



Highly effective and recoverable Pd(II) catalyst immobilized on thermally stable Schiff base polymer containing phenol group: Production, characterization and application in Suzuki coupling reactions

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ARTICLE INFO

Article history:

Received 21 January 2018

Received in revised form

2 March 2018

Accepted 13 April 2018

Available online 16 April 2018

Keywords:

Catalyst

Oxidative polycondensation

Schiff base polymers

Polyphenols

Suzuki coupling reactions

Biaryl compounds

ABSTRACT

In this study, a novel highly efficient, recoverable, sustainable, and thermally stable Schiff base polymer-Pd(II) catalyst was designed for Suzuki coupling reactions in synthesis of biaryl compounds for the first time. Firstly, a novel Schiff base polymer containing phenol, Poly(4-((pyridine-2ylimino)methyl)benzene-1,3-diol) (P (4-PMB)), which was used as a support material in catalyst design, was synthesized in aqueous alkaline medium via oxidative polycondensation of 4-((pyridine-2ylimino)methyl)benzene-1,3-diol (4-PMB) with NaOCl oxidant. The effects of oxidant concentration, polymerization temperature, and time on yield and molecular weight of the polymer were investigated. The structures of the synthesized compounds were illuminated by UV–Vis, FTIR, ¹H NMR, XRD, TG/DTG, and SEM/EDAX methods. Then, Pd(II) complex of P (4-PMB) was produced, and its catalytic performance was tested in the synthesis of various biaryl compounds by Suzuki reactions using microwave irradiation technique which is a highly effective, fast, solvent-free and green method. The designed Pd(II) catalyst exhibited superior catalytic effect against syntheses of various biaryl compounds with high conversion yields (99%) and very low catalyst loading (0.01 mol%) for 5 min. Recyclability and reproducibility tests showed that the catalyst could be reused for seven successive runs without any great loss of its catalytic performance (84%).

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1. Introduction

Biaryls are widely preferred compounds in many industrial applications such as pharmacology, agrochemicals, cosmetics, and medicine thanks to their outstanding properties [1]. Thus, synthesis of biaryls have gained more interest in recent years, and various methods such as Stille [2], Heck [3], Negishi [4], Kumada [5] and Suzuki [6] coupling reactions have been developed for this process. Among the carbon–carbon formation reactions, Suzuki coupling reactions are extensively preferred thanks to their superior properties such as i) stability against temperature, air, and moisture; ii) tolerance to wide range of functional groups and water; iii) high selectivity; as well as iv) ease of removal of by-products [7]. Suzuki

coupling reactions have been usually executed in the presence of catalysts containing palladium, and heterogeneous catalyst systems are generally preferred by researchers for these processes [8]. It is because, heterogeneous catalysts have outstanding advantages such as ease of removal from the reaction medium and applicability in consecutive reactions compared to homogenous catalysts [9]. Also, the most important problems, which are encountered in catalytic systems such as low recycle ratios originating from leaching, difficulty in recovery, and high cost of the catalyst have been overcome via heterogeneous catalysts [10]. Thus, in recent years, heterogeneous catalysts have been hopeful materials for industrial applications. However, Suzuki coupling reactions also have some disadvantages which can be listed as I) use of toxic solvents, II) high reaction temperature, III) long reaction time, IV) labor-intensity [11]. To overcome these problems, researchers have improved microwave irradiation technique for Suzuki coupling

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reactions [12]. The novel efficient method produces high product yields in a very short reaction time, and thus high TON and TOF values are obtained. Also, this simple and fast technique eliminates requirement of toxic organic solvents [13]. All of them are important parameters for use in industrial applications.

In Suzuki coupling reactions, it is desired that support materials for catalysts should be thermally and mechanically stable to be industrially applicable. Schiff base polymers containing phenol groups may be alternative support materials for catalysts to synthesize biaryl compounds via Suzuki coupling reactions. Schiff base polymers containing phenol groups have been known as promising materials because of their semiconductive [14,15], antimicrobial [15,16], outstanding optic [17], fluorescent [18] and electrochemical [14,17], catalytic [19] as well as high thermal stability, and mechanical [20] properties. These polymers are generally synthesized using oxidative polycondensation reactions. This method is executed using NaOCl, H₂O₂, and O₂ as mild oxidants [21]. The most important advantages of this synthesis method are the cheapness of the used oxidants, ease of separation of oxidants from the reaction media, mild reaction conditions, production of polymers with high solubility, high molecular weight, good thermal and mechanical stabilities as well as formation of environmentally friendly byproducts (NaCl and H₂O) [20,21].

A thermally stable Schiff base polymer was used in this research as a support material for Suzuki coupling reactions in synthesis of biaryl compounds for the first time in the literature. Thus, a novel highly efficient, thermally resistant, easily recoverable Schiff base polymer-Pd (II) heterogeneous catalyst was designed for Suzuki coupling reactions. Firstly, the synthesis of P (4-PMB) Schiff base polymer was carried out by oxidative polycondensation of 4-PMB, using NaOCl oxidant in an aqueous alkaline medium. The effects of oxidant concentration and polymerization temperature and time were examined on yield and molecular weight of P (4-PMB). Various characterization techniques were used to verify the structures. Secondly, P (4-PMB)-Pd (II) catalyst was synthesized, and its catalytic performance was investigated in Suzuki coupling reactions for synthesis of various biaryl compounds using a simple, fast, solvent-free microwave irradiation technique. Recycle and recoverability performances of the catalyst were tested, and the results exhibited that the performance of the catalyst continues without any significant change even after many catalytic cycles.

