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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



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1. Introduction

Palladium nanoparticles (NPs) have diverse applications in the field of both homogeneous and heterogeneous catalysis [1]. Suzuki and Heck reactions are the most important coupling reactions in the synthesis of great variety of simple to complex molecules which have tremendous application in the field of drugs, pharmaceuticals, agrochemicals and advanced materials [2]. Homogeneous Pd catalysts always exhibit better reaction rate, activity and selectivity but heterogeneous catalysts have many advantages over their homogeneous counterparts such as recycling, cost effectiveness and ease of catalyst/product separation [1-2]. Nowadays, much attention have been paid to investigate biocompatible solid support to provide thermo and air stable metal NPs as the synthetic solid support (carbon [3], zeolites [4], metal oxides [5], sol-gel [6], clays [7], dendrimers [8], polymers [9]) or the stabilizing ligands (phosphine, etc. [10]) are expensive, toxic, and in large-scale applications they may become more tedious for solid waste disposals.

In recent years, biogenic synthesis of metal NPs using different plant extracts received much attention both from environment and economy points of view. It was assumed that different flavonoids and polyphenols present in these plant extracts act as bio-reductant and stabilizing agent in NPs' synthesis. Biogenic synthesis eliminates the use of toxic, expensive

ABSTRACT

A simple, convenient and green protocol has been developed for the synthesis of cellulose supported Pd(0) nanoparticles (NPs) using hearth wood extract of Artocarpus lakoocha Roxb-as a bioreductant. Novel one-step method for the isolation of active bioreductant oxyresveratrol (2, 3', 4, 5'-tetrahydroxy-trans-stilbene) present in the hearth wood extract of A. lakoocha Roxb is also disclosed. Synthesized cellulose supported Pd(0) NPs have been used as an efficient catalyst for Suzuki and Heck coupling reactions in water under microwave irradiation. The prepared Pd(0) NPs were characterized by Ultraviolet-visible (UV-vis), Fourier transform-infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Transmission electron microscopy (TEM). The catalyst can be recycled up-to ten times without losing its activity significantly.

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and non-biodegradable chemical reagents (N₂H₄·H₂O, NaBH₄, DMF, etc.) as well as high temperature and pressures. Hence economically viable, environmentally safer plant based biogenic synthetic protocols for NPs synthesis are more advantageous [11-13]. Numerous metal NPs such as Au, Ag, Pd, Pt, Cu and bimetallic Ag-Au, Au-Pd, and Cu-Au can successfully be synthesized by different plant extracts [14]. These NPs have potential application in the field of catalysis [15]. In this research work, we report the successful isolation of oxvresveratrol, the active bio-reductant present in the hearth wood extract of Artocarpus lakoocha Roxb, a medicinal plant available in NE region of India in the synthesis of Pd(0) NPs. To enhance the surface area per volume, the NPs should be anchored on a suitable solid support so as to increase the catalyst robustness as well as reusability of the catalyst. In this endeavour, in continuation of our earlier works [16-20], we used microgranullar cellulose as a sustainable solid support for Pd(0) NPs to make the catalyst more stable and recyclable in the study on Suzuki and Heck coupling reaction in aqueous media under microwave heating. Cellulose consists of anhydroglucose units joined by β-1-4 glycosidic linkage to form a molecular chain. The intra-chain hydrogen bonding between hydroxyl groups and oxygens of the adjoining ring molecules stabilizes the linkage and results in the linear configuration of the cellulose chain. Cellulose contains microfibrils up to 30 nm width that are three dimensionally connected to each other. The metal NPs can be stabilized in these cavities via oxygen-metal electrostatic interaction. Depending upon the pore size of cellulose microfibrils the size of the metal NPs also varies. That is how cellulose can act as a solid support for the metal

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NPs' synthesis [21]. Biogenic synthesis of cellulose supported Pd(0) NPs using hearth wood extract of *A. lakoocha* Roxb and their application as a versatile and efficient catalyst in Suzuki and Heck coupling is the first protocol that we depicted herein (Scheme 1). We performed all the reactions under microwave heating. As being energy efficient, microwaves can enhance the rate of reactions and improve product yields [22].

