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Authors: Vishal Kandathil, Manjunatha Kempasiddaiah, Sasidhar B. S., Siddappa A. Patil

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From Agriculture Residue to Catalyst Support; A Green and Sustainable Cellulose-Based Dip Catalyst for C-C Coupling and Direct Arylation

Vishal Kandathil^a, Manjunatha Kempasiddaiah^a, Sasidhar B. S.^b, Siddappa A. Patil^{a,*}

^aCentre for Nano and Material Sciences, Jain University, Jain Global Campus, Kanakapura, Ramanagaram, Bangalore 562112, India.

^bOrganic Chemistry Section, National Institute for Interdisciplinary Science and Technology (CSIR), Trivandrum 695019, India.

Corresponding author: Dr. Siddappa A. Patil Tel: +91 80 27577254 Fax: +91 80 27577211 E-mail: p.siddappa@jainuniversity.ac.in/patilsiddappa@gmail.com

Highlights

- ✤ Dip catalyst was designed and synthesized in an environmentally benign approach.
- Cellulose isolated from agriculture residue in a facile method.
- ◆ Pd NPs synthesized using biogenic method avoiding hazardous chemicals.
- Dip catalyst was efficient in catalyzing C-C coupling as well as direct arylation reactions.
- Easily recoverable and highly recyclable.

Abstract:

The core characteristics of a perfect catalyst include good activity, simple design, excellent stability, easy recovery from reaction mixture, recyclability, and have the provision for easy scale up. The ease in synthesis, recyclability and scale up makes the dip catalyst a major contender in this regard which possess most of the aforementioned characteristics. In this work, we report a dip catalyst made of cellulose, isolated from agriculture residue (sugarcane bagasse), in which biogenically synthesized palladium nanoparticles were dispersed. The prepared dip catalyst was characterized by FESEM, EDS, XRD, ATR-IR, TGA, TEM, XPS and ICP-OES analysis. Also, the activity of the dip catalyst was studied in the Suzuki-Miyaura cross-coupling reaction and was found to give excellent conversion with 15 recycles. Further, the activity of dip catalyst in C5-arylation of 2-substituted thiophenes was evaluated for which promising yields were obtained.

Keywords: Bagasse; Cellulose; C-C coupling; C-H activation; Dip catalyst; Palladium nanoparticles

1. Introduction

Metal nanoparticles (MNPs) find huge applications in diverse fields of science which include electronics (Kumar et al., 2018), optics (Burda, Chen, Narayanan, & El-Sayed, 2005; Kelly, Coronado, Zhao, & Schatz, 2003), drug delivery (Albrecht, Evans, & Raston, 2006), water purification (Albertini, Ribeiro, Alves, Baleizão, & Farinha, 2018), energy (Ni et al., 2018; X. Xu

et al., 2018), catalysis (Liu & Corma, 2018; Rothfuss, Knofel, Roesky, & Barner-Kowollik, 2018) and so on. The distinctive properties of MNPs which make them suitable for various applications can be attributed to the large surface to volume ratio they have. In the catalysis field, diverse research is underway to effectively utilize the noble MNPs for catalyzing different reactions and for the convenient recovery of those MNPs for further recycles. Being nano in size, their recovery is quite difficult from reaction mass which results in the incomplete recovery and also has the consequences of MNPs aggregation (Hotze, Phenrat, & Lowry, 2010). The carbon-carbon, carbonheteroatom bond formation and C-H activation reactions are some important applications where the astonishing properties of these MNPs can be implemented (Cheng, Zhang, Li, & Liu, 2014; Chng, Erathodiyil, & Ying, 2013). Among the various MNPs available, palladium nanoparticles appear to be one of the most important MNPs which is indispensable from catalyzing various organic transformations of industrial and academic interest (Yin & Liebscher, 2007).

The immobilization of palladium nanoparticles on various supports has been studied widely and much effort has been taken in this regard (Khalafi-Nezhad & Panahi, 2011; Shylesh, Schunemann, & Thiel, 2010). Among the various kinds of supports which include metal oxides (Jin et al., 2012; Okumura, Kobayashi, Tanaka, & Niwa, 2003), silica (Martínez et al., 2015; Yang et al., 2012), polymers (Modak, Mondal, Sasidharan, & Bhaumik, 2011; Modak, Pramanik, Inagaki, & Bhaumik, 2014) etc., biogenic and green supports are of high priority due to the greenness and sustainability involved (Baran, Aciksoz, & Mentes, 2016; Baran, Inanan, & Mentes, 2016; Baran, Sargin, Kaya, & Mentes, 2016; Baran, Yılmaz Baran, & Menteş, 2018a, 2018b; Khazaei, Khazaei, & Rahmati, 2015; Khazaei, Rahmati, Hekmatian, & Saeednia, 2013). Cellulose is a good candidate in this regard as it falls in green and sustainable group of supports (Mtibe et al., 2015; Yilmaz Baran, Baran, & Mentes, 2018). The natural polymer, cellulose, is available in

abundant in nature and can be isolated by various means (Xie et al., 2016; Zhao, Moser, Lindstrom, Henriksson, & Li, 2017). The strong beta-(1-4) glycosidic linkage makes the cellulose strong enough to withstand most of the reaction conditions which is applicable in various organic transformations (Kaushik & Moores, 2016). Sugarcane bagasse, which is a rich source of cellulose and an agriculture residue, is produced in large quantity as a byproduct from sugar mills, of which some quantity goes to boiler industries and paper industries (Mandal & Chakrabarty, 2011). The cellulose can be isolated from bagasse without much effort and can be utilized in production of various value added products ranging from membranes to paper (Habibi, Lucia, & Rojas, 2010; Teixeira et al., 2011). The biodegradability, abundance, low cost, and greenness are some of the key advantages of cellulose which gives them an upper hand among other reported synthetic supports (Habibi et al., 2010).

Amongst the various cross-coupling reactions, Suzuki-Miyaura cross-coupling still stands lucrative because of the ease in performing this reaction, use of mild reaction conditions, high yield, and wide range of functional group tolerance (Baran, 2018a, 2018b; Phan, Van Der Sluys, & Jones, 2006). Even though there is a tremendous increase in research on new catalytic system with high catalytic activity for Suzuki-Miyaura cross-coupling reactions, a very few are commercialized (Blaser, Indolese, Naud, Nettekoven, & Schnyder, 2004). Some of the core reasons behind the non-commercialization of the palladium based catalyst can be attributed to the high cost in production, multi-step synthesis, stability of the catalyst, difficulty in the recovery of the catalyst and recycling (Blaser et al., 2004). Direct arylation reaction (C5-arylation) of 2substituted thiophenes with aryl halides is another class of reaction which is very important in organic chemistry since there is a wide range of products that can be synthesized by this strategy ranging from active pharmaceutical ingredients to various agro products (Rossi, Bellina, Lessi, &

Manzini, 2014; Steinmetz et al., 2012). There is an urgent need in this field for further development of catalysts which can catalyze the arylation under mild reaction conditions, which can be easily recovered and recycled and also results in high yield. So in this regard "dip catalysts" are getting more attention because of the ease of recovery and recycling associated with them (Ahmad, Kamal, Khan, & Asiri, 2016; Hariprasad & Radhakrishnan, 2012; Mourya, Choudhary, Basak, Tripathi, & Guin, 2018; Xiang, Chen, Liu, & Lu, 2018; Zheng, Polavarapu, Liz-Marzán, Pastoriza-Santos, & Pérez-Juste, 2015).

