and 4 of the

aromatic ring were investigated. It was observed that electron donating groups gave higher yields in shorter period of time against electron withdrawing groups as seen with 4-iodoanisole, 4-iodophenol, 4-bromotoulene, 4-bromonitrobenzene, 4-bromoacetophenone, 4-bromobenzaldehyde substituted aryl bromides and phenylboronic acid (Table 2, entries 2, 7, 10, 16, 18, 19 and 22). Also, steric interaction in 2-substituted aryl halides hampered the cross-coupling observed in the case of 2-benzaldehyde & 4-benzaldehyde with phenyl boronic acid (Table 2, entries 19 and 20). Aryl iodides provided better conversion in the cross-coupling reaction when compared to their corresponding analogues of bromides or chlorides (Table 2, entries 2, 5-7, 11-13, 16, 17, 22 and 23). This can be credited to iodides being better leaving group than bromides and chlorides. However, aryl chlorides may yield acceptable results at elevated temperatures. The presence of substituents on the arylboronic acid influenced the cross-coupling reaction as well. Alternatively, the presence of electron withdrawing substituents (Cl and COOH at position 4) on the phenyl ring of boronic acid moiety afforded lower conversion in contrast to unsubstituted phenylboronic acid. Both 4-chlorophenylboronic acid and 4-carboxyphenylboronic acid by and large gave comparable results (Table 2, entries 3, 4, 14 and 15) except in the case of 4-iodophenol, where the 4-carboxyphenylboronic acid took longer time (Table 2, Entry 9).

3.4. Catalytic activity of Cellu@NHC-Pd heterogeneous catalyst in Mizoroki-Heck cross-coupling reaction

Inspired with the catalytic activity of the developed Cellu@NHC-Pd heterogeneous catalyst for Suzuki-Miyaura cross-coupling reaction we further explored the activity of catalyst for Mizoroki-Heck cross-coupling reaction. Aforementioned in the Suzuki-Miyaura reaction, the Mizoroki-Heck cross-coupling reaction was also carried out under facile and eco-friendly method to curb the environmental pollution. Hence, with this consideration we carried out the optimization study in presence of 4-iodoanisole (1.0 equiv.) and *tert*-butyl acrylate (1.2 equiv.) as model reagents. The effect of various parameters such as base, solvent, temperature, time and catalyst loading were studied (Table 3). We first examined the performance of various bases. Among the studied bases K_2CO_3 gave the best results at 60 °C temperature and in 3 h (Table 3, entry 18). Similarly solvents effect was also studied in which EtOH:H₂O (1:1) gave excellent yield. Further, the activity of catalyst was investigated at different temperature and time interval and indicated that the best results were obtained at 60 °C in 3 h depicting the required temperature and time for the model reaction to provide best results. Sequentially, catalyst loading up to 2.22 mol% Pd demonstrated 80 to 95% yield. Herein the optimized reaction conditions suggests that K_2CO_3 as base, EtOH:H₂O (1:1) as solvent, 60 °C temperature, 2.22 mol% Pd as catalyst loading gave best results in 3h (Table 3, entry 18).

3.4.1. Effect of base on Mizoroki-Heck cross-coupling reactions

To study the catalytic activity of the developed heterogeneous catalyst we first examined the performance with different bases such as Na_2CO_3 , KOH, Cs_2CO_3 , K_2CO_3 , and KF was studied and is tabulated in Table 3 (entries 1-5). The examined bases exhibited excellent results, among which K_2CO_3 showed best results of 80% at 60 °C temperature in 3 h towards Mizoroki-Heck cross-coupling reaction (Table 3, entry 18).

3.4.2. Effect of solvents on Mizoroki-Heck cross-coupling reactions

The Cellu@NHC-Pd heterogeneous catalyst was subjected to the model reaction in order to examine the effect of polar and non-polar solvents, namely EtOH:H₂O (1:1), H₂O, EtOH, acetonitrile, DMF, THF, toluene and 1,4-dioxane. (Table 3 entries 6-12). The reaction took place predominantly in the presence of polar solvents while the others did not provide any considerable results. It might be possibly due to low solubility of K₂CO₃ in other solvents as seen in section 3.3.1. The excellent result was achieved with greener solvent EtOH:H₂O (1:1) mixture (Table 3, entry 18).

3.4.3. Effect of temperature on Mizoroki-Heck cross-coupling reactions

To investigate the effect of temperature conditions required for the effective collision of substrates to give desired product the model reaction was carried out at different temperature (Table 3, entries 13-15). The Mizoroki- Heck cross coupling reaction required 60 °C temperature to give best results of 80% and further on increase in temperature no effective increase in yield was observed (Table 3, entry 18).

3.4.4. Effect of time on Mizoroki-Heck cross-coupling reactions

The activity of Cellu@NHC-Pd heterogeneous catalyst was inspected at various time intervals (Table 3, entries 13-15) in order to examine the pace of the reaction. In this investigation, it was observed that the catalyst provided the greatest conversion of 80% in 3 h (Table 3, entry 18) and no further rise in yield was seen with increase in time. (Table 3, entry 13-15). As a result, 3 h was determined to be the optimal period for the creation of the cross-coupled product.