2. Experimental section

2.1. General remarks

Cellulose (CAS: 9004-34-6, microcrystalline, 20 µm, pH: 5-7), PdCl₂ (99.9%), all arylbromides, all phenylboronic acids, methyl acrylate, acrylonitrile, bases, and all solvents were purchased from Sigma Aldrich, USA and were used without any further purification. X-ray diffraction (XRD) analysis was performed with a scanning rate of 3° min⁻¹ and two theta values ranging from 5 to 100° using a Rigaku X-ray diffractometer (model: ULTIMA IV, Rigaku, Japan) with a Cu K α X-ray source ($\lambda = 1.54056$ Å) at a generator voltage of 40 kV and a generator current of 40 mA. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a IEM-2100 electron microscope (Transmission Electron Microscope, NEHU, Shillong, India) operated at an accelerating voltage of 60-200 kV. UV-visible spectra were recorded using Specord 200 and Spectrum 100 FTIR-Spectrometer (resolution: 4 cm^{-1}) was used for recording IR data. All microwave (MW) reactions were carried out in CEM, Discover microwave reactor. All NMR (¹H, ¹³C) spectra were recorded on a Bruker Avance DPX 500 MHz spectrometer. Chemical shifts were reported on the δ scale (ppm) downfield from TMS $(\delta = 0.0 \text{ ppm})$ using the residual solvent signal at $\delta = 7.26 \text{ ppm}$ (¹H) or $\delta = 77$ ppm (¹³C) as an internal standard. All products were purified by column chromatography using silica gel (200-300 mesh) and petroleum ether (60-90 °C).

2.2. General procedures

2.2.1. Synthesis of Pd(0) NPs on cellulose [Pd(0) NPs@cellulose] using hearth wood extract of A. lakoocha Roxb

200 mg nanoporous cellulose and 10 mg palladium(II) chloride were added to a 250 mL round bottom flask containing 100 mL hearth wood extract of *A. lakoocha* Roxb. The hearth wood extract of *A. lakoocha* Roxb was prepared by grinding the dry heart wood of *A. lakoocha* Roxb and extracted with water. The mixture was stirred for 30 min at room temperature and then warmed (50 °C) for 15 min until the light brown solution turned into black colour. No further colour change was observed after 15 min. The black precipitate was filtered, washed, vacuum dried, and finally stored under N₂ atmosphere in a dessicator. The synthesized Pd NPs were characterized by UV–visible spectroscopy, FT-IR spectroscopy, XRD and TEM analysis.

2.2.2. Isolation of active bio-reductant present in hearth wood extract of A. lakoocha Roxb

2.2.2.1. Method A. 10 g of dried and ground hearth wood of A. lakoocha Roxb was treated with 100 mL petroleum ether (40–60 °C) and kept overnight for removing fatty materials. After filtration, these wood materials were taken in 100 mL water, refluxed for 6 h, filtered off at hot condition, concentrated to one fourth of the volume under reduced pressure, and kept in a refrigerator for overnight. Separated deep brown solid materials were filtered, washed with cool water (50 mL) and vacuum dried. These solid materials are identified as oxyresveratrol (2, 3', 4, 5'-tetrahydroxy-trans-stilbene), yield: 500 mg (5%), melting point: 200 °C, (Lit. Mp 201 °C [23–25]).

2.2.2.2. Method B. 10 g of dry and powdered wood material was taken in 100 mL acidic water solution (pH = 4) and 20 mL accelerase enzyme [Aldrich] was added to the solution. The mixture was heated for 5 h at 40 °C, hot filtered, extracted with ethyl acetate (3×50 mL), the organic layer washed with 5% NaHCO₃ solution and dried over anhydrous so-dium sulphate for 5 h. The solvent was distilled off under reduced pressure to give deep brown solid oxyresveratrol (2, 3', 4, 5'-tetrahydroxy-trans-stilbene), yield: 600 mg, (6%). The compound was analysed and found as above.

2.2.3. Reaction of arylbromides with phenylboronic acids using Pd (0) NPs@cellulose under microwave heating [Suzuki coupling]

In a 10 mL microwave glass vial 0.5 mol% (0.028 g) Pd(0) NPs@cellulose, 0.5 mmol arylbromides, 0.75 mmol phenylboronic acid and 1.5 mmol K₂CO₃ were mixed in 5 mL water. The mixture was stirred at



Scheme 1. Schematic diagram of fabrication of Pd(0) NPs on cellulose by biogenic method and its catalytic activity towards Suzuki and Heck coupling reaction.