In continuation of our strategy to work towards a green and sustainable approach in catalysis (Kandathil, Dateer, Sasidhar, Patil, & Patil, 2018; Kandathil, Fahlman, Sasidhar, Patil, & Patil, 2017; Kandathil, Koley, et al., 2018; Manjunatha et al., 2018; Vishal, Fahlman, Sasidhar, Patil, & Patil, 2017), herein we report a new, efficient, economical, recyclable, and environmentally benign palladium based dip catalyst. Here, cellulose pulp was separated from agriculture residue, sugarcane bagasse, to which biogenically synthesized palladium nanoparticles were incorporated and was made into strips. This dip catalyst was characterized by various analytical techniques like ATR-IR, XRD, FESEM, EDS, TGA, TEM, XPS and ICP-OES and studied for their activity in Suzuki-Miyaura cross-coupling reactions and C5-arylation of 2-substituted thiophenes.

2. Experimental

2.1. Materials

Palladium nanoparticles were synthesized according to our previous report (Kandathil, Dateer, et al., 2018). The sugarcane bagasse was collected from local juice shop in Bangalore, India. Unless otherwise stated, all reactions were performed under aerobic conditions in oven-

dried glassware with magnetic stirring. Palladium acetate, aryl halides, 2-substituted thiophenes, sodium carbonate, pivalic acid, phenylboronic acid, silver oxide and sodium sulphate were purchased from Sigma-Aldrich and Avra chemical company and were used without further purification. Heating was accomplished by either a heating mantle or silicone oil bath. Reactions were monitored by thin-layer chromatography (TLC) performed on 0.25 mm Merck TLC silica gel plates, using UV light as a visualizing agent. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230-400 mesh). Yields refer to chromatographically pure material. Concentration *in vacuo* refers to the removal of volatile solvent using a rotary evaporator attached to a dry diaphragm pump (10-15 mm Hg), followed by pumping to a constant weight with an oil pump (<300 mTorr).

2.2. Characterization

Attenuated total reflectance infrared spectra were recorded with a Bruker Alpha Eco-ATR spectrometer. The elemental palladium content in dip catalyst was determined by Perkin Elmer Optima 5300 DV inductively coupled plasma optical emission spectrometer. Transmission electron microscope images were obtained using Jeol/JEM 2100 microscope. A JEOL JSM 7100F field-emission scanning electron microscope (FESEM), fitted with energy dispersive X-ray spectroscopy (EDS), was used to observe the morphology and elemental distributions of samples. Thermogravimetric analysis was carried out using a thermal analyzer (TGA/DTA) (STA-2500, NETZSCH, GERMANY) with a heating rate of 10.0 °C/min. X-ray powder diffraction patterns were obtained using Rigaku X-ray diffraction Ultima-IV. X- ray photoelectron spectroscopy study was performed using PHI 5000 Versa probe- Scanning ESCA Microprobe, Physical Electronics, USA. ¹H NMR spectra were recorded at 400 MHz, and are reported relative to CDCl₃ (87.27) and

DMSO- d_6 (δ 2.49). ¹H NMR coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet).

2.3. Preparation of palladium nanoparticles – cellulose pulp composite

The sugarcane bagasse was air died initially to remove the moisture content and then cut into small pieces of ~1 cm length. The dried bagasse chunks were then taken in a beaker with 5% sodium hydroxide solution and heated to 85 °C under mechanical stirring for 5-6 hours. After that the pulp was separated by centrifugation and washed till neutral pH with distilled water to remove the inorganic salts present.

The palladium nanoparticles were synthesized biogenically according to method reported in our previous work (Kandathil, Dateer, et al., 2018). A suspension of biogenically synthesized palladium nanoparticles in ethanol (1 M) was added to the pulp prepared as above and kept under stirring for 4-5 hours. The pulp with palladium nanoparticles was then poured to a laboratory made set up to get a sheet of palladium nanoparticles-cellulose strip which was then cut into required size and length after drying at 40-45 °C for catalysis applications.

2.4. General procedure for Suzuki-Miyaura cross-coupling reaction

In a 10 mL glass vial equipped with a cap containing 5 mL of ethanol:water (1:1) mixture, aryl halide (1 equiv), phenylboronic acid (1.1 equiv), K_2CO_3 (2.5 equiv) were added followed by dipping of the dip catalyst into the reaction mixture which was then stirred magnetically at room temperature for required time. The progress of the reaction was monitored by thin layer chromatography (TLC). After reaction completion, the dip catalyst was simply removed from the reaction mass and washed with ethanol (1 x 5 ml) and water (1 x 5 ml) and was reused without purifying further. The product was extracted using dichloromethane (2 x 10 mL) and the combined organic layer was subjected to water wash (2 x 10 mL) followed by drying of the organic layer

over Na₂SO₄. The dried organic layer was concentrated *in vacuo*, and the product was purified by column chromatography using *n*-hexane and ethyl acetate as eluents to afford the corresponding products in good to excellent yields. All the coupled products were known molecules and were confirmed by comparing with our previous standards (Kandathil et al., 2017; Vishal et al., 2017).

2.5. General procedure for the C5-arylation of 2-substituted thiophenes

Aryl halide (1 equiv), 2-substituted thiophene (0.8 equiv), Na₂CO₃ (1.5 equiv), PivOH (1.5equiv), Ag₂O (0.75 equiv) were added to a 10 mL glass vial equipped with a cap containing 5 mL of DMF followed by dipping the dip catalyst in to the reaction mass. The reaction mass was stirred at 120 °C for required time. TLC was employed for monitoring the reaction progress. The dip catalyst was easily removed from the reaction mass following reaction completion and washed with ethanol (5 ml) and water (5 ml) and was used in next cycle. The product was then extracted with dichloromethane (2 x 10 ml). The combined organic layer was subjected to water wash (1 x 10 ml) and brine wash (1 x 10 ml). The final organic layer was dried over Na₂SO₄ and concentrated *in vacuo*. The product was purified by column chromatography using *n*-hexane and ethyl acetate as eluents to afford the corresponding products in good yields. All the coupled products were known molecules and were confirmed by comparing the ¹H NMR (see supplementary data for details) with literature reports.