3.4.5. Effect of the catalyst ratio on Mizoroki-Heck cross-coupling reactions

The catalyst ratio used in the reaction is an important factor that impact rate of the reaction. The effect of catalyst loading ranging from 1.67 to 2.78 mol% of palladium (Table 3, entries 20-23) concerning aryl halides was employed in the model reaction. This allowed us to determine the appropriate amount of Cellu@NHC-Pd heterogeneous catalyst that was necessary. This demonstrates that 2.22 mol% Pd was adequate for a successful reaction (Table 3, entry 18).

3.4.6. Mizoroki-Heck cross-coupling reactions of different aryl halides

To investigate the effect of optimized reaction conditions, various aryl halides including 4-iodoanisole, 4-iodobenzene, 4-iodophenol, 2-iodoanisole, and 2-fluoroiodobenzene, reacted in presence alkenes such as *tert*-butyl acrylate and heterogeneous catalyst Cellu@NHC-Pd under optimum conditions such as EtOH:H₂O (1:1) as green solvent and at 60 °C temperature as indicated in Table 4. The results revealed that the higher activity was shown by aryl iodides 4-iodoanisole, 4-iodobenzene, 4-iodophenol, 2-iodoanisole and 2-fluoroiodobenzene with *tert*-butyl acrylate as the coupling was quicker and resulted in high yields 80%-95% (Table 4, entries 1-9). Furthermore, we studied the coupling of aryl bromide and aryl

chlorides with *tert*-butyl acrylate using Cellu@NHC-Pd heterogeneous catalyst which yielded lower than substituted aryl iodide (Table 4, entries 2, 4, 6 and 10). Subsequently, as seen in the Suzuki-Miyaura cross-coupling reaction, the iodine being the better leaving group when compared to bromide and chloride thereby gave higher yield. Based on these findings, it can be concluded that the Cellu@NHC-Pd heterogeneous catalyst can be proficiently used for Mizoroki-Heck cross-coupling reaction.

3.5. Plausible mechanism for Suzuki-Miyaura cross-coupling

The prevalent Suzuki-Miyaura cross-coupling reaction involves the reaction of organoboronic acid with various aryl halides in the presence of a palladium catalyst and a base to form biaryl as the product. In the Suzuki-Miyaura cross-coupling reaction, the mechanism involves oxidative addition, transmetallation, and reductive elimination in a catalytic cycle. The oxidative addition of aryl halide to the metal core to generate an organometallic complex is the first step. Furthermore, the addition of base produces the intermediate as a result of transmetallation between boronic acid and palladium, resulting in the formation of the organopalladium complex. The initial palladium catalyst is restored after reductive elimination of the desired product, completing the catalytic cycle (Scheme S1).

3.6. Plausible mechanism for Mizoroki-Heck cross-coupling

The well-established Mizoroki-Heck cross-coupling reactions are facts that in-order to get the desired product in the quantitative yields. The proposed plausible reaction mechanism for Mizoroki-Heck cross-coupling reaction involved the addition reaction of the aryl halide and *tert*-butyl acrylate to give substituted esters as the desired product. The first step involves the oxidative addition of palladium itself in the aryl halide and form the π -complex with the alkene. In the further step, the palladium metal inserts itself in the palladium-carbon bond followed by the β -hydride elimination to give a π -complex again (Step 3). Further gives the generation of product and regeneration of catalyst (Scheme S2).

3.7. Catalyst recyclability for Suzuki- Miyaura and Mizoroki-Heck cross-coupling reactions

A major consideration in use of catalyst to be economical and greener is their ability to be recovered and reused. Hence, subsequent to investigating substrate scope the Cellu@NHC-Pd heterogeneous catalyst was subjected to recyclability studies under optimized conditions of the model reaction. The heterogeneous nature of the Cellu@NHC-Pd heterogeneous catalyst assists in the recovery of the catalyst from the reaction medium by simple filtration. The recovered catalyst was washed with EtOH and distilled H₂O and dried in an oven at 50 °C before subjecting it to the next cycle. The recovered Cellu@NHC-Pd heterogeneous catalyst was recycled up to three cycles (Fig. 8) which showed considerable decrease in activity which could be due to the leaching of Palladium from the active site. The chemical structure and morphology of the recovered Cellu@NHC-Pd heterogeneous catalyst, after the third recycle was

characterized by FT-IR (Fig. 2b & c) and FE-SEM analyses (Fig. 3d & e) and compared with the fresh catalyst.

3.8. Leaching studies

For the better understanding of the heterogeneity of the Cellu@NHC-Pd catalyst leaching studies by hot filtration test was carried out. The Cellu@NHC-Pd heterogeneous catalyst was treated with the base and stirred under the optimized condition for half an hour. The catalyst was separated before the model reactants were added and further stirred for one hour occasionally monitoring the reaction by TLC. The product formation was observed with indicating partial leaching out of the active species of the Cellu@NHC-Pd heterogeneous catalyst. This could be due to the loss of the palladium nanoparticles formed on the cellulose support under the reaction conditions. This indicates that some of the loosely held palladium bond to the cellulose may be lost, while most of the palladium(II) are strongly adhered to the NHC precursor in the heterogeneous catalyst.

3.9. Comparison of catalytic activity

To examine the novelty of the synthesized Cellu@NHC-Pd heterogeneous catalyst, comparison study was carried out with other supported heterogeneous catalysts for the Suzuki-Miyaura and Mizoroki-Heck cross-coupling reaction. The Cellu@NHC-Pd heterogeneous displayed high catalytic activity with good results in less time and in greener circumstances. Which helps to explain the importance of the synthesized Cellu@NHC-Pd heterogeneous catalyst.