Scheme 2. Photograph of (A) hearth wood extract of *A. lakoocha* Roxb in water; (B) solution A with cellulose; (C) Solution B with PdCl₂; (D) Solution C after 15 min warming in heating bath at 60 °C; (E) solid recyclable Pd(0) NPs@cellulose.

80 °C for the stipulated time in a microwave. After completion of the reaction [monitored by TLC], the catalyst was filtered off and washed with acetone and stored for further reactions. The filtrate was concentrated and then extracted with ethyl acetate (2×20 mL). The organic layer was washed with water (2×10 mL), brine (15 mL), dried over anhydrous Na₂SO₄, concentrated, and purified by column chromatography.

2.2.4. Reaction of arylbromides with alkenes using Pd(0) NPs@cellulose under microwave heating [Heck coupling]

0.5 mol% (0.028 g) Pd(0) NPs@cellulose, 0.5 mmol arylbromides, 1.0 mmol alkene (e.g. methyl acrylate) and 1.5 mmol K₂CO₃ were mixed in 5 mL water in a 10 mL microwave glass vial and heated under microwave for a stipulated time period. Progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered off and washed with acetone. The filtrate was concentrated and then extracted with ethyl acetate (2 × 20 mL). The organic layer was washed with water (2 × 10 mL), brine (15 mL), dried over anhydrous Na₂SO₄, concentrated, and purified by column chromatography.

3. Results and discussions

3.1. Isolation of oxyresveratrol

Oxyresveratrol was isolated from the hearth wood of *A. lakoocha* Roxb available in North-East part of India. The isolation methods (methods A & B) are disclosed. These two methods eliminate multistep chemical synthesis [23] and long tedious separation and purification processes [24]. It was found that method B for the isolation of oxyresveratrol gave better yield than method A. In spite of using longer synthetic process, this eco-friendly protocol will be highly beneficial for industrial purposes as our protocol do not require the use of expensive chemicals [25].

3.2. Characterization of Pd(0) NPs@cellulose

Synthesis of Pd(0) NPs@cellulose using hearth wood extract of *A. lakoocha* Roxb was initially assumed from the colour changes. A light



Fig. 1. A comparative UV-visible spectra of PdCl₂, cellulose, oxyresveratrol and Pd(0) NPs@cellulose.



Fig. 2. Comparative FT-IR spectra of pure cellulose and Pd(0) NPs@cellulose. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

brown colour of aqueous solution of oxyresveratrol, PdCl₂ and cellulose, C gradually changed to black colour, D. The black solid deposited on the bottom of the test tube E is solid Pd(0) NPs@cellulose (Scheme 2).

replaced by a broad and continuous absorption band in the UV–visible spectrum of black solid Pd/cellulose matrix, this indicates the formation of Pd(0) NPs@cellulose [26].

UV-visible study of the synthesized nanocomposites revealed the formation of Pd(0) NPs (Fig. 1). The UV-visible spectrum of $PdCl_2$ exhibits an absorption maximum in the range of 400–430 nm, due to the absorption of Pd(II) ions. As this peak completely disappeared and

Comparative FTIR spectra of cellulose and cellulose supported Pd are shown in Fig. 2. The red line indicates the FTIR of cellulose supported Pd and the blue line indicates the FTIR of pure cellulose. Strong absorption peak at 3349.6 cm^{-1} corresponds to the O–H stretching intramolecular



Fig. 3. Powder XRD spectra of Pd(0) NPs@cellulose.