2.6. Procedure for the recovery of the dip catalyst

After the reaction completion, the dip catalyst was taken out effortlessly using forceps followed by dipping the same in ethanol and water. The washed dip catalyst was then dried at 40-45 °C and reused in further cycles without further purification.

3. Results and Discussion

3.1. Biogenic synthesis and characterization of palladium nanoparticles

The palladium nanoparticles were synthesized biogenically using black pepper extract as per our previous report (Kandathil, Dateer, et al., 2018). The palladium nanoparticles were characterized by ATR-IR, FESEM, EDS, UV-Visible spectrophotometry and XRD and were found in accordance with the previous report (Kandathil, Dateer, et al., 2018).

3.2. Isolation of cellulose from sugarcane bagasse and casting of the dip catalyst

The sugarcane bagasse is a fibrous residue obtained as a byproduct in sugar industries after extraction of sugar. The cellulose was isolated from sugarcane bagasse and the dip catalyst was prepared step-wise as depicted in Fig. 1. Initially, the sugarcane bagasse collected was dried in sunlight and cut into small pieces and were subjected to base hydrolysis for removing the lignin and hemicelluloses. Lignin can be effectively removed by alkaline pretreatments which is even cost effective when compared with other pretreatments which work at high temperature and pressure (Rabelo, Fonseca, Andrade, Filho, & Costa, 2011). After delignification, the pulp obtained was washed with water thoroughly up to neutral pH. The cellulose pulp was casted to strips (cellulose strip) and was characterized by ATR-IR, FESEM, and XRD to find out the chemical composition and morphology.





Fig. 1. Steps involved in the preparation of dip catalyst from sugarcane bagasse and conceptualized representation of cellulose-palladium nanoparticles interaction.

The pulp obtained was then mixed with 1M dispersion of palladium nanoparticles in ethanol and stirred for 4-5 hours at room temperature. During this period the palladium nanoparticles will be stabilized and immobilized on cellulose support by the strong bonding interactions of hydroxyl groups present in cellulose as shown in Fig. 1 (He, Kunitake, & Nakao, 2003; C. Xu, Cheng, Shen, & Liu, 2007). The Vander Waals force of attraction plays the major role in interaction of palladium with hydroxyl groups of cellulose (Zheng, Kaefer, et al., 2015). Also, being highly oxyphilic in nature, palladium encompasses strong attraction with the hydroxyl groups present on the cellulose (Rosario et al., 2014).Thus the hydroxyl groups on cellulose may act as the points of anchoring for the immobilization of palladium nanoparticles through electrostatic interaction which also prevents the aggregation of the Pd NPs (He et al., 2003; C. Xu et al., 2007).

3.3. Spectroscopic and microscopic characterization of dip catalyst

To begin with the structure of prepared cellulose strip as well as dip catalyst was evaluated by ATR-IR (Fig. 2). The ATR-IR spectrum of cellulose strip (Fig. 2a) shows a broad band at \sim 3335 cm⁻¹ which is the characteristic peak due to O-H stretching. Also, the peak at \sim 1643 cm⁻¹ is

due to the O-H overtone vibrations. The intense peak at 1029 cm⁻¹ is due to the C-O-C skeletal vibrations of pyranose ring. Additional peaks at 2854 cm⁻¹, 1424 cm⁻¹ and 1369 cm⁻¹ are due to the aliphatic C-H stretching, CH₂ symmetric bending and C-H bending respectively. A small peak at 896 cm⁻¹ indicates the C-O-C, C-C-O and C-C-H deformation and stretching vibrations (Baran, Baran, & Menteş, 2018; Baruah, Das, Hazarika, & Konwar, 2015). Thus ATR-IR spectrum confirms the structure of cellulose extracted from sugar cane bagasse and also it shows that the delignification process was effective due to the absence of any other peaks, for instance, peaks which can be attributed to carbonyl groups and other aromatic stretching vibrations. From the ATR-IR spectrum of dip catalyst (Fig. 2b), no new peaks can be observed when compared with Fig. 2a, but a slight shift in the wavenumbers is observed for all the peaks which can be ascribed to the bonding interactions between palladium nanoparticles and the cellulose (Baruah et al., 2015).



Fig. 2. ATR-IR spectra of (a) cellulose strip and (b) dip catalyst.

The X-ray diffractograms recorded in the range of 10-80° for palladium nanoparticles, cellulose strip and the dip catalyst are shown in Fig. 3. The peaks (Fig. 3a) at 20 value 40.0°, 46.5° and 68.1° corresponds to the lattice planes (111), (200) and (220) respectively which confirms face centered cubic crystal structure of palladium nanoparticles. The XRD pattern of cellulose (Fig. 3b) show peaks at 20 value 15.8°, 22.4° and 35.2° corresponding to the (110), (200) and (004) planes which represents cellulose-I structure (Gong, Li, Xu, Xiang, & Mo, 2017). To identify the crystallinity of the isolated cellulose, crystallinity index (CrI) was determined using Segal's equation (Du et al., 2016; Segal, Creely, Martin Jr., & Conrad, 1959). The CrI for the cellulose strip was found to be 55.4% where as for the dip catalyst it was 60.4%. The increase in crystallinity in the case of dip catalyst can be attributed to the hydrolysis of hemicellulose and amorphous regions of cellulose (Du et al., 2016). After the incorporation of palladium nanoparticles on cellulose (Fig. 3c), there was no change in the peak position but the peak intensity of palladium nanoparticles of cellulose.

The thermal stability of the dip catalyst was assessed using thermogravimetric analysis. Fig. 4 depicts the thermogram for the dip catalyst in which the removal of moisture resulted in the initial weight loss of ~5% up to a temperature of 110 °C. The second sharp weight loss was observed from 225 °C to 370 °C which is due to the cellulose degradation. The higher thermal stability of the dip catalyst can be attributed to the higher crystallinity of the cellulose support.



Fig. 3. X-ray diffraction pattern of (a) palladium nanoparticles, (b) cellulose strip and (c) dip catalyst.



Fig. 4. TG curve for dip catalyst.



Fig. 5. FESEM images of (a) cellulose strip, (b) dip catalyst and (c) dip catalyst cross-section.

