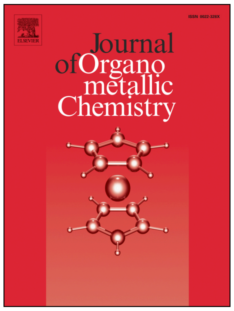

Palladium nanoparticles decorated on a novel polyazomethine as a highly productive and recyclable catalyst for Suzuki coupling reactions and 4-nitrophenol reduction

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Palladium Nanoparticles Decorated on a Novel Polyazomethine as a Highly Productive and Recyclable Catalyst for Suzuki Coupling Reactions and 4-nitrophenol Reduction

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Abstract

This report displays the procedure in preparation of fast, highly productive, reusable, and easily retrievable Pd nanoparticles (NPs) as a heterogeneous catalyst (Pd NPs@P(3-MPAP)) immobilized on a novel polyazomethine with phenol group, Poly(3-methyl-4-((pyridin-2-ylmethylene)amino)phenol) (P(3-MPAP)), and the investigation of its catalytic efficiency in fabrication of several biaryl compounds by Suzuki coupling reactions and reduction of 4-nitrophenol to 4-aminophenol. The structures of the synthesized monomer, polymer support material and nanocatalyst were identified by UV-Vis, FT-IR, ^{1}H-NMR, TGA, XRD, SEM and EDS methods. The catalytic activity of Pd NPs@P(3-MPAP) catalyst in the synthesis of various biaryls by Suzuki coupling reactions was explored using microwave irradiation, which is rapid, easy, solventless and environmentally friendly method. The nanocatalyst presented outstanding advantageous methodology containing easy work-up with high reaction yield (99%) at very short reaction time (5 min.) in solventless media using very low catalyst loading (0.007 mol%) in the synthesis of biaryls. Additionally, the harmful 4-nitrophenol was completely reduced to industrially useful 4-aminophenol in the presence of Pd NPs@P(3-MPAP) with low catalyst amount (1 mg), at very short reaction time (60s) without any toxic solvent (in water) at room temperature. Additionally, reproducibility test results for both catalytic reactions show that the highly productive nanocatalyst was easily retrievable and reusable for six and five sequential cycles, respectively, for Suzuki coupling reactions and reduction of 4-NP without any notable loss in its catalytic activity.

Keywords: Catalyst; Pd nanoparticles; Polyazomethines; reduction of 4-nitrophenol; Suzuki coupling reactions.

1. Introduction

Palladium catalyzed cross coupling reactions emerged as extraordinarily method to form carbon-carbon bonding in synthetic organic chemistry [1]. These coupling reactions have been intensively utilized in the production of polymers and biaryls which play a key role in various vital industrial applications thanks to their use in pharmaceutical intermediates, agrochemicals, biologically active, and natural products [2-5]. Thus, palladium catalyzed cross coupling reactions have attracted great attention of researchers in recent years. Among these reactions, Suzuki coupling reactions, which have been performed by the reactions of arylboronic acids with aryl halides, have been intensively preferred by many researchers because of their outstanding properties such as mild reaction conditions, ease of separation of byproducts from the reaction mixture, and high tolerance towards a wide range of functional groups [6]. Homogeneous and heterogeneous palladium catalysts have been used for these powerful synthetic organic reactions. Heterogeneous catalysts have gained enormous relevance in terms of their superiorities such as ease of purification and separation of catalyst and product, ease of retrievability, high reusability, high performance and selectivity of catalyst, and minimization of palladium leaching, which make them stupendous candidates for industrial applications, compared to homogeneous catalysts [7-9]. However, drawbacks such as requirement of high temperature, long reaction time and toxic organic solvent in traditional Suzuki coupling reactions led researchers to seek a new ways [10, 11]. Thus, several modern methods such as ultrasound irradiation, microwave irradiation, photo-activated methods have been recently developed to overcome these problems [12, 13]. Among these techniques, microwave irradiation has been evaluated as a promising method for industrial applications due to its priorities such as unnecessity of harmful organic solvent, requirement of very short reaction time, low reaction temperature, less energy, low workforce and, attainable high product yield [14].

Aromatic nitro compounds such as 4-nitrophenol (4-NP) are considered as the most common organic pollutants in wastewaters. These harmful organic compounds are produced from wastes of dye, explosive, and pharmaceutical factories, and their existence in water even at minimum level threatens human, plant and aquatic life due to their high toxic, mutagenic and carcinogenic effects [15, 16]. They have also been reported as high priority toxic pollutants by the United States Environmental Protection Agency [17]. Thus, their removal or degradation process is of great importance from the point of view life of all living creatures and environmental. Therefore, various methods such as thermal decomposition [18], adsorption [19], electrochemical degradation [20], biological degradation [21], photo catalysis [22], electro-Fenton method [23] and catalytic reduction have been developed. Among them, catalytic reduction which is an effective, economic, safe and green is the most preferred method [24]. In catalytic reduction of 4-NP, this harmful compound is converted into 4-aminophenol (4-AP) which is very useful and effective for many applications such as photographic developer, anticorrosion lubricant, corrosion inhibitor, and analgesic and antipyretic drugs [16, 25].

In this study, a novel polyazomethine containing phenol group supported Pd NPs catalyst which was reusable, easily retrievable, fast and highly effective was designed for both the synthesis of biaryls via Suzuki coupling reactions and the reduction of 4-NP to 4-AP. Firstly, P(3-MPAP) was synthesized as support material via oxidative polycondensation reaction of 3-methyl-4-((pyridin-2-ylmethylene)amino)phenol (3-MPAP) Schiff base in aqueous alkaline medium with NaOCl oxidant. Then, Pd NPs was immobilized on P(3-MPAP) support material. The structures of all the generated materials was illuminated by various characterization methods. Then, the catalytic efficiency of Pd NPs@P(3-MPAP) was investigated for I) the synthesis of various biaryl compounds by Suzuki coupling reactions using microwave irradiation technique and II) the reduction of highly hazardous 4-NP to 4-

AP. Moreover, reusability and recoverability tests for Pd NPs@P(3-MPAP) were performed in both catalytic conversion reactions. The obtained results revealed that the designed nanocatalyst was highly active towards both Suzuki coupling reactions and reduction of 4-NP and it could be easily regenerated and reused without any great loss in its catalytic efficiency in both catalytic reactions.

2. Experimental

2.1. Materials

4-Amino-3-methylphenol**,** 2-pyridinecarboxaldehyde, phenyl boronic acid, aryl halides, Palladium(II) chloride ($PdCl_2$), 4-nitrophenol, cesium carbonate (Cs_2CO_3), potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), magnesium sulfate ($MgSO_4$), Sodium borohydride ($NaBH_4$), methanol, ethyl acetate, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and toluene were purchased from Merck Chem. Co. (Germany). Sodium hypochlorite (NaOCl, 15% aqu.) was obtained from Pl-dess Chemistry Co. (Turkey).

