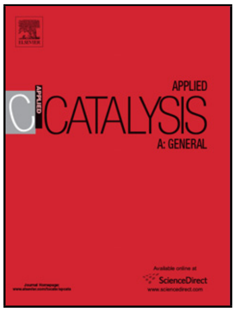

Title: Fabrication and application of cellulose Schiff base supported Pd(II) for fast and simple synthesis of biaryls via Suzuki coupling reaction

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PII: S0926-860X(16)30590-7
DOI: http://dx.doi.org/doi:10.1016/j.apcata.2016.12.005
Reference: APCATA 16090

To appear in: *Applied Catalysis A: General*

Received date: 6-10-2016
Revised date: 18-11-2016
Accepted date: 3-12-2016

Please cite this article as: Nuray Yılmaz Baran, Talat Baran, Ayfer Menteş, Fabrication and application of cellulose Schiff base supported Pd(II) for fast and simple synthesis of biaryls via Suzuki coupling reaction, Applied Catalysis A, General http://dx.doi.org/10.1016/j.apcata.2016.12.005

Fabrication and application of cellulose Schiff base supported Pd(II) for fast and simple synthesis of biaryls via Suzuki coupling reaction

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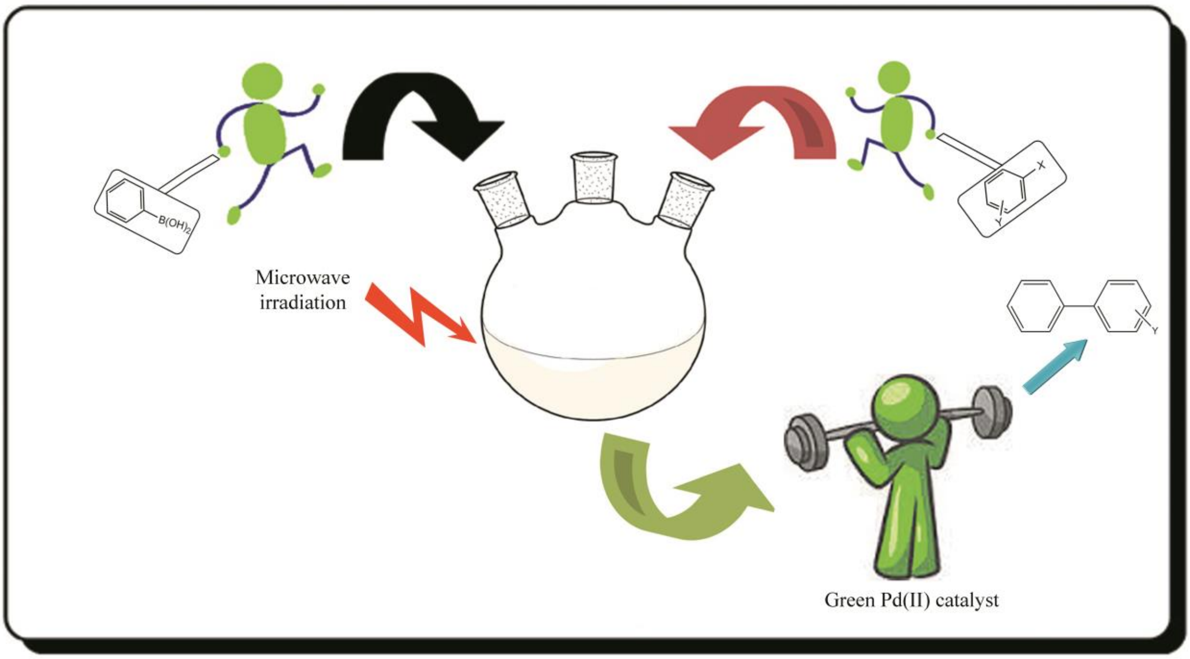
Graphical Abstract



Highlights

Cellulose supported Pd(II) catalyst exhibited better performance in Suzuki coupling reactions

Catalyst was characterised by FTIR, TGA, SEM-EDAX, XRD, ICP-OES and magnetic moment

This green catalyst showed a better recycles performance

Abstract

Bio-supported catalysts, due to their green nature, are promising materials for coupling reactions. In this paper, the design and application of a new green cellulose Schiff base supported Pd(II) catalyst (CL-Sc-Pd) for the synthesis of different biaryls under microwave irradiation without the use of any organic solvent is reported. Firstly, a silane-modified cellulose Schiff base (CL-Sc) was synthesized as a support material, and then its heterogonous Pd(II) catalyst was easily prepared in water for the Suzuki coupling reaction. The synthesized materials were then characterized with various analytical tools. Finally, the catalytic performance of the green catalyst was investigated towards various C-C reactions using a green, simple and fast microwave technique. The catalyst indicated excellent selectivity and activity in a very short time (6 min) under a solvent-free media. In addition, outstanding TON (19,800) and TOF (198,000) values were obtained with the green Pd(II) catalyst. The longevity of the green Pd(II) catalyst was studied and it was found to be reusable for at least eight runs. CL-Sc-Pd catalyst showed perfect catalytic efficiency for the Suzuki C-C reaction when it was compared to commercial palladium catalysts.