2. Experimental

2.1. Materials

2,4-dihydroxybenzaldehyde, 2-aminopyridine, potassium hydroxide (KOH), disodium tetrachloropalladate (Na₂PdCl₄), sodium carbonate (Na₂CO₃), cesium carbonate (Cs₂CO₃), potassium carbonate (K₂CO₃), magnesium sulfate (MgSO₄), phenyl boronic acid, aryl halides hydrochloric acid (HCl, 37%), iodine, acetone, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethyl acetate, methanol, ethanol, *n*-methylpyrrolidone, 1,4-dioxane, *n*-heptane, tetrahydrofuran (THF) and toluene were supplied by Merck Chem. Co. (Germany). Sodium hypochlorite (NaOCl, 15% aqu.) was provided from Birpa Co. (Turkey). All chemicals were used as received without further purification.

2.2. Method

2.2.1. Synthesis of 4-PMB

4-PMB Schiff base monomer was synthesized by general condensation reaction of 2,4-dihydroxybenzaldehyde and 2-

aminopyridine (Scheme 1). A solution of (10 mmol, 1.38 g) 2,4-dihydroxybenzaldehyde in 15 mL methanol was added on 10 mmol (0.94 g) of 2-aminopyridine dissolved in 5 mL methanol. The mixture was continuously stirred at 40 °C. The completion of the reaction was intermittently checked by FTIR and TLC techniques. After 24 h, the mixture which contained the precipitated reddish product was filtered out and then washed with cold methanol to remove unreacted amine and aldehyde. Recrystallization of 4-PMB was performed from heptane and the purified Schiff base monomer was dried in vacuum desiccator (Yield: 91%).

2.2.2. Synthesis of P(4-PMB)

P (4-PMB) was obtained by oxidative polycondensation reaction of 4-PMB using NaOCl oxidant in aqueous alkaline medium (Scheme 1). 1 mmol (0.214 g) of 4-PMB was dissolved in aqueous solution of KOH (10%, 1 mmol) by refluxing under nitrogen atmosphere. After the dissolution was completed and determined reaction temperature was reached, 1 mmol of NaOCl was added to the reaction medium dropwise for 10 min. As soon as the oxidant was added, the reddish color of the monomer solution turned into dark brown. When the determined polymerization time was completed, the obtained polymer solution was cooled to room temperature and precipitated by neutralizing with HCl (37%). The precipitated product was filtered and washed with hot water and heptane to separate from mineral salts and unpolymerized monomer, respectively. The brown polymer was dried in an oven at 80 °C and weighed. The yield of the polymer (Yield, %) was determined according to Equation (1):

$$\text{Yield (\%)} = \frac{W_p}{W_m} \times 100 \quad (1)$$

where w_p and w_m describe the obtained polymer and initial monomer weights, respectively.

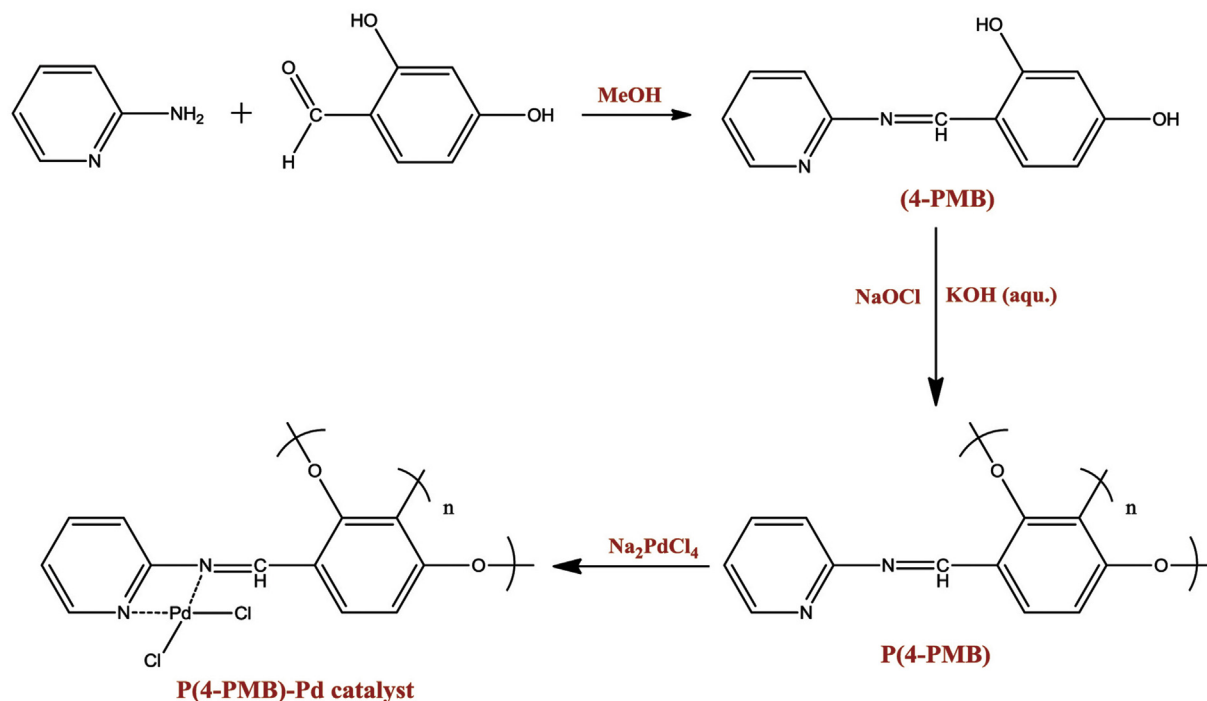
2.2.3. Synthesis of P(4-PMB)-Pd catalyst