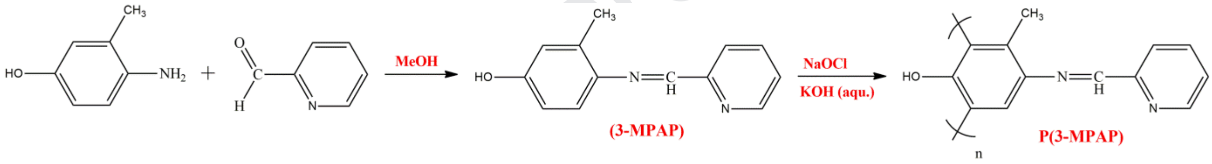
2.2. Method

2.2.1. Synthesis of 3-MPAP

3-MPAP was synthesized as Schiff base monomer by condensation reaction of 4-amino-3-methylphenol and 2-pyridinecarboxaldehyde (Scheme 1). A solution of 2-pyridinecarboxaldehyde (10 mmol, 0.98 mL) in 5 mL methanol was added into the solution of 4-amino-3-methylphenol (10 mmol, 1.23g) in 15 mL methanol. The reaction was performed by stirring at 60 ºC for 6 h. The finalization of the reaction was intervally monitored by TLC and FTIR techniques. It was seen that yellow crystals formed in the red reaction mixture after the reaction. The yellow crystals were filtered and washed with methanol. The obtained Schiff base monomer was recrystallized twice from methanol and dried at room temperature. (Yield: 86%)

2.2.2. Synthesis of P(3-MPAP)

P(3-MPAP) was attained by oxidative polycondensation reaction of 3-MPAP Schiff base monomer in aqueous alkaline medium using NaOCl oxidant. 1 mmol (0.212 g) of 3-MPAP was dissolved in 0.01 M 10 mL KOH solution. When the determined polymerization temperature was reached, 1 mmol NaOCl was dribbled to the dark yellow monomer solution and it was seen that the color of the solution immediately turned to blackish brown. After the decided reaction time ended up, the obtained solution was cooled and the synthesized polymer was precipitated by adding 0.1 M HCl solution. Then, the acquired polymer was washed with hot water (3x100 mL) and ethyl acetate (3x50 mL) to remove mineral salts and unreacted monomer, respectively. It was dried in an oven at 80 °C.



Scheme 1. Synthesis of 3-MPAP and P(3-MPAP).

2.2.3. Preparation of Pd NPs@P(3-MPAP) catalyst

0.25 g of P(3-MPAP) which was dissolved in 10 mL ethanol was added to the solution of 0.05 g of $PdCl_2$ in 20 mL ethanol. The reaction was performed at 70 °C for 24 h by continuously stirring under reflux. Then, the obtained reaction product was filtered, washed with ethanol, and dried at 80 °C. (Yield: 90%)

2.2.4 General procedure for Suzuki coupling reactions

In the process of determination of the fabricated catalyst efficiency in Suzuki coupling reactions, microwave irradiation technique, which is very fast, easy to use, highly productive and nontoxic, was used. Firstly, the reaction of phenylboronic acid and 4-iodoanisol was selected as the model coupling reaction for the synthesis of biaryl compounds by Suzuki coupling reactions. Then, the effects of catalyst loading, reaction time, base type, and microwave irradiation power on the biaryl product yield were investigated on the chosen model coupling reaction. After the optimum reaction conditions were found, the general method which was performed for the fabrication of different biaryls by Suzuki coupling reactions was as follows: 1.87 mmol of phenyl boronic acid, 1.12 mmol of the selected aryl halide, 3.75 mmol of potassium carbonate, and 0.007 mol% of Pd NPs@P(3-MPAP) were added in a Schlenk tube. The coupling reactions were performed in solvent-free medium using 400W microwave irradiation for 5 min. The obtained mixture was cooled to room temperature (RT) at the end of the reaction. 5 mL toluene was added on the cooled mixture and it was filtered. Then, the filtrate was extracted with 5 mL water twice. $MgSO_4$ was added on the separated organic phase which contains biaryl product to completely eliminate water. Then, toluene in the obtained product was evaporated at room temperature. Finally, the product yield was calculated and its chemical structure was identified by GC/MS analysis.

2.2. Catalytic reduction procedure of 4-nitrophenol

Aqueous solution of freshly prepared $NaBH_4$ (0.05 M, 0.1 mL) was added on aqueous solution of 4-NP (1.25×10^{-4} M, 2 mL) in a tube and the mixture was stirred at room temperature for 2 min. 1 mg of Pd NPs@P(3-MPAP) catalyst was added in the prepared mixture and stirred until the yellow color of the mixture completely turned into colorless. The reduction process was monitored by UV-Vis analysis. After the reduction reaction was completed, the nanocatalyst was removed from the reaction mixture by filtering. The nanocatalyst was reused after it was washed and dried in an oven.

2.3. Characterization

GPC analysis of the polymer was done using Shimadzu Prominence Gel Permeation Chromatography with Nucleogel GPC 103-5 VA300/7.7 column (detector: refractive index detector (RID), eluent: dimethylformamide (DMF), flow rate: 0.5 mL/min, temperature: 40 °C). UV-Vis spectra of 3-MPAP, P(3-MPAP) and Pd NPs@P(3-MPAP) were obtained by Shimadzu UV-1700 PharmaSpec UV-Visible Spectrophotometer in DMSO in the wavelength range of 260-800 nm. FTIR spectra of all the fabricated materials were recorded by Perkin Elmer FTIR Spectrometer in the wavenumber range of 4000-650 cm^{-1}. ^{1}H-NMR spectra of 3-MPAP and P(3-MPAP) were attained by Bruker Avance 500 MHz NMR in DMSO at 25 °C. Thermal analyses of 3-MPAP, P(3-MPAP) and Pd NPs@P(3-MPAP) catalyst were done using EXSTAR S11 7300 Thermal Analyzer (nitrogen atmosphere, heating range: 30-1200 °C, heating rate: 10°C/min). X-ray diffraction (XRD) pattern of Pd NPs@P(3-MPAP) catalyst was attained from Rigaku Smart Lab X-Ray Diffractometer (at 40 kV, 30 mA, and 2θ with a scan angle of 5−80°). SEM micrographs of 3-MPAP, P(3-MPAP) and Pd NPs@P(3-MPAP) and EDS spectrum and EDS mapping analysis of Pd NPs@P(3-MPAP) were obtained by FEI Quanta 450 FEG FE-ESEM-EDS. Palladium ion content of Pd NPs@P(3-MPAP) catalyst was detected by Perkin Elmer Optima 2100 DV Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES). The chemical structures of the synthesized biaryl products were illuminated by GC-MS Agilent GC-7890 A- MS 5975.

