

RESEARCH PAPER

Highly Efficient of Cross-Coupling Reaction Supported Green Synthesized Palladium Nanoparticles Coated Natural Ligands as Heterogeneous Reusable Nanocatalyst

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ARTICLE INFO

Article History:

Received 28 May 2019

Accepted 08 July 2019

Published 01 October 2019

Keywords:

Cross-Coupling Reaction

Heterogeneous Catalysis

Palladium Nanoparticles

ABSTRACT

An efficient procedure and green route has been developed by using eco-friendly green synthesized palladium nanoparticles (Pd-NPs) as reusable heterogeneous nanocatalyst (Pd@nanocat) for the synthesis of diaryl ethers from the cross coupling reaction of the aryl halides with the phenol in the presence of dimethylsulfoxide (DMSO) as a solvent at 110 °C under natural ligand condition capped Pd-NPs. The generated Pd-NPs were characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) techniques. Structural characterization of diaryl ether was done by nuclear magnetic resonance spectroscopy (NMR). The nanoparticles exhibited stability, reusability with excellent catalytic activity and the results of this study demonstrate the possible application of biosynthesized Pd-NPs as heterogeneous nanocatalyst in environmental remediation. Application of the cheaper base, shorter reaction time, cost-effective, high yield and environmentally friendly make our conditions potentially useful and more suitable to other reported works, which could be amenable to scale-up.

How to cite this article

Mahdavi Shahri M. Highly Efficient of Cross-Coupling Reaction Supported Green Synthesized Palladium Nanoparticles Coated Natural Ligands as Heterogeneous Reusable Nanocatalyst. J Nanostruct, 2019; 9(4): 669-678. DOI: 10.22052/JNS.2019.04.009

INTRODUCTION

The synthesis and utilization of diaryl ethers is interesting because they are not only important structures in a variety of biologically active natural products, fragrances, biological materials, pharmaceuticals and herbicides, but also common backbone molecules in polymer industries and materials science [1-3].

The transition metal catalyzed cross-coupling of aryl halides with phenols is the most conventional forward and regular method for the synthesis of biaryl ethers [4].

Nevertheless, there are some problems in the other study due to use of toxic, expensive and sensitive to air or moisture ligands, low yields, extended reaction times, side products caused environments pollution and use of

homogeneous catalysts. In palladium catalyzed coupling reactions, homogeneous catalysts have been extensively examined, but less expensive heterogeneous catalysts received more attention. the difficulty in separating and recycling, low catalytic efficiency, and the high leaching of metal species caused homogeneous Pd catalysts are not used in industrial application. In order to solve the problem, new strategies should be developed. The recovery and reusability of catalysts is a very important and significant from the viewpoints of green chemistry and practical application especially in the case of noble metal (Pd) catalyzed C-C coupling reaction. Therefore, several methods have been applied for recycling catalysts, containing the use of Pd complexes supported by silica gel [5], polymers [6], metal nanoparticles [7], natural compounds from plant [this study] and

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bulky proazaphosphatane ligands [8].

These noticeable structures of nanoparticles led us to focus on the palladium nanoparticles, as nanocatalyst for the formation of carbon-oxygen bond [9]. The simplest and straight forward way to synthesize diaryl ethers includes the direct formation of aryl-oxygen bond from an aryl halide. Palladium nanoparticles are routinely used as catalysts in various organic transformations including Suzuki-cross coupling, Mizoroki-Heck, Stille and Sonogashira coupling reactions because of high catalytic activity [10]. Pd-NPs as homogeneous or heterogeneous nanocatalyst, are extensively applied in various filed such as hydrogen sensor, photography, automotive catalytic converter and plasmonic wave guides [11]. Initially, palladium strongly selects the oxidation states 0 and +2, which are separated by a relatively narrow energy gap, making palladium an excellent catalyst for both oxidation and reduction reactions. Lastly, Pd is moderately electronegative, resulting in a rather nonpolar Pd-C bond, suppressing the reactivity towards polar functional groups [12].