0.2 g of P (4-PMB) was dissolved in 15 mL methanol at 70 °C and Na₂PdCl₄ (0.2 g) solution which was prepared in 10 mL water was added into the polymer solution. The reaction mixture was continuously stirred under reflux for 24 h. Then, the precipitated dark brown product was filtered and rinsed with water and methanol to remove unreacted Na₂PdCl₄ and polymer, respectively (Yield: 92%).

2.2.4. General procedure for Suzuki coupling reactions

Firstly, the coupling reaction of 4-bromoanisole and phenylboronic acid was determined as the model reaction. Then, to detect ideal reaction conditions, the effects of base system, reaction time, and catalyst amount on the yield of the biaryl compounds were investigated for the model coupling reaction which occurred in the presence of the synthesized P (4-PMB)-Pd (II) catalyst.

As a result of the determined optimum conditions, several aryl halides (1.12 mmol), phenyl boronic acid (1.87 mmol), potassium carbonate (3.75 mmol), and P (4-PMB)-Pd catalyst (0.01 mol%) were put into a Schlenk tube and mixed. The reactions were actualized by microwave irradiation technique using 400 W power in solventless media for 5 min. At the end of the coupling reactions, toluene (4 mL) was added on the obtained products and filtered. Then, extraction of the supernatant was done with water (2 mL) for three times, and the organic phase, which contained synthesized biaryl compound, was separated from water using separatory funnel. To remove the water completely, MgSO₄ was added on the organic phase. Then, toluene was removed at room temperature,



Scheme 1. Synthesis of 4-PMB, P(4-PMB) and P(4-PMB)-Pd catalyst.

and the yield of biaryl compound which was completely dried was calculated. To verify the structures of the biaryl compounds, they were analyzed by GC/MS technique.

2.3. Characterization

To determine molecular weight distributions (M_n , M_w and PDI values) of the synthesized polymers, Shimadzu Prominence Gel Permeation Chromatography was used as equipped with a preparative Nucleogel GPC 103-5 VA300/7.7 column (eluent: dimethylformamide (DMF), flow rate: 0.5 mL/min temperature: 40 °C), and monodisperse polystyrene standards was used for the calibration. UV–Vis spectra of 4-PMB, P(4-PMB), and P(4-PMB)-Pd were obtained from their solution prepared in DMSO in the wavelength range of 260–700 nm by Shimadzu UV-1700 PharmaSpec UV–Visible Spectrophotometer. FTIR spectra of the synthesized products were taken in the wavenumber range of 4000–650 cm^{-1} using Perkin Elmer FTIR Spectrometer. To identify the molecular structures of 4-PMB and P(4-PMB), their ^1H NMR spectra were recorded from their solutions in DMSO by Bruker Avance 500 MHz NMR at 25 °C. Thermal behaviors of 4-PMB, P(4-PMB), and P(4-PMB)-Pd were investigated by TG/DTG techniques taken under nitrogen atmosphere in the temperature range of 30–1200 °C at heating rate of 10 °C/min in a platinum crucible using EXSTAR S11 7300 thermal analyzer. Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku smart lab system (at 40 kV, 30 mA, and 2θ with a scan angle of 10–70°). The surface morphologies of the products were obtained by coating with platinum using QUANTA-FEG 250 ESEM. An EDAX-Metek was used to determine the presence of palladium ion on polymer. Palladium ion content of the Pd catalyst was also analyzed by Perkin Elmer Optima 2100 DV Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES). Verification of the structures of the synthesized biaryl compounds was done by GC–MS Agilent GC-7890 A- MS 5975. Catalytic tests were done with a domestic

microwave oven.

3. Results and discussion

3.1. Effect of synthesis conditions on polymer yield and molecular weight distribution of P(4-PMB)

3.1.1. Oxidant concentration

The changes of the yield and molecular weight distribution of the polymer with oxidant concentration were investigated and the obtained data are presented in Table 1. As seen in the table, the polymer yield increased to 0.1 mol/L NaOCl concentration but the yield did not significantly change after this concentration [22].