Keywords: Schiff base; microwave irradiation; biaryls; bio-material; longevity

1. Introduction

Environmental friendly materials, such as chitosan, cotton, chitin and alginate and zeolite have gained much recent attention as support materials for catalytic systems due to their unique properties, such as renewable, nontoxic, low cost and abundance in nature [1-8]. The most important natural polymer is cellulose (CL), which has high thermal stability and metal binding capacity. More importantly, the hydroxyl groups on cellulose easily enable chemical modifications, like carboxymethylation, silylation and periodate oxidation, to improve the physical and chemical properties [9-11]. Especially, silylation can be easily obtained with the reactive hydroxyl groups on the polymer chain of cellulose with silane containing agents. This modification plays an important role in catalytic systems [12, 13]. With all these significant features, cellulose and its derivatives are considered to be good support materials for catalyst systems.

Biaryl compounds, which are produced via Suzuki coupling reactions in the presence of palladium catalysts, have been widely used in various areas, such as cosmetics, medicine and pharmacology [14, 15]. In recent years, different homogenous or heterogeneous palladium catalytic systems have been designed and their activities have been tested towards the synthesis of biaryl compounds in Suzuki C-C reactions [16-25]. Homogeneous catalytic systems have serious disadvantages such as short life time, high operational costs, labour-intensive and the difficulty of separation from the reaction mixture [26]. These problems affect the reaction yields and recyclability of the catalyst. Especially in the last 10 years, to improve the selectivity and longevity of the catalyst, solid supported heterogeneous palladium catalysts have been extensively used in Suzuki C(sp^2)- C(sp^2) reactions due to their ease of removal from the reaction media [27-32]. In addition, these catalyst derivatives have outstanding advantages, such as ease of use, low cost and thermal and chemical satiability.

These important properties determine whether a catalyst is feasible for various industrial operations.

In this study, a new CL-Sc-Pd catalyst was designed for Suzuki coupling reactions. The support material for palladium ions was prepared as follows: firstly, silylation of cellulose (CL-NH_2) was carried out using 3-aminopropyltriethoxysilane (APTES). Then, the condensation reaction of CL-NH_2 with 2-amino pyridine was achieved. Finally, the Pd(II) catalyst was easily synthesized in water. The chemical structure of the support material and Pd(II) catalyst was characterized with FTIR, SEM-EDAX, XRD, TG-DTG, ICP-OES and magnetic moment techniques. The catalytic performance of CL-Sc-Pd catalyst was investigated in the green synthesis of various biaryl compounds via Suzuki coupling reactions under mild conditions by employing microwave irradiation in a solvent-free medium. The biaryl products were identified on GC-MS. Longevity tests of the catalyst were done. The catalytic activity of the catalyst was compared with different commercial palladium salts. Catalytic tests showed that the CL-Sc-Pd catalyst has excellent selectivity as well as TON and TOF values with low catalyst loading. In addition, the catalyst retained its activity even after eight cycles.

2. Materials and method

2.1. Materials

CL, 2-aminopyridine, APTES, $PdCl_2$, Na_2PdCl_4, all aryl halides, phenyl boronic acid, K_2CO_3, NaOH, Na_2CO_3, KOH, $MgSO_4$, toluene, ninhydrin and ethanol were purchased from Sigma-Aldrich.

2.2. Instrumentation

FT-IR spectra of the all compounds were analyzed on a Perkin Elmer Spectrum 100 FTIR spectrophotometer. X-ray diffractograms were recorded on a Rigaku D max 2000 system (at

40 kV, 30 mA and 2θ with a scan angle: 5−70°). Thermal and mechanical stability of the samples were performed on an EXSTAR S11 7300 (nitrogen atmosphere; heating range: 30-650°C). The surface images were obtained on a QUANTA-FEG 250 ESEM. The analyses of palladium, chloride and silane ions on the catalyst were determined using an EDAX-Metek. Palladium ion content of the catalyst was performed by using Perkin Elmer Optima 2100 DV Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES). Characterization of biaryl compounds were done on GC-MS Agilent GC-7890 A- MS 5975. Magnetic moment analysis of the catalyst was measured using Sherwood magnetic susceptibility balance. In the catalytic performances tests a domestic microwave oven was used.