Now days, biosynthesis of metal nanoparticles using plant materials has received much attention as an appropriate alternative to get the experimental conditions more environmentally friendly [13]. Although various methodologies have been developed for the synthesis of palladium nanoparticles, including chemical and electrochemical reduction [14], ion exchange [15], thermal decomposition [16] and polyol method [17]. *Camellia sinensis* leaves (*white tea*) have been reported to contain extensive amounts of flavones and many polyphenols. The reduction potential of these polyphenols in *white tea* is sufficient to reduce metals [18]. Therefore, the present work investigated green synthesis of palladium nanoparticles (Pd-NPs) by *white tea* extract as both the reducing and stabilizing agent. The obtained Pd-NPs were characterized by, scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction pattern. To test the efficiency of the Pd-NPs as heterogeneous nanocatalyst (Pd@*nanocat*), we chose to focus our initial studies on the cross-coupling of phenol with iodobenzene as model substrates under natural ligand from *white tea* plant. Structural characterization was concluded by using nuclear magnetic resonance spectroscopy (NMR).

MATERIALS AND METHODS

Materials

White tea plant were bought from a local herbal store in Shiraz and washed several times using distilled water, dried under sunlight and then, crushed into powder. PdCl₂ (99.98%) was purchased from Merck (Darmstadt, Germany) and used as palladium precursor. A combination of phenol (C₆H₆O), iodobenzene (C₆H₅I), Potassium phosphate (K₃PO₄), dimethylsulfoxide (DMSO) as solvent in organic synthesis and ethyl acetate (C₄H₈O₂), used in the experiment were purchased from Merck (Darmstadt, Germany).

Preparation of white tea aqueous extract

The *white tea* were washed several times using distilled water to remove possible impurities present on the leaves. The cleared leaves were dried under sunlight to remove moisture completely, and then ground into powder. *White tea* powder sample (3 g) was dispersed in 100 mL distilled water by magnetic stirring and heated at 100 °C for 20 min. The extract was cooled down to room temperature and filtered through normal filter paper. The filtrate was then stored at 4°C which is to be used for further characterization and future works.

Synthesis of palladium nanoparticles as nanocatalyst (Pd@*nanocat*) under natural ligand

The Erlenmeyer flask containing 50 mL of PdCl₂ (1 mM) solution was mixed with 50 mL of the aqueous extract of *white tea* and stirred at 40 °C. The colour of the reaction mixture gradually turned from yellow to dark brown over 30 min indicating the formation of palladium nanoparticles. After 2 hours, the solid product was collected through centrifugation for 10 min. After washing several times with distilled water, a black powder Pd-NPs was dried in an oven at 60°C.

General procedure for the C-O cross-coupling reaction under Pd@*nanocat*

A mixture of iodobenzene (2 mmol), phenol (2.5 mmol), Pd@*nanocat* (0.15 mmol), K₃PO₄ (4 mmol) and DMSO (8 ml) in a sealed tube was stirred at 120 °C under N₂ atmosphere for 7 h. Subsequently, the reaction was cooled to room temperature and the catalyst were filtered off, washed with ethanol, dried and then reused directly for the next cycle of reaction without further purification. The resultant organic layer was extracted with

