ORIGINAL PAPER



Synthesis and characterization of chitosan pyridyl imine palladium (CPIP) complex as green catalyst for organic transformations

Narendra Singh Chundawat¹ · Sultan Pathan¹ · Girdhar Pal Singh¹ · Arup Saha Deuri² · Payam Zarrintaj³ · Narendra Pal Singh Chauhan¹

Received: 17 September 2020 / Accepted: 19 January 2021 / Published online: 3 February 2021 © Institute of Chemistry, Slovak Academy of Sciences 2021

Abstract

In this work, the modification of chitosan using 2-acetyl pyridine has been used to prepare an intermediate, chitosan pyridyl imine (CPI), in first step and then in second step it is further reacted with Pd(OAc)₂ to develop chitosan pyridyl imine palladium (CPIP) complex catalyst in a very simplistic way. The formed CPIP has been extensively characterized with respect to raw chitosan utilizing methods including FT-IR, pyrolysis GC–MS, XRD, XPS, FE-SEM, EDS, TGA-DTG and DSC. TG-DSC study suggested that the catalyst is thermally stable up to 300 °C. This catalyst shows an excellent activity in the reduction of toxic pollutant nitrobenzene to less toxic aniline. CPIP complex has also been found to give magnificent results in Suzuki–Miyaura and Heck cross-coupling reactions, and therefore, using this green catalyst, the toxic phosphine ligand can be excluded from cross-coupling reactions. This study furnishes an economic and eco-friendly catalyst for organic transformation in sustainable chemistry.

Keywords Chitosan · Pyridyl · Characterization · Palladium catalyst · Suzuki · Heck reaction · Reduction · Azo dye

Introduction

Nitrobenzene compounds are major pollutant due to their explosive nature and high toxicity, carcinogenicity and other adverse effects to living beings and environment. The study by U.S. Environmental Protection Agency (EPA) found that nitrobenzene content in water must be less than 17 ppm (Sun et al. 2016,2019). Thus, it is important and equally necessary to reduce nitrobenzene into relatively less toxic aniline by using eco-friendly process. Suzuki–Miyaura and Heck crosscoupling reactions requires ligand like phosphine which is toxic and can cause disruption of neural tissues performance, blocked energy metabolism and altered the cellular redox

Narendra Singh Chundawat and Sultan Pathan have contributed equally to this work.

Narendra Pal Singh Chauhan narendrapalsingh14@gmail.com

- ¹ Department of Chemistry, Faculty of Science, Bhupal Nobles'University, Udaipur 313001, India
- ² Balakrishna Industries Lt (BKT), Bhuj, Gujrat, India
- ³ School of Chemical Engineering, Oklahoma State University, 420 Engineering North, Stillwater, OK 74078, USA

level (Anderson 2006). Thus, it is environmental need to develop process which can facilitate to get rid of such pollutants by greenway.