Table 5 Comparison of results for the Cellu@NHC-Pd heterogeneous catalyst with other catalysts for the Suzuki-Miyaura cross-coupling reaction between 4-iodoanisole and phenylboronic acid

Entry	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)	Ref
1	h-BN@NHC-Pd	EtOH-H ₂ O (1:1)	RT	0.5	95	(Antony et al. 2021)
2	Pd NPs@CS	EtOH-H ₂ O (1:1)	65	3	99	(Li et al. 2017)
3	HEC-NHC-Pd	EtOH:H ₂ O (3:2)	60	2	97	(Dong et al. 2020)
4	Cell-NHC-Pd	DMF:H ₂ O (1:1)	80	2	94	(Wang et al. 2014)
5	NHC-Pd@MNPs	EtOH-H ₂ O (1:1)	70	1	95	(Vishal et al. 2017)
6	Cellu@NHC-Pd	EtOH-H₂O (1:1)	RT	0.5	95	Present work

Bold represent the most effective reaction conditions.

Table 6 Comparison of results for the Cellu@NHC-Pd heterogeneous catalyst with other catalysts for the Mizoroki-Heck cross-coupling reaction between 4-iodoanisole and *tert*-butylacrylate

Entry	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)	Ref
1	NO ₂ -NHC-Pd@Fe ₃ O ₄	MeCN	80	6	92	(Kandathil et al. 2017)
2	Pd-NHC-MIL-101 (Cr)	DMF	110	10	92	(Niknam et al. 2021)
3	PdNP@ChNC	MeCN:H ₂ O (1:1)	90	24	100	(Jin et al. 2020)
4	PdNPs/rGO-NH ₂	DMF	120	4	100	(Mirza-Aghayan et al. 2020)
5	PS-Pd-salen complex	DMF	110	10	93	(Balinge and Bhagat 2019)
6	Cellu@NHC-Pd	EtOH-H₂O (1:1)	60	3	95	Present work

Bold represent the most effective reaction conditions.

4. Conclusion

To summarize, a new *N*-heterocyclic carbene-palladium (II) complex immobilized on cellulose support (Cellu@NHC-Pd) was synthesized and successfully used as a heterogeneous catalyst in Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions. The Cellu@NHC-Pd heterogeneous catalyst was characterized by various techniques: microscopic, spectroscopic and thermal, to understand its chemical and physical nature. The main advantages of this catalyst are its simplicity in synthesis from biogenic material, high catalytic performance and ease in recovery of the catalyst from the reaction mass by simple filtration. Subsequently, the developed catalyst showed excellent catalytic activity for various substrates in Suzuki-Miyaura and Mizoroki-Heck cross-coupling reaction. Modifications can be incorporated to reduce the leaching of active site to further improve its efficiency. Additionally, the Cellu@NHC-Pd heterogeneous catalyst can be explored for its use in other important organic transformations such as other coupling reactions, C-H activation, N/O-arylation, oxidation/reduction reactions as well as other applications. Also, we can explore for the catalytic activity of cellulose-based heterogeneous catalysts immobilized with other common and abundantly available transition metal complexes for diverse applications.

Declarations

Ethics approval and consent to participate

Authors declare that the manuscript is not submitted to any other journal at the time of submission for simultaneous consideration, that the submitted work is original and has not been published elsewhere in any form, that this work is not part of a single study, that results are presented under the principles of honesty, without fabrication falsification or inappropriate data manipulation and that no data, text or theories by others are presented as our own.

Consent for publication

All authors have revised the last version of the submitted manuscript and we approve its submission.

Availability of data and materials

The datasets generated and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at.

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Tables and Schemes

Tables 1-4 and Scheme 1 are available in the supplementary files section.