The morphological study was carried out using FESEM analysis (Fig. 5). The FESEM images of the cellulose strip, dip catalyst and cross section of dip catalyst are shown in Fig. 5a, 5b and 5c respectively. The cellulose strip showed a rough surface which may be the result of removal of outer non-cellulosic layer like lignin and hemicelluloses during the base hydrolysis process. A uniform distribution of palladium nanoparticles on cellulose support can be observed in the case of dip catalyst from Fig. 5b which further underlines the dispersion of palladium nanoparticles on cellulose as inferred from XRD results. A cross section image of dip catalyst was obtained for finding out the thickness of the same and a thickness of ~ 42μ m was observed which is shown in Fig. 5c. TEM analysis of the dip catalyst in dispersion form shows the even distribution of the palladium nanoparticles on cellulose support (Fig. 6) which further confirms the FESEM analysis results.



Fig. 6. TEM images of the dip catalyst

The palladium content and composition of the dip catalyst was evaluated using EDS analysis as shown in Fig. 7. The EDS spectrum confirms the presence of palladium along with carbon and oxygen. The percentage of palladium from EDS analysis was found to be 4%. Also, elemental mapping of the dip catalyst proved the uniform distribution of palladium nanoparticles in dip catalyst as shown in Fig. 7. From survey XPS spectrum, the presence of palladium, carbon and oxygen was confirmed a fresh (Fig. S1). Also, from XPS analysis, the presence of Pd(0) and Pd(II) was revealed. The formation of PdO can be imputed to the surface oxidation of the Pd(0) during the XPS sampling procedure (Celebi, Yurderi, Bulut, Kaya, & Zahmakiran, 2016). The ICP-OES analysis was performed to check the exact palladium content of the dip catalyst and found that the palladium content was 4.19 wt% which closely matches with the EDS analysis result.





Fig. 7. EDS spectrum and elemental mapping of the dip catalyst.

3.4. Application of the dip catalyst in Suzuki-Miyaura cross-coupling reaction

After understanding the chemical composition, surface morphology and thermal behavior of the dip catalyst, Suzuki-Miyaura cross-coupling reaction was selected for the initial catalytic activity studies. The cross-coupling of iodobenzene with phenylboronic acid was chosen as a model reaction for the optimization of reaction conditions with the dip catalyst. A series of reactions were carried out to find out the optimum temperature, time, catalyst loading, solvent and base for the Suzuki-Miyaura cross-coupling reaction (Table S1). Fig. 8 represents a typical reaction set up used for the catalytic studies with dip catalyst.

The palladium weight percentage was calculated for the dip catalyst with dimension of 1.5 cm width and 3.0 cm length. The dimensions of the dip catalyst can be varied according to the reaction conditions and reaction set up requirement. In our study, we have varied the starting material loading and kept the dip catalyst dimensions constant to find out the optimum catalyst loading. The optimum catalyst loading was found to be 0.15 mol% of palladium with respect to aryl halide.



Fig. 8. Typical reaction setup with dip catalyst.

The dip catalyst was found stable in most of the solvent system at room temperature. A mixture of ethanol:water (1:1) solvent system appeared to be the best solvent for Suzuki-Miyaura cross-coupling with the dip catalyst with good stability. When ethanol facilitates the solubility of organic substrates, the water helps to dissolve the base. Also, the palladium nanoparticles in the interior layers of the dip catalyst are made more available for the reactants by the weakening effect of the hydrogen bonding network of cellulose fiber matrix by the presence of water (Shen & Gnanakaran, 2009). Among the different bases employed, potassium carbonate was the finest. Strong bases like sodium hydroxide and potassium hydroxide resulted in fewer yields. In ethanol:water system with potassium carbonate base, 30 minutes was sufficient for the reaction to complete with highest conversion and yield at room temperature. Increase in time does not increase the yield further and decrease in time resulted in lesser yield. Also, increase in conversion and yield were negligible at higher temperatures when compared to that of at room temperature. Thus, the reaction at room temperature for 30 minutes in presence of potassium carbonate base and 0.15 mol% of palladium in ethanol:water (1:1) mixture as solvent turned out to be the optimized reaction condition for Suzuki-Miyaura cross-coupling using the dip catalyst to get an isolated yield of 98 %.

After optimization of the reaction conditions, we proceeded to study the substrate scope in Suzuki-Miyaura cross-coupling reaction to find out the applicability of the dip catalyst for a broad range of aryl halides with different functional groups and arylboronic acid. The functional groups involved were either electron withdrawing or electron donating in nature. Also, among aryl halides, both aryl iodides and bromides were employed. Among aryl halides, iodides being easy leaving group when compared with bromides reacted at a faster rate due to the faster oxidative addition step during the reaction cycle of Suzuki-Miyaura cross-coupling. In addition, the aryl halides with electron withdrawing groups were faster to give products when compared with those aryl halides containing electron donating groups. Again, this can be attributed to the ease in oxidative addition of aryl halide on to the catalyst because of the electron withdrawing effect of the functional group present on the aryl halide. From the result obtained (Table 1) it can be substantiated that the dip catalyst is very efficient in Suzuki-Miyaura cross-coupling with high yield and excellent functional group tolerance and at the same time the yields obtained were good to excellent when compared with other reported dip catalysts (Hariprasad & Radhakrishnan, 2012; Xiang et al., 2018; Zheng, Kaefer, et al., 2015).

 Table 1. Suzuki-Miyaura cross-coupling of different aryl halides with arylboronic acid using dip

 catalyst^a



^aReaction conditions: Aryl halide (1.0 equiv), phenylboronic acid(1.1 equiv), dip catalyst(0.15 mol% palladium with respect to aryl halide), K_2CO_3 (2.2 equiv) and EtOH:H₂O (5 mL) in air. Yields given are isolated yield after column chromatography; average of two runs.

To evaluate the applicability of the dip catalyst in drug molecule synthesis, a non-steroidal anti-inflammatory drug, Felbinac (Kylmälä, Tois, Xu, & Franzén, 2009), was also synthesized via Suzuki-Miyaura cross-coupling reaction (Entry 3p, Table 1). The optimized condition was well suited for the synthesis of Felbinac with above 90 % yield within two hours of time at room temperature. The use of green solvent system and mild base at room temperature with easily recoverable dip catalyst for the synthesis of Felbinac is noteworthy.

3.5. Recyclability of the dip catalyst in Suzuki-Miyaura cross-coupling reaction

One of the key visions while designing and employing the dip catalyst was the ease of recovery and recyclability which makes the dip catalyst exceptionally greener. In our case, after the successful execution of the dip catalyst in Suzuki-Miyaura cross-coupling reaction, we advanced with recyclability studies on the model reaction. The dip catalyst can be easily removed from the reaction mass using forceps and washed as discussed in section 2.6. The recovered dip catalyst was reused in new reaction cycle without further purification. There was no any change in the conversion and yield up to 13 cycles which is depicted in Fig. S4, but there was a slight decrease in the yield from 14th cycle onwards. Moreover, after 15th recycle, the edges of the dip catalyst slowly started disintegration which can be attributed to the abrasion caused by the magnetic stir bar.