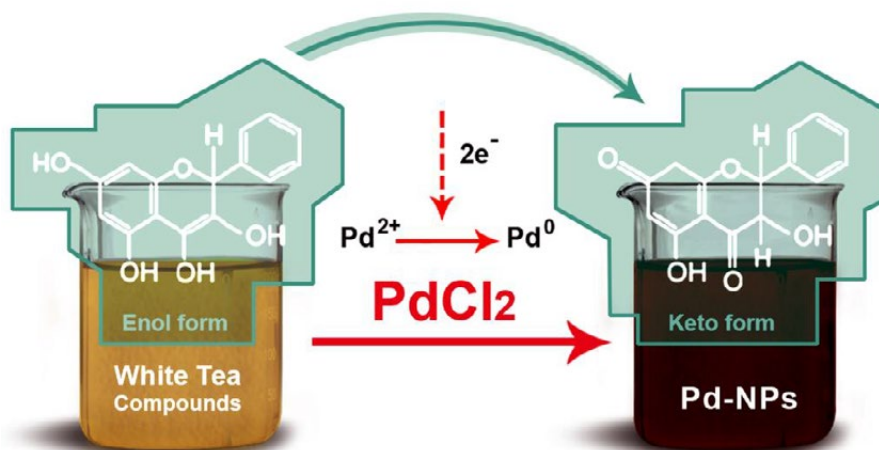


Fig. 1. The aqueous extract of *white tea* (A) before and (B) after synthesis of Pd-NPs.

ethyl acetate. The organic phases were dried over MgSO_4 , followed by evaporation by rotary to remove the solvent. The residue was purified by column chromatography on silica gel to afford the desired product and the purity of the product was confirmed by NMR spectroscopy.

Characterization methods and instruments

Phase purity and particle size were determined by X-ray diffractometer (XRD-6000; Shimadzu) at 40 kV with nickel-filtered Cu ($\lambda = 1.542 \text{ \AA}$) in the range of 10° to 80° . Scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM) analysis was carried out to determine the morphology and the mean particle size of nanoparticles. SEM was performed using a Philips XL-30 instrument (Philips, Eindhoven, Netherlands). The powder sample was put on the carbon stub by using carbon tape and then gold-coated using a sputter coater. The energy dispersive X-ray fluorescence spectrometry (EDXRF) was carried out on a DX-700HS spectrometer (Shimadzu). TEM was done using HITACHI (H-7650) at an operating voltage of 80 kV. The sample was sonicated for 15 min. A drop of this solution was loaded on carbon-coated copper grids, and allowed to evaporate for TEM analysis. Nuclear magnetic resonance spectroscopy (NMR) is used to characterize organic structure. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance-DPX-250/400 spectrometer operating at 250 and 62.5 MHz, respectively.

RESULTS AND DISCUSSION

The reduction of palladium ion (Pd^{2+}) and

formation of the corresponding palladium nanoparticles (Pd-NPs) by using of *white tea* extracts containing of many poly phenols and flavones as both reducing and stabilizing agent could be followed by the colour change of the reaction solution from yellowish (*white tea* extract) to dark brown after 2 h of incubation as shown in Fig. 1. The colour change in aqueous solution is due to the excitation of surface plasmon resonance in the Pd-NPs, which indicated the formation of Pd^0 [19]. The mechanism of Pd^{2+} reduction most likely involved oxidation of phenolic hydroxyl groups which are very abundant in flavonoids and catechins. The main mechanism in green synthesized is hydrogen abstraction due to the OH groups in the polyphenol therefore Keto-enol Tautomerization [20] can take place (Fig. 1).

Characterization of Pd-NPs

The crystalline structure of the Pd@*nanocat* was determined by the X-ray diffraction and showed in Fig. 2A. There are five distinct reflections peaks at 40.1° (111), 46.3° (200), 68.5° (220), 82.1° (311), and 86.2° (222) could be attributed to the crystallographic planes of the fcc of Pd-NPs [21]. A broad peak at 2θ of 13.5° may be attributed to the natural compounds in *white tea* extract which coated the Pd@*nanocat*. According to the Scherrer's equation, the crystallite size was found to be around 15 nm. Control on the size, morphology and distribution of nanoparticles plays an important role in the properties of nanocomposites. Fig. 2B exhibits the morphological characteristics of the as-synthesized Pd-NPs under scanning electron

