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Title: Synthesis, Characterization, and Catalytic Activity in Suzuki Coupling and Catalase-like Reactions of New Chitosan Supported Pd Catalyst

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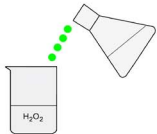
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**Synthesis, Characterization, and Catalytic Activity in Suzuki Coupling and Catalase-like Reactions of New Chitosan Supported Pd Catalyst**

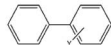
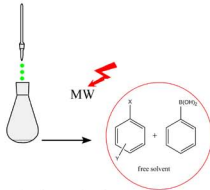
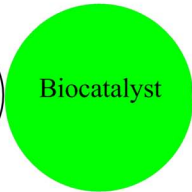
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Catalase-like activity



Suzuki coupling reaction

**Highlights**

- Catalase-like activity of biomaterial supported Pd catalyst decreased by only 12.9 % at the end of 10 cycle.
- Synthesis of biaryl using free solvent at 4 min. under MW was succeeded.
- TON and TOF values for both applications determined high.
- Suzuki reaction exhibited high selectivity and no homo-coupling by-products.

**Abstract:**

The aim of this study is to analyze the synthesis of a new chitosan supported Pd catalyst and examination of its catalytic activity in:

- 1) Suzuki coupling reactions by improving a simple, fast, and solvent-free microwave method
- 2) H<sub>2</sub>O<sub>2</sub> decomposition reaction to find out its redox potential.

Pd catalyst was synthesized using chitosan as a biomaterial and characterized with FTIR, TG/DTG, XRD, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, SEM-EDAX, ICP-OES, Uv-Vis spectroscopies, and magnetic moment, along with molar conductivity analysis. Biomaterial supported Pd catalyst indicated high activity and long life time as well as excellent turnover number (TON) and turnover frequency (TOF) values in Suzuki reaction. Biomaterial supported Pd catalyst catalyzed H<sub>2</sub>O<sub>2</sub> decomposition reaction with considerable high activity using comparatively small loading catalyst (10 mg). Redox potential of biomaterial supported Pd catalyst was still high without negligible loss (13 % decrease) after 10 cycles in reusability tests. As a consequence, eco-friendly biomaterial supported Pd catalyst has superior properties such as high thermal stability, long life time, easy removal from reaction mixture and durability to air, moisture and high temperature.

**Keywords:** Biomaterial supported Pd catalyst, Suzuki coupling reaction, redox potential, microwave irradiation, solvent-free

## 1. Introduction

Green chemistry is one of the most attracted subjects nowadays (H. Clark, 1999). It is concerned with catalysis, environmentally favorable solvents, supercritical fluids, and some techniques such as microwave and real time analysis for pollution prevention (Fuji, 1993; H. Clark, 1999; Li, 2005; Nuchter, Ondruschka, Bonrath & Gum, 2004). Catalysts are most favored materials with superior properties such as ease of preparation, reusability, and selectivity (Makha, Raston, Skelton & White, 2004). TON and TOF are significant parameters due to their influence on both the commercial sustainability and the catalyst potential for clean chemistry.

Biomaterial supported catalysts have attracted much attention in last 20 years due to their eco-friendliness, non-toxicity, low-cost, bio-degradable features, and high metal adsorption capacity (Sin, Yi & Lee, 2010; Yi, Lee, Sin & Lee, 2007). They have the advantages of being economic and being used as eco-friendly reagents under mild reaction conditions (Calo et al., 2004) Thus, solid supported biocatalysts, homogenous or heterogeneous, are operated in Suzuki-coupling, Heck, decomposition, and aerobic oxidation reactions (Sin, Yi & Lee, 2010).

Chitin, chitosan, cellulose, silica, zeolite, and carbon are widely used biomaterial based catalysts (Cui, Zhang & Li, 2005; Puthiaraj & Pitchumani, 2014; Zhu, Wang, Wang, Li & Diao, 2013). Chitosan (CS) is one of the most important and majorly used biomaterials due to its several applications in different areas such as waste water treatment, radioactive element and textile waste removal, medicine, agriculture, biotechnology, and food and pharmaceutical industries (Muzzarelli, 2011; Zeng, Zhang, Shao, Qi & Zhang, 2012).

The synthesis of biaryls in the presence of palladium catalysts are generally performed by Suzuki coupling reactions (Miyaura & Suzuki, 1995). Suzuki coupling reactions require high

reaction temperature, long reaction time, large amounts of energy and solvents, and inert atmosphere (Alonso & Najera, 2010; Das, Sarmah, Tairai & Bora, 2011). To improve these drawbacks, microwave irradiation techniques are popularly utilized for Suzuki coupling reactions (S. Varma, 1999; Singh, Kaval, Tomar, Van der Eycken & Parmar, 2008). Advantages of microwave irradiation techniques can be sorted as ease of work-up, safety, high reaction yield in short time, clean synthesis, and high selectivity, and good economic and environmental conditions (Hajipour, Karami & Pirisedigh, 2011).

In addition, several metal ions supported biomaterial catalysts have redox potential (Gupta & Abdulkadir, 2008). Thus, these chemically modified new catalysts find application areas for decomposition reactions (Demetgul, 2012; Gupta & Abdulkadir, 2008). The catalytic activities of metal supported catalysts are investigated by choosing catalase-like decomposition reaction of  $H_2O_2$  as a model reaction. It has been reported that complexation of metal ions with different ligands affect the reactivity of metal complexes in decomposition of  $H_2O_2$ .

In the current study, synthesis and characterization of a new biomaterial supported Pd catalyst were aimed, and catalytic activity of the new catalyst was tested in two different reactions:

- a) Synthesis of biaryls by Suzuki coupling reactions that uses a new solvent-free microwave irradiation technique in a short reaction time of 4 minutes.
- b) Investigation of redox potential of biomaterial supported Pd catalyst in catalase-like reaction of  $H_2O_2$  and optimization of reaction conditions such as time, substrate concentration, temperature, and amount of catalyst.

The newly synthesized biomaterial supported Pd catalyst was illuminated with fourier transform infrared (FTIR), thermal gravimetric analysis (TG/DTG), X-Ray Diffraction (XRD), proton and carbon nuclear magnetic resonance ( $^1H$ -NMR and  $^{13}C$ -NMR), scanning



electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDAX), inductively coupled plasma atomic emission spectroscopy (ICP-OES), ultraviolet visible (Uv-Vis) spectroscopies and magnetic moment, and molar conductivity analysis. Catalytic activity results ensure that biomaterial supported Pd catalyst shows high conversion yield and long life time at small catalyst loading. TON and TOF values of biomaterial supported Pd catalyst proved to be higher than the ones in the previous studies (Karthikeyan, Vanitha, Radhika, Suresh & Sugumaran, 2013; Leonhardt et al., 2010; Liu, Li, Gao, Wang & Jin, 2015). As a consequence, the catalyst can easily find potential uses in different industrial and pharmaceutical applications.