3. Results and Discussion

3.1. Determination of optimum polymerization conditions

The effects of NaOCl concentration, polymerization temperature, and time parameters on the yield of P(3-MPAP) were investigated to determine optimum polymerization conditions and the obtained results are given in Fig. 1. As seen in Fig.1.a., the polymer yield increased with increasing NaOCl concentration up to 0.2 mol/L concentration (94.3%). It was observed that the monomer precipitated at higher NaOCl concentration than 0.2 mol/L and thus the polymerization process stopped. The polymer yield also increased with increasing polymerization temperature up to 80 ˚C. After this temperature, the yield decreased with increasing temperature (Fig.1.b.). Additionally, the polymer yield also increased with increasing polymerization time up to 5 h when it was reached the highest yield (Fig.1.c.). Then, the yield decreased after longer durations. The reason of decrease in the polymer yield at higher temperatures and periods may be explained by the fact that polymer chains could be broken at high temperatures and periods. These short broken chains may be removed by dissolving during washing in the purification process [26-28]. Consequently, the highest polymer yield was obtained at 80 ˚C for 5 h using 0.2 mol/L NaOCl concentration and P(3-MPAP) which was synthesized under the determined optimum polymerization conditions was used in all following process.

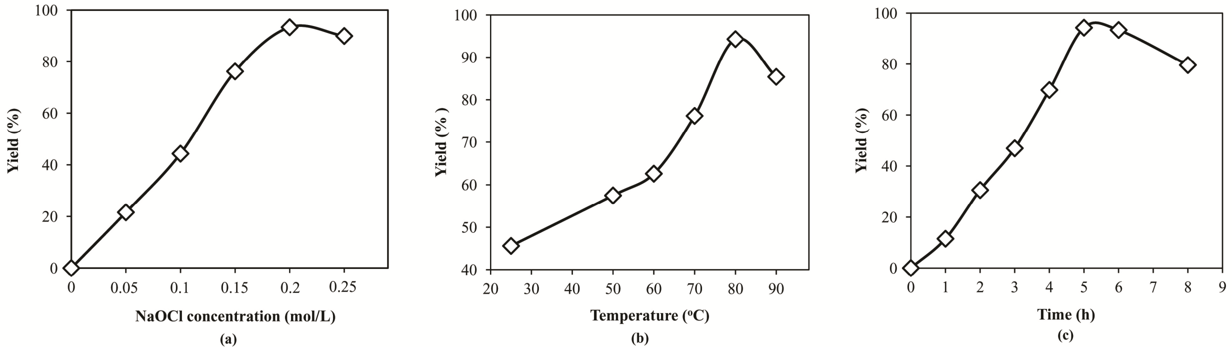


Figure 1. The effect of (a) NaOCl concentration, (b) polymerization temperature and (c) time on the yield of P(3-MPAP).

3.2. Molecular Weight Distribution of P(3-MPAP)

Molecular weight distribution of P(3-MPAP) support material was determined by GPC analysis. The analysis result showed that P(3-MPAP) had broad monomodal molecular weight distribution. Number average molecular weight (M_n), weight average molecular weight (M_w)

and polydispersity index (PDI) values of P(3-MPAP) which were obtained at determined optimum conditions were found as 85390, 23146 g/mol and 3.68, respectively.

3.3. Structures of 3-MPAP, P(3-MPAP) and Pd NPs@P(3-MPAP) catalyst

3.3.1. UV-Vis spectra

UV-Vis spectra of 3-MPAP, P(3-MPAP) and Pd NPs@P(3-MPAP) catalyst are given in Fig. 2. While two distinct bands were observed at 285 and 356 nm in the spectrum of the monomer, the same bands were seen at 287 and 365 nm as imperceptible broad shoulder-shaped in the broadened polymer spectrum. These bands can be ascribed to π-π* transitions of benzene ring (-C=C) and imine functional groups and n-π* transitions of OH functional group for the monomer and the polymer, respectively. When the polymer spectrum was compared to that of the monomer, I) broadening, imperceptibility and shifting of bands and II) broadening and extension of spectrum (to 700nm) were observed in the polymer spectrum. These changes refer that the polymerization process was successfully achieved [29-32]. Additionally, only a broad band at 323 nm was observed in the UV spectrum of Pd NPs@P(3-MPAP) catalyst compared to P(3-MPAP) spectrum. This band originates from surface plasmon resonance corresponding to the reduction of Pd^{II} to Pd^{0} and the formation of Pd NPs [33].

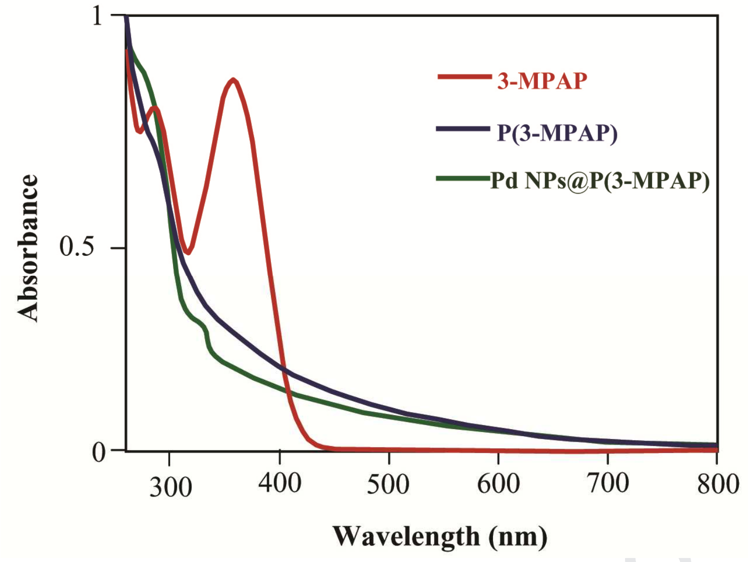


Figure 2. UV-Vis spectra of 3-MPAP, P(3-MPAP) and Pd NPs@P(3-MPAP) catalyst.

3.3.2. FTIR Spectra

FT-IR spectra of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst are displayed in Fig. 3. The vibration peaks of HC=N- functional group, which are typical for Schiff bases, their polymers and all derivatives, are detected at 1627, 1631, and 1617 cm^{-1} for 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst, respectively. The existence of this peak in the polymer spectrum indicates that azomethine structure was also preserved in the polymer backbone without degradation [26, 29, 30]. Other important peaks in the spectra of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst are summarized as follows: OH vibrations at 3054, 3129, 3206 cm^{-1}; C-H stretching vibrations at 2989, 2962, 2960 cm^{-1}; C=C vibrations at 1584-1440; 1589-1434 and 1591-1441 cm^{-1}; the plane aliphatic C-H bending vibrations at 1348, 1374, 1375 cm^{-1}; C-O vibrations at 1221, 1211, and 1212 cm^{-1}; C-N vibrations at 1047, 1094 and 1099 cm^{-1}.