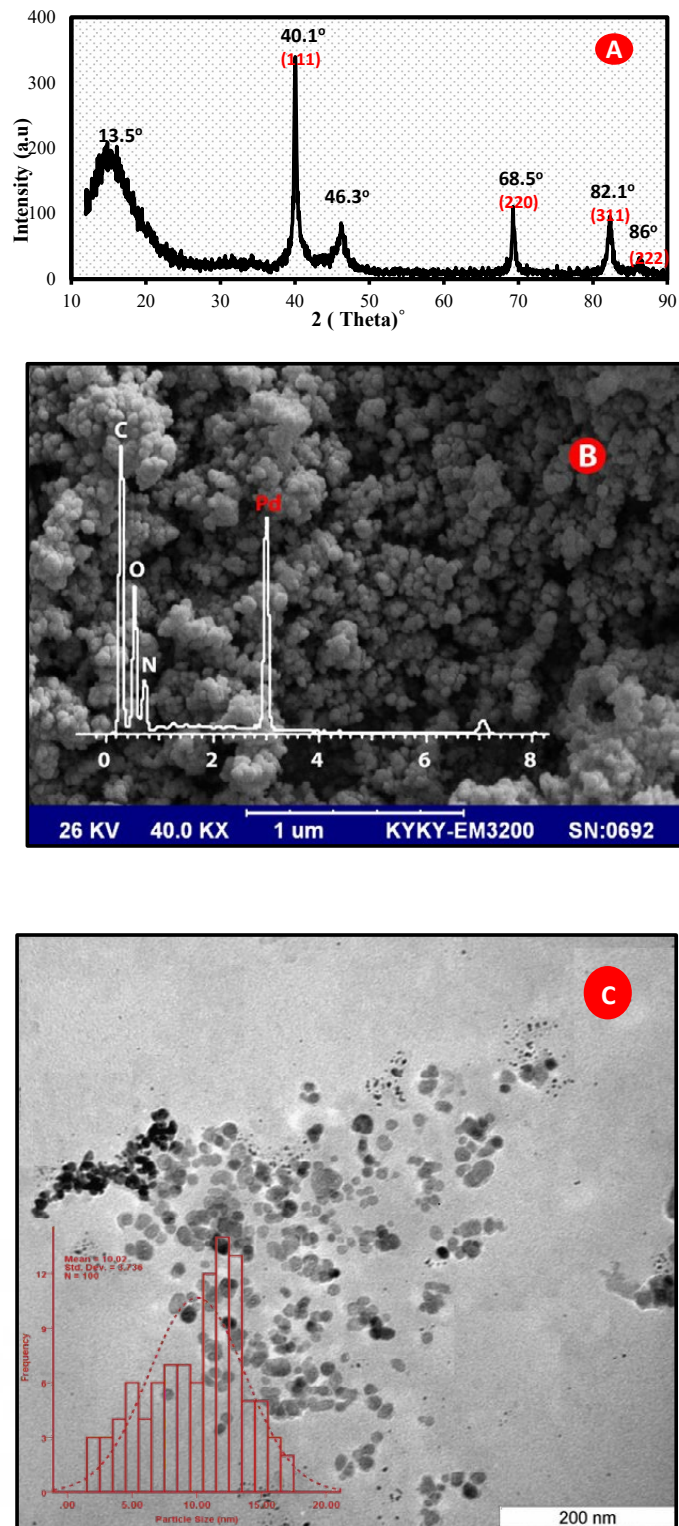


Fig. 2. XRD pattern (A), SEM image with EDX spectra (B) and TEM image with particle size distribution of Pd@nanocat (C).

microscopy (SEM). The nanoparticles are of spherical morphology and have very narrow size distributions. Furthermore, the Pd NPs might also have been stabilized due to the interactions such as hydrogen bond and electrostatic interactions between the bioorganic capping molecules that have bound to the Pd-NPs. As shown in Fig. 2B for the energy dispersive X-ray fluorescence spectra, the strong peak at 3.0 keV is related to the binding energies of Pd-NPs and other existing elements included carbon, oxygen, and nitrogen confirmed the organic compounds present in the *white tea* extract [22].

Transmission electron microscopy (TEM) image and particle size distribution of Pd@*nanocat* are shown in Fig. 2C. The particle sizes distributed in the range of 6–18 nm, with an average particle size of 11 ± 1.97 nm synthesized (Inset Fig. 2C). It was interesting to note that the dispersed colloidal Pd-NPs were surrounded by bio-polymers layer, which appeared to be responsible for reducing and stabilizing the nanoparticles.