Chitosan is a linear polysaccharide composed of randomly distributed N-acetyl-D-glucosamine and D-glucosamine (Jalali et al., 2016). Chitin's deacetylation results in the formation of chitosan. Chitosan is used for adsorbent of metals, wound dressings, drug dispensing and ophthalmic lenses, and it can be easily developed into foils or fibrils (Kumar 2000; Vincent and Guibal 2001). Chitosan plays important role in catalysis support, and its activity has been reported in various literature, e.g., in chromate reduction (with use of Pd) (Huang et al. 2012; Molnár 2019), phenol (Pd) (An et al. 1994; Tang et al. 1994), and nitro-aromatics (Ni, Cu, Cr, Zn) (Han et al. 1996). Yin et al. narrated asymmetric hydrogenation (Yin et al. 1999). The hydrophilic characteristic of chitosan was used by Quignard et al. to develop aqueous phase catalysts supported by chitosan, for the allylic substitution reaction by palladium catalyst. (Buisson and Quignard 2002; Quignard et al. 2000) The chitosan can be redesigned by inducing various functional groups (Functionalization) to prepare divergent co-ordination sites which can provide catalysts for olefins cyclopropanation (Cu-Schiff's base) (Sun et al. 2002), alkylbenzenes oxidation (Mn or Ni-Schiff's base) (Chang et al. 2002), and DOPA (3,4-dihydroxyphenylalanine) oxidation (Hu et al. 2001). The oxidation of DOPA involved the homogeneous phase due to chitosan solubility in acetic acid, functionalization and re-precipitation, while the others involved the direct functionalization of the solid chitosan. N-allylation of amines has been made utilizing a biodegradable and recyclable heterogeneous chitosan-supported palladium (Pd) catalyst (Baig et al. 2015; Kawatsura et al. 2008; Plietker 2006; Polet et al., 2006; Welter et al. 2004). Pd nanoparticles encapsulated on thiourea-chitosan are utilized for green Suzuki reaction (Affrose et al. 2015; Hajipour et al. 2015; Sin et al. 2010), reduction of nitro to amine (Krogul-Sobczak et al. 2019; Su et al. 2016; Wang et al., 2017) and Heck reaction (Hajipour et al. 2015; Sin et al. 2010; Kurandina et al. 2018; Shao and Qi 2017). Cross-coupling reaction has tremendous application in pharmaceuticals, agrochemical and fine chemicals (Barder et al. 2005; Buchwald 2008; Corbet and Mignani 2006; Magano and Dunetz 2011; Sedghi et al. 2019; Torborg and Beller 2009; Chauhan et al. 2019; Chauhan and Chundawat 2019; Marziale et al. 2011).

Chitosan forms Schiff's base with 2-acetyl pyridine to give chitosan pyridyl imine (Kim et al. 2004; Li and Liu 2004). These N-heterocyclic imines behave as nitrogenbased ligand which replaces phosphine ligands. N-heterocyclic imine is used as metal ligand; imine has more oxidizing tendency than that of phosphine ligands that enhances the stability of corresponding palladium toward the gases like O₂, etc., water and heat. Ligand N-heterocyclic imine has the similar σ -donor and small π -acceptor properties, and thus, N-heterocyclic imine forms firm bond with Co (Someya et al. 2007), Pd (Peris and Crabtree 2004), Cu (Hu et al. 2004) and Ni (Dorta et al. 2005) metals. In cross-coupling reactions, Pd metal complexes with N-heterocyclic imine are better catalyst to achieve outstanding catalytic activities, and this complex facilitates the reduction of nitro compounds into amine. N-heterocyclic imine supports oxidative addition of reagent and can aid in the reductive elimination of bi aryl compounds due to its strong σ -donating properties (Fortman and Nolan 2011; Li et al. 2012; Pathan et al. 2020).

'Green' cross-coupling reactions have concentrated on scheming readily reclaimable catalysts, thus facilitating the segregation of product and clinging to green chemistry (Kashin et al. 2018; Lipshutz et al. 2010; Mai et al. 2019; Sun et al. 2015; Sydnes 2017). Chitosan-supported silver nanoparticles have been used for reduction of 4-nitrophenol to 4-aminophenol in the presence of NaBH₄ (Hasan et al. 2019). Chitosan Fe₃O₄–Pd nanoparticles as heterogeneous catalyst were fabricated for Suzuki and Heck coupling reactions in water. (Hasan 2020).

Herein, we demonstrate a facile synthesis of green catalyst, chitosan pyridyl imine complex catalyst using raw chitosan, 2-acetylpyridine and $Pd(OAc)_2$. It has been

characterized by FT-IR, XRD, Py-GC–MS, XPS FE-SEM–EDS, BET surface area, TG-DTG and DSC. Surprisingly, it has been found that the prepared CPIP complex catalyst displayed excellent catalytic performance in Suzuki–Miyaura and Heck coupling reactions at elevated temperature without any phase transfer agents, toxic solvents and inert atmosphere, achieving a green chemical synthesis.