The results of GPC analysis of P(4-PMB) show that the molecular weight values increased to 0.1 mol/L NaOCl concentration but after this concentration, they decreased (Table 1). The decrease which was determined at higher concentrations can be explained by the increase in the number of active centers. Therefore, the growing chains remain short due to this increase [23]. Since the highest polymer yield and molecular weight values ($M_w = 36710$, $M_n = 20890$ g/mol and PDI = 1.75) were obtained using 0.1 mol/L NaOCl, the subsequent experiments were performed with 0.1 mol/L NaOCl concentration.

Table 1

The effect of NaOCl concentration on the yield and the molecular weight distribution of P(4-PMB).

NaOCl concentration (mol/L)	Yield (%)	M_w (g/mol)	M_n (g/mol)	PDI
0.05	49.6	10798	8870	1.21
0.1	74.3	36710	20890	1.75
0.2	76.2	11641	4353	2.67
0.3	75.6	7812	3672	2.12

([4-PMB] $_0$ = [KOH] $_0$ = 0.1 mol/L, polymerization temperature: 80 °C, time: 6 h).

3.1.2. Polymerization temperature and time

The effects of polymerization temperature and time on the polymer yield were investigated and the molecular weight values and the obtained results were exhibited in Table 2. When the change of polymer yield with polymerization temperature was examined, it was seen that the polymer yield decreased with increasing temperature [24]. While 81.4% yield was obtained at 90 °C, the yield was determined to be 95.6% at 25 °C. This case can be explained by breaking of the polymer chains due to increasing temperature. Short chains which form after breaking of the chains may be removed by dissolving during washing of polymer, and thus the polymer may be obtained with low yield.

On the other hand, molecular weight values of the polymer increased with increase in temperature (Table 2). M_w , M_n and PDI values of the polymer which was synthesized at 25 °C were 4882, 3552 g/mol and 1.37, respectively. The values for the polymer which was synthesized at 90 °C were measured as 93199, 51700 g/mol and 1.80, respectively. This increase is an expected phenomenon for polycondensation reactions in the literature [22,25]. Moreover, thermal stabilities of the polymers which were synthesized at 25 °C and 90 °C were compared by TG/DTG analysis. It was determined that while the polymer which was obtained at 25 °C completely degraded at 600 °C, the weight loss of the polymer obtained at 90 °C continued to 1200 °C. Thus, when the polymer was evaluated in terms of thermal stability and molecular weight values, the subsequent experiments were performed at 90 °C.

When Table 2 is examined in terms of the change of polymerization time, it is seen that the polymer yield increased up to 3 h and reached 96.8%. After this polymerization time, the yield decreased with the increase in polymerization time. These obtained results are in accord with the literature [22,26,27]. This may be explained by breaking of the polymer chains. The polymeric chains which were synthesized at high temperature for higher durations may remain short due to the breaking and the short chains may move away by dissolving during washing of the polymer.

Moreover, the change of the molecular weight values of P (4-PMB) with polymerization time was analyzed (Table 2) and a gradually decrease in molecular weight values of P (4-PMB) was determined with the increase in polymerization time. The highest molecular weight values ($M_w = 223362$, $M_n = 139350$ g/mol and PDI = 1.60) were obtained at the end of 1 h. This can be explained by breaking of the polymer chains synthesized at high temperature during higher durations [22].

3.2. Structures of 4-PMB, P(4-PMB), and P(4-PMB)-Pd catalyst

3.2.1. UV–Vis spectra

UV–Vis spectra of 4-PMB, P (4-PMB) and its palladium (II)

Table 2

The effect of polymerization temperature and time on the yield and the molecular weight distribution of P (4-PMB).

Temperature (°C)	Time (h)	Yield (%)	M_w (g/mol)	M_n (g/mol)	PDI
25	6	95.6	4882	3552	1.37
50	6	88.2	15841	9511	1.66
70	6	86.2	17797	11320	1.57
80	6	84.3	36710	20890	1.75
90	6	81.4	93199	51700	1.80
90	1	50.2	223362	139350	1.60
90	2	79.8	157940	88160	1.79
90	3	96.8	125380	68640	1.82
90	4	84.3	105790	57828	1.83
90	6	81.4	93199	51700	1.80
90	15	68.6	9071	7004	1.29

$([4\text{-PMB}]_0 = [\text{KOH}]_0 = [\text{NaOCl}]_0 = 0.1 \text{ mol/L})$.

catalyst were recorded by dissolving in DMSO. In UV–Vis spectrum of 4-PMB, two bands were observed at the wavelengths of 290 and 342 nm. The presence of these bands can be referred to π – π^* transitions belonging to benzene ring ($\text{C}=\text{C}$) and π – π^* transitions of the imine functional group. The same transitions were detected at 295 and 386 nm in the spectrum of P (4-PMB). In the spectrum of P (4-PMB)-Pd, a new band was seen at 537 nm which originates from d–d transitions of palladium ion in addition to the bands of π – π^* transitions at 297 and 392 nm [28]. This new band confirms that the complexation was achieved. When the spectra of the monomer and the polymer were compared to each other, it was determined that the spectrum of the polymer broadened to 700 nm while the monomer spectrum terminated at 500 nm. Moreover, all the bands of the polymer shifted to red and broadened too much. All these differences originate from the increasing conjugation and verify that the polymerization was accomplished [15,19,29,30].