Figures

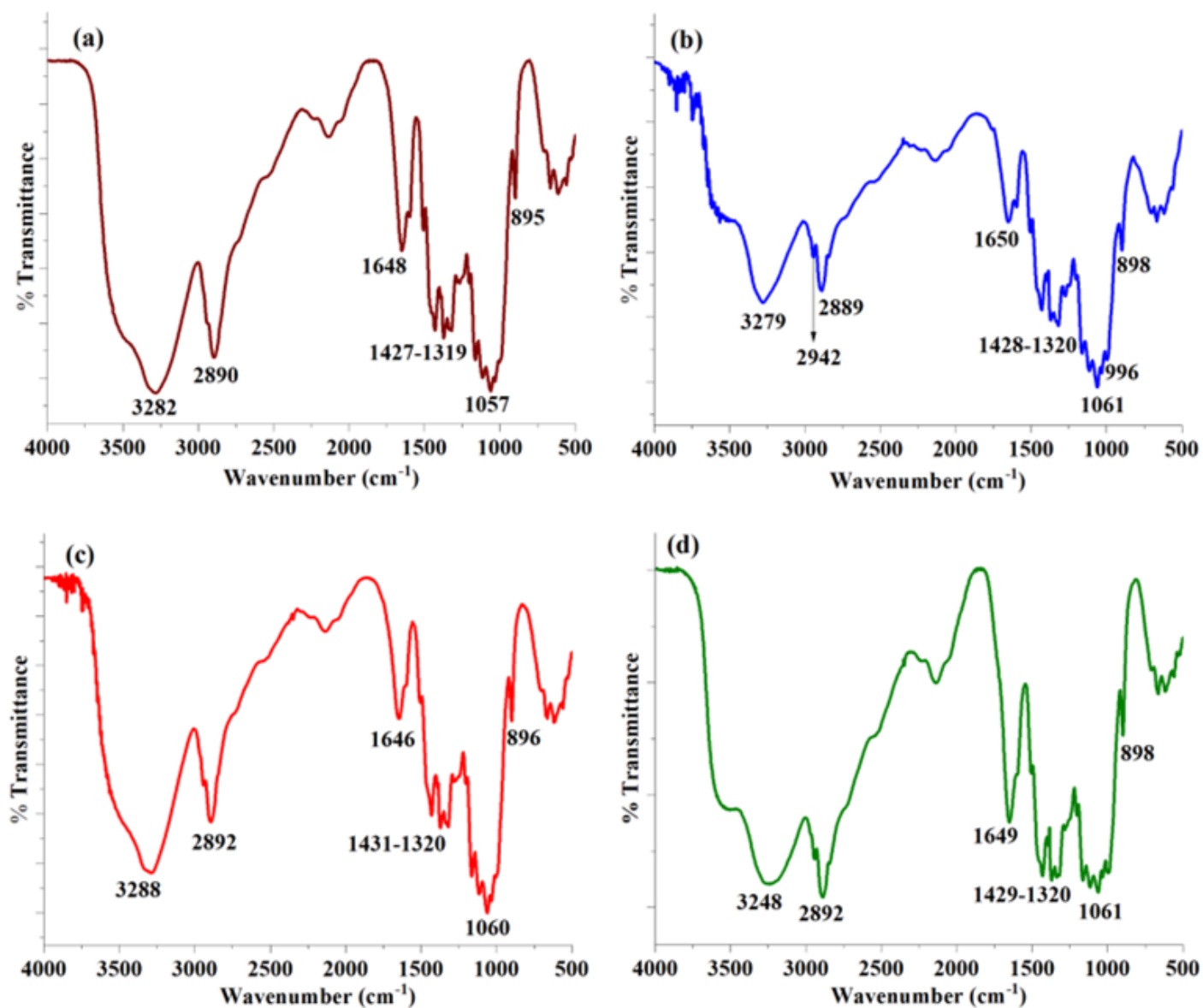


Figure 1

FT-IR spectra of (a) cellulose, (b) Cellu@SC, (c) Cellu@NHC and (d) Cellu@NHC-Pd heterogeneous catalyst.

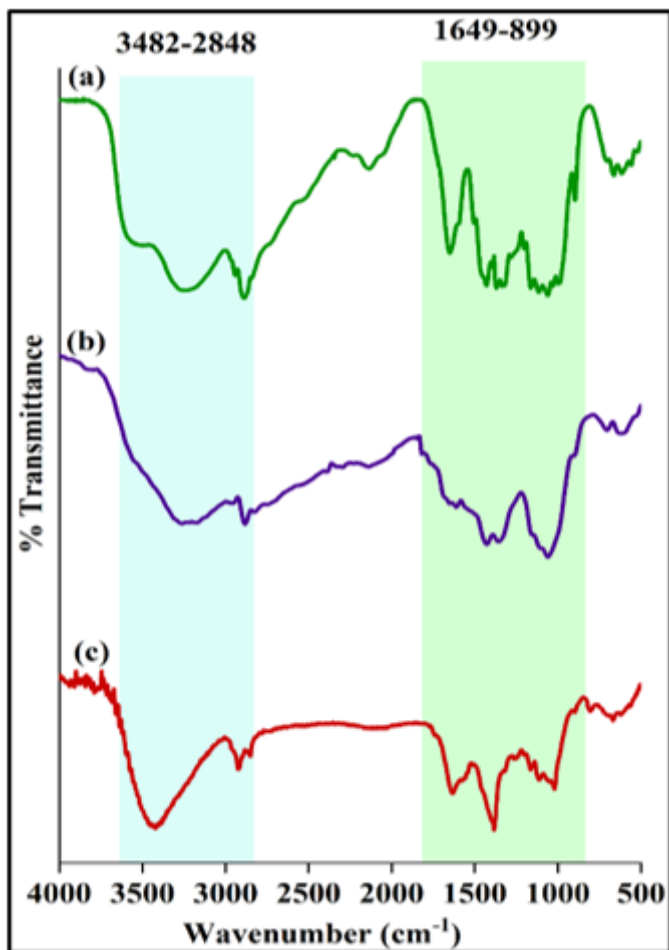


Figure 2

FT-IR spectra for (a) fresh, three times recycled (b) Suzuki-Miyaura and (c) Mizoroki-Heck cross-coupling reactions Cellu@NHC-Pd heterogeneous catalyst.