3. Experimental studies

3.1. Preparation of support material for palladium ion

3.1.1. Synthesis of CL-NH_2

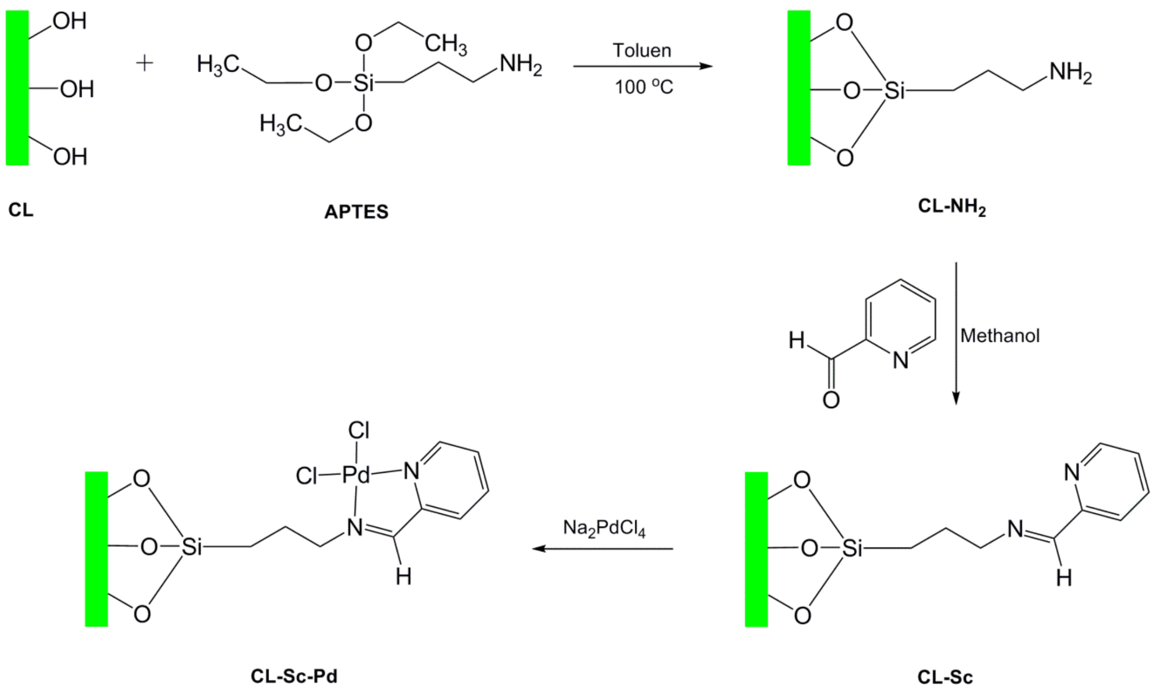
CL-NH_2 was prepared by refluxing cellulose (2 g) with APTES (10 mL) in anhydrous toluene for 48 h. Following the reaction, the product was filtered and rinsed with ethanol and dried in an oven (Scheme 1).

3.1.2. Preparation of CL-Sc

CL-NH_2 (1 g) and 2-aminopyridine (3 mL) were refluxed in 50 mL of ethanol for 72 h. The condensation reaction was followed by the FTIR technique. Following the reaction, light yellow Schiff base product was filtered and washed hot ethanol (Scheme 1).

3.2. Synthesis CL-Sc-Pd catalyst

CL-Sc was suspended in water at room temperature for 2h. Then water solution of Na_2PdCl_4 (0.4 g) was added into the reaction media and stirred for 6 h. At the end of the reaction, brown product was filtered and rinsed with hot water to remove unreacted palladium salts. Finally, the product was dried at room temperature (Scheme 1).



……………………………….…………**Scheme 1**………..………...……………….

3.3. General procedure for synthesis of biaryls via Suzuki C-C reactions

A mixture of 1.12 mmol aril halides, 1.18 mmol phenyl boronic acid, 3.75 mmol K_2CO_3 and CL-Sc-Pd catalyst ($5x10^{-3}$ mol %) was irradiated in a microwave oven at 50 °C and 400 W for 6 min in solvent-free medium. After the reaction, the mixture was cooled and extracted with toluene:water solution (2:1). The organic phase was separated with separatory funnel and $MgSO_4$ was added to completely remove the water. Finally, the organic phase, which contained the biaryl compounds, was sent for GC/MS and ^{1}H-NMR analysis.