The ATR-IR and FESEM analysis of the dip catalyst after 15th recycle was performed to identify the state of the catalyst which is given in Fig. S2b and Fig. S3a respectively. From ATR-IR analysis, the chemical composition was found unaltered. Even though the chemical composition was unaltered, the FESEM image shows the transformation of palladium nanoparticles from spherical to needle like morphology. The change in morphology adds to the decreased activity of the dip catalyst (Hu & Liu, 2005).

3.6. Application of the dip catalyst in C5-arylation of 2-substituted thiophenes

Direct arylation reactions are of prime importance in organic chemistry field due to the wide spread applications of these reactions in the synthesis of various drug molecules and intermediates. After the successful application of the dip catalyst in Suzuki-Miyaura crosscoupling reaction, we explored the feasibility of C5-arylation of 2-substituted thiophenes with dip catalyst for the first time. The C5-arylation of thiophene-2-carboxaldehyde with 1-bromo-4nitrobenzene was selected as the model reaction for optimizing the reaction conditions. Table S2 shows the different reactions carried out during the optimization of C5-arylation of thiophene-2carboxaldehyde. A broad screening of solvents revealed that polar aprotic solvents like N,Ndimethylformamide (DMF) and N,N-dimethylacetamide (DMA) were suitable for arylation with dip catalyst. Even though the dip catalyst was stable in most of the solvent system, disintegration was observed when DMA and water was used as solvents at higher temperatures and for our surprise the dip catalyst was extremely stable in DMF even at elevated temperatures. At lower temperature there was no any starting material conversion but at higher temperature the product formation was observed. A temperature up to 120 °C was optimal for the maximum conversion and good yield. Also, the optimal catalyst loading was found to be 0.25 mol% of palladium. An increase in catalyst loading does not show any remarkable improvement in conversion and a decrease in catalyst loading resulted in lower yields. The carbonate bases proved to be good enough for arylation in our case and the choice of the base ended up in sodium carbonate as it is milder and cost effective than potassium carbonate and cesium carbonate. The presence of silver salt as oxidant and pivalic acid as an additive was proved to be essential for the reaction to proceed with the dip catalyst. There was zero or less conversion in the absence of silver oxide and pivalic acid during the arylation reaction. The Ag(I) is believed to abstract the halide ion from the Pd(II)

complex formed during oxidative addition thereby making the Pd(II) complex a more electrophilic intermediate (Lebrasseur & Larrosa, 2008; Rene & Fagnou, 2010). The pivalate generated during the reaction of pivalic acid with sodium carbonate is expected to play an important role in cleavage of C-H bond (Lafrance & Fagnou, 2006; Pardo, Prendergast, Nolan, Ó Muimhneacháin, & McGlacken, 2015). The methodology we present here for the direct arylation reaction is based on this reasoning even though the precise role of additives is still ambiguous.

Subsequent to the optimization of the reaction conditions for arylation, we then proceeded to explore the substrate scope for the arylation reactions under optimized conditions (Table 2). The dip catalyst was successful in catalyzing C5-arylation of 2-substituted thiophenes with aryl halide substrate containing both electron donating as well as electron withdrawing groups. In addition, the dip catalyst was capable to generate comparable yield with both aryl iodides as well as aryl bromides but with aryl bromides the reaction took longer time than their aryl iodide counterparts.

Table 2. Substrate scope for the C5-arylation reaction of 2-substituted thiophenes with aryl halides

 in the presence of dip catalyst.



^aReaction conditions: Aryl halide (1.0 equiv), 2-substituted thiophene (0.8 equiv), base (2.0 equiv), Ag_2O (0.75 equiv), PivOH (1.0 equiv), dip catalyst (0.25 mol% of palladium with respect to aryl halide) and DMF (5 mL) in air; Isolated yield after purification by column chromatography; average of two runs.

3.7. Recyclability of the dip catalyst in C5-arylation of 2-substituted thiophenes

The recyclability of the dip catalyst was studied for C5-arylation of 2-substituted thiophenes on the model reaction. Even though the activity of fresh dip catalyst was exemplary, especially as this is the first ever dip catalyst applied in C-H activation reaction, the recyclability was not that appreciable. There was a steady decrease in the yield from first recycle onwards as shown in Fig. S5. The key reason for the decreased yield in arylation reaction can be attributed to the deposition of silver salts on the strip there by blocking the active palladium sites. In order to

prove this, apart from ATR-IR and FESEM analysis, EDS analysis was also performed for the dip catalyst after the third recycle which is given in Fig. S6. The EDS results confirm the presence of Ag on the dip catalyst surface. The ATR-IR analysis of the dip catalyst after 3rd recycle (Fig. S2c) revealed a similar IR spectrum as fresh catalyst but an extra peak was observed at 1473 cm⁻¹ which may be due to the aromatic reactants left out on the surface of the dip catalyst even after washing while the FESEM analysis of the same (Fig. S3b) confirmed the agglomeration and deposition of palladium as well as silver nanoparticles on the surface of the dip catalyst which was confirmed by EDS as well.

3.8. Leaching study

In order to understand the heterogeneity of the dip catalyst and palladium leaching, we performed the leaching study on the model Suzuki-Miyaura cross-coupling reaction under optimized condition. After 15 minutes of reaction time, the dip catalyst was removed from the reaction mass and the reaction was allowed to continue for further 3-4 hours. But the yield obtained was 68% which shows that the reaction did not proceed after the removal of the dip catalyst. In order to further confirm the leaching out of palladium from the dip catalyst during reaction, the palladium content in the reaction mass from both applications were also analyzed by ICP-OES and the palladium content in the reaction mass was found to be 2.1 ppm in the case of Suzuki-Miyaura cross-coupling and 8.42 ppm in the case of C5-arylation of 2-substituted thiophenes. Also, the palladium content of the dip catalyst after 15th recycle from Suzuki-Miyaura cross-coupling was found to be 3.70 % w/w and that of the dip catalyst after 3rd recycle from C5-arylation of 2-substituted thiophenes was found to be 3.86 % w/w from ICP-OES analysis, which was initially 4.12 % w/w. The removal of palladium from the surface of dip catalyst, while performing the washings of the same, after reaction completion during each cycle can also account for the slight

decrease in the palladium content after recycles. From all these results it can be accomplished that the electrostatic interaction of palladium nanoparticles with hydroxyl groups of cellulose is strong enough for holding palladium nanoparticles during the course of reaction.