Experimental

Reagents

All reagents and solvents were procured from mercantile sources. Chitosan was purchased from Loba Chem. Compound confirmed by TLC and analyzed against analytical grade standard reference compound which is available in market.

Synthetic method

Reflux for around 6 h was carried out after addition of chitosan (2.0 g, equivalent to 12 mmol NH_2), 2-acetylpyridine (2.05 g, 12 mmol to ethanol (75 ml) and acetic acid (20 ml). The solid was filtered from the resultant mixture after cooling. Approx. 3.75 g of chitosan pyridyl imine (CPI) was obtained after ethanol wash and 6 h of vacuum drying.

Stirred 1 (2.0 g) with palladium acetate (0.25 g, 0.5 mmol) in acetone (100 ml) for 8 h at 25–30 °C. After Pd adsorption, the solid was washed completely to draw out any unadsorbed Pd. The catalyst was rinsed with ethanol 50 g, dried to solid at 75 °C for 8 h under vacuum to give 2.05 g chitosan pyridyl imine palladium (CPIP) complex catalyst (Fig. 1). The intrinsic viscosity and viscosity average molecular weight of CPI (η = 3.4 dL/g and Mv = 1.48 × 10⁵ Da) and CPIP (η = 3.5 dL/g and Mv = 1.63 × 10⁵ Da) were determined by Ubbelohde viscometer using acetic acid as solvent. It is clearly revealed from these results that both intrinsic viscosity average molecular weights directly impact the functional groups present in chitosan.

Instrumentations

FT-IR spectrometer (Perkin Elmer) in set up of KBr pellets over the range of 400–4000 cm⁻¹ wave numbers was used for the Fourier transform infrared (FT-IR) studies. NMR test was performed with 400 and 500 MHz spectrometers for ¹H NMR and 100 MHz for ¹³C NMR on Bruker Supercon Magnet Avance DRX-300 spectrometers in deuterated solvents with TMS as a reference (chemical shifts δ in ppm, coupling constant *J* in Hz.). Multiplicities are described as follows: singlet (s), doublet (d), triplet (t), multiplet (m), and broad singlet (br s). The ESI positive ion mode is used for mass



Fig. 1 The chitosan pyridyl imine complex synthesis and conversion of it to corresponding Pd complex

spectra and HRMS. The progression of reaction was surveilled by thin-layer chromatography (TLC) on pre-coated silica gel plates. All compounds were identified and characterized by TLC, ¹H NMR, 13C NMR, MS and HRMS.

Py-GC/MS instrument was designed by Agilent technologies (Santa Clara, California, United States). Singleshot pyrolyser unit from frontier laboratories with a platinum coil and a quartz sample tube was coupled to column. Samples were heated up in furnace at 700 °C and an interface at 280 °C@ 7 °C/min and held at this temperature for 1 min. The pyrolysis products were divided on an Ultra alloy HP-5MS column (frontier laboratories, Tokyo, Japan) with helium (99.998% pure) as carrier gas (100 kPa). The pyrolysis chamber was maintained at 250 °C and purged with helium (99.998% pure). The GC was programmed from 75 °C (1 min) to 280 °C at 7 °C /min (elution time 40.28 min). The mass spectrometer was conducted with a scan range of m/z = 15-450 in electron impact mode, and the products were discovered by comparing to mass spectral library of NIST and results in the previous researches. XRD apparatus is equipped with x' Celerator solid-state detector. The apparatus contains vertical theta-theta goniometer $(0^{\circ} < 2\theta < 160^{\circ})$. The radiation utilized is Cu K-alpha-1, whereas nickel metal is utilized as beta filter.