3.4. Recycle Tests

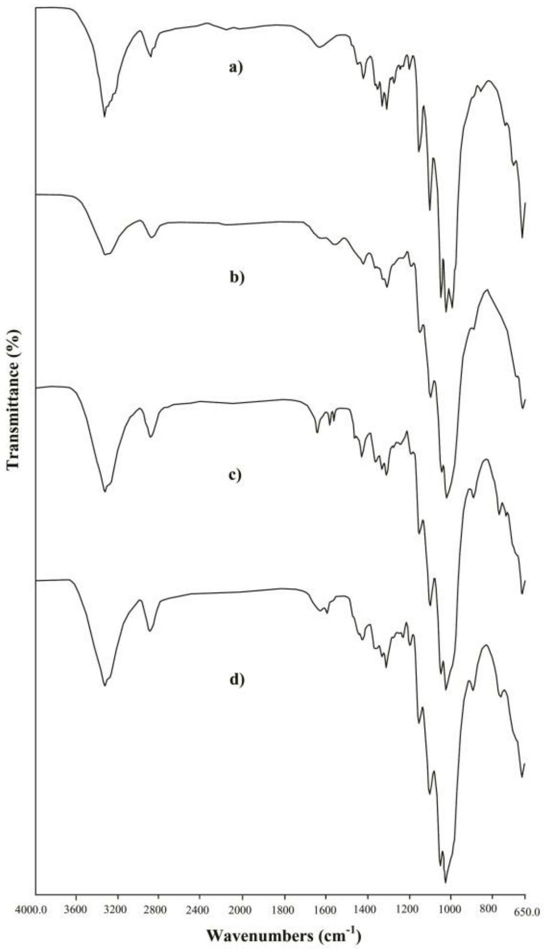
After the model coupling reaction was completed, the Pd(II) catalyst was filtered and washed with hot water and methanol to reactive the catalyst. The same process was applied after the ensuing runs and recyclability tests were performed on the model reaction.

4. Results and discussion

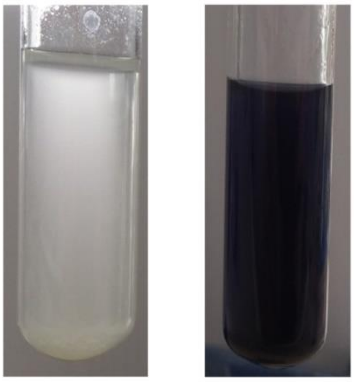
4.1. Characterization the catalyst

4.1.1. FTIR analysis

The FTIR spectra of CL, CL-NH_2, CL-Sc and CL-Sc-Pd catalyst are presented in Fig.1. In the spectrum of CL-NH_2 (Fig 1b), the decrease in the intensity of the peak that belongs to the –OH group (3337 cm^{-1}) of cellulose demonstrated that the APTES molecules bonded via the hydroxyl groups of CL. In addition, the peaks at 3336 and 2886 cm^{-1} were assigned to stretching of the N–H and O-H as well as C–H groups, respectively [33]. On the other hand, the Si-O-Si peak could not be precisely defined because this peak fell in the stretching region of C-O-C belonging to CL. Thus, to confirm the silane modification of the CL, a ninhydrin color test was done according to the literature (Fig. 2) [34]. As shown in Fig. 2, the color of the CL-NH_2 sample turned from light yellow to dark purple, by refluxing CL-NH_2 with ninhydrin in the ethanol. This sharp color conversion indicates that the silane molecules were loaded on the CL chain. Following the condensation reaction of CL-NH_2 and 2-aminopyridine, a new sharp peak was observed at 1648 cm^{-1} in the spectrum of the CL-Sc which is attributed to imine bond (Fig. 1c) [27]. In addition, the stretching of the $(\text{-C=C})_{\text{aromatic rings}}$ groups of 2-aminopyridine appeared at 1588 and 1567 cm^{-1} in the spectrum. All these significant peaks show that the Schiff base modification of CL was achieved. On the other hand, after the coordination of the palladium ion to its ligand, the imine bond was shifted to lower wavenumber (1624 cm^{-1}) in the spectrum of the catalyst (Fig. 1d). This change indicated that the metal ions were coordinated to the ligand via the imine groups of the CL-Sc [35].



……………………………….…………Figure 1………..…………..……………….