4. Conclusion

In this work, we were able to develop a green and sustainable protocol for the design of the dip catalyst with cellulose as a support, which was isolated from the agriculture residue, and biogenically synthesized palladium nanoparticles by following a simple and efficient as well as economical method. The strong electrostatic interaction between the hydroxyl groups of the cellulose and palladium nanoparticles leads to the immobilization of the nanoparticles on the substrate. The dip catalyst proved to be efficient in Suzuki-Miyaura cross-coupling reaction and the yields obtained were good to excellent when compared with other reported dip catalysts. Also, the applicability of the dip catalyst was studied in the synthesis of a non-steroidal antiinflammatory drug, Felbinac, which resulted in excellent yield. The dip catalyst also proved to be an excellent catalyst in C5-arylation of 2-substituted thiophenes. The ease of recovery from the reaction mass and the increased number of recycles makes the dip catalyst very significant among various heterogeneous catalysts. In addition, the dip catalyst can also be easily scaled up due to the ease of synthesis and green protocol involved along with the choice of deployment of the dip catalyst in the reaction set up. Moreover, the cellulose residue which is available in abundance in nature can be isolated by following the simple protocol presented here and can be utilized efficiently in the field of catalysis.

Conflicts of interest

There are no conflicts to declare.

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Supplementary data

XPS spectra of the dip catalyst, ATR-IR spectra and FESEM images of the recovered dip catalyst, optimization table for Suzuki-Miyaura cross-coupling and direct arylation reactions, recyclability studies, the analysis data and ¹H NMR spectra of cross-coupled products and direct arylated products is available in the supplementary data.

References

- Ahmad, I., Kamal, T., Khan, S. B., & Asiri, A. M. (2016). An efficient and easily retrievable dip catalyst based on silver nanoparticles/chitosan-coated cellulose filter paper. *Cellulose*, 23, 3577 - 3588.
- Albertini, F., Ribeiro, T., Alves, S., Baleizão, C., & Farinha, J. P. S. (2018). Boron-chelating membranes based in hybrid mesoporous silica nanoparticles for water purification. *Mater Design*, 141, 407 - 413.
- Albrecht, M. A., Evans, C. W., & Raston, C. L. (2006). Green chemistry and the health implications of nanoparticles. *Green Chem*, 8, 417 432.
- Baran, T. (2018a). Pd(0) nanocatalyst stabilized on a novel agar/pectin composite and its catalytic activity in the synthesis of biphenyl compounds by Suzuki-Miyaura cross coupling reaction and reduction of o-nitroaniline. *Carbohydr Polym*, 195, 45-52.

- Baran, T. (2018b). Ultrasound-accelerated synthesis of biphenyl compounds using novel Pd(0) nanoparticles immobilized on bio-composite. *Ultrason Sonochem*, 45, 231-237.
- Baran, T., Aciksoz, E., & Mentes, A. (2016). Highly efficient, quick and green synthesis of biarlys with chitosan supported catalyst using microwave irradiation in the absence of solvent. *Carbohydr Polym*, 142, 189-198.
- Baran, T., Baran, N. Y., & Menteş, A. (2018). Preparation, structural characterization, and catalytic performance of Pd (II) and Pt (II) complexes derived from cellulose Schiff base. J Mol Struct, 1160, 154 - 160.
- Baran, T., Inanan, T., & Mentes, A. (2016). Synthesis, characterization, and catalytic activity in Suzuki coupling and catalase-like reactions of new chitosan supported Pd catalyst. *Carbohydr Polym*, 145, 20-29.
- Baran, T., Sargin, I., Kaya, M., & Mentes, A. (2016). Green heterogeneous Pd(II) catalyst produced from chitosan-cellulose micro beads for green synthesis of biaryls. *Carbohydr Polym*, 152, 181-188.
- Baran, T., Yılmaz Baran, N., & Menteş, A. (2018a). A new air and moisture stable robust biopolymer based palladium catalyst for highly efficient synthesis of biaryl compounds. *Appl Organomet Chem*, 32(2), e4076.
- Baran, T., Yılmaz Baran, N., & Menteş, A. (2018b). Sustainable chitosan/starch composite material for stabilization of palladium nanoparticles: Synthesis, characterization and investigation of catalytic behaviour of Pd@chitosan/starch nanocomposite in Suzuki-Miyaura reaction. *Appl Organomet Chem*, 32(2), e4075.
- Baruah, D., Das, R. N., Hazarika, S., & Konwar, D. (2015). Biogenic synthesis of cellulose supported Pd(0) nanoparticles using hearth wood extract of Artocarpus lakoocha Roxb —

A green, efficient and versatile catalyst for Suzuki and Heck coupling in water under microwave heating. *Catal Commun*, 72, 73 - 80.

- Blaser, H. U., Indolese, A., Naud, F., Nettekoven, U., & Schnyder, A. (2004). Industrial R&D on Catalytic C-C and C-N Coupling Reactions: A Personal Account on Goals, Approaches and Results. *Adv Synth Catal*, 346, 1583 - 1598.
- Burda, C., Chen, X., Narayanan, R., & El-Sayed, M. A. (2005). Chemistry and Properties of Nanocrystals of Different Shapes. *Chem Rev*, 105, 1025 1102.
- Celebi, M., Yurderi, M., Bulut, A., Kaya, M., & Zahmakiran, M. (2016). Palladium nanoparticles supported on amine-functionalized SiO2 for the catalytic hexavalent chromium reduction. *Appl Catal B*, 180, 53-64.
- Cheng, T., Zhang, D., Li, H., & Liu, G. (2014). Magnetically recoverable nanoparticles as efficient catalysts for organic transformations in aqueous medium. *Green Chem*, 16, 3401 3427.
- CHNG, L. L., ERATHODIYIL, N., & YING, J. Y. (2013). Nanostructured Catalysts for Organic Transformations. *Acc Chem Res*, 46, 1825 - 1837.
- Du, H., Liu, C., Zhang, Y., Yu, G., Si, C., & Li, B. (2016). Preparation and characterization of functional cellulose nanofibrils via formic acid hydrolysis pretreatment and the followed high-pressure homogenization. *Indus Crop Prod*, 94, 736 - 745.
- Gong, J., Li, J., Xu, J., Xiang, Z., & Mo, L. (2017). Research on cellulose nanocrystals produced from cellulose sources with various polymorphs. *RSC Adv*, 7, 33486 33493.
- Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications. *Chem Rev*, 110, 3479 3500.
- Hariprasad, E., & Radhakrishnan, T. P. (2012). Palladium Nanoparticle-Embedded Polymer Thin
 Film " Dip Catalyst" for Suzuki Miyaura Reaction. ACS Catal, 2, 1179 1186.