The XPS assay was conducted with a spectrometer (model MULTILAB 2000 Base system with X-ray, Auger and ISS attachments), using an Mg-K α source (1253.6 eV) (Twin Anode Mg/Al (300/400 W) X-ray Source.). The X-ray source was operated at a power of 300 W (10 keV and 30 mA). The pressure inside the vacuum chamber was 5×10^{-8} torr. A hemispherical analyser with 110 mm was employed with 4 variable analyzer slits, viz 5, 2, 1 mm and 4 mm, which operates in constant analyser energy (CAE) and constant retard ratio (CRR) modes. The CCD camera and zoom microscope for optical viewing was utilized to check the spectrum and to identify the analysis area size. All spectra were achieved utilizing a 900-µm-diameter analysis zone. Chitosan and PDIP complex were launched on a stainless steel sample holder and incubated for 12 h under vacuum before transferring to the spectrometer analysis chamber.

Morphology of the synthesized PDIP complex was visualized through field emission scanning microscopy (FE-SEM) on Hitachi-SU8010 microscope. Elemental analysis of the yields was determined from EDS coupled with FE-SEM apparatus. Dried pattern images were taken utilizing Carl Zeiss Axio Imager 2Am microscope. Images were analyzed using axio-vision software. The surface of catalyst was evaluated by the Brunauer–Emmett–Teller (BET) technique on a Quanta chrome NOVA 2200E BET device; before each assessment, the sample was heated to 50 °C and maintained at such temperature for 12 h. The BET surface area was computed based on the adsorption data in the relative pressure range of 0.05 to 0.25.

The thermal stability of the chitosan and PDIP complex was investigated using thermo-gravimetric analysis instrument (PerkinElmer TGA 8000) from 30 to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere, and then, after from 600 to 850 °C, oxygen was purged. The transition temperature of both chitosan and PDIP complex was determined using differential scanning calorimetry (PerkinElmer DSC 4000) from 40 to 180 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

Results and Discussions

FT-IR analyses

The FT-IR spectra of the pristine chitosan and CPIP complex in the 4000–400 cm⁻¹ ranges are depicted in Fig. 2. The absorption bands for chitosan at 3300–3350 related to the N–H group and 2700–3000 cm⁻¹ are ascribed to methylene (-CH₂) group. The wide band peak at 3450 attributed to the



Fig. 2 FT-IR spectra of a chitosan, b CPIP complex catalyst

hydroxyl groups (Hada et al. 2019; Mozafari and Chauhan 2019; Sudheesh et al. 2010). The FT-IR spectrum of the CPIP complex catalyst which was almost identical to the corresponding chitosan except carbonyl stretching in acetyl group, which was at 1640 cm⁻¹, has completely vanished in CPIP complex catalyst, which clearly revealed that de-acetylation was completely done. The strength of the IR bond at 3300-3350 cm⁻¹ reduced suggesting the stabilizing of the palladium nanoparticles in the chitosan medium. The presence of new peaks at 1300–1500 cm⁻¹ is attributed to C=N groups of pyridyl moieties present in CPIP complex catalyst.

Pyrolysis GC–MS

To analyze the intact insoluble organics, pyrolysis GC–MS was used as it is uphill task to analyze them by traditional chromatographic techniques. Pyrolysis decomposes insoluble samples into volatile molecules and facilitates the segregation and identification of decomposed fragments by gas chromatography followed by mass spectrometry (Chauhan et al. 2011). The mechanism of polymer degradation in pyrolysis (GC/MS) is a technique founded on the volatile fragments production by thermal energy and analyzed by GC/MS (Chauhan et al. 2012; Chauhan 2013; Furuhashi et al. 2009).

The degradation of polymers is basically a free radical procedure commenced by bond separation at the pyrolysis