Evaluation of the catalytic activity of Pd-Nps through the C-O cross coupling reaction

In this paper, we develop an ecofriendly, non-toxic, inexpensive procedure to prepare a highly efficient, reusable Pd-NPs coated with natural compounds as a nanocatalyst. Moreover, the biologically active molecules involved in the

green synthesis of Pd-NPs act as functionalizing ligands, making these NPs more suitable for catalysis activity. Natural compounds in *White tea* contains many polyphenols especially epigallocatechingallate, flavonoids and catechins coated the Pd-NPs and can be act as natural ligand [23]. The catalytic activity of Pd@*nanocat* for synthesizing diaryl ether under natural ligands was evaluated (Fig. 3).

The results found in our studies support the oxidative addition/reductive elimination type of reaction mechanism for C-O cross-coupling reaction [24]. The first step is oxidative addition. In general, to be useful as a pre-catalyst, the palladium source should be a “bench-stable” 16- or 18-electron species. This complex must quickly become an activated 14-electron species through the loss of two ligands in solution. This catalytically active Pd^0L_2 species then coordinates to the π -system in the electrophile, followed by the migration of Pd to a possible transition state, where the metal binds in a π^2 fashion over the C-X bond in the electrophile. The actual mechanism involves the cleavage of one covalent bond (C-X) to form two new bonds (R-Pd-X). For this reason, a non-bonded electron pair on palladium becomes involved in a new bond which results in an increase in the oxidation state of Pd from 0 to +2. The oxidation of Pd will change the tetrahedral geometry into a square planar complex. Generally,

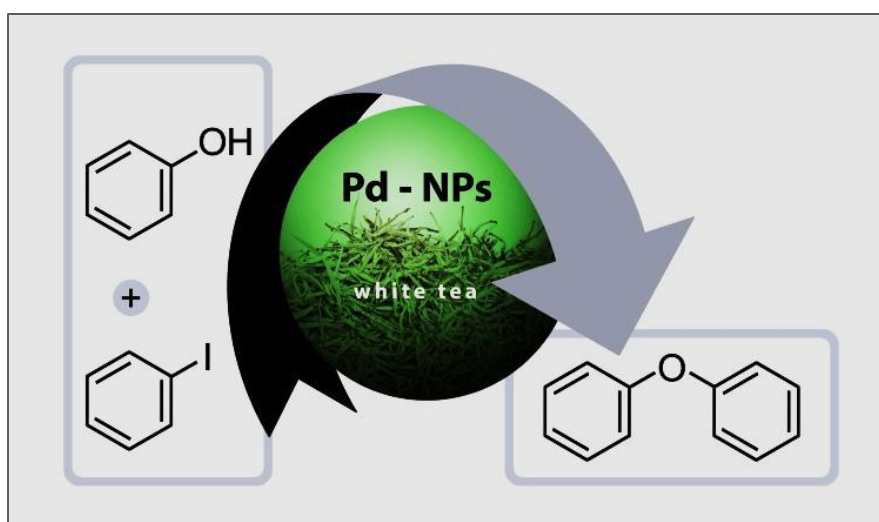


Fig. 3. Diaryl ether formation reaction.