- He, J., Kunitake, T., & Nakao, A. (2003). Facile In Situ Synthesis of Noble Metal Nanoparticles in Porous Cellulose Fibers. *Chem Mater*, 15, 4401 - 4406.
- Hotze, E. M., Phenrat, T., & Lowry, G. V. (2010). Nanoparticle Aggregation: Challenges to Understanding Transport and Reactivity in the Environment. J Environ Qual, 39, 1909 -1924.
- Hu, J., & Liu, Y. (2005). Pd Nanoparticle Aging and Its Implications in the Suzuki Cross-Coupling Reaction. *Langmuir*, 21, 2121 - 2123.
- Jin, M., Park, J.-N., Shon, J. K., Kim, J. H., Li, Z., Park, Y.-K., & Kim, J. M. (2012). Low temperature CO oxidation over Pd catalysts supported on highly ordered mesoporous metal oxides. *Catal Today*, 185, 183 - 190.
- Kandathil, V., Dateer, R. B., Sasidhar, B. S., Patil, S. A., & Patil, S. A. (2018). Green Synthesis of Palladium Nanoparticles: Applications in Aryl Halide Cyanation and Hiyama Cross-Coupling Reaction Under Ligand Free Conditions. *Catal Lett*, 148, 1562 - 1578.
- Kandathil, V., Fahlman, B. D., Sasidhar, B. S., Patil, S. A., & Patil, S. A. (2017). A convenient, efficient and reusable N-heterocyclic carbene-palladium(II) based catalyst supported on magnetite for Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions. *New J Chem*, 41, 9531 - 9545.
- Kandathil, V., Koley, T. S., Manjunatha, K., Dateer, R. B., Keri, R. S., Sasidhar, B. S., . . . Patil,
 S. A. (2018). A new magnetically recyclable heterogeneous palladium(II) as a green catalyst for Suzuki-Miyaura cross-coupling and reduction of nitroarenes in aqueous medium at room temperature. *Inorg Chim Acta*, 478, 195 210.
- Kaushik, M., & Moores, A. (2016). Review: nanocelluloses as versatile supports for metal nanoparticles and their applications in catalysis. *Green Chem*, 18, 622 637.

- Kelly, K. L., Coronado, E., Zhao, L. L., & Schatz, G. C. (2003). The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *J Phys Chem B*, 107, 668 - 677.
- Khalafi-Nezhad, A., & Panahi, F. (2011). Immobilized palladium nanoparticles on a silica–starch substrate (PNP–SSS): as an efficient heterogeneous catalyst for Heck and copper-free Sonogashira reactions in water. *Green Chem*, 13, 2408 - 2415.
- Khazaei, A., Khazaei, M., & Rahmati, S. (2015). A green method for the synthesis of gelatin/pectin stabilized palladium nano-particles as efficient heterogeneous catalyst for solvent-free Mizoroki–Heck reaction. J Mol Catal A-Chem, 398, 241-247.
- Khazaei, A., Rahmati, S., Hekmatian, Z., & Saeednia, S. (2013). A green approach for the synthesis of palladium nanoparticles supported on pectin: Application as a catalyst for solvent-free Mizoroki–Heck reaction. J Mol Catal A-Chem, 372, 160-166.
- Kumar, G., Tibbitts, L., Newell, J., Panthi, B., Mukhopadhyay, A., Rioux, R. M., . . . Chandler, B.D. (2018). Evaluating differences in the active-site electronics of supported Au nanoparticle catalysts using Hammett and DFT studies. *Nat Chem*, 10(3), 268-274.
- Kylmälä, T., Tois, J., Xu, Y., & Franzén, R. (2009). One step synthesis of Diflunisal using a Pddiamine complex. *Cent Eur J Chem*, 7, 818 - 826.
- Lafrance, M., & Fagnou, K. (2006). Palladium-Catalyzed Benzene Arylation: Incorporation of Catalytic Pivalic Acid as a Proton Shuttle and a Key Element in Catalyst Design. *J Am Chem Soc*, 128, 16496 16497.
- Lebrasseur, N., & Larrosa, I. (2008). Room Temperature and Phosphine Free Palladium Catalyzed Direct C-2 Arylation of Indoles. *J Am Chem Soc*, 130, 2926 - 2927.

- Liu, L., & Corma, A. (2018). Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles. *Chem Rev*, 118(10), 4981-5079.
- Mandal, A., & Chakrabarty, D. (2011). Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization. *Carbohydr Polym*, 86, 1291 1299.
- Manjunatha, K., Koley, T. S., Kandathil, V., Dateer, R. B., Balakrishna, G., Sasidhar, B. S., . . . Patil, S. A. (2018). Magnetic nanoparticle- tethered Schiff base–palladium(II): Highly active and reusable heterogeneous catalyst for Suzuki–Miyaura cross- coupling and reduction of nitroarenes in aqueous medium at room temperature. *Appl Organomet Chem*, 32, e4266.
- Mart, M., Tylus, W., & Trzeciak, A. (2018). Pd/DNA as Highly Active and Recyclable Catalyst of Suzuki–Miyaura Coupling. *Catalysts*, 8(11), 552-567.
- Martínez, A., Krinsky, J., Peñafiel, I., Castillón, S., Loponov, K., Lapkin, A., . . . Claver, C. (2015).
 Heterogenization of Pd-NHC complexes onto a silica support and their application in the Suzuki-Miyaura coupling under batch and continuous flow conditions. *Catal Sci Technol*, 5, 310 319.
- Modak, A., Mondal, J., Sasidharan, M., & Bhaumik, A. (2011). Triazine Functionalized Ordered Mesoporous Polymer: A Novel Solid Support for Pd-Mediated C-C Cross-Coupling Reactions in Water. *Green Chem*, 13, 1317 - 1331.
- Modak, A., Pramanik, M., Inagaki, S., & Bhaumik, A. (2014). Triazine functionalized porous organic polymer: Excellent CO2 storage material and support for designing Pd nanocatalyst for C-C cross-coupling reactions. *J Mater Chem A*, 2, 11642 11650.
- Mourya, M., Choudhary, D., Basak, A. K., Tripathi, C. S. P., & Guin, D. (2018). Ag-Nanoparticles-Embedd ed Filter Paper: An Efficient Dip Catalyst for Aromatic

Nitrophenol Reduction, Intramolecular Cascade Reaction, and Methyl Orange Degradation. *ChemistrySelect*, 3, 2882 - 2887.