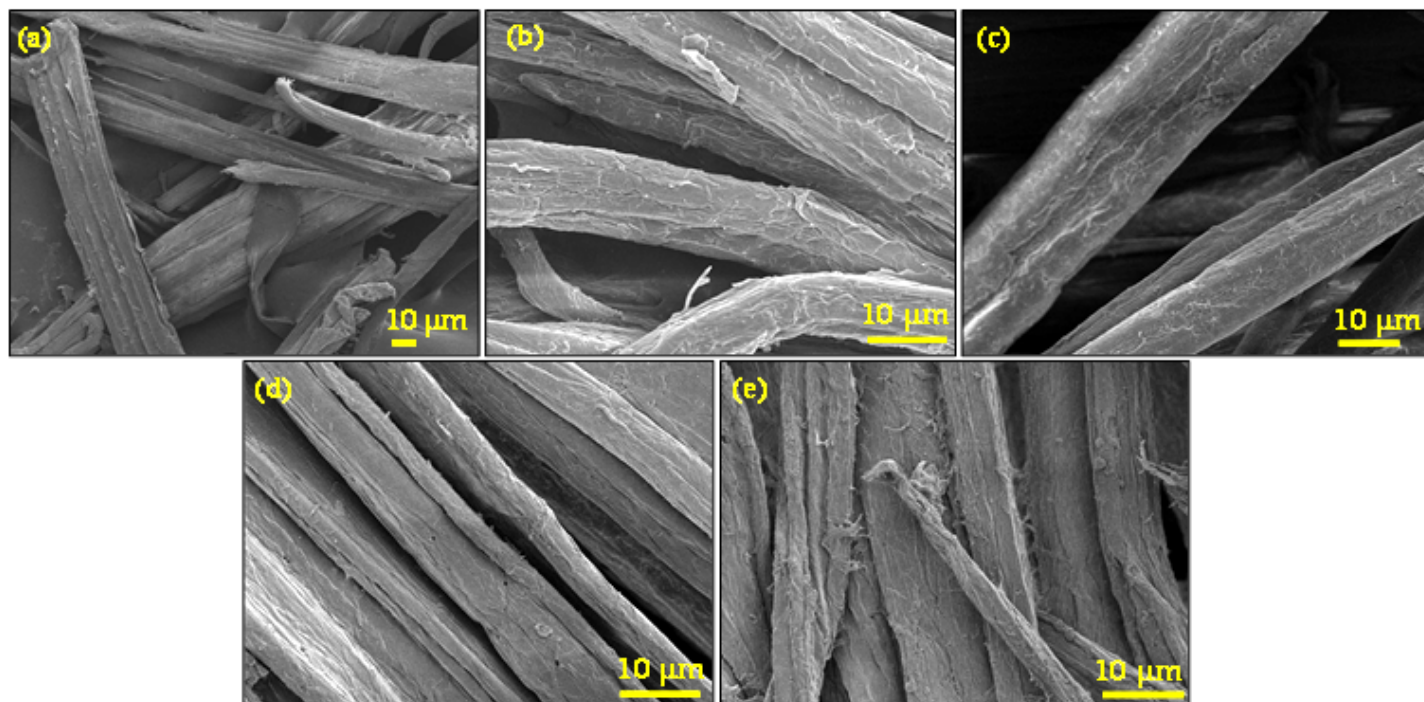


Figure 3

FE-SEM images of (a) cellulose, (b) Cellu@NHC, (c) fresh Cellu@NHC-Pd heterogeneous catalyst and; three times recycled Cellu@NHC-Pd