Cellulose solution

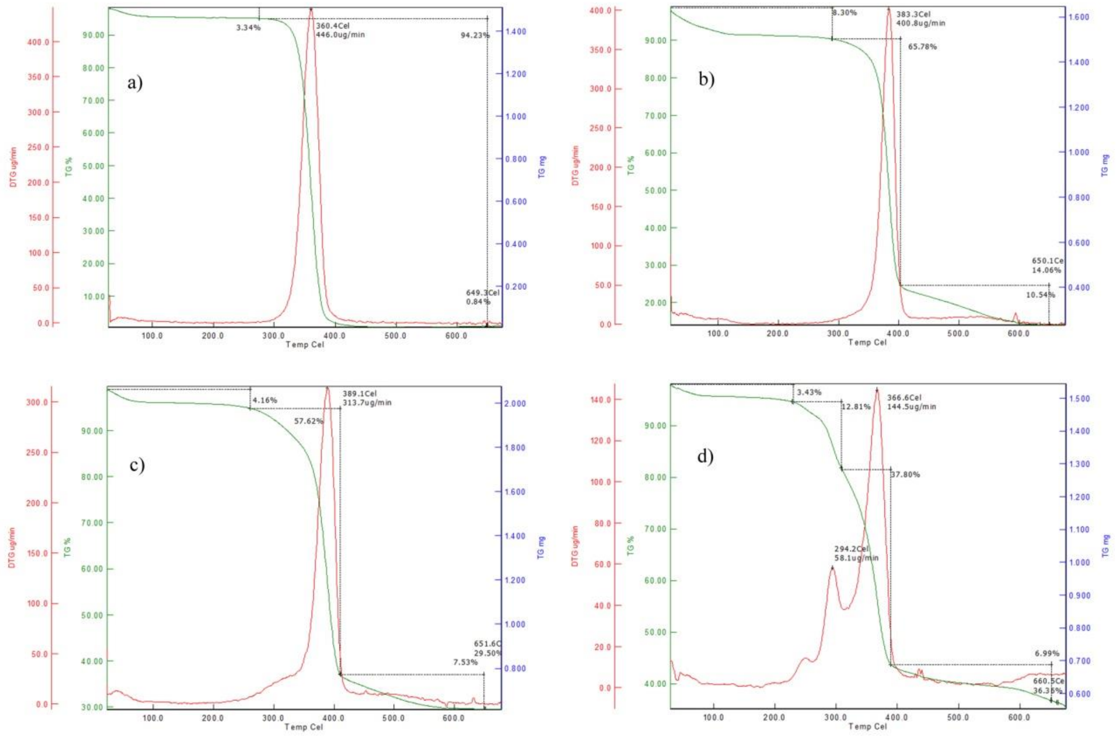
APTES-functionalized
cellulose solution

……………………………….…………Figure 2………..…………..……………….

4.1.2. TG/DTG analysis

Chemical and mechanical durability in catalyst are desirable properties because it can be used in different industrial operations. Thus, the thermal stabilities of CL, CL-NH_2, CL-Sc and CL-

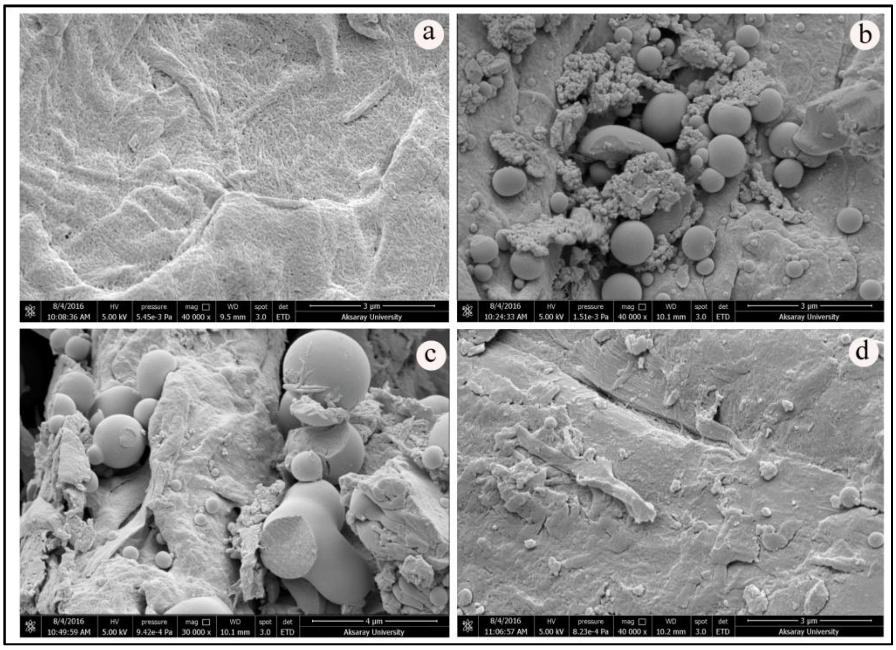
Sc-Pd catalyst were investigated and the results are given in Fig.3. The maximum decomposition temperature (T_{max}) of CL was determined to be 360 °C (Fig. 3a). After the silane and Schiff base formation of CL, the thermal stabilities were recorded as 383 and 389 °C, respectively (Fig. 3b,c). These results show that CL-NH_2 and CL-Sc have higher thermal stability compared to CL. On the other hand, thermal durability of the catalyst was recorded to be 366 °C (Fig. 3d). This result indicates that the catalyst is suitable for different coupling reactions due to its higher thermal mechanical stability. The negligible decrease in the thermal stability of the catalyst may be attributed to the catalytic effect of the palladium ions on the degradation of the CL structure [36].