3.2.2. FTIR spectra

FTIR analysis was used to support the structures of the synthesized samples, and the obtained spectra for 4-PMB, P (4-PMB), and P (4-PMB)-Pd are presented in Supplementary Fig. S1. When the spectra are investigated, the peaks at 3038, 3075, and 3094 cm^{-1} are due to the vibrations of phenolic OH groups for 4-PMB, P (4-PMB) and P (4-PMB)-Pd, respectively. While $\text{CH}=\text{N}$ – vibration, which is characteristic for Schiff bases and their polymers, is seen at 1610 cm^{-1} in the monomer spectrum, the peaks which belong to this vibration are observed at 1621 and 1605 cm^{-1} in the polymer and its Pd(II) catalyst spectra, respectively. The presence of azomethine peak in the polymer spectrum also demonstrate that these characteristic groups are protected without degradation during polymerization [15]. The other peaks for 4-PMB, P (4-PMB), and P (4-PMB)-Pd are observed at 1584–1432, 1591–1436, and 1587–1434 cm^{-1} (aromatic $\text{C}=\text{C}$ vibrations); 1205, 1229, and 1233 cm^{-1} (C–O stretching vibrations); 1143, 1170, and 1081 (C–N vibrations of pyridine ring), respectively. When FTIR spectrum of the polymer is compared to that of the monomer, (i) shifting of $\text{CH}=\text{N}$ – vibration to higher wavenumber, (ii) broadening of the peaks, and (iii) the decrease in the peak number are detected in the polymer spectrum. All of these findings originate from the increase in the conjugation length and prove that polymeric structure is achieved [15,19,22,29,30]. Moreover, shifting of $\text{CH}=\text{N}$ – vibration of Pd(II) catalyst from 1621 cm^{-1} to 1605 cm^{-1} compared to that of the polymer, shows that the palladium ion was coordinated to the polymeric structure through the nitrogens of azomethine groups.

3.2.3. ^1H NMR spectra

To illuminate the structure of 4-PMB and P (4-PMB), their ^1H NMR spectra were recorded and are displayed in Supplementary Fig. S2. The signals of the protons of OH and $\text{CH}=\text{N}$ – functional groups in ^1H NMR spectra of 4-PMB are observed at 9.90 (s, 1H) and 9.32 (s, 1H) ppm, respectively. The same signals which belong to the polymer are seen at 11.65 (s, 1H) and 9.81 (s, 1H) ppm, respectively. The other signals which verify the aromatic structure of 4-PMB are determined at $\delta = 8.47$ (s, 1H); 7.87 (d, 1H); 7.54 (d, 1H); 7.36 (d, 1H); 7.08 (t, 1H); 7.33 (d, 1H); and 7.27 (d, 1H) ppm. Additionally, the signals which prove the aromatic structure of P (4-PMB) are found at $\delta = 7.95$ (d, 1H); 7.85 (t, 1H); 7.55 (d, 1H); 6.95 (d, 1H); 6.83 (t, 1H); and 6.67 (d, 1H) ppm. When ^1H NMR spectrum of polymer is compared to that of the monomer, broadening in aromatic signals of the polymer occurs because several polymer chains with different molecular weights have different chemical environments.

Moreover, (I) the absence of the aromatic singlet signal of the monomer, in the polymer spectrum and (II) the observation of OH signal of the polymer with 1H integration compared to OH signal of the monomer with 2H integration, express that the polymerization

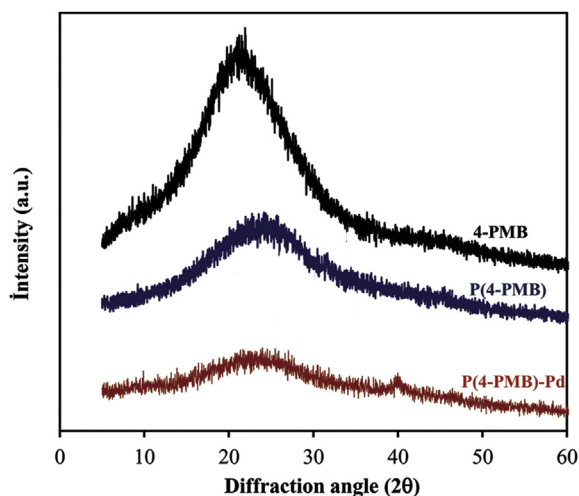


Fig. 1. XRD patterns of 4-PMB, P (4-PMB), and P (4-PMB)-Pd catalyst.

process continues from C-O-C and C-C couplings which occur from OH groups and ortho positions of OH groups during polymerization, respectively [14,15,22,30].