heterogeneous catalyst (d) Suzuki–Miyaura and (e) Mizoroki-Heck cross-coupling reactions.

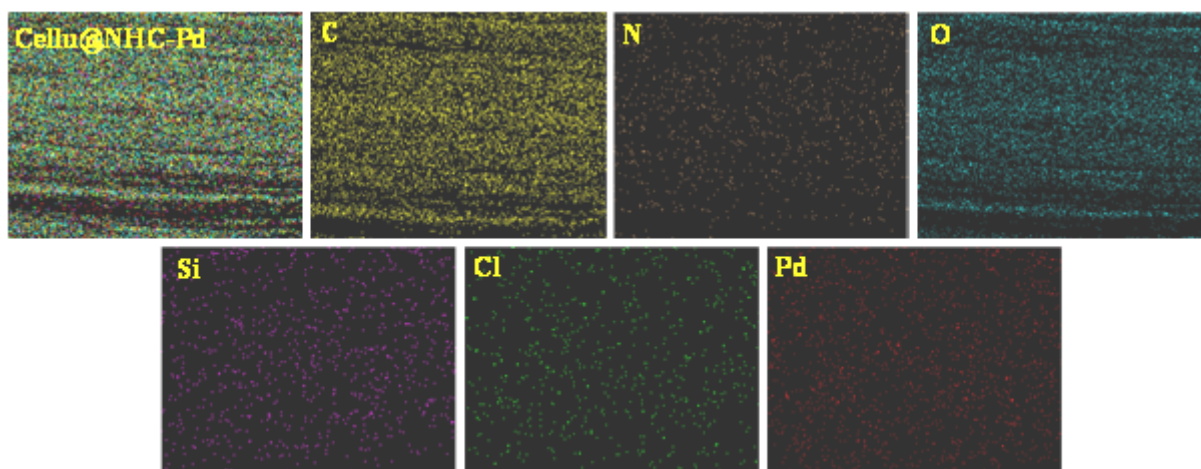
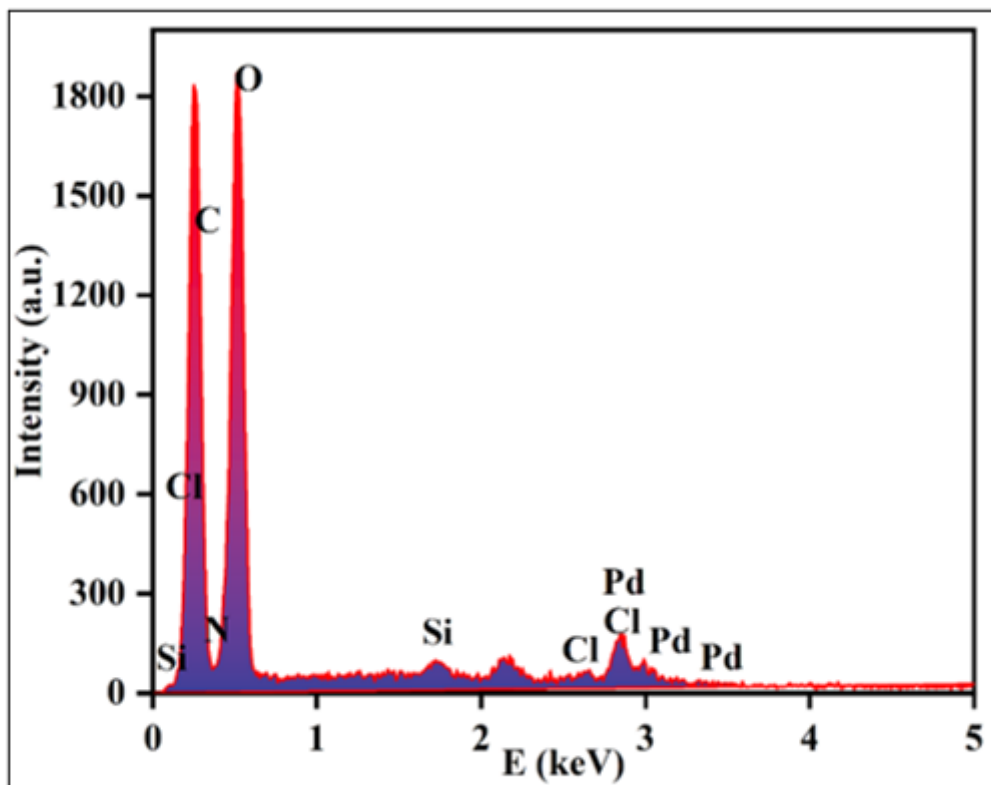