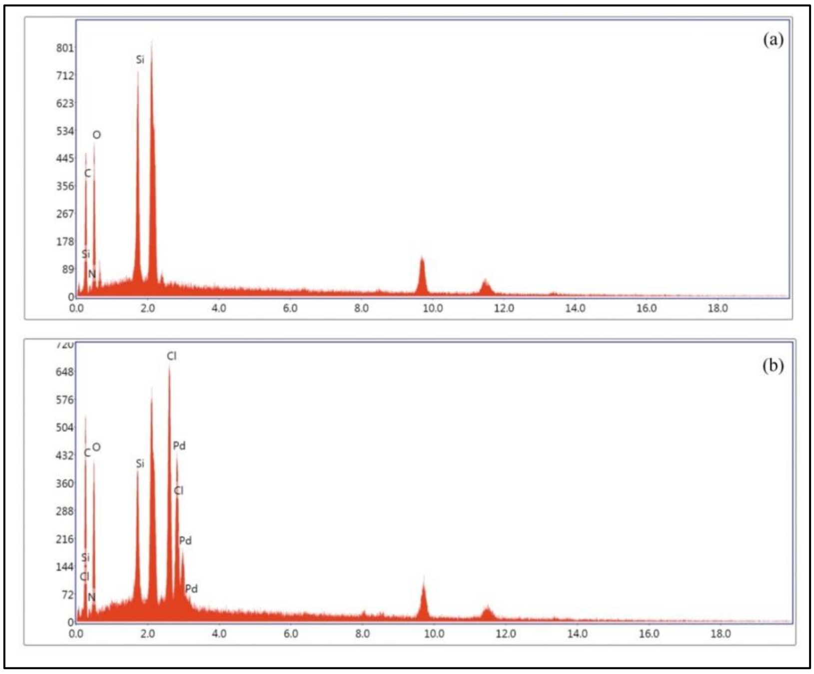
…………………………………….……………Figure 3………...…………..……………….

4.1.3. SEM-EDAX analysis

The surface morphologies of CL, CL-NH_2, CL-Sc and CL-Sc-Pd catalyst were investigated with scanning electron microscope (SEM) and their images are given in Fig. 4. As seen in Fig. 4a, while the CL has a practically flat structure, the surface images of the CL-NH_2 and the CL-Sc were completely changed following the chemical modifications (Fig. 4b,c). On the other hand, the surface image of the catalyst showed a regular surface image (Fig. 4d). It can be concluded from the SEM image that the palladium ions were coordinated with CL-Sc. We also conducted EDAX analysis to confirm the silylation of CL and the formation of the green palladium catalyst (Fig 5). In the spectra, Si, Pd and Cl peaks were observed (Fig. 5a,b). These observations confirm that chemical modification of the CS was achieved.



……………………………………….……………Figure 4………...…………..………………..



……………………………………….……………Figure 5………...…………..………………..