temperature. The whole ion chromatograms for chitosan and CPIP pyrolysis were discovered by utilizing the Nist library. For chitosan, there were five peaks in pyrogram, which may be due to acetic acid (RT 2.44 min; RA = 98%) derived from chitin, pyrrol (RT 3.02 min; RA = 85%) derived from chitin/chitosan, methylpyridine (RT 3.56 min; RA = 95%) derived from chitosan, acetylpyridine (RT 6.25 min; RA = 95%) derived from chitosan and an unknown compound (RT 9.15 min; RA = 75%)) derived from chitin, whereas for CPIP complex catalyst there were three large peaks in pyrogram, which may be due to acetic acid (RT 2.39 min; RA = 99%) derived from chitin, pyrazine (RT 2.87 min; RA = 97%) derived from chitosan, pyridine (RT 2.93 min; RA = 93%) derived from chitin, acetamide (RT 3.22 min; RA = 93%) derived from chitin, methyl pyrazine (RT 3.47 min; RA = 97%) derived from chitosan and acetylpyrazine (RT 6. 13 min; RA = 74%) derived from chitosan. These results suggest that pyrolysis mechanism may be owing to unzipping, random scission and side group removal. In such polymers, pyrolysis provides fragmentation to tinier segments and unzipping to monomer. The attached groups to the side chain were weaker rather than backbone bonds. The side groups are detached from the backbone before cracked into tinier pieces; therefore, monomer and oligomers were not observed.

XRD analyses

The 2 θ values are in between 10° and 20° in XRD pattern for chitosan, which is probably attributed to hydrogen bonding between –OH and –NH₂ groups. XRD data for chitosan and CPIP complex catalyst are given in Table 1. The characteristic semicrystalline peaks of pure chitosan are observed at 9.4792° and 20.08° (Fig. 3). In the case of CPIP complex, a change in the intensity of the chitosan peaks (8.9197° and 20.2420°) was observed on the addition of Pd(OAc)₂ to chitosan pyridyl imine. Shift in the peaks of chitosan is owing

to the interaction with palladium acetate clearly suggested the proposed structure of CPIP complex catalyst.

XPS analysis

XPS (X-ray photo-electron spectroscopy) is a powerful method to examine how metal ions bind onto these patterns. To further investigate the mechanism of catalyst formation and also the interaction present in between Pd and CPI, the high-resolution C 1*s* XPS, N 1*s* XPS, Pd 3*d* v and O 1*s* XPS spectra are depicted in Fig. 4a–h, and data for different runs

Table 1 XRD data of raw chitosan and CPIP complex catalyst	Compound	Pos. (°2 θ)	FWHM total (°2 θ)	d-spacing (Å)	Rel. Int. (%)
	Raw chitosan	9.4792	3.6553	9.32258	69.32
		20.0801	2.5878	4.41845	100.00
	CPIP complex catalyst	8.9197	2.8663	9.90607	28.71
		20.2420	2.6531	4.38348	100.00



Fig. 3 X-ray diffractogram for a chitosan and b CPIP complex catalyst



Fig. 4 XPS analyses (a, b) C 1s (c, d) N 1s, Pd 3d (e, f) and O 1s plus Pd 3p (g, h) for CPIP complex catalyst

Element	Start BE	Peak BE	End BE	Height (counts per second)	FWHM eV	Atomic %	Assignments
C1s scan A	289.6	283.51	280.95	12,421.72	1.39	15.98	C–C or adventitious carbon
C1s Scan B	289.6	285.04	280.95	22,845.94	1.36	28.56	C–N, C=N, C–O or C–O–C
C1s Scan C	289.6	286.57	280.95	8156.23	1.77	13.32	0–C–O, C=O
Pd3d5 Scan A	345.05	334.78	331.95	4469.16	1.88	0.68	_
Pd3d5 Scan B	345.05	336.55	331.95	6766.66	1.82	1	-
O1s Plus Pd 3p3 Scan A	536.05	531.15	527.45	11,092.64	1.06	4.03	Pd–O
O1s Plus Pd 3p3 Scan B	536.05	530.34	527.45	12,040.92	1.95	8.03	Pd–O
O1s Plus Pd 3p3 Scan C	536.05	531.71	527.45	29,038.1	1.31	13.02	Pd–O
O1s Plus Pd 3p3 Scan D	536.05	532.12	527.45	11,453.78	1.96	7.69	Pd–O
O1s Plus Pd 3p3 Scan E	536.05	534.18	527.45	1259.27	1.9	0.82	Pd–O
N1s Scan A	402.25	398.51	394.9	6316.68	1.83	6.56	C–N

are given in Table 2. There are three N 1 s peaks located at 398.5 eV that are attributed to the existence of the nitrogen atom present in pyridine moiety, which is in very close agreement with 398.7 eV for pyridine mentioned in previously published literature (Jansen and Bekkum 1995). The XPS spectrum of Pd 3*d* in the CPIP complex catalyst consists of single and intensive doublet (336.3 and 342 eV) which may belong to the +2 oxidation state of Pd (Fig. 4e, f) (Mauriello et al. 2015; Sun et al. 2014).