Figure 4

(a) EDS spectrum and (b) elemental mapping of Cellu@NHC-Pd heterogeneous catalyst.

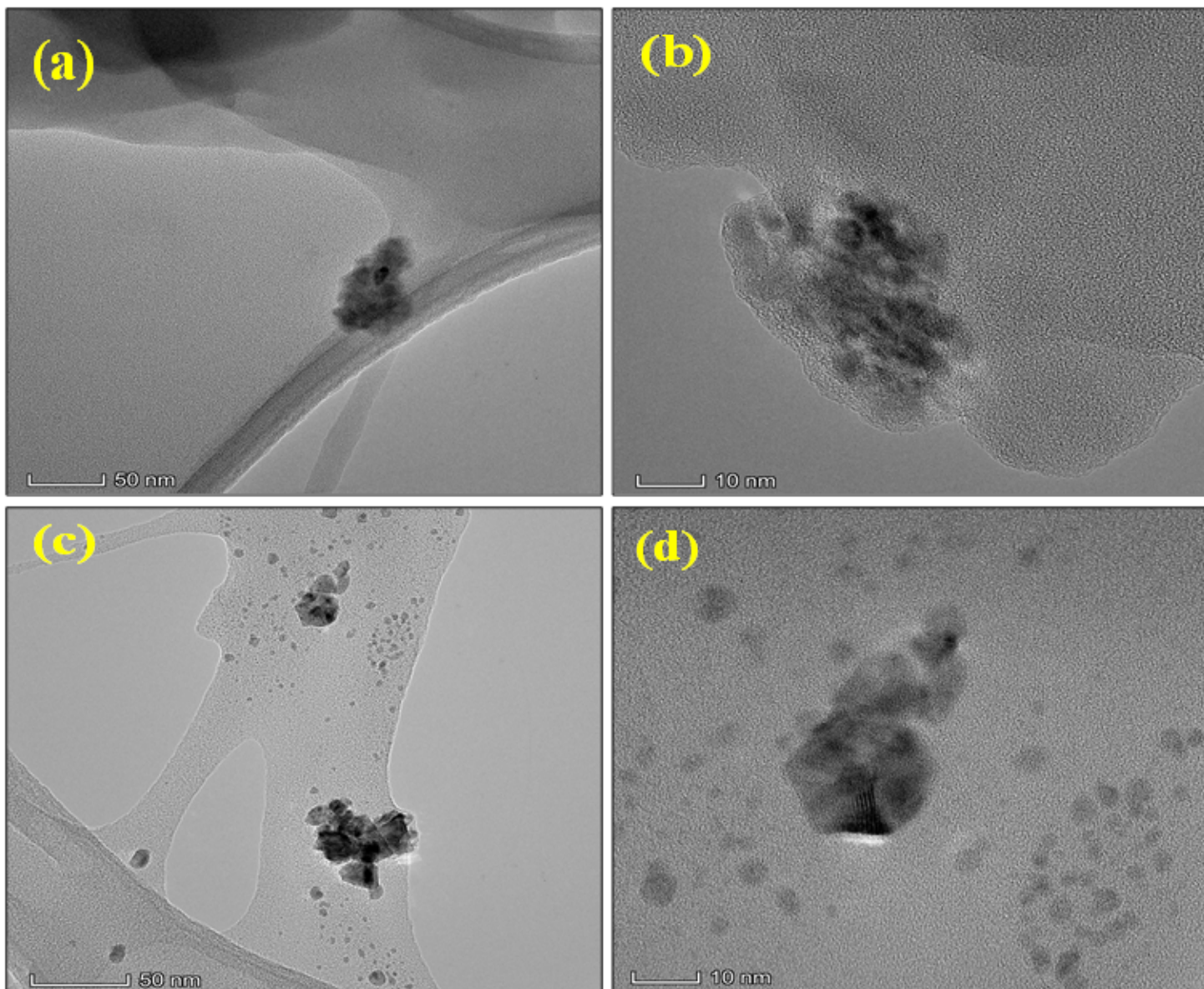


Figure 5

HR-TEM images of (a, b) cellulose and (c, d) Cellu@NHC-Pd heterogeneous catalyst at different magnifications.

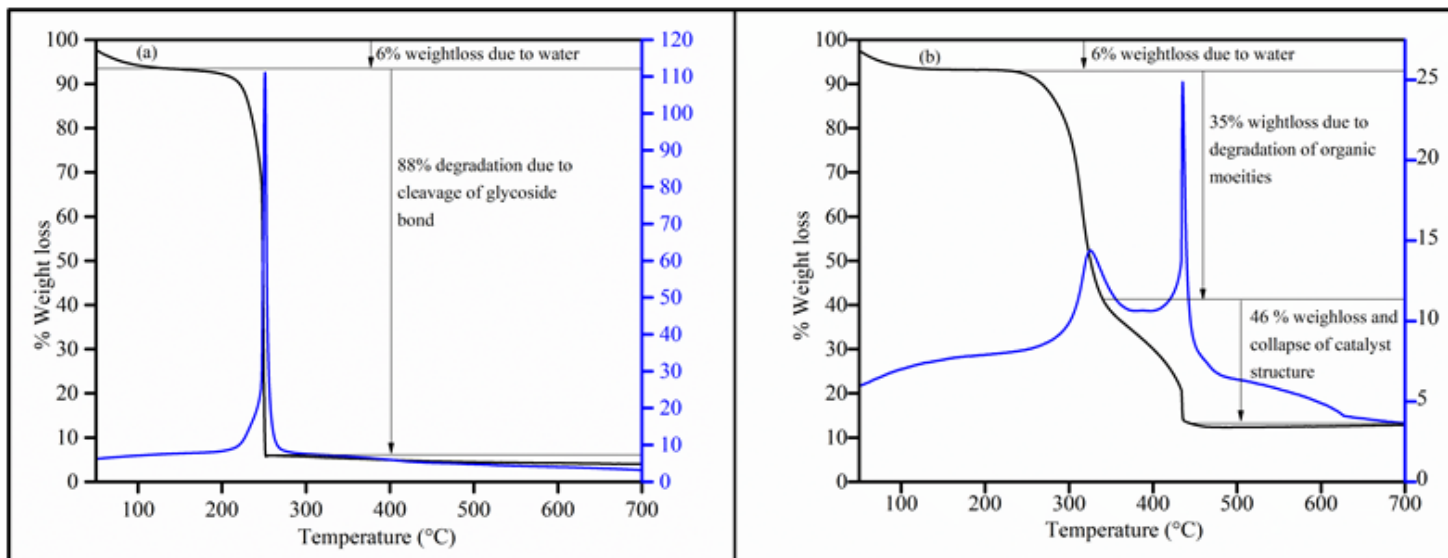


Figure 6

TG/DTA curves of (a) cellulose and (b) Cellu@NHC-Pd heterogeneous catalyst.