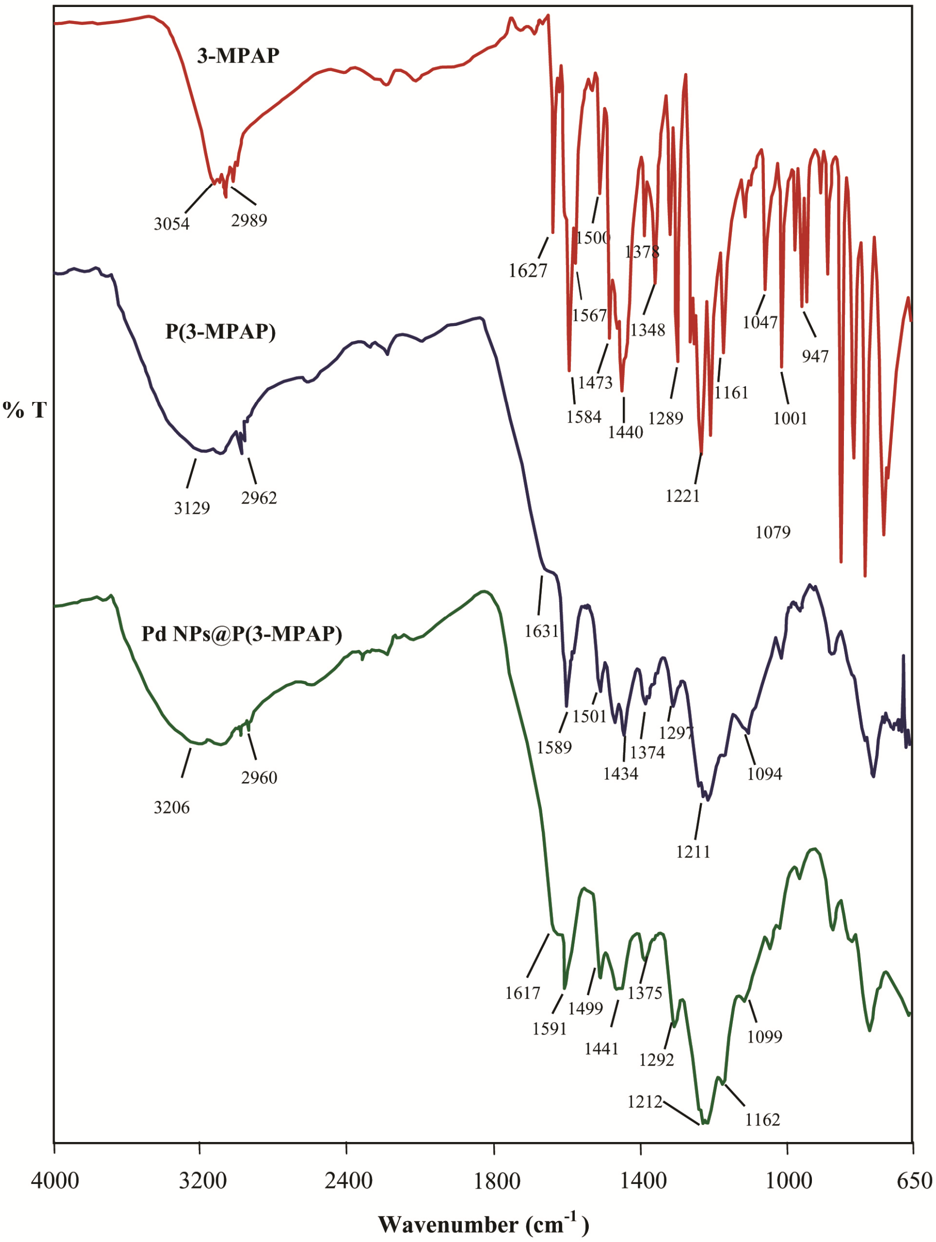


Figure 3. FTIR spectra of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst.

3.3.3.^{1}H-NMR Spectra

^{1}H-NMR analyses were carried out to determine the chemical structure of the synthesized monomer and polymer support material. The signals of the proton of characteristic -OH functional groups, –CH=N- and –CH$_3$ groups are seen at 9.94 (s, 1H), 9.40 (s, 1H) and 2,48 (s, 3H) ppm and 10.19 (s, 1H), 9.60 (s, 1H) and 2,37 (s, 3H) ppm in the spectra of 3-MPAP and P(3-MPAP), respectively. While the signals of protons belonging to aromatic structure of 3-MPAP were recorded at δ= 8.65 (s, 1H,); 8.47 (d, 1H); 8.12 (d, 1H); 7.90 (t, 1H); 7.45 (t, 1H); 7.10 (d, 1H,); 6.65 (d, 1H); ppm, these signals were observed at δ= 8.20 (d, 1H); 8.09 (d, 1H); 7.95 (t, 1H); 7.60 (t, 1H); 7.21 (s, 1H) ppm for P(3-MPAP). When the obtained signals are evaluated, it is seen that the synthesis of 3-MPAP and P(3-MPAP) were successfully carried out.

3.3.4.Thermal Degradation Process

Thermal degradation behaviors of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst were determined by TGA and the obtained curves are given in Fig. 4. Additionally, the measured thermal degradation data for all the synthesized materials are presented in detail in Table 1. When the thermal behaviors of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst are compared to each other, the temperatures at which 50% weight losses occurred are determined as 413, 788, and 831, respectively. These data indicate that while the polymeric support material is more thermally stable than the monomer due to increasing conjugation, the nanocatalyst is also more thermally stable than the polymeric support material due to Pd^0 content. Additionally, carbon residue of the monomer, polymer and nanocatalyst at 1200 °C were determined as 16.5%, 30.4%, and 31.6%, respectively. The increment of undecomposed part of Pd NPs@P(3-MPAP) catalyst is due to Pd NPs content.