## **2. Materials and Method**

### **2.1 Materials**

All chemicals used in the study were purchased from Sigma-Aldrich. The FTIR spectra of the all compounds were analyzed on a Perkin Elmer Spectrum 100 FTIR spectrophotometer. The  $^1\text{H}$ -NMR spectra of the biaryls were recorded on Agilent 600 MHz spectrometer using Acetone- $\text{d}_6$  solvents. The  $^{13}\text{C}$ -NMR spectra of Schiff base ligand (SBL) and O-carboxymethyl chitosan Schiff base ([OCMCS-SBL]) were measured with Agilent 600 MHz spectrometer using DMSO- $\text{d}_6$  and  $\text{D}_2\text{O}$  solvent, respectively. TG/DTG curves of CS, [OCMCS-SBL], and biomaterial supported Pd catalyst were performed with an EXSTAR S11 7300 at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . XRD spectra of CS, [OCMCS-SBL], and biomaterial supported Pd catalyst were measured with a Rigaku Dmax 2000 system at 40 kV, 30 mA, and  $2\theta$  with a scan angle from  $5^\circ$  to  $50^\circ$ . GC/MS spectra of biaryls were obtained with Agilent GC-7890 A-MS 5975. Surface images were acquired using a QUANTA-FEG 250 ESEM. The EDAX spectrum of the Pd catalyst was obtained with an EDAX-Metek. The metal content of biomaterial supported Pd catalyst was studied with a Perkin Elmer Optima 2100 DV

Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES). UV-Vis spectrum of biomaterial supported Pd catalyst was recorded with a Genesys 10S UV-Vis spectrophotometer. Magnetic susceptibility of biomaterial supported Pd catalyst was measured with a Sherwood magnetic susceptibility balance at 25 °C. The molar conductivity of biomaterial supported Pd catalyst was determined using a tabletop-digital conductivity-meter CD-2005 at 25 °C. Domestic microwave oven was used in the synthesis of biaryl.

Crystallinity indexes of CS, [OCMCS-SBL], and biomaterial supported Pd catalyst were calculated by using the equation below:

$$(1) \text{Crystalline index}(\%) = [(I_{110} - I_{am}) / I_{110}] \times 100$$

$I_{110}$  is the maximum intensity at  $\sim 20^\circ$ .

$I_{am}$  is the intensity of amorphous diffraction at  $16^\circ$ .

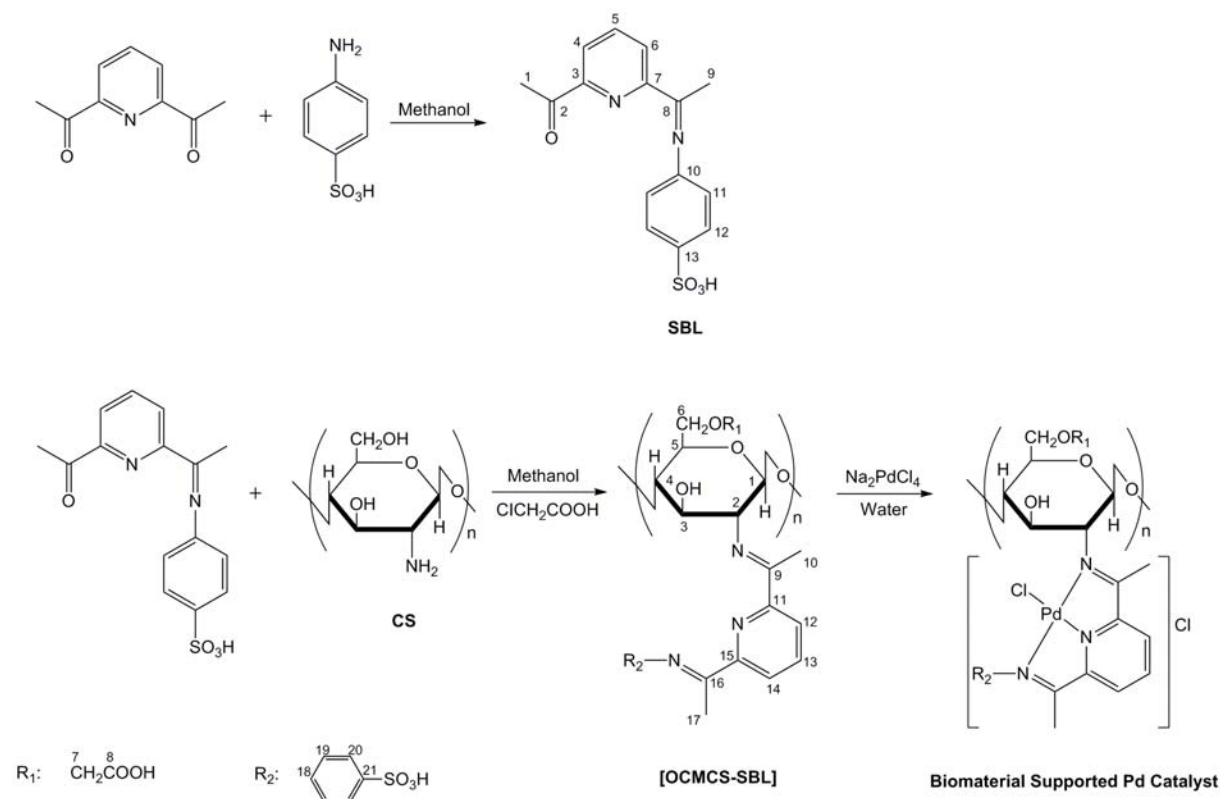
## 2.2 Synthesis of mono-imine Schiff base ligand (SBL)

4-aminobenzenesulfonic acid (1 g, 5.77 mmol) and 2,6-diacetylpyridine (0.94 g, 5.77 mmol) were dissolved in methanol (40 mL) and refluxed for 72 hours. The reaction was followed with FTIR and thin layer chromatography (TLC). At the end of the reaction time, participated yellowish product was filtered and washed with cold methanol and ether (92 % yield).

## 2.3 Synthesis of chitosan supported Pd catalyst

[OCMCS-SBL] was synthesized according to our previous study (Baran, Menteş & Arslan, 2015). Briefly, condensation of SBL with chitosan was refluxed and stirred for 48 h. Then, monochloroacetic acid was added, the reaction mixture was stirred at 60°C. After 7 days, water soluble [OCMCS-SBL] derived from biomacromolecule was achieved (79 %

yield). 0.2 g [OCMCS-SBL] was dissolved in water (10 mL) and mixed with  $\text{Na}_2\text{PdCl}_4$  solution (0.35 g in 10 mL water) at room temperature for 5 h. Yellow-green product was filtered and rinsed with water to remove unreacted reactants, and biomaterial supported Pd catalyst was successfully obtained (71 % yield) (Scheme 1).



.....Scheme 1.....