3.2.4. Thermal degradation process

TG and DTG curves were recorded to determine thermal behaviors of 4-PMB, P (4-PMB), and P (4-PMB)-Pd catalyst (Supplementary Fig. S3). As seen in TG curve of 4-PMB, the monomer began to degrade at 99 °C and degraded in three steps. While 37.2% weight loss was seen in the first step in the temperature range of 99–300 °C, 22.8% weight loss was determined for the second step in the temperature range of 300–452 °C, and 40% weight loss was defined in the third step (452–600 °C). The maximum degradation temperatures ($T_{\max}$) belonging to these degradation steps were determined from DTG curves at 232, 354 and 635 °C, respectively.

Additionally, TG curve of P (4-PMB) was recorded up to 1200 °C, and the degradation of the polymer actualized in three steps. Firstly, the weight loss of 3.37% in the temperature range of 30–122 °C can be ascribed to the removal of adsorbed water. The other weight losses in the temperature ranges of 122–518, 518–852, and 852–1200 °C were determined as 37.31%, 17.87%, and 14.2%, respectively. $T_{\max}$ values which belong to these degradation steps were also found as 260, 585 and, 1036 °C, respectively.

As seen in TG curve of P (4-PMB)-Pd catalyst, the catalyst degraded in three steps up to 1200 °C. The weight loss in the temperature range of 30–142 °C (4.5%) can be attributed to the removal of adsorbed water. The weight losses which belong to degradation steps of the catalyst were determined as 19.2%, 8.0%,

13.7%, and 10.2% in the temperatures ranges of 142–378, 378–520, 520–873, and 873–1200 °C, respectively.

When the thermal behaviors of the monomer, polymer and Pd(II) catalyst were compared to each other, 30% weight loss took place at 260, 360, and 480 °C, and 50% weight loss occurred at 369, 622, and 1018 °C, respectively. These findings indicate that the thermal stability of the polymer is higher than that of the monomer due to the increasing conjugation in the polymer structure. Moreover, while 4-PMB did not leave any carbon residue, P (4-PMB) and P (4-PMB)-Pd catalyst had carbon residues at 1200 °C which were found as 27.5% and 44.4%, respectively. The reason why the catalyst has the highest residue also originates from metal oxide residue [15,19,30].

3.2.5. XRD analysis

To learn about the crystalline structures of 4-PMB, P (4-PMB) and P (4-PMB)-Pd catalyst, XRD patterns were recorded in the region of $2\theta = 5\text{--}60^\circ$ and are illustrated in Fig. 1. A broad diffraction peak which is centered at about $22\text{--}25^\circ$ (2θ) is observed for all synthesized samples. It means that the prepared samples have amorphous nature. As seen in the figure, the diffraction peak of the polymer is broader than the monomer peak, and it shifted to 25° (2θ) from 22° (2θ). This broadening expresses a decrease of crystallinity and an increase of amorphous nature which verify that the polymerization occurred successfully. Moreover, the peak of Pd(II) catalyst is also broader than that of the polymer. This phenomenon is also seen in literature and explained by the coordination of palladium ion with the polymer [31]. On the other hand, two new weak peaks were observed at 40.12 (2θ) and 46.78 (2θ) in the diffraction pattern of Pd(II) catalyst. These diffraction peaks can be attributed to the presence of palladium species [32].

3.2.6. SEM/EDAX and ICP-OES analysis

SEM micrographs of 4-PMB, P (4-PMB), and P (4-PMB)-Pd catalyst were obtained to show their surface morphologies and these images are displayed in Fig. 2. While the monomer surface is determined to consist uniform spheres, it is seen that the polymer surface has a layered structure. These differences emphasize that the surface changed following condensation polymerization. When P (4-PMB)-Pd catalyst surface is analyzed, it is seen that the particles of palladium ions homogeneously covered the polymer surface had layered structure.

Moreover, EDAX analysis of Pd(II) catalyst was carried out to confirm the presence of palladium ions coordinated to the polymeric structure (Fig. 3). In EDAX spectrum, palladium signals are apparently seen and verify that palladium ions were successfully coordinated. Additionally, the amount of the palladium ions was also found by ICP-OES and as 35% by mass.

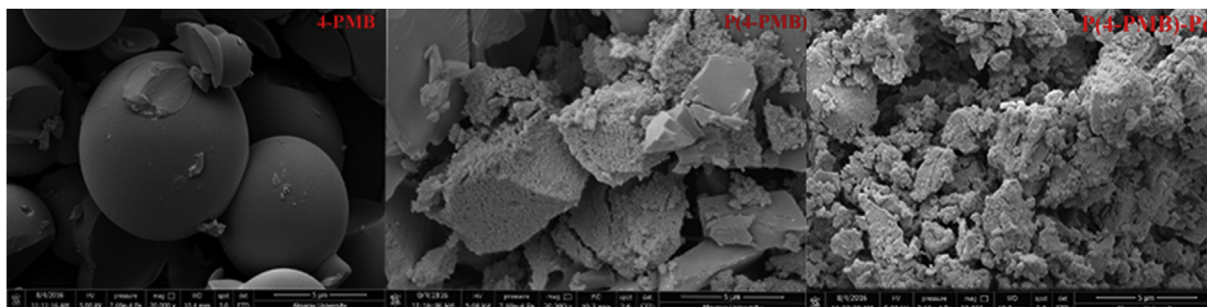


Fig. 2. SEM of micrographs of 4-PMB, P (4-PMB) and P (4-PMB)-Pd catalyst.