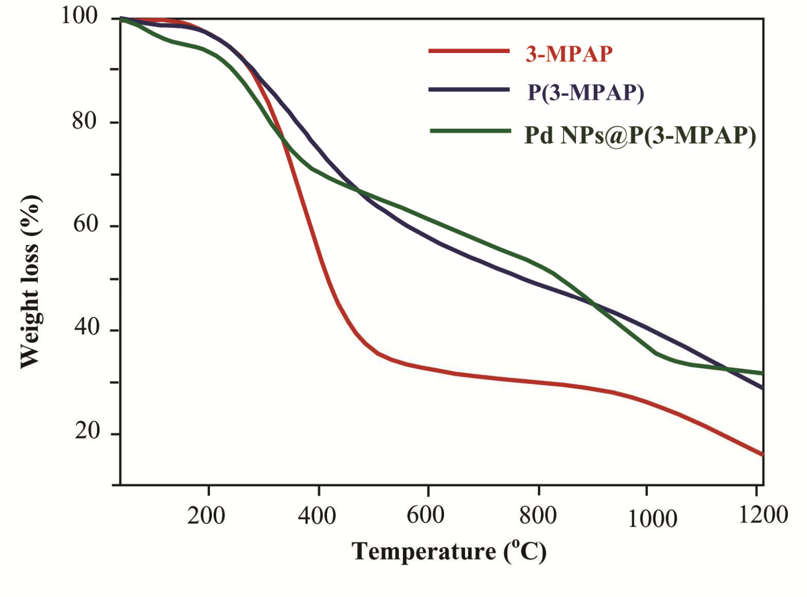


Figure 4. TG curves of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst.

Table 1. Thermal degradation data of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst.

Compound	T_{on}^{a} (°C)	Temperature ranges of weight loss stages (°C)	Weight losses at each stage (%)	T_{max}^{b} (°C)	$T_{50\%}$ (°C)	Residue at 1200 °C (%)
3-MPAP	122	122-220 220-600 600-1200	4.4 62.9 16.2	185 361 -	413	16.5
P(3-MPAP)	124	30-124 124-832 832-1200	1.3 49.8 18.4	75 362 -	788	30.4
Pd NPs@P(3-MPAP)	134	30-134 134-1200 620-1200	4.8 35.2 28.4	62 289	831	31.6

T_{max} represents the temperature at the maximum weight loss rate.
T_{on} represents the onset degradation temperature.
$T_{50\%}$ represents the temperature at which 50% weight losses occurred.

3.3.5.XRD Analysis

XRD analysis was performed to identify both the crystalline structure of Pd NPs@P(3-MPAP) catalyst and the presence of Pd NPs in the catalyst structure (Fig. 5). Broad peaks at about 10° (2θ) and 25° (2θ) can be ascribed to the amorphous nature of the support material.

Three sharp diffraction peaks in the pattern of Pd NPs@P(3-MPAP) catalyst were determined at 40.4° (2θ), 46.5° (2θ) and 66.7 (2θ). These peaks can be indexed to (111), (200) and (220) planes of Pd and attributed to the face centered cubic palladium [16, 34-36] These diffractions confirm the crystalline structure of the nanocatalyst and verify the presence of Pd NPs (Pd^0) and their purity [16].

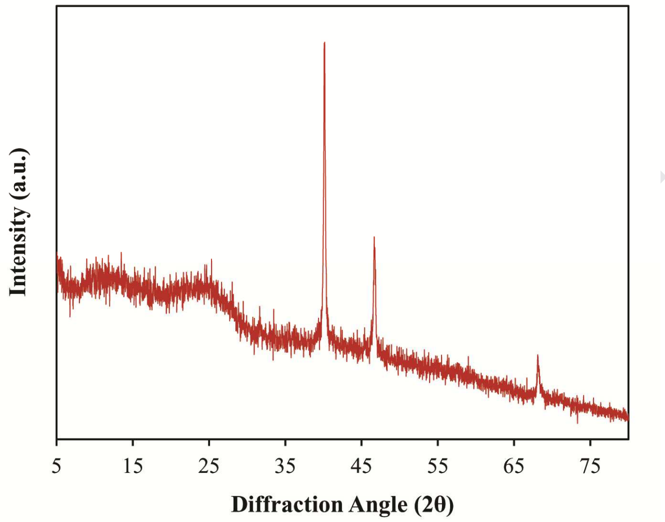


Figure 5. XRD patterns of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst.

3.3.6.SEM, EDS and ICP-OES analysis

The surface morphologies of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst were investigated by FE-SEM analysis. FE-SEM images of 3-MPAP and P(3-MPAP) in Fig. 6.a and 6.b show that while 3-MPAP had irregular platelike surface with fissures, P(3-MPAP) surface became more irregular surface with small particles after the oxidative polycondensation reaction. It is seen in the SEM image of Pd NPs@P(3-MPAP) catalyst (Figure 6.c) that Pd NPs had spherical shape and they were homogenously distributed on the support material surface. The size of immobilized Pd NPs on the support material is estimated about 50 nm.

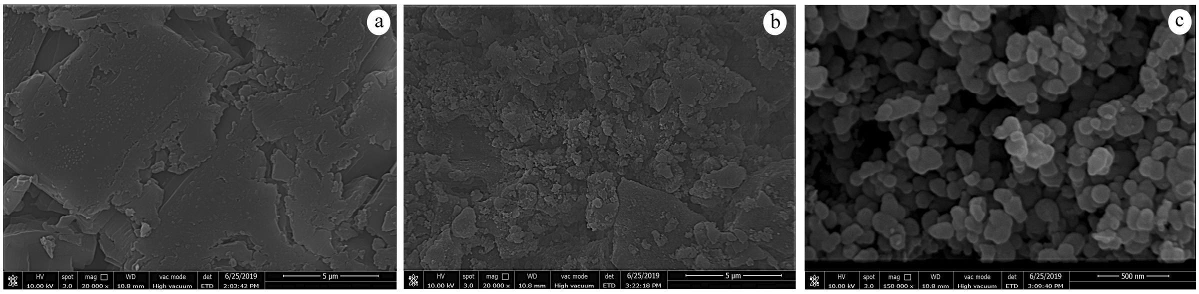


Figure 6. SEM of micrographs of (a) 3-MPAP, (b) P(3-MPAP), and (c) Pd NPs@P(3-MPAP) catalyst.

Additionally, EDS analysis was carried out for Pd NPs@P(3-MPAP) catalyst to determine the elemental composition. The presence and distributions of carbon, oxygen, nitrogen and palladium were determined by EDS spectrum and EDS mapping analysis, respectively (Fig. 7.). As seen in EDS mapping analysis, Pd NPs was homogenously distributed on the support material. Additionally, the signals belonging to palladium are obviously observed in EDS spectrum of Pd NPs@P(3-MPAP) catalyst. These results verify that the presence of palladium in the composition of Pd NPs@P(3-MPAP) catalyst. Furthermore, the content of palladium in Pd NPs@P(3-MPAP) catalyst was also found by ICP-OES technique. The quantity of palladium in the nanocatalyst was measured as 23.12% and 23.68% by mass with ICP-OES and EDS analyses, respectively.