Fig. 4. TEM images of Pd(0) NPs@cellulose: (A) dispersion of nanoparticles in cellulose; (B), (C) Size of the Pd(0) NPs with HRTEM image (inset); (D) Selected Area Electron Diffraction (SAED) of Pd(0) NPs [31,32].

hydrogen bonds for cellulose. Peak at 2903 cm⁻¹ is due to the C–H stretching vibration. Peak at 1650 cm⁻¹ is because of O–H bending vibration, 1430 cm⁻¹ (CH₂ scissoring motion), 1384 cm⁻¹(C-H bending), 1336 cm⁻¹ (O–H in plane bending), 1317 cm⁻¹ (CH₂ wagging), 1053 cm⁻¹ (C–O–C pyranose ring stretching vibration) and peak at 897 cm⁻¹ is associated with the cellulosic β-glycosidic linkages [27]. A decrease in intensity at 3346 cm⁻¹ of the cellulose supported Pd as compared to 3349.6 cm⁻¹ indicates the formation of Pd(0)–oxygen linkage, i.e. palladium metals are stabilized by the –OH groups of the cellulose moiety by metal–ligand interactions. Due to these interactions

 Table 1

 Optimization of the reaction conditions for the Suzuki cross-coupling reaction of 2-bromobenzaldehyde with phenylboronic acid.^a

B(OH) ₂				онс
		сно _	CHO Pd(0) Nps@cellulose		
	+	J			
Entry	Catalyst	Loading of catalyst	Base (1.5 mmol)	Temp (°C) (min)	/time Yield % ^b
1			K ₂ CO ₃	100/10	0
2	PdCl ₂	0.05 mmol	K ₂ CO ₃	100/15	25
3	Pd(0)NPs	0.5 mol%	K ₂ CO ₃	80/5	94
4	Pd(0)NPs	0.3 mol%	K ₂ CO ₃	100/5	82
5	Pd(0)NPs	1.0 mol%	K ₂ CO ₃	100/15	94
6	Pd(0)NPs	0.5 mol%	K ₂ CO ₃	140/15	94
7	Pd(0)NPs	0.5 mol%	NaOH	100/5	20
8	Pd(0)NPs	0.5 mol%	Et ₃ N	100/5	40
9	Pd(0)NPs	0.5 mol%	NaOAc	100/5	20
10	Pd(0)NPs	0.5 mol%	Cs ₂ CO ₃	100/5	68

^aReaction conditions: 2-bromobenzaldehyde (0.5 mmol), phenylboronic acid (0.75 mmol), Pd(0) NPs@cellulose (0.5 mol%), K₂CO₃(1.5 mmol), H₂O (5 mL), 80 °C, microwave. The reaction was monitored by TLC. ^bIsolated vield. weaker absorption peaks were observed in the FTIR spectra of cellulose supported Pd. This results demonstrate that the –OH groups on microcrystalline cellulose acts as a stabilizing agent of metal nanoparticles, i.e. formation of Pd(0) NPs inside the cavities. Shifting of peaks in FTIR of cellulose supported Pd as compared to FTIR of pure cellulose is also an indication of the formation of Pd(0) NPs inside the cavities of cellulose template [28].

Powder X-ray diffraction study (XRD) (Fig. 3) showed that in combination with three cellulose peaks at 2θ values of 14.8° , 16.4° , and 22.9° corresponding to the Braggs planes (101), (101') and (002), there were five peaks at 2θ values of 40.2° , 46.5° , 67.9° , 81.7° and 85.7 corresponding to (111), (200), (220), (311) and (222) planes representing Pd(0) NPs on cellulose [29–30]. No peaks corresponding to any other impurity were observed. The intense reflection at 40.2° (111) in comparison with four other peaks may indicate the preferred growth direction of the nanocrystals [2].

The TEM images (Fig. 4, A–D) of synthesized nanocomposites showed that Pd(0) NPs were dispersed in the nanopores of cellulose matrix. The supported Pd(0) NPs were spherical in shape with sizes in the range of 10–30 nm. The HRTEM image (Fig. 4C, inset) of a single Pd(0) NPs showed the reticular lattice planes inside the nanoparticles indicating the crystalline nature. The selected area electron diffraction (SAED) image shows the Braggs planes.