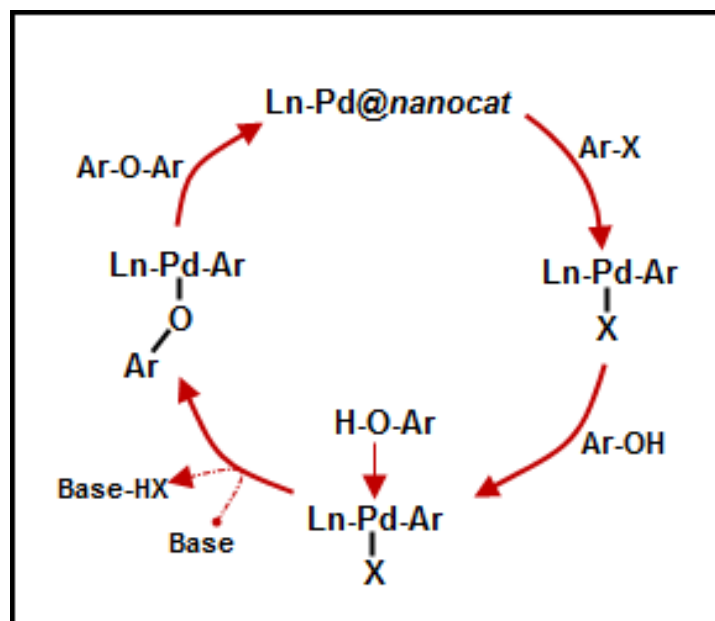


Fig. 4. Plausible mechanism for the catalytic synthesis of diaryl ether.

this step is favored by electron-donating monodentate of carbene ligands [25] or bidentate ligands with a small bite angle [26]. The next step is the coordination of oxygen to palladium. This process is defined as transmetalation and delivers the organonucleophile to the Pd center. The last step is reductive elimination. The chemoselectivity of the overall process depends strongly on relative rates of C-O bond-forming reductive elimination. The non-bonded electron pair in palladium that was involved in a new bond in the previous oxidative addition step is now returned and the catalytically active Pd^0L_2 species is regenerated. Based on these evidences, a reaction mechanism for coupling using the prepared nanocatalyst was proposed (Fig. 4).

The effect of Pd@nanocat on the rate of reaction was studied and the results are shown in Table 1. At the first, a controlled reaction was done in absence of catalyst, very less percentage of products even after 6 h was observed (15%). The reaction was then studied with different amount of Pd@nanocat (4–7%) at 110°C temperature. The results indicated that the product yield increased with catalyst concentration. Maximum yield was obtained by using 6 mol% loading of catalyst within a short reaction time.

The results indicated that nanocatalyst will increase but only up to certain amount, and further increase of amount of nanocatalyst will have no

effect. Consequently, the Pd@nanocat can be applied as a considerable function of accelerator promoting the time and cost impressive formation of organic compound.

Diaryl ether was obtained as a yellow liquid. ^1H NMR (400 MHz, DMSO, δ , ppm): 7.37-7.35 (m, 4H, ArH), 6.98-7.32 (m, 6H, ArH); ^{13}C NMR (400 MHz, DMSO, δ , ppm): 157.2, 130.3, 123.7, and 119, which is shown in Fig. 5.

The effect of temperature on the rate of reaction was also evaluated at different temperatures for the synthesis of diaryl ether in the presence of Pd@nanocat (Table 2). It was detected that the reaction

Table 1. Effect of Pd@nanocat on the yield of C-O cross-coupling reaction.

Entry	Catalyst/mol%	Time/h	Yield/%
1	4	9	62
2	5	8	85
3	6	7	94
4	7	7	94

Reaction conditions: Iodobenzene (2 mmol), phenol (2.5 mmol), MDF (8 mL), K_3PO_4 (4.0 mmol), 120 °C, 7h.

Table 2. Effect of temperature on the yield of C-O cross-coupling reaction.

Entry	Temperature/°C	Time/h	Yield/%
1	70	11	52
2	90	9	80
3	110	8	91
4	120	7	96

(2 mmol), phenol (2.5 mmol), MDF (8 mL), K_3PO_4 (4.0 mmol), Pd@nanocat (6 mol%), 7h.