Bands at 530.3 and 531.1 eV were discovered in the spectrum (Fig. 4g) which might be ascribed to N...Pd-O interaction present between CPI and Pd(OAc)₂. Through detailed peak fitting using the XPS peak software package, the peak amounts were given to the presence of interaction between Pd 3d and O 1s which indicated that $Pd(OAc)_2$ were more likely to bond with CPI. For the spectrum of O 1s, the band of the initial chitosan was comprised of two subbands, which are ascribed to the existence of OH (534.2 eV) and the -O- in the ring and feasibly -O- between the rings (532.1 eV) which are present in chitosan structure. The bands appeared at 283.1 eV (C-C), 285 eV (C-N, C=N, C-O or C-O) and 286.6 eV (C=O, O-C-O) also suggested the formation of CPI and CPIP complex catalyst. On the basis of above explanation, we speculated that $Pd (OAc)_2$ was tetracoordinated to two nitrogen atoms present in CPI and two oxygen present in acetate groups. The binding energy and atomic percentage for CPIP complex catalyst are given in Table 3 and XPS spectrum is shown in Fig. 5.

FE-SEM, and surface area analyses

The surface morphology of the CPIP complex examined by FE-SEM images at different scale measurements is depicted in Fig. 6, and its color image presented in Fig. 7 clearly depicts the layered structure of catalyst). The catalyst surface has a lower surface area, which is verified by the N_2

 Table 3 Binding energy (eV) and atomic concentration of O 2 s, C

 1 s, Pd 3d and N1s in CPIP complex catalyst

Element	Peak BE (eV)	Atomic %	
O 2 <i>s</i>	25.18	24.4	
C 1 <i>s</i>	285.06	66.14	
Pd 3 <i>d</i>	336.29	1.8	
N 1 <i>s</i>	398.86	7.3	



Fig. 5 XPS analysis (full) for CPIP complex catalyst

adsorption surveys. The BET surface area of the catalyst was discovered to be ~1.84 m² g⁻¹ with a pore diameter of 227 Å.

SEM–EDS analysis

SEM-EDS images of CPIP complex catalyst are displayed in Figs. 8 and 9. SEM image suggested the binding of chitosan







Fig. 7 FE-SEM image (color) showing layered structure of CPIP complex catalyst having well distribution of constituent elements carbon, oxygen, palladium and nitrogen using FE-SEM

pyridyl amine with $Pd(OAc)_2$. It has been assumed that the size and the uniformity of particles are related to the binding of chitosan pyridyl amine with palladium acetate (Fig. 8). EDS indicates that the CPIP comprised of carbon, oxygen,

palladium and nitrogen with wt% (atomic%, series) as 41.2 (49.9, K), 44.5 (40.5, K), 3.8 (0.52, L) and 8.29 (8.61, K) (Fig. 9).