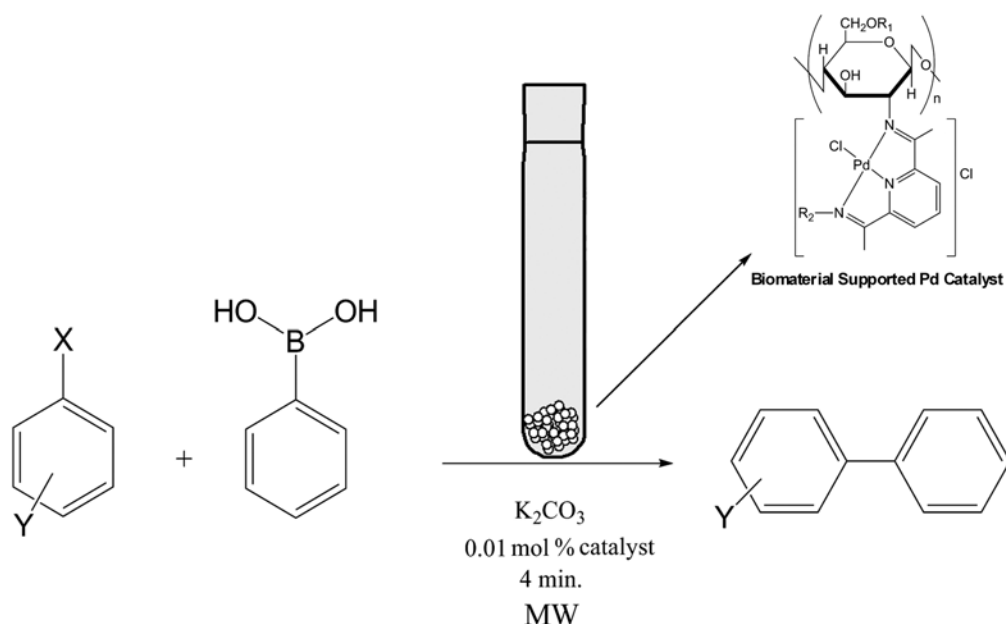
## 2.4 Suzuki coupling Reaction

Base system, reaction time, and catalysts amount parameters must be optimized to obtain C-C coupling reactions with high selectivity. Therefore, coupling reaction of 4-bromoanisole with phenylboronic acid was selected as the model reaction, and optimum conditions were determined for coupling reaction in the presence of biomaterial supported Pd catalyst.

To determine the optimum catalyst amount, biomaterial supported Pd catalyst was used at different loading catalyst (2.5, 5.0, 10.0, 20.0)  $\times 10^{-3}$  mol % under microwave irradiation at 400 W in solvent-free reaction mixture (50°C). Reaction time was investigated from 1 min to

5 min, and NaOH, K<sub>2</sub>CO<sub>3</sub>, KOH, and Cs<sub>2</sub>CO<sub>3</sub> base systems were examined for optimum coupling reaction condition.

Different aryl halides (1.12 mmol), K<sub>2</sub>CO<sub>3</sub> (3.75 mmol), phenylboronic acid (1.87 mmol), and biomaterial supported Pd catalyst (0.01 % mol) were mixed, and the reaction was allowed under microwave irradiation at 400 W in solvent-free media for 4 min (Scheme 2). At the end of the reaction period, the product was extracted with toluene:water (4:2, v:v). Organic phase was separated, and MgSO<sub>4</sub> was added to remove water. The chemical identifications of synthesized biaryls were illuminated with <sup>1</sup>H-NMR and gas chromatography-mass spectroscopy (GC-MS) analyses.

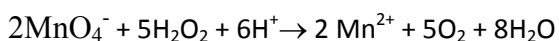


.....Scheme 2.....

At the end of the coupling reaction, biomaterial supported Pd catalyst was filtered and washed with hot water and methanol to re-activate the biocatalyst. Then, the same biomaterial supported Pd catalyst was used for recycling experiments for model reaction under optimum reaction conditions for 10 times. Leaching test was applied to supernatant of all recycle experiments to determine Pd ion in the solution.

## 2.5 Catalase-like activity of biomaterial supported Pd catalyst

Biomaterial supported Pd catalyst was applied for the catalase-like decomposition reaction of H<sub>2</sub>O<sub>2</sub>. Concentration of H<sub>2</sub>O<sub>2</sub> was followed by permanganate reaction in acidic media after decomposition reaction, and reaction equation was given as follows:



Decomposition or initial reaction solution (0.5 mL) was mixed with 0.1 M H<sub>2</sub>SO<sub>4</sub> (5 mL) and titrated with 0.01 M KMnO<sub>4</sub> until the solution became colorless. Conversion ratio was calculated using the initial and final concentrations of reaction media.

Decomposition reaction was investigated at different reaction periods (till 150 min.) to optimize the reaction period. H<sub>2</sub>O<sub>2</sub> concentrations ranged from 10 mM to 45 mM. The reaction temperature was investigated between 5 °C to 60 °C to obtain maximum conversion yield. Finally, biomaterial supported Pd catalyst was changed from 5 to 20 mg to optimize catalyst amount. To determine the reusability of biomaterial supported Pd catalyst, catalase-like reaction was repeated 10 times at optimum reaction conditions.

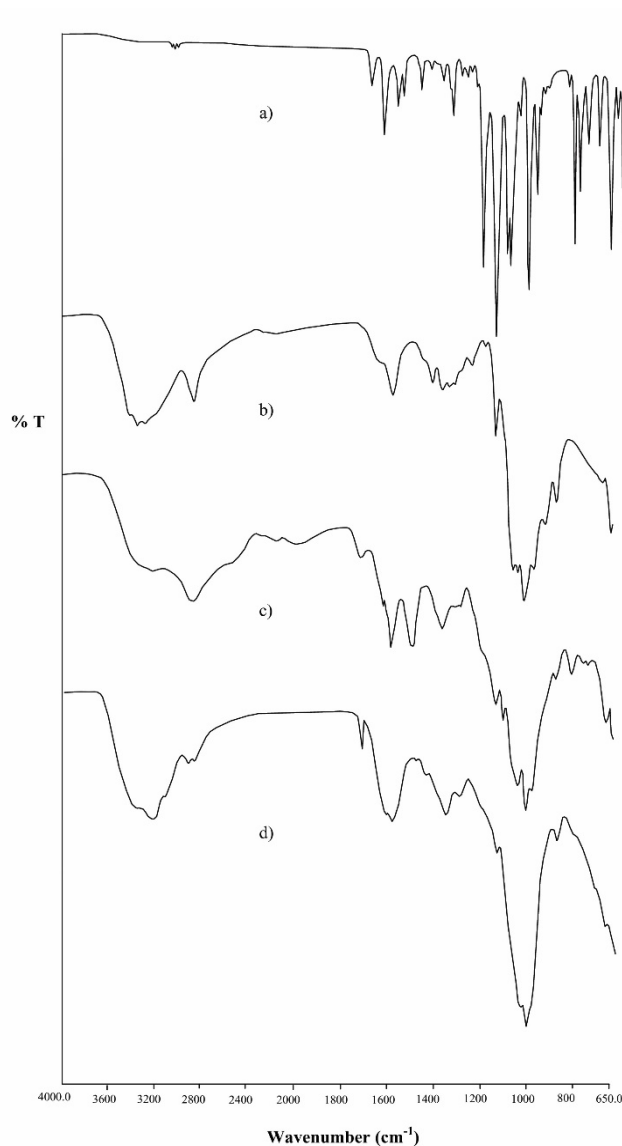
## 3. Results and Discussion

### 3.1 Characterization of biomaterial supported Pd catalyst

#### 3.1.1. FTIR analysis

FTIR spectra of SBL, [OCMCS-SBL], and biomaterial supported Pd catalyst are presented in Figure 1. In the FTIR spectrum of SBL, absence of NH<sub>2</sub> stretching of 4-aminobenzenesulfonic acid and new band at 1651 cm<sup>-1</sup> attribute to imine groups showed the condensation of 4-aminobenzenesulfonic acid with 2,6-diacetylpyridine. Stretching band at 1702 cm<sup>-1</sup> of free carbonyl groups of 2,6-diacetylpyridine decreased after condensation of 2,6-diacetylpyridine with 4-aminobenzenesulfonic acid. This change proved that the condensation