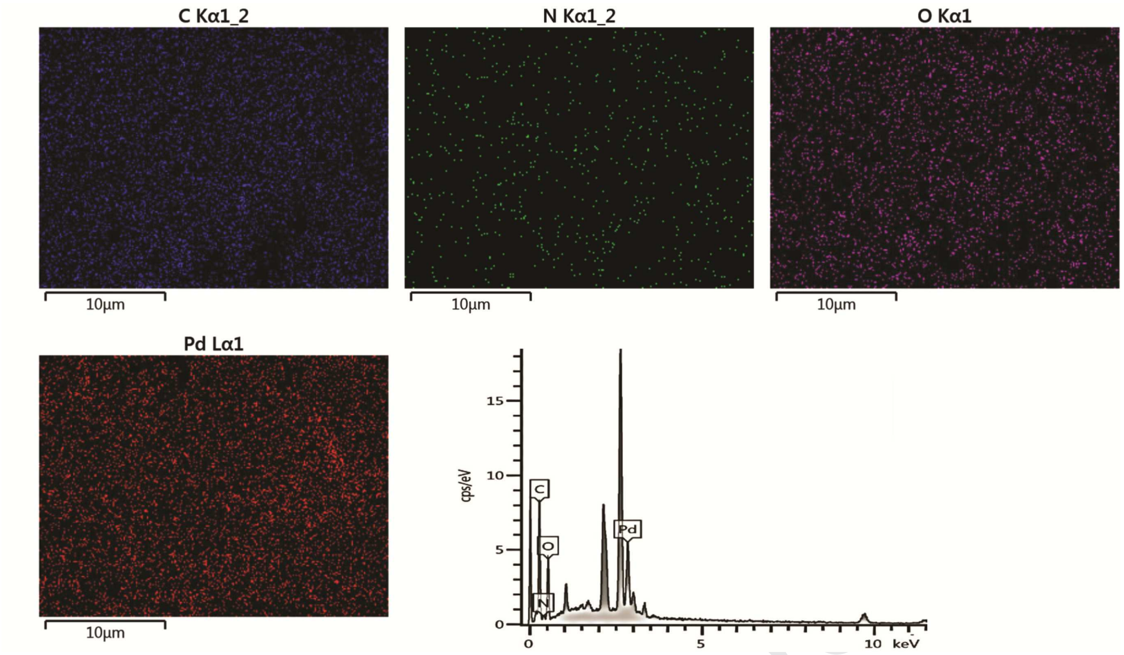


Figure 7. EDS mapping analysis and spectrum of Pd NPs@P(3-MPAP) catalyst.

3.4 Catalytic performance of Pd NPs@P(3-MPAP) catalyst

3.4.1 Catalytic activity of Pd NPs@P(3-MPAP) catalyst in Suzuki-Miyaura reactions

Catalytic effectiveness of the designed Pd NPs@P(3-MPAP) was tested in the production of biaryls by Suzuki coupling reactions using microwave irradiation which presents simple and fast methodology with high reaction yield in solvent-free media. The coupling reaction between 4-iodoanisole and phenylboronic acid was chosen as the representative reaction. To find ideal reaction parameters, preliminary experiments were carried out in the presence of Pd NPs@P(3-MPAP) catalyst and the obtained results are presented in Fig.8. As a result of the experiments which were performed using different catalyst loadings, reaction time, bases, and microwave powers, the highest reaction yield (99%) was reached with 0.007 mol% Pd NPs@P(3-MPAP) catalyst (Fig.8.a.), for 5 min. reaction time, (Fig.8.b.) K_2CO_3 as base (Fig.8.c.) and 400 W microwave power (Fig.8.d.), and these conditions were determined as the ideal reaction conditions. The catalytic performance of Pd NPs@P(3-MPAP) was evaluated in the synthesis of twenty different biaryls using microwave irradiation technique under the determined ideal reaction conditions and the results are summarized in Table 1. As seen in Table, Pd NPs@P(3-MPAP) was applied as the catalyst in Suzuki coupling reactions of aryl iodides, which have different functional groups, and the desired biaryls were synthesized with good yields up to 99%. Additionally, the activity of Pd NPs@P(3-MPAP) was also assessed against cross-couplings of phenylboronic acid with various aryl bromides and yields ranging between 97% and 65% were obtained. As the next step, coupling ability of Pd NPs@P(3-MPAP) was also investigated using aryl chlorides which have poor activity. It was found that Pd NPs@P(3-MPAP) catalyzed Suzuki coupling reactions of aryl chlorides with good product yields. These results indicated that Pd NPs@P(3-MPAP) has good catalytic performance against Suzuki cross coupling reactions by rapidly converting aryl halides into desired biaryls. This result facilitates the use of the fabricated nanocatalyst in industrial applications as an efficient material.

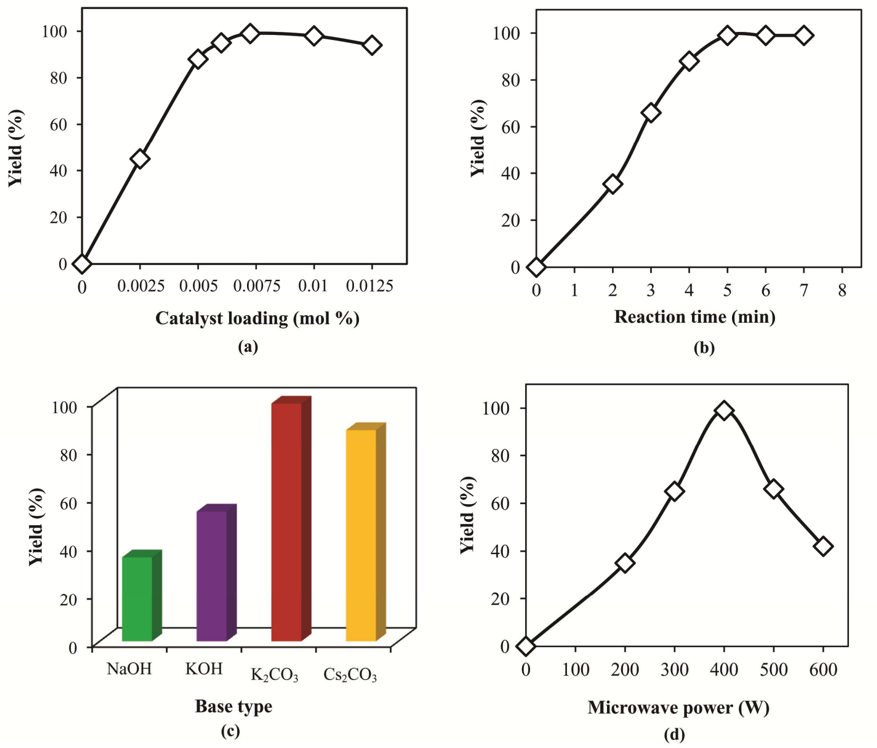
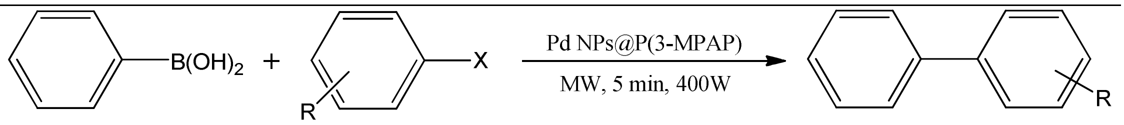


Figure 8. The effects of (a) catalyst loading, (b) reaction time, (c) base type and (d) microwave power on catalytic activity of Pd NPs@P(3-MPAP).