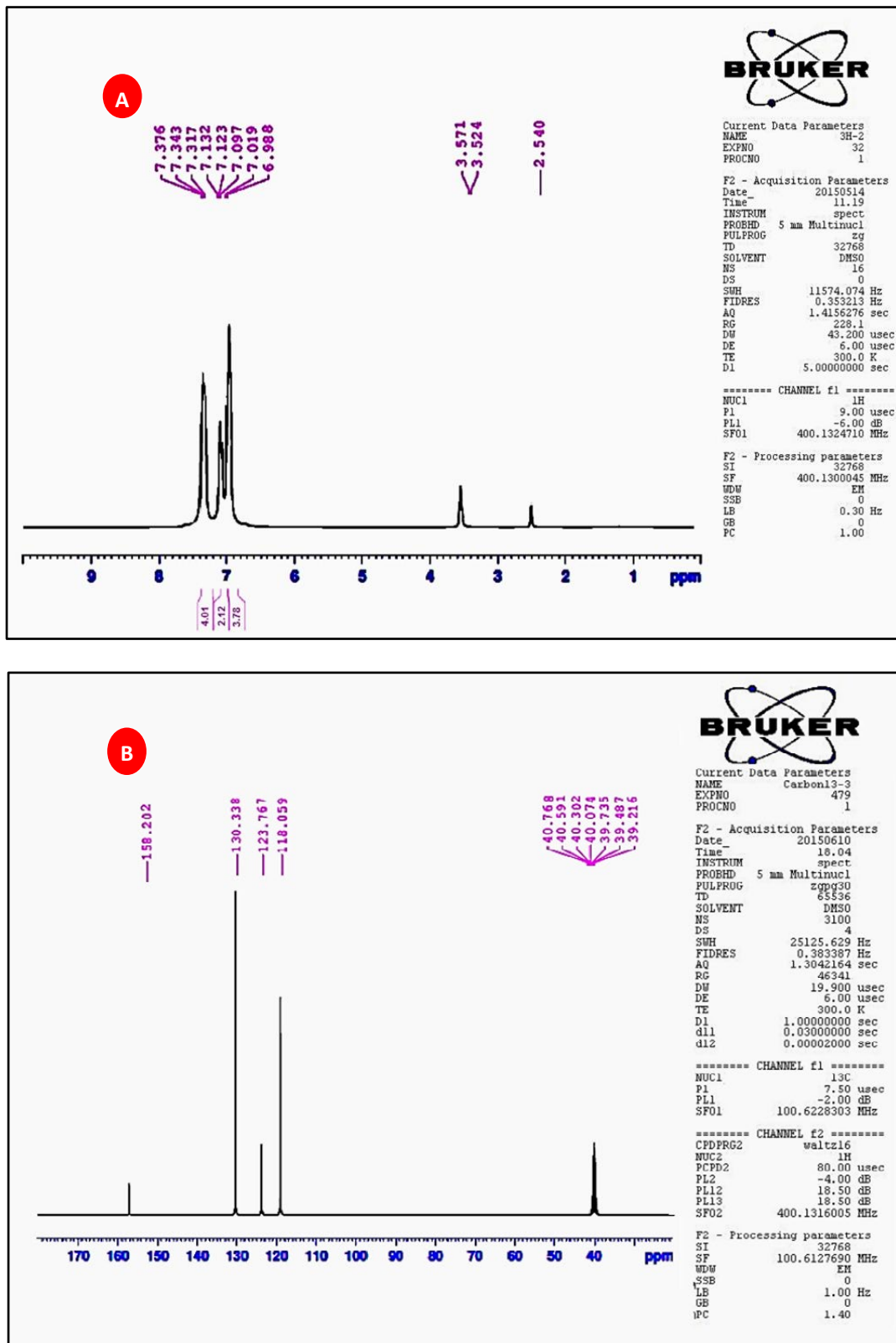


Fig. 5. ¹H NMR (A) and ¹³C NMR (B) analysis of diaryl ether.