was achieved at 1:1 ratio. The characteristic peaks of chitosan can be examined in detail in our previous study (Baran, Menteş & Arslan, 2015). As seen in the spectrum of [OCMCS-SBL],  $\text{NH}_2$  stretching of CS disappeared, and the imine band was observed at  $1635\text{ cm}^{-1}$ . This observation ensures the condensation of CS with SBL. The carbonyl stretching of carboxymethyl at  $1729\text{ cm}^{-1}$  indicated successful carboxymethylation of CS (Baran & Menteş, 2015; Baran, Menteş & Arslan, 2015). In addition, asymmetric and symmetric stretching of these carbonyl groups are shown at  $1599$  and  $1506\text{ cm}^{-1}$ , respectively (Fig.1). Also, lack of stretching belonging to primer hydroxyl groups at  $1029\text{ cm}^{-1}$  of CS indicated that the carboxymethylation occurred from the  $\text{C}_6\text{-O}$  of CS (Kaya, Cakmak, Baran, Asan-Ozusaglam, Menteş & Tozak, 2014; Liu, Zhao & Wang, 2013). In the spectrum of biomaterial supported Pd catalyst, imine band shifted to the lower wavelength ( $1623\text{ cm}^{-1}$ ) according to [OCMCS-SBL]. This alteration originated from the coordination of Pd ions to the nitrogen atoms of imine groups (Demetgul, Karakaplan & Serin, 2008).



.....**Figure 1**.....

### 3.1.2. $^{13}\text{C}$ -NMR Spectrum

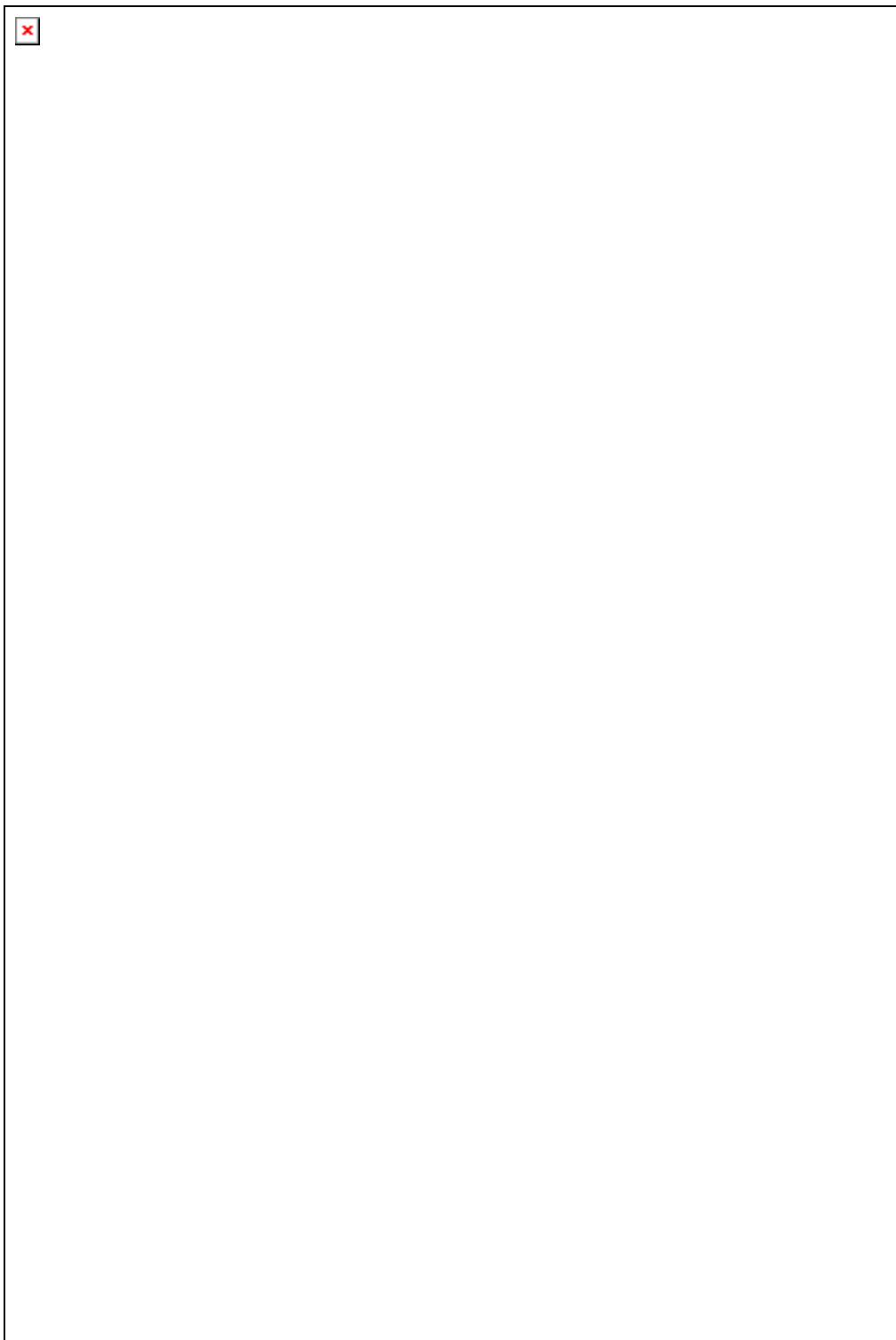
In the  $^{13}\text{C}$ -NMR spectrum of SBL, the signal of imine carbon atom seen at 167.18 ppm demonstrated condensation between 4-aminobenzenesulfonic acid and 2,6-diacetylpyridine (Fig. 2). Signal belonging to free carbonyl carbon at 199.29 ppm confirmed the formation of condensation reaction at 1:1 ratio. Other signals in the spectrum are listed below:

$^{13}\text{C}$  NMR : 25.79 C(1); 199.29 C(2); 155.11 C(3); 122.83 C(4); 136.52 C(5); 125.06 C(6); 149.28 C(7); 167.18 C(8); 16.42 C(9); 144.27 C(10); 122.96 C(11); 127.09 C(12); 138.04 C(13).