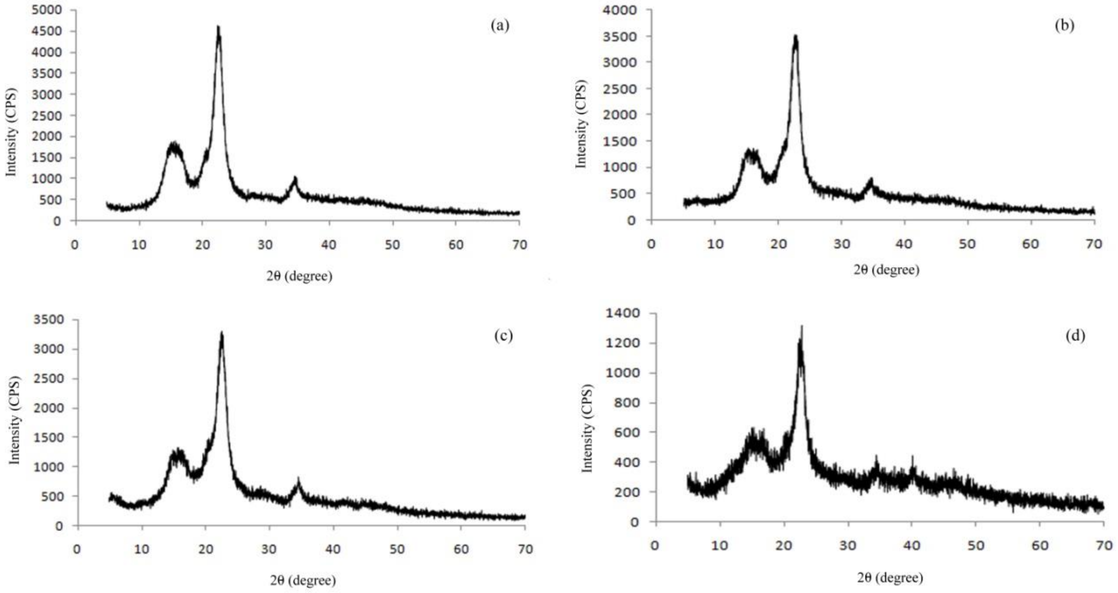
4.1.4. XRD

The crystalline nature of CL, CL-NH_2, CL-Sc and CL-Sc-Pd were investigated and crystalline index values (CrI) were calculated using the equation presented below [37]. In the XRD diagram of CL, two sharper peaks (~at 15 and 22°) and one small peak (~ at 34°) were observed [38] (Fig. 6a). The CrI value of CL was determined to be 81 %. On the other hand, decreases in the CrI values of CL-NH_2 (74 %) and CL-Sc were observed (69 %) (Fig. 6b,c). These decreases may be attributed to the deformation of the hydrogen bonds of CL following the chemical modifications. In addition, we determined a decrease in the CrI of the catalyst (64 %). The lower CrI value of the catalysts showed that palladium complex was formed and the catalyst has an amorphous nature (Fig. 6d). In addition, in the spectrum of the catalyst, palladium peaks seen at around 40.1 ° (Fig. 6d) indicate that designee of catalyst was achieved [39].

$CrI = [(I_{200}–I_{am})/I_{200}]\ x100$

I_{200} is the height of the 200 peak (I_{200}, $2\theta = 22.7°$).

I_{am} is the minimum between the 200 and 110 peaks (I_{am}, $2\theta = 18°$)



……………………………………….…………Figure 6………...…………..………………

4.1.5. Magnetic moment and ICP-OES analysis

It was reported that Pd(II) complexes that have square planar geometry (low spine) showed diamagnetic property [40, 41]. In this paper, to determine the geometry of the CL-Sc-Pd catalyst, magnetic moment analysis was performed at room temperature and it was seen that the catalyst had diamagnetic property. This result indicated that the catalyst has square planar geometry [42]. In addition, the metal content of the catalyst was explored and the palladium content was determined to be 18.2 (mass %).

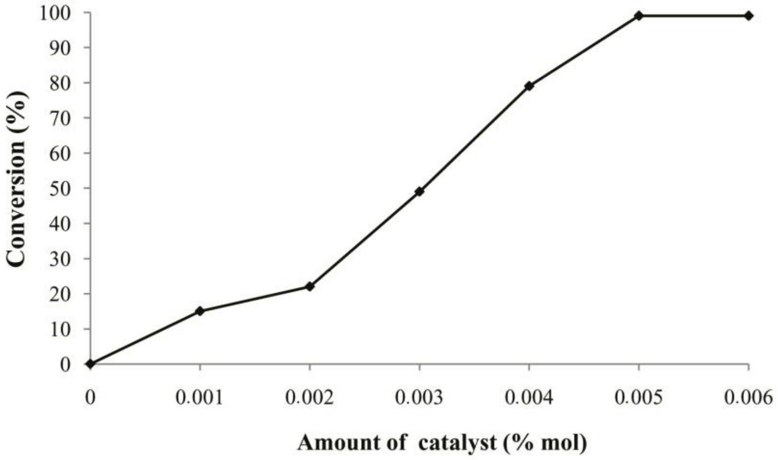
4.2. Catalytic activity of cellulose Schiff base supported Pd(II) catalyst