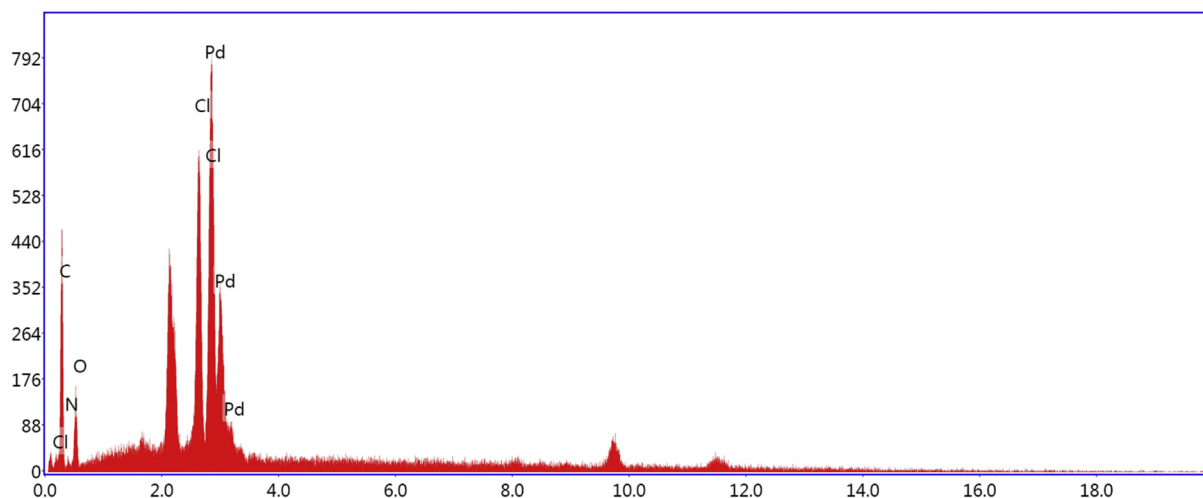


Fig. 3. EDAX spectrum of Pd(II) catalyst.

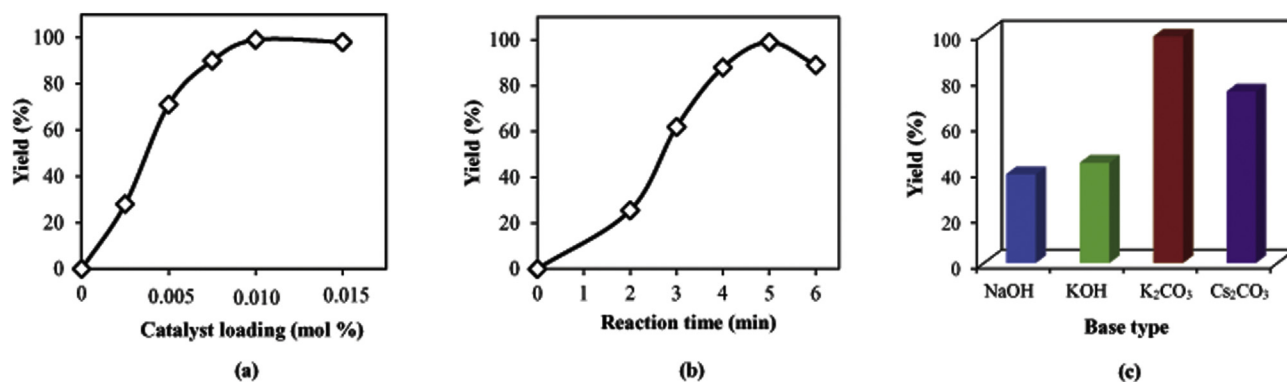


Fig. 4. The effects of catalyst loading (a), reaction time (b) and base type (c) on catalyst activity of P (4-PMB)-Pd.

3.3. Catalytic performance of P(4-PMB)-Pd catalyst

3.3.1. Optimal reaction conditions for Suzuki cross coupling reactions

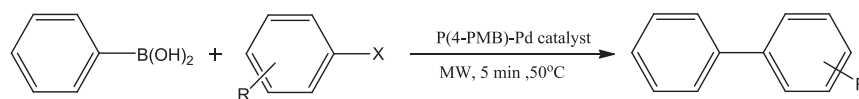
All Suzuki coupling reactions which were carried out for the synthesis of various biaryl compounds were performed with microwave irradiation technique which is simple, fast, solvent-free, and highly efficient. The reaction of *p*-bromoanisole and phenyl boronic acid was determined as model Suzuki coupling reaction to detect optimum reaction conditions. The effects of catalyst amount, base type, and reaction time on the yield of synthesized biaryl compound (4-methoxybiphenyl) were investigated and the obtained results are presented in Fig. 4a, b, and c, respectively. As seen in Fig. 4a, it was determined that the product yield increased up to 0.01 mol% catalyst amount, and after this catalyst amount, the yield gradually decreased with the increasing catalyst amount. Since the highest product yield was obtained with 0.01 mol% catalyst amount, the subsequent experiments were continued with this catalyst loading. To determine the effect of base type, the coupling reactions were tested in the medium of NaOH, KOH, Na_2CO_3 , CS_2CO_3 and K_2CO_3 (Fig. 4b). Since the highest biaryl yield (99%) was obtained with K_2CO_3 base, the following experiments were carried out with it. Additionally, the reaction time with the highest product yield (99%) was determined as 5 min (Fig. 4c). Thus, 5 min was used as the optimal reaction time for all Suzuki coupling reactions.