The carbonyl signal of SBL at 199.29 ppm disappeared after the condensation of CS with SBL. A new imine carbon signal at 168.43 ppm was also observed, and this change proved the condensation of SBL with CS (Fig. 2). Furthermore, carbonyl signal of carboxymethyl at 173.40 ppm was the other proof of accomplished carboxymethylation (Yin, Chen, Yuan, Lin, Ji & Liu, 2011). Important signals are presented as:

$^{13}\text{C}$  NMR : 97.48 C(1); 55.73 C(2); 69.99 C(3); 76.28 C(4); 74.70 C(5); 59.90 C(6); 42.46 C(7); 173.40 C(8); 168.43 C(9); 23.78 C(10); 154.44 C(11); 121.63 C(12); 131.69 C(13); 124.28 C(14); 149.90 C(15); 166.38 C(16); 13.40 C(17); 142.94 C(18); 122.08 C(19); 127.26 C(20); 138.47 C(21).

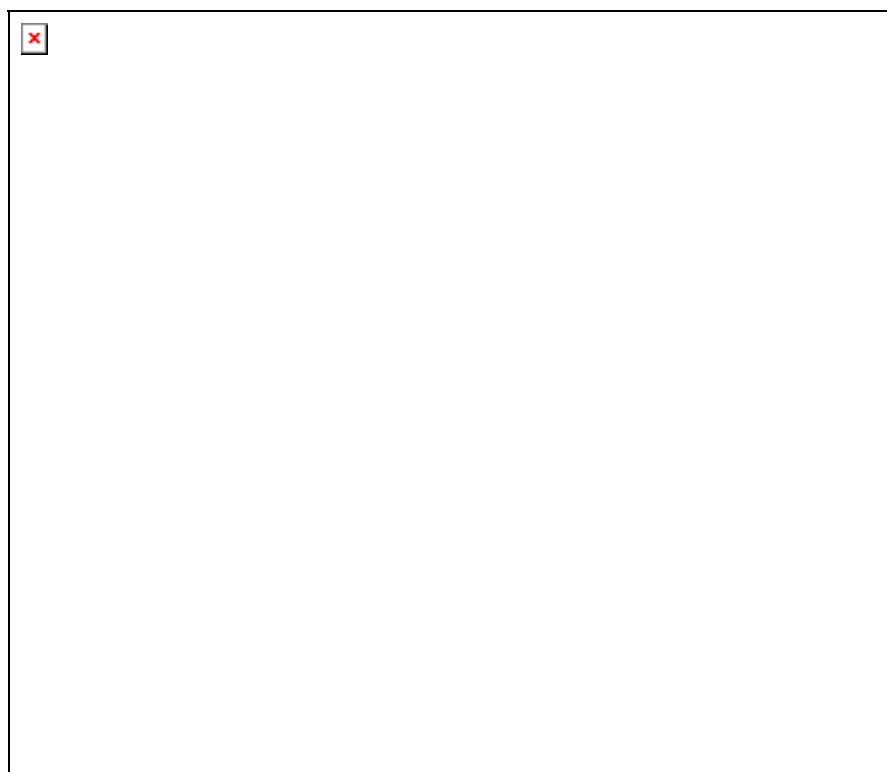




.....**Figure 2**.....

*3.1.3. TG/DTG and XRD Analysis*

It was reported that chemical modifications of chitosan (Schiff base, carboxymethylation, metal coordination, cyanoethylation, acylation, and sulfation) induce cleavage of hydrogen bonds (Antony, Manickam, Saravanan, Karuppasamy & Balakumar, 2013; Trimukhe & Varma, 2009). Thus, crystallinity value of CS decreases. All these alterations bring about a drastic decline at main thermal degradation temperature ( $DTG_{max}$ ) of CS. In the current study,  $DTG_{max}$  of CS was determined as 302 °C while  $DTG_{max}$  values of [OCMCS-SBL] and Pd biomaterial supported Pd catalyst were observed as 219 °C and 232 °C, respectively, after chemical modifications (Fig.3). Biomaterial supported Pd catalyst was detected to be thermally more stable than [OCMCS-SBL]. High thermal stability of the Pd catalyst ramps up the usage potential in different catalytic studies that require high reaction temperature.



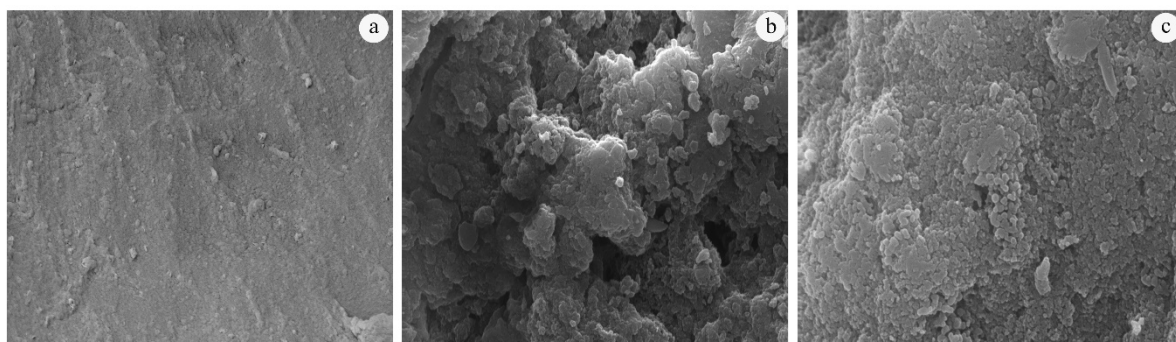
.....**Figure 3**.....

Crystallinity indexes of CS, [OCMCS-SBL], and biomaterial supported Pd catalyst were calculated (Zhang, Xue, Xue, Gao & Zhang, 2005) as 82, 55, and 15 %, respectively. As

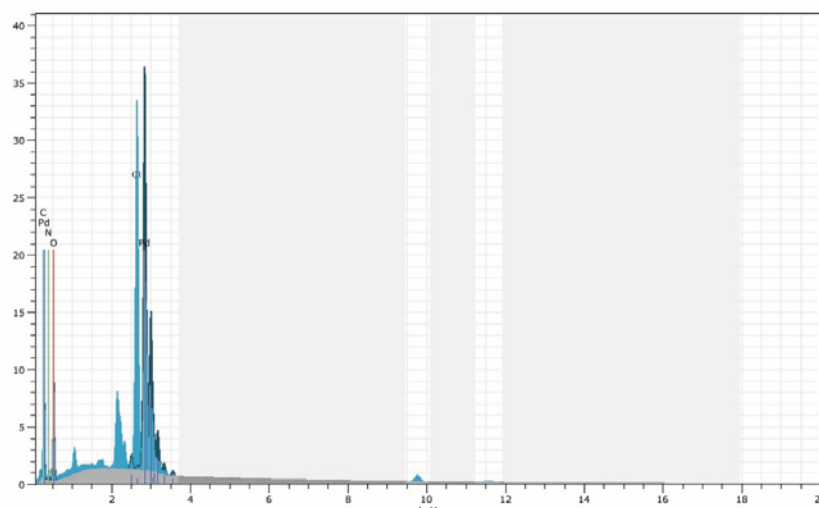
expected, biomaterial supported Pd catalyst has a more amorphous nature with regard to CS and [OCMCS-SBL].