Table 2. Suzuki coupling reactions of several aryl halides with phenylboronic acid in the presence of Pd NPs@P(3-MPAP) catalyst.



Entry	X	R	Yield
1	I	4-OCH_3	99
2	I	3-NO_2	93
3	I	4-NH_2	86
4	I	2-CH_3	67
5	I	3-CH_3	71
6	I	4-CH_3	81
7	Br	2-OCH_3	91
8	Br	3-OCH_3	92
9	Br	4-OCH_3	97
10	Br	4-CN	98
11	Br	3-NO_2	90
12	Br	4-NO_2	97
13	Br	3-NH_2	78
14	Br	4-NH_2	81
15	Br	3-CH_3	65
16	Br	4-CH_3	69
17	Cl	2-OCH_3	69
18	Cl	3-OCH_3	73
19	Cl	4-OCH_3	79
20	Cl	3-NO_2	77

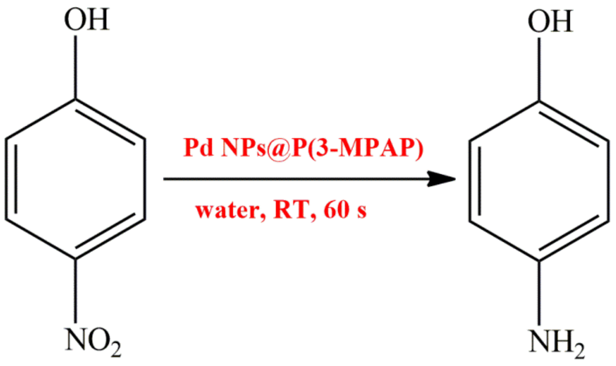
Reaction conditions: 1.8 mmol aryl halides, 1.2 mmol phenyl boronic acid, 3.5 mmol K_2CO_3 and 0.007mol% Pd NPs@P(3-MPAP) catalyst, 5 min, 400 W.

3.4.1 Catalytic activity of Pd NPs@P(3-MPAP) catalyst in the reduction of 4-NP

4-NP is one of the most common organic pollutants in wastewaters and known to have carcinogenic, toxic and mutagenic effect for human beings and animals. Thus, degradation of this harmful chemical to a harmless product is of great importance for all living creatures from both industrial and environmental points of view. 4-AP which is reduction product of 4-NP, is a byproduct used in fabrication of antipyretic and analgesic drugs and, hair dying agents [37]. Thus, the reduction of harmful 4-NP to harmless 4-AP is a desirable eco-friendly catalytic reaction. To be useful industrially and environmentally, the catalytic ability of the fabricated nanocatalyst was also assessed toward the reduction of 4-NP to 4-AP with $NaBH_4$ in water at room temperature (Scheme 2.) and the catalytic reduction studies were monitored by UV-Vis analysis. As seen in Fig.9, 4-NP has a strong absorption band at 317 nm. When $NaBH_4$ was added into 4-NP solution, the band of 4-NP shifted to 400 nm because of the production of 4-nitrophenolate ion (4-NPT) [38]. The yellow color of 4-NP solution simultaneously turned to bright yellow with the addition of $NaBH_4$ which justifies the fabrication of 4-NPT. After the addition of prepared nanocatalyst into the resulting mixture, the intensity of absorbance peak at 400 nm decreased gradually as the catalytic reaction progressed and finally disappeared within 60 s. Additionally a new band appeared at 296 nm, which is attributed to the formation of 4-AP, in parallel with the catalytic reaction [39]. Moreover, after the catalytic reaction was completed, bright yellow reaction solution turned to colorless. These results indicated that the catalytic reduction of 4-NP to 4-AP was successfully performed in 60 s in the presence of Pd NPs@P(3-MPAP) catalyst. On the other hand, a control experiment was carried out without catalyst to reveal the catalytic activity of the catalyst, and it was found that there is no reduction without its presence. This finding reveals that the prepared nanocatalyst is necessary for the catalytic reduction of 4-NP. The catalytic reduction of 4-NP followed pseudo-first-order kinetic and the rate constant was determined as 0.04 s^{-1} by using the formula in below.

$$\ln(A/A_0)=\ln(c/c_0) = -kt$$

where c_0 and c correspond to the initial concentration of 4-NP and concentration of 4-NP at the measured reaction time, respectively, and k (s^{-1}) is the rate constant.



Scheme 2. Reduction of 4-NP to 4-AP in the presence of Pd NPs@P(3-MPAP).

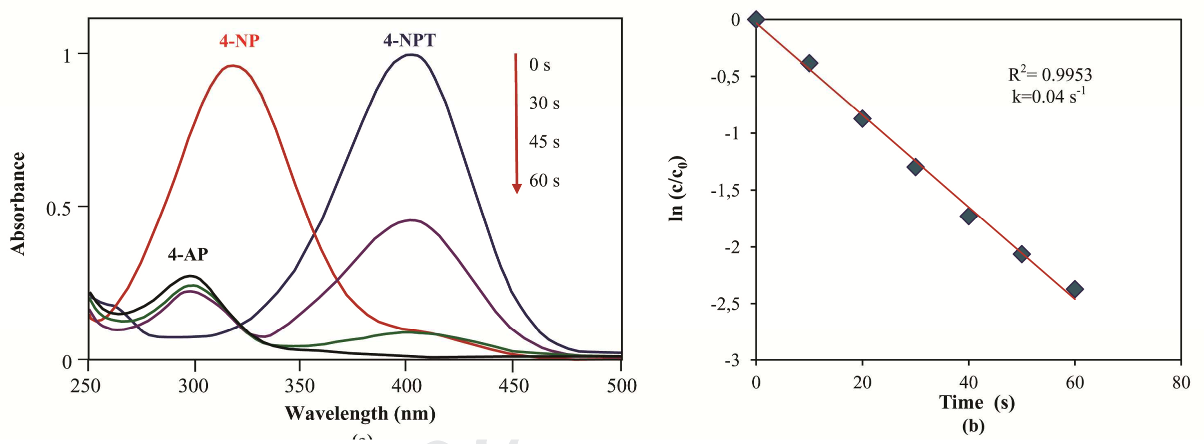


Figure 9. (a) UV–Vis absorption spectrum for the catalytic reduction of 4-NP in the presence of Pd NPs@P(3-MPAP) catalyst and (b) linear dependence graph between ln (c/c_0) and time. (Reaction conditions: 4-NP: 1.25×10^{-4} M, $NaBH_4$: 0.05 M, Pd NPs@P(3-MPAP): 1 mg, in water, at RT)