- Mtibe, A., Linganiso, L. Z., Mathew, A. P., Oksman, K., John, M. J., & Anandjiwala, R. D. (2015).
 A comparative study on properties of micro and nanopapers produced from cellulose and cellulose nanofibres. *Carbohydr Polym*, 118, 1-8.
- Ni, C., Carolan, D., Rocks, C., Hui, J., Fang, Z., Padmanaban, D. B., . . . Mariotti, D. (2018). Microplasma-assisted electrochemical synthesis of Co3O4 nanoparticles in absolute ethanol for energy applications. *Green Chem*, 20, 2101 - 2109.
- Okumura, K., Kobayashi, T., Tanaka, H., & Niwa, M. (2003). Toluene combustion over palladium supported on various metal oxide supports. *Appl Catal B*, 44, 325 331.
- Pardo, L. M., Prendergast, A. M., Nolan, M. T., Ó Muimhneacháin, E., & McGlacken, G. P. (2015). Pd/Pivalic Acid Mediated Direct Arylation of 2- Pyrones and Related Heterocycles. *Eur J Org Chem*, 2015, 3540 - 3550.
- Phan, N. T., Van Der Sluys, M., & Jones, C. W. (2006). On the nature of the active species in palladium catalyzed Mizoroki–Heck and Suzuki–Miyaura couplings–homogeneous or heterogeneous catalysis, a critical review. *Adv Synth Catal*, 348, 609 - 679.
- Rabelo, S. C., Fonseca, N. A. A., Andrade, R. R., Filho, R. M., & Costa, A. C. (2011). Ethanol production from enzymatic hydrolysis of sugarcane bagasse pretreated with lime and alkaline hydrogen peroxide. *Biomass Bioenergy*, 35, 2600 - 2607.
- Rene, O., & Fagnou, K. (2010). Room-temperature direct arylation of polyfluorinated arenes under biphasic conditions. *Org Lett*, 12(9), 2116-2119.

- Rosario, J. A. D., Ocon, J. D., Jeon, H., Yi, Y., Lee, J. K., & Lee, J. (2014). On the Enhancing Role of Nickel in Nickel-Palladium Bilayer for Electrocatalytic Oxidation of Ethanol in Alkaline Media. *J Phys Chem C*, 118, 22473-22478.
- Rossi, R., Bellina, F., Lessi, M., & Manzini, C. (2014). Cross- Coupling of Heteroarenes by C-H Functionalization: Recent Progress towards Direct Arylation and Heteroarylation Reactions Involving Heteroarenes Containing One Heteroatom. *Adv Synth Catal*, 356, 17 117.
- Rothfuss, H., Knofel, N. D., Roesky, P. W., & Barner-Kowollik, C. (2018). Single-Chain Nanoparticles as Catalytic Nanoreactors. *J Am Chem Soc*, 140(18), 5875-5881.
- Segal, L., Creely, J. J., Martin Jr., A. E., & Conrad, C. M. (1959). An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. . *Tex Res J*, 29, 786 – 794.
- Shen, T., & Gnanakaran, S. (2009). The stability of cellulose: a statistical perspective from a coarse-grained model of hydrogen-bond networks. *Biophys J*, 96, 3032 3040.
- Shylesh, S., Schunemann, V., & Thiel, W. R. (2010). Magnetically separable nanocatalysts: bridges between homogeneous and heterogeneous catalysis. *Angew Chem Int Ed Engl*, 49(20), 3428-3459.
- Steinmetz, M., Ueda, K., Grimme, S., Yamaguchi, J., Kirchberg, S., Itami, K., & Studer, A. (2012).
 Mechanistic Studies on the Pd- catalyzed Direct C□ H Arylation of 2- Substituted
 Thiophene Derivatives with Arylpalladium Bipyridyl Complexes. *Chem Asian J*, 7, 1256
 1260.

- Teixeira, E. d. M., Bondancia, T. J., Teodoro, K. B. R., Corrêa, A. C., Marconcini, J. M., & Mattoso, L. H. C. (2011). Sugarcane bagasse whiskers: Extraction and characterizations. *Indus Crop Prod*, 33, 63 - 66.
- Vishal, K., Fahlman, B. D., Sasidhar, B. S., Patil, S. A., & Patil, S. A. (2017). Magnetic Nanoparticle-Supported N-Heterocyclic CarbenePalladium(II): A Convenient, Effient and Recyclable Catalyst for Suzuki–Miyaura Cross-Coupling Reactions. *Catal Lett*, 147, 900 -918.
- Xiang, Z., Chen, Y., Liu, Q., & Lu, F. (2018). A highly recyclable dip-catalyst produced from palladium nanoparticle-embedded bacterial cellulose and plant fibers. *Green Chem*, 20, 1085 - 1094.
- Xie, J., Hse, C. Y., De Hoop, C. F., Hu, T., Qi, J., & Shupe, T. F. (2016). Isolation and characterization of cellulose nanofibers from bamboo using microwave liquefaction combined with chemical treatment and ultrasonication. *Carbohydr Polym*, 151, 725-734.
- Xu, C., Cheng, L., Shen, P., & Liu, Y. (2007). Methanol and ethanol electroox idation on Pt and Pd supported on carbon microspheres in alkaline media. *Electrochem Commun*, 9, 997 -1001.
- Xu, X., Xiao, L., Jia, Y., Wu, Z., Wang, F., Wang, Y., . . . Huang, H. (2018). Pyro-catalytic hydrogen evolution by Ba_{0.7}Sr_{0.3}TiO₃ nanoparticles: harvesting cold–hot alternation energy near room-temperature. *Energy Environ Sci*, 11, 2198 - 2207.
- Yang, X., Chen, D., Liao, S., Song, H., Li, Y., Fu, Z., & Su, Y. (2012). High-performance Pd–Au bimetallic catalyst with mesoporous silica nanoparticles as support and its catalysis of cinnamaldehyde hydrogenation. *J Catal*, 291, 36 - 43.

- Yilmaz Baran, N., Baran, T., & Mentes, A. (2018). Production of novel palladium nanocatalyst stabilized with sustainable chitosan/cellulose composite and its catalytic performance in Suzuki-Miyaura coupling reactions. *Carbohydr Polym*, 181, 596-604.
- Yin, L., & Liebscher, J. (2007). Carbon–Carbon Coupling Reactions Catalyzed by Heterogeneous Palladium Catalysts. *Chem Rev*, 107, 133 - 173.
- Zhao, Y., Moser, C., Lindstrom, M. E., Henriksson, G., & Li, J. (2017). Cellulose Nanofibers from Softwood, Hardwood, and Tunicate: Preparation-Structure-Film Performance Interrelation. ACS Appl Mater Interfaces, 9(15), 13508-13519.
- Zheng, G., Kaefer, K., Mourdikoudis, S., Polavarapu, L., Vaz, B., Cartmell, S. E., ... Perez-Juste, J. (2015). Palladium Nanoparticle-Loaded Cellulose Paper: A Highly Efficient, Robust, and Recyclable Self-Assembled Composite Catalytic System. *J Phys Chem Lett*, 6(2), 230-238.
- Zheng, G., Polavarapu, L., Liz-Marzán, L. M., Pastoriza-Santos, I., & Pérez-Juste, J. (2015). Gold
 Nanoparticle-loaded Filter paper: A Recyclable "Dip-Catalyst" for Real-Time Reaction
 Monitoring by Surface Enhanced Raman Scattering. *Chem Commun*, 51, 4572 4575.