3.3. Catalytic activity of Pd(0) NPs@cellulose under microwave heating

Cellulose supported Pd(0) NPs were tested as a catalyst in the Suzuki cross/homo coupling and Heck reactions under microwave heating. Initially, we have chosen the coupling reaction of 2-bromobenzaldehyde (0.5 mmol) and phenylboronic acid (0.75 mmol) as model substrates for the development of optimized conditions under microwave heating taking water as a solvent. Several bases such as Et_3N , NaOH, NaOAc, Cs_2CO_3 , K_2CO_3 , etc. were used in order to find the optimized reaction condition (Table 1). Study with different bases indicates that they

have remarkable effect on the yields of the product. Among the tested bases, K₂CO₃ (entry 3, Table 1) gave the highest yield of 1a, (94%) as compared to all other bases (entries 7-10, Table 1). These results imply that K₂CO₃, among the bases under study, was the most effective for activating this catalytic system in the Suzuki cross coupling reaction. Next we studied the catalytic behaviour of Pd(0) NPs@cellulose as well as loading of the catalyst in this coupling reaction. Control experiments showed that no product formation took place in the absence of Pd (0) NPs@cellulose in aqueous medium under microwave irradiation (entry 1, Table 1). However, addition of the catalyst to this mixture has rapidly increased the formation of product in high yields. Taking PdCl₂ salt as a catalyst for this coupling reaction under the same reaction condition gave disappointing result (entry 2, yield 30%, Table 1) as compared to Pd(0) NPs@cellulose which showed more than 90% product yield. A decrease in the catalyst loading from 0.5 mol% to 0.3 mol% lowered the product yield (entry 4, Table 1). On the other hand, increasing the catalyst loading did not improve the yield of the product significantly (entry 5, Table 1). 0.5 mol% of the catalyst was found to be optimal for the coupling reaction (entry 3, Table 1). The optimum temperature for the reaction is 80 °C and only 5–10 min time is required to complete the reaction under microwave heating. The best result was obtained with 0.5 mmol of 2-bromobenzaldehyde, 0.75 mmol of phenylboronic acid, 0.5 mol% (0.028 g) of catalyst, 1.5 mmol of K₂CO₃ and 5 mL of H₂O at 80 °C, which gave the product an excellent yield. Furthermore two comparative cross coupling reactions were performed using the same substrates, one in microwave heating and the other in conventional heating using oil bath at 100 °C to find the best reaction condition. It was observed that reactions performed under microwave heating require shorter time and afforded maximum yield as compared to the conventional heating. Taking water as a solvent we got very high yield of products, therefore, studies of the reactions in other solvents was excluded.

Table 2

Suzuki cross-coupling reaction between phenylboronic acid and substituted arylbromides under microwave heating.^a



^aReaction conditions: arylbromides (0.5 mmol), phenylboronic acid (0.75 mmol), Pd (0) NPs@cellulose (0.5 mol%), K₂CO₃(1.5 mmol), H₂O (5 mL), 80 °C, microwave. The reactions were monitored by TLC. ^bIsolated yield.

Table 3

Pd(0) mediated Suzuki homocoupling reaction of phenyl boronic acids.^a



^aReaction conditions: arylbromide (1.0 mmol), Pd(0) NPs@cellulose (0.5 mol%), K₂CO₃ (1.5 mmol), H₂O (5 mL), 60 °C, microwave. The reactions were monitored by TLC. ^bIsolated yield.

After optimization of reaction conditions, we explored the scope and limitations of this protocol towards the coupling reactions. As illustrated in Table 2, it was subsequently extended to a wide range of substituted aryl bromides and phenylboronic acids as substrates for Suzuki cross coupling reaction. In general, all the reactions gave excellent yields of coupling product under microwave heating. However, arylbromides containing electron withdrawing groups as substrates gave slightly more yields (1a, 1c) as compared to the electron donating counterparts. This protocol was found to be well tolerated towards the hetero aryl bromides (1e, 1i) and *ortho* substituted aryl bromide (1a, 1g, 1h, 1j, 1k) as substrates. Overall, steric and electronic factors of the substrates do not affect significantly the yield of the products because of the high catalytic activity of Pd(0) NPs@cellulose system.

Next, we tried to study the homocoupling reactions of arylboronic acids, Table 3. It was observed that Pd(0) NPs@cellulose system efficiently catalyses the homocoupling reaction with high yield percentage of desired product regardless of the nature of boronic acids under microwave heating (2a–2d). In homocoupling reaction the requirement of time as well as temperature is somewhat less than the cross coupling reactions. All the products were well characterized by the comparison of their physical characteristics (TLC Rf value and melting point) and spectral data (¹H & ¹³C NMR) with those of the authentic samples.