3.4.3 Reusability performance of Pd NPs@P(3-MPAP) catalyst in the catalytic systems

Reusability performance of any catalyst is an important parameter from the point of industrial applicability and continuity by reducing cost [40]. Thus, reusability performance of Pd NPs@P(3-MPAP) catalyst was investigated for both Suzuki coupling reactions and the reduction of 4-NP. The reusability test of Pd NPs@P(3-MPAP) catalyst in Suzuki coupling reactions was performed for the chosen model reaction under the found ideal reaction conditions using microwave irradiation technique. After the completion of model reaction, the filtered catalyst was washed with hot water and methanol for recovery process. The easily and fast recovered catalyst was reused and these recovery and reuse processes were recurrently repeated. At the end of the sixth subsequent cycle, the designed catalyst fabricated the desired biaryl with a conversion of 84%.

The reusability performance of Pd NPs@P(3-MPAP) catalyst was also tested for the reduction of 4-NP. In this process, the catalyst was filtered by simple filtration from the mixture in which the reduction reaction was completed and washed ethanol and water. After the obtained catalyst was dried in 80 ºC in an oven, it was used in other cycle. Even after four recovery and recycle processes, the designed catalyst reduced 4-NP without no loss of its catalytic efficiency.

Additionally, FTIR spectra which was recorded after the recycle processes indicated that the spectra of the fresh and the recycled catalysts for both catalytic reactions were similar. These results display that the chemical structures of the six and four times recovered and recycled catalyst for Suzuki coupling reaction and reduction of 4-NP could be invariably preserved.

These results show that Pd NPs@P(3-MPAP) is an ideal nanocatalyst in production of biaryls and the reduction of 4-NP for industrial applications in terms of its fast and easily recoverability, high efficiency, good recyclability without any valuable loss of its catalytic activity.

Hot filtration test

After model Suzuki coupling reaction was carried out for 3 min under optimum reaction conditions, Pd NPs@P(3-MPAP)catalyst was filtered out from the reaction media and 55% product yield was obtained in this process. Then, the reaction was allowed with the filtrate (without catalyst) for another 2 min and no increase was observed in the reaction yield. Additionally, after the reaction, palladium leaching in the filtrate was checked by ICP analyses and no palladium content was detected. These findings showed that Pd NPs@P(3-MPAP) catalyst had heterogeneous nature.

4. Conclusions

In summary, a novel highly effective, easily recoverable, repeatedly reusable, robust and thermally stable Pd NPs@P(3-MPAP) catalyst was fabricated for the synthesis of several biaryl compounds by Suzuki coupling reactions and the reduction of harmful 4-NP to 4-AP. Thermal analysis results display that both the newly synthesized polyazomethine derivative P(3-MPAP) support material and Pd NPs@P(3-MPAP) catalyst have high thermal stability. This property could enable their utilization in industrial materials necessitating thermal durability. The catalytic efficiency of the fabricated Pd NPs@P(3-MPAP) catalyst was investigated against i) the synthesis of twenty different biaryl compounds by Suzuki coupling reactions using simple, fast and nontoxic microwave irradiation technique and ii) the reduction of 4-NP to 4-AP. Pd NPs@P(3-MPAP catalyst provided high product yield (up to 99%) with low catalyst loading (0.007 mol%) in solventless media at short reaction time (5 min) using microwave irradiation technique with simple work-up procedure for all Suzuki coupling reactions. Additionally, the designed catalyst entirely reduced 4-NP, which is very harmful for all creatures and environment, to 4-AP (100% yield), in mild reaction conditions (at RT and in water) at very short reaction time (60 s). Moreover, reproducibility tests showed that Pd NPs@P(3-MPAP)catalyst was an easily retrievable material with simple and rapid procedure and could be reused at least six and four times with no valuable loss in Suzuki coupling reaction and 4-NP reduction, respectively. The effective reusability and easy recoverability of the fabricated nanocatalyst play a key role for commercial and industrial applications to decrease cost. This paper reveals that polyazomethines can be good stabilizers for different metallic nanoparticles and their catalysts can be used in various catalytic systems.

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Figure Captions

Figure 1. The effect of (a) NaOCl concentration, (b) polymerization temperature and (c) time on the yield of P(3-MPAP).

Figure 2. UV-Vis spectra of 3-MPAP, P(3-MPAP) and Pd NPs@P(3-MPAP) catalyst.

Figure 3. FTIR spectra of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst.

Figure 4. TG curves of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst.

Figure 5. XRD patterns of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst.

Figure 6.SEM of micrographs of (a) 3-MPAP, (b) P(3-MPAP), and (c) Pd NPs@P(3-MPAP) catalyst.

Figure 7.EDS mapping analysis and spectrum of Pd NPs@P(3-MPAP) catalyst.

Figure 8. The effects of (a) catalyst loading, (b) reaction time, (c) base type and (d) microwave power on catalytic activity of Pd NPs@P(3-MPAP).

Figure 9. (a) UV–Vis absorption spectrum for the catalytic reduction of 4-NP in the presence of Pd NPs@P(3-MPAP) and (b) linear dependence graph between ln (c/c_0) and time. (Reaction conditions: 4-NP= 1.25×10^{-4} M, $NaBH_4$ =0.05 M, Pd NPs@P(3-MPAP)=1 mg)

Scheme 1. Synthesis of 3-MPAP and P(3-MPAP).

Scheme 2. Reduction of 4-NP to 4-AP in the presence of Pd NPs@P(3-MPAP).

Table Captions

Table 1. Thermal degradation data of 3-MPAP, P(3-MPAP), and Pd NPs@P(3-MPAP) catalyst.

Table 2. Suzuki coupling reactions of several aryl halides with phenylboronic acid in the presence of Pd NPs@P(3-MPAP).

Highlights

- Pd NPs immobilized on a novel polyazomethine.
- Catalytic efficiency of Pd NPs@P(3-MPAP) was tested Suzuki coupling reactions.
- Reduction of 4-NP to 4-AP was accomplished in the presence of Pd NPs@P(3-MPAP).
- Pd NPs@P(3-MPAP) could be reused for six runs in production of biaryls (85%).
- Pd NPs@P(3-MPAP) could be recycled for four runs without any loss catalytic activity.