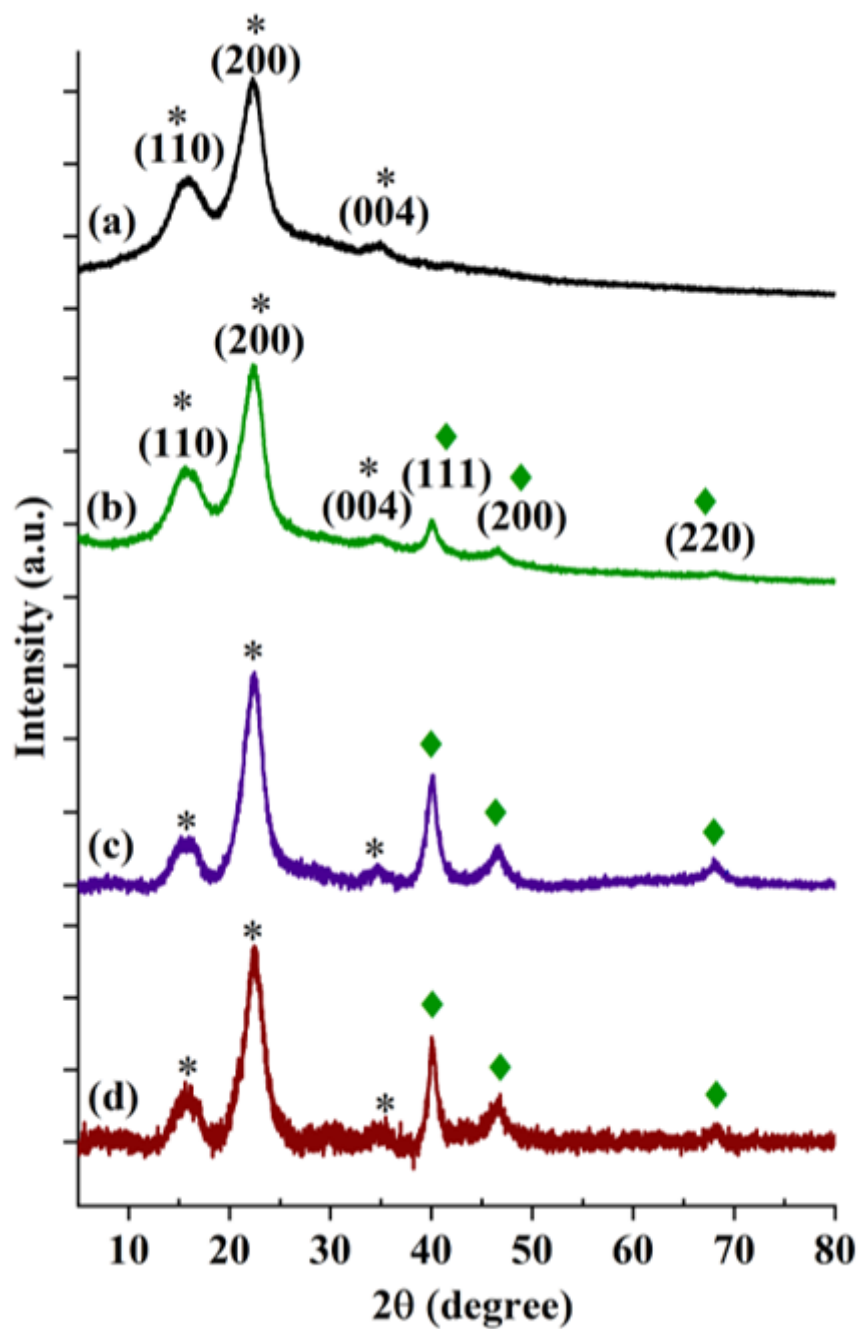


Figure 7

p-XRD pattern of (a) cellulose and (b) Cellu@NHC-Pd heterogeneous catalyst; three times recycled Cellu@NHC-Pd heterogeneous catalyst (c) Suzuki–Miyaura and (d) Mizoroki–Heck cross-coupling reactions.

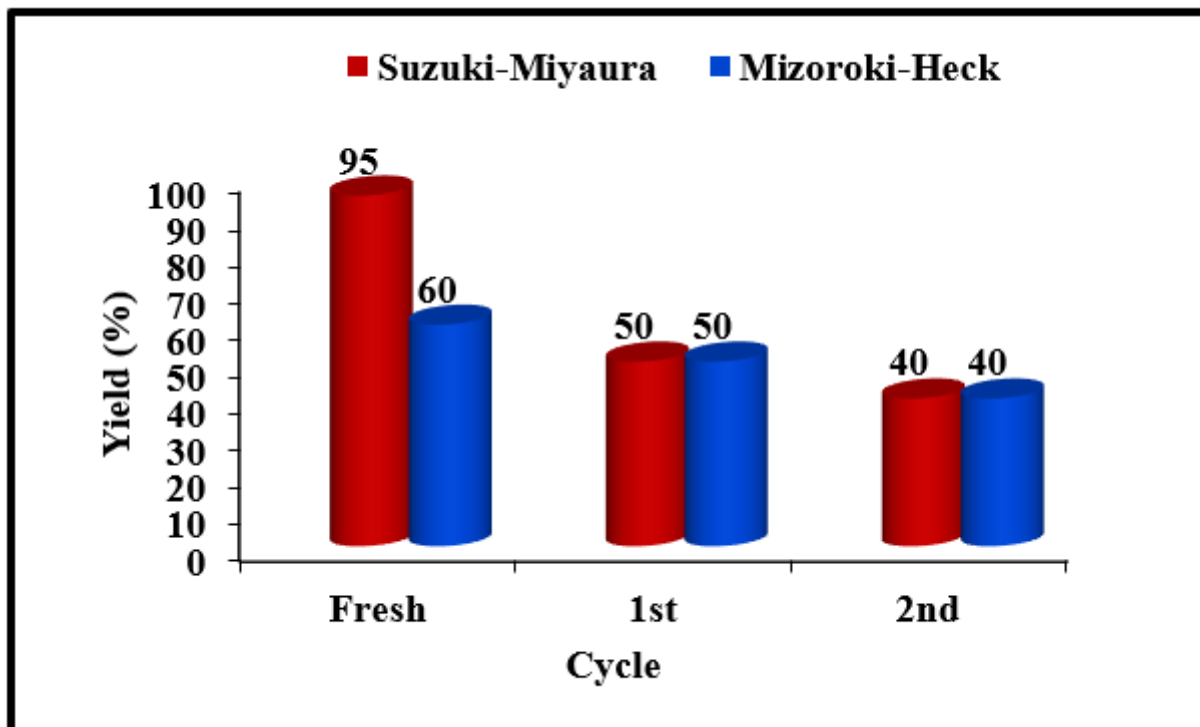


Figure 8

Recyclability study of Cellu@NHC-Pd heterogeneous catalyst in Suzuki-Miyaura and Mizoroki-Heck cross-coupling reaction.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SchemeandTables.docx](#)
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