We investigated the catalytic activity of Pd(0) NPs@cellulose towards the Heck reaction (Table 4). 15–20 min time is required for successful completion of all Heck reactions under study. To find the optimized reaction condition we used iodobenzene (0.5 mmol) and methyl acrylate (1.0 mmol) as substrates. Regardless of the substituents present in arylbenzenes and alkenes (3a–3d, Table 4), the catalyst

Heck reaction of aryl halides and olefins under microwave heating catalysed by Pd(0) NPs@cellulose.^a



^aReaction conditions: arylhalides (0.5 mmol), alkene (0.75 mmol), Pd(0) NPs@cellulose (0.5 mol%), K₂CO₃(1.5 mmol), H₂O (5 mL), 80 °C, microwave. The reactions were monitored by TLC.

^bIsolated yield.

Table 4

^cReaction time is 15 min.

^dReaction time is 20 min.

^elodobenzene as a substrate.

^fSubstituted bromobenzene as a substrate.

Table 5

Reusability of Pd(0) NPs@cellulose in the Suzuki cross-coupling reaction of 2bromobenzaldehyde and phenyl boronic acid under microwave heating.^a



^aReaction conditions: arylbromides (0.5 mmol), phenylboronic acid (0.75 mmol), Pd (0) NPs@cellulose (0.5 mol%), K₂CO₃(1.5 mmol), H₂O (5 mL), 80 °C, microwave. ^bIsolated yield.

effectively catalysed the Heck coupling reactions with excellent yields in aqueous media under microwave heating.

3.4. Reusability of Pd(0) NPs@ cellulose

The reusability of Pd(0) NPs@cellulose catalyst was investigated by using the Suzuki cross-coupling reaction between phenyl boronic acid and 2-bromobenzaldehyde under the abovementioned optimized conditions in microwave heating. After completion of the reaction the catalyst was separated from the mixture by simple filtration, washing it with H₂O and acetone alternatively and finally vacuum dried. Then it was reused directly for the next cycle without any further treatment. This experiment showed that our catalyst can be recycled up to ten times without major loss of yield of product. At the end of the 5th and 10th runs we were able to collect 89% and 71% yield of the product respectively (Table 5). The recovered catalyst (after the 5th run) was further investigated by powder XRD and TEM studies (Fig. 5). The appearance of low intensity peaks as compared to the fresh one may indicate the aggregation and leaching of Pd(0) NPs in the surface of cellulose. Due to these combined effects of aggregation and leaching reduction of catalytic activity was observed after multiple runs. The catalyst can also be reusable in Heck reactions.

4. Conclusion

In summary, we have demonstrated a green biogenic approach for the synthesis of Pd(0) NPs@cellulose using the hearth wood extract of A. lakoocha Roxb. We have also depicted a novel one step approach for the isolation of active bioreductant oxyresveratrol from the hearth wood extract of A. lakoocha Roxb. This novel procedure for isolation of oxvresveratrol will be highly beneficial for industrial production of potent therapeutic agents in human health, e.g. tyrosinase inhibitor, antioxidant, antiglycation, free radical scavenger, and neuroprotection [23-25]. This eco-friendly protocol for the synthesis of metal NPs provides thermo and air stable crystalline spherical shaped NPs without requiring harmful reducing agents, toxic nitrogenous ligands, solid waste disposals, etc. Pd (0) NPs@cellulose exhibit versatile catalytic activity towards the Suzuki and Heck reactions in water under microwave heating with very high product yield. The main advantages of this environmentally benign protocol are such as ease of catalyst preparation, ease of work up procedure, high catalytic activity, stability, reusability up-to ten times without measurable Pd leaching, etc. Pd (0) NPs@cellulose may be regarded as a very effective alternative for Suzuki and Heck reaction considering the green chemistry point of view.

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Fig. 5. The powder XRD pattern and TEM image of recovered catalyst.

Appendix A. Supplementary data

Characterization data and copies of the NMR spectra of all the products. This material is available free of charge via the Internet at http://dx. doi.org/10.1016/j.catcom.2015.09.011.

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