TG-DTG and DSC analyses

The thermal behavior of chitosan and CPIP complex catalyst are depicted in Fig. 10. Chitosan and CPIP complex catalyst have three main weight losses 30-250 °C; 250-600 °C; and 600–850 °C. The first weight loss of ~10% was ascribed to the elimination of physical adsorbed water molecules. The second phase weight loss of 53.7% (chitosan) and 51.7% (CPIP complex catalyst) is because of the decomposition of the polysaccharide chain and decomposition of the polysaccharide framework and also loss of side chains such as pyridyl groups, etc., and third stage weight loss for both chitosan and CPIP complex catalyst is due to oxidation of organic substance in form of carbon monooxide and carbon dioxide because in experiment oxygen was purged from 600 to 850 °C. CPIP complex catalyst has higher decomposition temperature ($T_{d,1}$ =300.6 °C, $T_{d,2}$ =614.1 °C) than chitosan $(T_{d,1}=297.9 \text{ °C}, T_{d,2}=610.1 \text{ °C})$ which clearly suggest that CPIP complex catalyst is slightly more thermally stable. TG-DTG and DSC data for raw chitosan and CPIP complex catalyst are given in Table 4.



Fig.8 Layered structure seen from FE-SEM (a) and Al mapping of the constituents elements present in CPIP complex catalyst by EDS (b-e)



Fig. 9 Energy-dispersive X-ray spectrum for CPIP complex catalyst



r¹³⁸⁵

2843

Fig. 10 TG-DTG thermogram a chitosan, b CPIP complex catalyst

The volatilization heat of polymers was calculated using DSC where region beneath the endothermic peak was shown to be linearly related to the volatilization heat. Melting transition temperature and heat of melting in endotherm for

Compound	Stage	Δw(%)	Temperature range (°C)	Maximum weight change speed (mg/s)	Char yield (%)	Transition temperature(Tm; $^{\circ}$ C) and enthalpy change (ΔH ; J/g) by DSC	
Chitosan	I	101	30–250	_	1.1	127; 165	
	II	53.7	250-600	297.9			
	III	35.2	600-850	610.1			
CPIP complex catalyst	Ι	10.4	30-250	-	1.2	120.8; 179.8	
	II	51.7	250-600	300.6			
	III	36.7	600-850	614.1			

Table 4 TG-DTG and DSC data for chitosan and CPIP complex catalyst



Fig. 11 DSC thermograms for a chitosan, b PDIP complex catalyst

chitosan were observed at 127.8 °C and 165 J/g, whereas for CPIP complex catalyst it was 12.8 °C and 179.8 J/g (Fig. 11).

Organic transformation

The weight % of Pd loading in catalyst is the real measure of activity of the catalyst. It was found that 0.018 wt% of Pd loading in catalyst and 0.138 mol% Pd were the active concentration present in catalyst.

General procedure for hydrogenation of nitro aryl to amino aryl (1a)

Nitro aryl compound (4.06 mmol) stirred in the presence of CPIP (50 mg) and under hydrogen atmosphere in ethanol

(20 ml) for 6 h. Reaction monitor on TLC. Catalyst recovered by filtration and amino aryl isolated by distillation of ethanol, isolated yield 99% (Table 5).

Recovered catalyst was reused with 10% top-up fresh catalyst, yield 97–98%; five recycling of catalyst was performed (Fig. 12).

General procedure for Suzuki–Miyaura cross-coupling reaction

Aryl halide (5.0 mmol), phenylboronic acid (6.0 mmol), potassium carbonate (15.0 mmol) and 50 mg of CPIP were heated in sealed tube at 70–75 °C (under nitrogen atmosphere) in 30 ml ethanol/water (1:1) for 3hrs. After completion of the reaction, catalyst recovered by filtration. Filtrated ethanol/water, distilled and compound, was purified through



 Table 5
 Hydrogenation of nitro

aryl to amino aryl



Reaction conditions: 4.06 mmol nitrobenzene, hydrogen gas, 25 mg CPIP, ethanol, stir at 25–30 °C, Isolated yields were reported after distillation of ethanol from reaction



Fig. 12 Yield chart with five recycling of catalyst (hydrogenation of nitrobenzene to aniline)

a short column chromatography (silica gel 100–200 mesh) using ethyl acetate and n-hexane (20% ethyl acetate in n-hexane) to get the pure biaryl, isolated yield > 97%, (Table 6). Chlorobenzene was also tested, but the results were not satisfactory and inactive in these reactions.