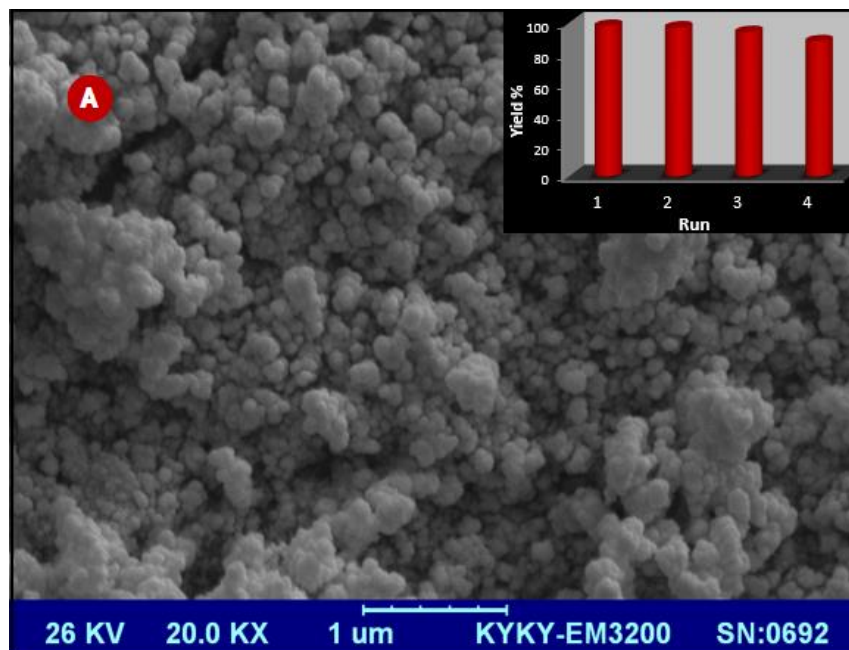


Fig. 6. SEM image of recovered Pd@nanocat (A) and recyclability chart (inset).

seems to be very slow at room temperature. The reaction proceeded smoothly at 50°C and more enhance in temperature to 70 and 120°C increased the rate of reaction. Consequently, the products were obtained in short reaction time and excellent yields at 120°C. Compared with other study, the outstanding features of our technique are (1) the reaction system is simple, (2) elimination of toxic ligands and homogeneous catalysts, (3) the reaction proceed with higher yields, (4) the reactions are relatively more environmentally friendly with easy and efficient recyclability of the catalyst, (5) the use of *white tea* extract as an economic and effective alternative represents an interesting fast and clean synthetic route for the large scale synthesis of Pd-NPs.

Reusability the Pd@nanocat in the cross-coupling reaction

The reusability and recyclability of the catalysts is an important step as it reduces the cost of the process, which makes them useful for commercial applications. More studies were achieved to verify the catalyst stability and recyclability in cross-coupling reaction. After completion of the reaction, catalyst was separated by centrifugation from the reaction mixture and washed with deionized water and ethanol. After that, it was

dried in an oven and the recycled catalyst was saved for the next reaction. The dried recovered catalyst was successively used for four fresh runs with no significant loss of catalytic performance as illustrated in inset of Fig. 6. This reusability demonstrates the high stability of catalyst under operating conditions. In addition, the SEM and TEM image of the recovered Pd@nanocat indicated that the morphology and size of the nanocatalyst remains unchanged, even after the last cycle which is shown in Fig.6 and Fig. 7 respectively.

Catalyst leaching

To investigate the heterogeneity of nanocatalyst, which is an important factor, the metal leaching of Pd-NPs was considered by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis before and after reaction. The results suggested that less than 0.3% of the total amount of the original palladium species was lost into solution during the course of a reaction.

CONCLUSION

In summary, a novel Pd@nanocat via the reduction of aqueous Pd²⁺ ions using bioactive *white tea* extract was synthesized. The polyols and carbonyl groups present in the aqueous extract

act as both reducing and capping/stabilizing agents. In addition, we have established that the heterogeneous Pd@nanocat capped by biomolecules as natural ligand is a highly efficient, stable and recyclable catalyst for the synthesis of diaryl by the cross coupling reaction.

Application of the cheaper base, shorter reaction time, cost-effective, high yield and environmentally friendly make our conditions potentially useful and more suitable to other reported works, which could be amenable to scale-up.

ACKNOWLEDGMENT

The authors are grateful to the staff of the Department of Chemistry, Shiraz Branch, Islamic Azad University for their help with this research.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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