### 3.1.4. SEM/EDAX

Surface morphology of CS was examined, and a smooth surface was detected. Surface picture and particle size of [OCMCS-SBL] were altered due to the chemical modification of CS. The drastic change on the surface morphology of biomaterial supported Pd catalyst in comparison to CS and [OCMCS-SBL] demonstrated the coordination of Pd with [OCMCS-SBL] (Antony, Manickam, Saravanan, Karuppasamy & Balakumar, 2013; Demetgul, 2012) (Fig.4). EDAX spectrum of biomaterial supported Pd catalyst was recorded to determine the existence of Pd ions. The coordination of Pd ions with [OCMCS-SBL] was proved with the appearance of both Pd ions and metal coordinated chlorine ions (Fig.5).



.....**Figure 4**.....



.....**Figure 5**.....

### *3.1.5. Uv-Vis Spectroscopy and Magnetic Moment/Molar Conductivity Measurements*

It is known that Uv-Vis spectrum of CS has no transition in the range of 200-800 nm (Kumar, Nigam, Ghosh, Dutta, Yadav & Pandey, 2010). Two transitions were observed at 260 and 320 nm when Uv-Vis spectrum of [OCMCS-SBL] was recorded. These transitions were attributed to aromatic ring  $\pi$ - $\pi^*$  and imine groups (C=N)  $n$ - $\pi^*$  (Antony, David, Saravanan, Karuppasamy & Balakumar, 2013; Demetgul, 2012). They shifted to higher wavelength compared to [OCMCS-SBL] in the spectrum of biomaterial supported Pd catalyst due to the coordination of Pd ions with nitrogen atoms of imine groups (Antony, Manickam, Saravanan, Karuppasamy & Balakumar, 2013). In addition, two weak d-d transitions which were determined at 360 and 465 nm supported the square planar geometry of biomaterial supported Pd catalyst (Anan, Hassan, Saad, Butler & Mostafa, 2011; Mostafa & Badria, 2008).

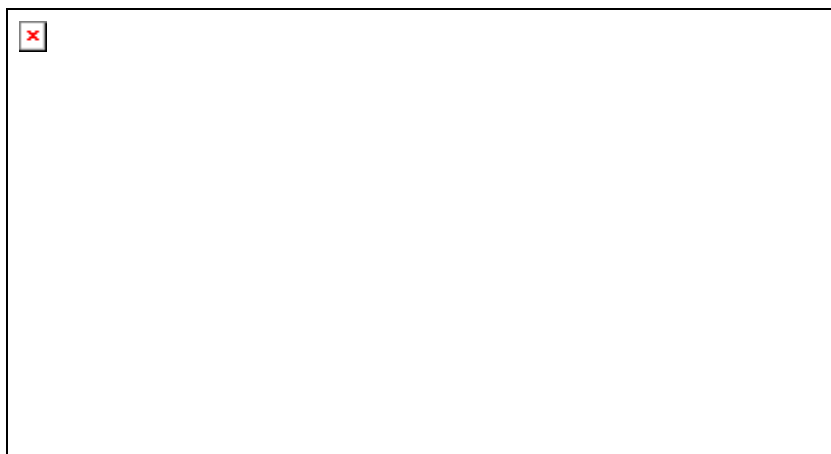
Magnetic moment and molar conductivity measurements were performed to promote geometry the catalyst. Magnetic moment measurements showed that biomaterial supported Pd catalyst had diamagnetic properties. Molar conductivity value of biomaterial supported Pd catalyst at room temperature was measured as  $58 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . This value was compatible with 1:1 electrolyte nature of biomaterial supported Pd catalyst (Al-Nahary, 2009). Furthermore, both magnetic moment and molar conductivity values ensured the square planar geometry of biomaterial supported Pd catalyst.

## **3.2 Suzuki Coupling Reaction**

### *3.2.1. Optimization of Suzuki reaction conditions*

In the current study, catalytic activity of biomaterial supported Pd catalyst was investigated by developing a new technique under microwave irradiation using solvent-free media for 4 min at 400 W to use energy more efficiently, to reduce waste products by preventing formation of by-products and to have higher reaction yield in a shorter reaction time. Amount of biomaterial supported Pd catalyst, base system, and reaction time parameters must be optimized to achieve high conversation yield in C-C coupling reaction.

Preliminary experiments were applied with different loading mol percentages of biomaterial supported Pd catalyst to determine the optimum biomaterial supported Pd catalyst amount. As seen in Figure 6, the optimum Pd catalyst amount was chosen as 0.01 mol %.



.....**Figure 6**.....

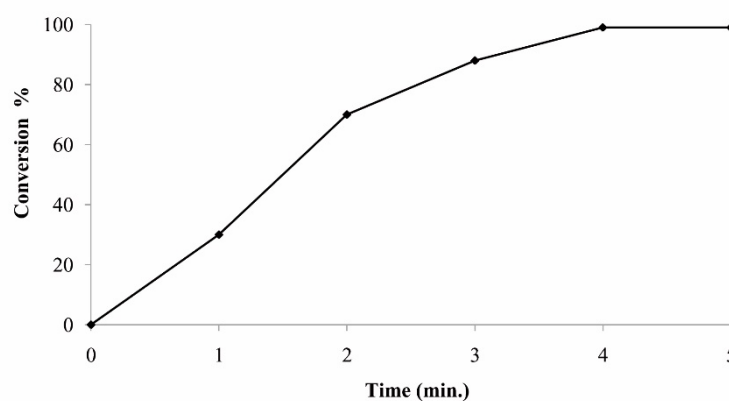
Base plays a significant role in transmethylation step thus; choice of base is a critical parameter for coupling reactions. Thus, different base systems were tested in model reaction, and the results are presented in Table 1.  $K_2CO_3$  was selected as the suitable base system for more selective coupling reaction.

**Table 1.** Base Optimization for Suzuki reaction

Base	Yield (%)
NaOH	59
KOH	55
Cs <sub>2</sub> CO <sub>3</sub>	88
K <sub>2</sub> CO <sub>3</sub>	>99

Reaction conditions: 1.12 mmol 4-bromoanisole, 1.87 mmol phenyl boronic acid, 3.75 mmol base, 0.01 mol % catalyst, 50 °C, 4 min under MW.

Reaction time was ranged from 1 to 5 min (Fig.7) under microwave irradiation, and maximum reaction yield was achieved at 4 min.



.....**Figure 7**.....

### 3.2.2. Investigation of catalytic activity of biomaterial supported Pd catalyst

TON and TOF values which were calculated for all C-C coupling reactions with several halides are given in Table 2. These TON and TOF values which were achieved with notably small biomaterial supported Pd catalyst loading were higher than those in literatures (Karthikeyan, Vanitha, Radhika, Suresh & Sugumaran, 2013; Leonhardt et al., 2010; Liu, Li, Gao, Wang & Jin, 2015).