Recovered catalyst was reused with 20% top-up fresh catalyst, yield 97–98%; five recycling of catalyst was performed (Fig. 13).

Reaction condition: 5 mmol aryl bromide, 6 mmol phenylboronic acid, 50 mg CPIP, 15 mmol K_2CO_3 , 30 ml ethanol/water (1:1), 70–75 °C; Isolated yields were reported after column chromatography. Table 6 Suzuki–Miyaura cross-

coupling reaction



97

96.5

General procedure for heck cross-coupling reaction

Aryl halide (5.0 mmol), alkenes (6.0 mmol), cesium carbonate (15.0 mmol) and 50 mg of CPIP were heated in sealed tube at 100–105 °C (under nitrogen atmosphere) in 30 ml toluene for 3 h. After completion of the reaction, catalyst recovered by filtration. Filtrated toluene distilled and compound purified through a short column chromatography (silica gel 100–200 mesh) using ethyl acetate and n-hexane (20% ethyl acetate in n-hexane) to get the pure vinylbenzene, isolated yield 75–92% (Table 7).







 Table 7
 Heck cross-coupling

 reaction





Figure14 Yield chart with five recycling of catalyst (heck cross-coupling reaction of bromobenzene with 3,3-dimethyl-1-butene)

Recovered catalyst was reused with 20% top-up fresh catalyst, yield 75–92%; five recycling of catalyst was performed (Fig. 14).

Reaction conditions: 5.0 mmol aryl bromide, 6.0 mmol alkene, 50 mg catalyst 2, 15 mmol Cs_2CO_3 , 30 ml toluene, 100–105 °C. Isolated yields were reported after column chromatography.

General procedure for degradation of aniline yellow dye

Aniline yellow (5 mmol) stirred in presence of CPIP (50 mg) and under hydrogen atmosphere in methanol (30 ml) (Fig. 15) for 6 h. Initial yellow color of reaction disappears during reaction hold period. Two spots corresponding to aniline and benzene-1,4-diamine was observed on TLC system using 0.5% methanol and chloroform as solvent.

The primary objective of the present paper was to develop a heterogeneous green catalyst that is recyclable and reduces hazardous waste. We have done five recycling tasks with the top catalytic converter. This catalyst at is at the first stage of generation, and there is a possibility of further improvement in its activities and applications. There is a high demand for further efforts to develop sustainable catalysts and appropriate means of recovery, reactivation and regeneration (Molnár and Papp 2017). Of course, catalytic deactivation in industrial processes requires special attention, and regeneration is a key issue in terms of economy and sustainability. Nowadays in commercial production, the catalyst is preferably recycled with top-up. This is because there is a possibility of a stuck reaction between the two if we use a catalyst without a top-up. Top-up always increases the catalytic activity of the reaction.

Conclusion

In summary, we introduce a facile and green technique to synthesize chitosan pyridyl imine palladium (CPIP) complex catalyst from chitosan, 2-acetylpyridine and Pd(OAc)₂. It has been characterized using FT-IR, Py (GC–MS), XRD, XPS, FE-SEM, BET adsorption, EDX, TG-DT and DSC. From XPS study, it was revealed that Pd (OAc)₂ has been tetracoordinated to two nitrogen atoms present in CPI and two oxygen present in acetate groups. TG-DTG results suggested that this catalyst is thermally stable up to 300 °C. This catalyst has proved to be active and recyclable catalysts for both Suzuki and Heck reactions. It also exhibits excellent catalytic performance for the nitrobenzene and azo dye reduction. Benefited from increased catalytic performance, high stability and ease of synthesis, CPIP complex catalyst is very promising for applications in organic transformation.





Acknowledgements The authors are thankful to SAIF, Punjab University, Chandigarh for characterization like SEM, TEM, FT-IR and XRD. We are also thankful to CECRI, Karaikudi, for XPS. Authors are also thankful R &D, BKT tyre for py (GC-MS), TG-DTG, DSC, nitrogen adsorption and FT-IR for analyses.

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