3.3.2. Catalytic activity of P(4-PMB)-Pd catalyst in the Suzuki-Miyaura reactions

The catalytic performance of the prepared P (4-PMB)-Pd catalyst was studied in Suzuki cross coupling reactions under the aforementioned optimization conditions by using microwave irradiation technique, and the results are given in Table 3. The catalyst gave excellent biaryl yields with aryl bromides containing electron-withdrawing group (Table 3). For example, when *p*-bromonitrobenzene and *p*-bromobenzonitrile were used as the substrate, 91% and 89% conversion yields, respectively, were reached (Table 3, entry 4,5). In addition, good biaryl yields were obtained with aryl bromides bearing -meta and -para substituted electron-donating groups ($-CH_3$) (Table 3, entry 7,8). The catalytic activity of the catalyst was also tested with electronically different aryl iodides, and the perfect reaction yields were reached in the presence of the catalyst (Table 3, entry 9,10). For example, the cross coupling reaction of *p*-iodoanisole with phenyl boronic acid produced excellent yield (99%). Aryl iodide with meta-substituted- NO_2 gave an isolated yield of 90%. We also investigated the activity of the catalyst in the presence of aryl chlorides, and biaryl yields were lower than aryl bromides and iodides, as expected (Table 3, entry 11,12). For example, the coupling reaction gave 55% yield with *p*-chloroanisole and 65% yield with 1-chloro-3-nitrobenzene. These lower reaction yields can be explained by poor activities of aryl chlorides in Suzuki coupling reactions [31]. Performed tests revealed that the designed catalyst is highly effective towards

Table 3

Suzuki coupling reactions of several aryl halides with phenylboronic acid using P (4-PMB)-Pd catalyst.



Entry	Phenyl boronic acid	Aryl halide	Product	Yield (%)
1				99
2				95
3				88
4				89
5				91
6				87
7				79
8				73
9				99
10				90
11				55
12				65

Reaction conditions: 1.12 mmol aryl halides, 1.87 mmol phenyl boronic acid, 3.75 mmol K₂CO₃, 0.01 mol% Pd catalyst, 50 °C, 0.08 h under MW.

Suzuki cross coupling reactions.

3.3.3. Reproducibility capacity of P(4-PMB)-Pd catalyst

Reproducibility performance for catalysts is one of the most important parameters from the view point of industrial applicability [33]. Thus, the reusability performance of the designed catalyst was examined on the model reaction under the determined optimum reaction conditions. After the model reaction was completed, the filtered catalyst was washed with hot water and methanol to renew the catalyst and the regenerated catalyst was reused in Suzuki coupling reaction. This process was repeated for each cycle. The catalyst provided 84% product conversion even after seven recycles. This result shows that the designed reproducible and reusable catalyst is ideal for industrial applications to reduce operational cost. FTIR spectra of the recycled catalyst and the fresh

catalyst were compared to determine whether there was any change in the catalyst structure after recycle tests, and no significant change was observed. It indicates that the recovered and reused catalyst preserved its chemical structure without any changes. This reproducibility of the designed catalyst makes it a promising material for industrial applications.

4. Conclusions

In conclusion, a novel Schiff base polymer-Pd(II) catalyst, which is highly efficient, thermally stable, renewable, and sustainable, was fabricated for Suzuki coupling reactions for the first time in the literature. A novel Schiff base polymer containing phenol group which was used as support material was produced by oxidative polycondensation reaction of 4-PMB in an aqueous alkaline

medium in the presence of NaOCl oxidant. The effect of the change of polymerization conditions on molecular weight monitoring of P (4-PMB) was monitored since the molecular weight is one of the most important parameters for polymers in terms of industrial applications. Thermal analysis data revealed that the polymer is thermally more stable than its monomer which means that the polymer can be used in industrial materials that require high thermal stability. Moreover, the fabricated Pd(II) catalyst was investigated in terms of its catalytic activity for Suzuki coupling reactions in the synthesis of various biaryls compounds. The catalytic performance experiments were carried out using microwave irradiation technique which is easy, rapid, and solvent free, and require low workforce and power. The designed catalyst gave outstanding catalytic activities by producing high biaryl yields. Additionally, the reproducibility tests revealed that the catalyst is renewable and can be reused seven times without any great loss from its catalytic ability. The reproducibility performance of the catalyst plays a key role for industrial applications in terms of cost reduction.

Acknowledgments

The authors would like to thank Aksaray University Research Funds for the financial support of this work (Project No. 2016-022).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jorganchem.2018.04.022>.

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