Coupling reactions between different aryl halides with phenyl boronic acid were conducted under optimum reaction conditions to determine the effect of several functional groups of substrates on Suzuki coupling reactions, and the reaction yields of several halides are given in Table 2. It was determined that coupling reactions with withdrawing bromides occurred at considerably higher selectivity than electron-donor aryl bromides (entries 2-8). Conversion yields of coupling reactions in the presence of aryl iodides were (entries 9-13) determined to be higher than the one in the presence of aryl chlorides (entry 14). As expected, low conversion yields with aryl chlorides originated from the poor activity of aryl chlorides in Suzuki reactions (Littke, Dai & Fu, 2000). It is thought that various conversion yields obtained with several aryl halides was caused by the radii of halogens and bond dissociation energy (Baran, Açıksöz & Menteş, 2015; Makhubela, Jardine & Smith, 2011). Finally, para-substitue groups were the most effective while orto-substitue groups showed lower reaction yield.

Coupling reaction between 4-bromoanisole and phenyl boronic acid was also carried out with conventional heating method (100 °C, 48h). It is clearly understood from the conversion yields in Table 2 that microwave heating method catalyzed coupling reaction with higher conversion yield in a shorter reaction time compared to conventional heating method (entry 15).

Different commercial Pd compounds were investigated for model reaction at optimum reaction conditions (0.01 mol % biomaterial supported Pd catalyst,  $K_2CO_3$ , under microwave irradiation at 400 W, and 4 min), and results are given in Table 2 (entries 16-17).

The newly synthesized biomaterial supported Pd catalyst had excellent catalytic activity compared to commercial Pd compounds. Furthermore, blank experiments (without the catalyst) were performed under microwave irradiation, but no conversion was obtained. These

results indicate that biomaterial supported Pd catalyst ensures C-C coupling reaction successfully with perfect conversion yield.



**Table 2.** The effects of biomaterial supported Pd catalyst on Suzuki cross-coupling reaction.

	X	Y	Yield (%)	TON yield / per mol of Pd	TOF TON/reaction time	
1	Br	2-OCH <sub>3</sub>	93	9300	140909	
2	Br	3-OCH <sub>3</sub>	96	9600	145454	
3	Br	4-OCH <sub>3</sub>	>99	10000	151515	
4	Br	3-CH <sub>3</sub>	64	6400	96967	
5	Br	4-CH <sub>3</sub>	74	7400	112121	
6	Br	3-NH <sub>2</sub>	80	8000	121212	
7	Br	4-NH <sub>2</sub>	82	8200	124242	
8	Br	3-NO <sub>2</sub>	88	8800	133333	
9	I	2-CH <sub>3</sub>	57	5700	86364	
10	I	3-CH <sub>3</sub>	41	4100	62121	
11	I	4-CH <sub>3</sub>	54	5400	81818	
12	I	4-NH <sub>2</sub>	78	7800	118182	
13	I	3-NO <sub>2</sub>	74	7400	112121	
14	Cl	3-NO <sub>2</sub>	57	5700	86364	
15*	Br	4-OCH <sub>3</sub>	58	5800	121	Reacti on
16 <sup>†</sup>	Br	4-OCH <sub>3</sub>	55	5500	83333	conditi ons:
17 <sup>#</sup>	Br	4-OCH <sub>3</sub>	45	4500	68182	1.12 mmol

aryl halide, 1.87 mmol phenyl boronic acid, 3.75 mmol K<sub>2</sub>CO<sub>3</sub>, 0.01 mol % catalyst, 50 °C, 4 min, under MW.

\*Conventional Method: 1.12 mmol aryl halide, 1.87 mmol phenyl boronic acid, 3.75 mmol K<sub>2</sub>CO<sub>3</sub>, 0.01 mol % catalyst, 100 °C, 48 h, 6 mL toluene.

<sup>†</sup>Commercial Pd catalyst; Reaction conditions: 1.12 mmol aryl halide, 1.87 mmol phenyl boronic acid, 3.75 mmol K<sub>2</sub>CO<sub>3</sub>, 0.01 mol % Na<sub>2</sub>PdCl<sub>4</sub>, 50 °C, 4 min, under MW.

<sup>#</sup>Commercial Pd catalyst; Reaction conditions: 1.12 mmol aryl halide, 1.87 mmol phenyl boronic acid, 3.75 mmol K<sub>2</sub>CO<sub>3</sub>, 0.01 mol % PdCl<sub>2</sub>, 50 °C, 4 min, under MW.

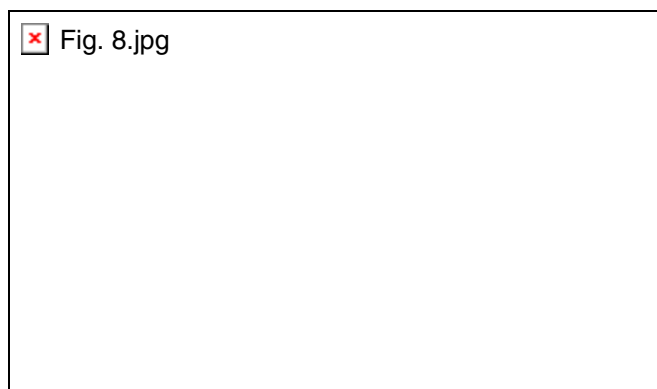
Characterization of all biaryls compounds which were synthesized by C-C coupling reaction using various aryl halides were defined with  $^1\text{H-NMR}$  and GC-MS. It is observed on the spectra of biaryls that coupling reaction exhibited high selectivity and generated no homo-coupling by-products.

### 3.3 Catalase-like activity of biomaterial supported Pd catalyst

#### 3.3.1. Optimization of decomposition reaction conditions

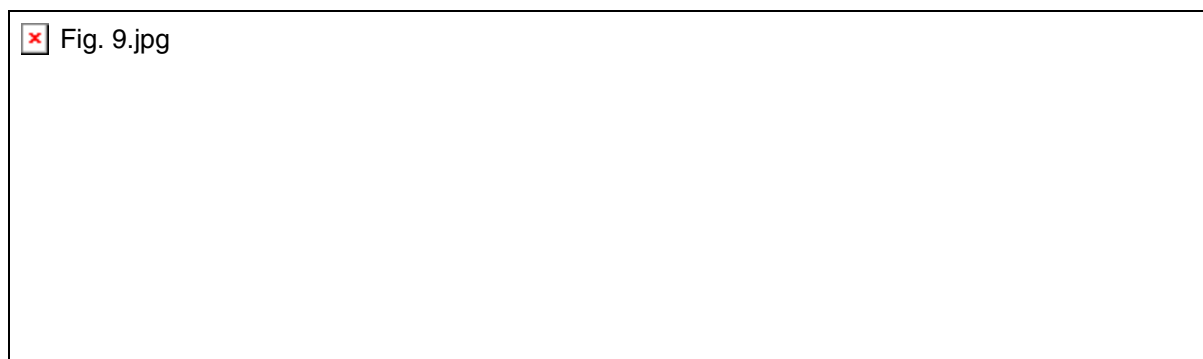
Reaction time, substrate concentration, temperature, and catalyst amount parameters were tested for the optimization of catalase-like activity reaction. Conversion of  $\text{H}_2\text{O}_2$  was followed until 150 min using both 15 mM and 25 mM  $\text{H}_2\text{O}_2$  solutions with 20 mg biomaterial supported Pd catalyst (Fig.8). For both concentrations, conversion reaction reached a plateau value at 120 min and did not change after then. Thus, all experiments were performed for 120 min.

A linear equation ( $y:-0.0005 x + 3.2136, R^2:0.9915$ ) which was obtained from the plot of  $\log$  (converted  $\text{H}_2\text{O}_2$  concentration) with reaction time(s) demonstrated that catalase-like decomposition obviously agreed with the first order kinetics (Gupta & Abdulkadir, 2008). Using the equation given above, rate constant ( $k$ ) for catalase-like reaction was calculated as  $5 \times 10^{-4} \text{ s}^{-1}$ .



.....**Figure 8**.....

Several substrate concentrations in the range of 10 mM to 45 mM H<sub>2</sub>O<sub>2</sub> were investigated and are given in Fig.9a. Non-significant difference at conversion yield was observed between 10 and 35 mM H<sub>2</sub>O<sub>2</sub> although conversion yield decreased at 45 mM H<sub>2</sub>O<sub>2</sub>. Effect of temperature, as seen in Fig. 9b, was tested using 25 mM H<sub>2</sub>O<sub>2</sub> solution because maximum conversion was observed at this concentration. The results showed that temperature positively effected decomposition reaction. All of H<sub>2</sub>O<sub>2</sub> (99%) was decomposed by 20 mg biomaterial supported Pd catalyst at 40°C and 60°C. This result made us think that high conversion yields could be achieved by using lower catalyst amounts at high reaction temperatures. Therefore, decomposition reaction was investigated using 5 mg and 10 mg biomaterial supported Pd catalyst both at 40°C and 60°C, and the results are seen in Fig. 9c. The decomposition of all H<sub>2</sub>O<sub>2</sub> (99%) was succeeded with 5 mg biomaterial supported Pd catalyst at 60°C. As a result, optimum conditions were specified as 120 min, 25 mM H<sub>2</sub>O<sub>2</sub> with 5 mg biomaterial supported Pd catalyst at 60°C.



.....**Figure 9**.....

### 3.4. Reusability of biomaterial supported Pd catalyst

The reusability potential of biomaterial supported Pd catalyst was investigated on model reaction at optimum reaction conditions and are given in Table 3. After 10 cycles, biomaterial supported Pd catalyst still exhibited high conversion. Biomaterial supported Pd catalyst is economical and proper for industrial applications due to its high conversion yields at small

amounts. In addition, leaching test was applied for all runs, and negligible amounts of Pd ions (< 0.5 %) were determined by ICP-OES.

Reusability studies for decomposition reaction were performed by using 25 mM H<sub>2</sub>O<sub>2</sub> with 5 mg biomaterial supported Pd catalyst at 60°C for 120 min. At the end of 10 cycles, redox potential of the catalyst decreased by 12.9 %. This result demonstrated long life time of biomaterial supported Pd catalyst for decomposition reaction. TON values for each cycle at 60°C (Table 3) are in accordance with the results of biomaterial supported Pd catalyst nature.

**Table 3.** Reusability of biomaterial supported Pd catalyst

The number of cycle	*Suzuki C-C reaction		+Catalase like reaction	
	Yield (%)	TON	Yield (%)	TON
1 <sup>st</sup>	>99	10000	99	1234
2 <sup>nd</sup>	97	9700	96	1203
3 <sup>rd</sup>	97	9700	95	1184
4 <sup>th</sup>	97	9700	91	1131
5 <sup>th</sup>	95	9500	93	1156
6 <sup>th</sup>	92	9200	89	1106
7 <sup>th</sup>	88	8800	88	1094
8 <sup>th</sup>	79	7900	89	1116
9 <sup>th</sup>	78	7800	90	1132
10 <sup>th</sup>	78	7800	86	1074

\*Reaction conditions: 1.12 mmol 4-bromoanisole, 1.87 mmol phenyl boronic acid, 3.75 mmol base, 0.01 mol % catalyst, 50 °C, 4 min under MW

+Reaction conditions: 25 mM H<sub>2</sub>O<sub>2</sub>, 0.08 mol % catalyst, 60 °C, 120 min.

#### 4. Conclusion

In the current study, a new biomaterial supported Pd catalyst was synthesized and characterized with FTIR, TG/DTG, XRD,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , SEM-EDAX, ICP-OES, Uv-Vis spectroscopy, magnetic moment, and molar conductivity analysis. Catalytic activity of environment friendly biomaterial supported Pd catalyst was evaluated in Suzuki coupling under microwave irradiation without solvent in a short time. Furthermore, its redox potential in  $\text{H}_2\text{O}_2$  decomposition reaction was investigated, and effects of time, substrate concentration and catalyst amount were optimized. TON and TOF values were higher than those in previous studies for both Suzuki coupling and decomposition reactions. Reusability of biomaterial supported Pd catalyst was tested for 10 cycles for catalytic studies. Biomaterial supported Pd catalyst can be used economically for several applications since it catalyses without significant loss in activity after 10 cycles. The new biomaterial supported Pd catalyst can also find different applications in environmental technologies, textile, and pharmaceutical industries owing to its superior features such as high catalytic activity at small loading catalyst, simple work-up, short reaction time in solvent-free media, durability to air, moisture, and high reaction temperature.

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**Scheme 1.** The synthesis pathway of biomaterial supported Pd catalyst

**Scheme 2.** General reaction procedure of Suzuki coupling reactions

**Fig.1.** FTIR spectra of a) SBL, b) CS, c) [OCMCS-SBL], d) biomaterial supported Pd catalyst

**Fig.2.**  $^{13}\text{C}$ -NMR spectra of a) SBL, b) [OCMCS-SBL]

**Fig. 3.** TG/DTG spectra of a) CS, b) [OCMCS-SBL], c) biomaterial supported Pd catalyst

**Fig.4.** SEM images of a) CS (30000x), b) [OCMCS-SBL] (30000x) c) biomaterial supported Pd catalyst (40000x)

**Fig.5.** SEM-EDAX spectrum of biomaterial supported Pd catalyst

**Fig.6.** The effect of catalyst (mol %) on Suzuki coupling reactions

**Fig.7.** The effect of reaction time on Suzuki coupling reactions

**Fig.8.** The effect of reaction time on catalase-like reactions (25 °C, 20 mg biomaterial supported Pd catalyst)

**Fig.9.** The effect of a) substrate concentration (25 °C, 120 min., 20 mg biomaterial supported Pd catalyst), b) temperature (120 min., 25 mM  $\text{H}_2\text{O}_2$ , 20 mg biomaterial supported Pd catalyst), c) amount of catalyst on catalase-like reactions (120 min., 25 mM  $\text{H}_2\text{O}_2$ ).