Before performing the catalytic activity test on the catalyst with various substrates containing aril halides, the effects of catalyst loading, base and reaction time parameters on the C-C reaction yield were investigated. To determine optimum reaction conditions, the synthesis reaction of 4-methoxybiphenyl, which is obtained via the coupling reaction of phenyl boronic acid with 4-bromoanisole, was selected as a model reaction under microwave irradiation and solvent-free media. To detect the suitable catalyst loading, the coupling reactions were carried out using a different amount of catalyst (Fig. 7). As seen from Fig. 7, the best conversion yield was obtained with $5x10^{-3}$ mol % catalyst. We also explored the effect of the reaction time (Fig. 8) and base system on the model reaction (Table 1). We determined that the highest conversion yield (99 %) was obtained at 6 min with the K_2CO_3 base system at 50°C under microwave heating without any organic solvent.

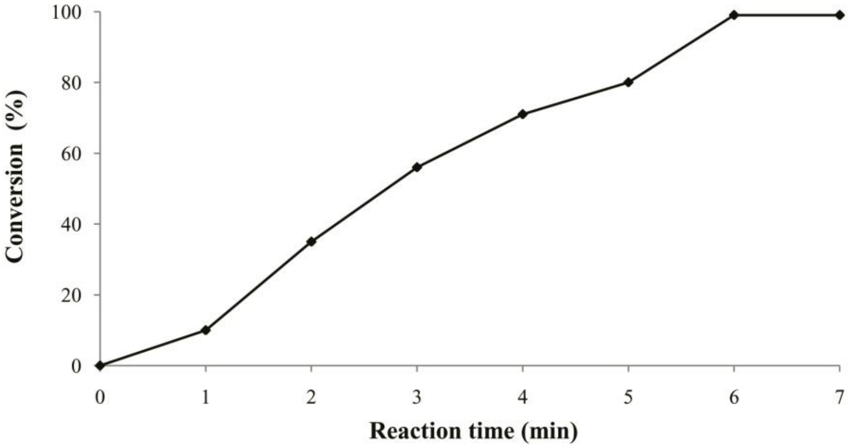
Table 1. The effect of the base system on the Suzuki reaction

Base	Yield (%)	TON	TOF
NaOH	40	8000	80000
KOH	55	11000	110000
Na_2CO_3	39	7800	78000
K_2CO_3	99	19800	198000

Reaction conditions: 1.12 mmol 4-bromoanisole, 1.87 mmol phenyl boronic acid, 3.75 mmol base, $5\text{x}10^{-3}$ % mol catalyst, 50 °C, 0.1 h under MW and solvent-free media



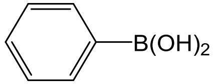
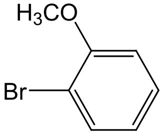
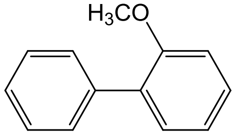
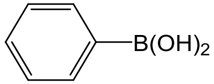
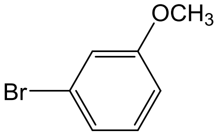
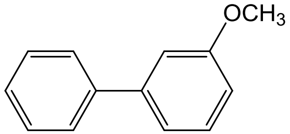
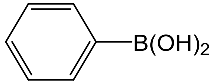
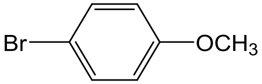
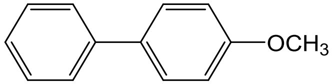
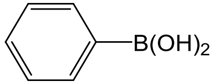
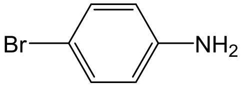
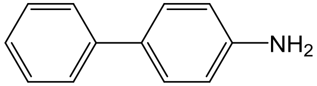
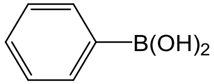
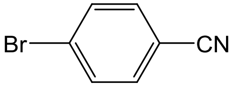
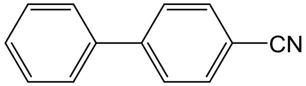
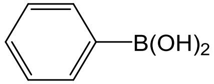
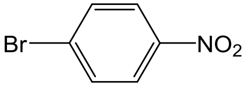
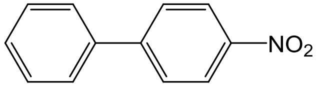
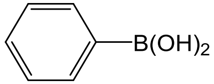
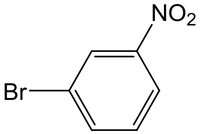
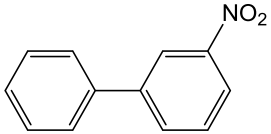
…………………………………..……………Figure 7………...…………..……………….

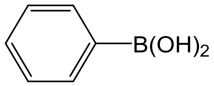
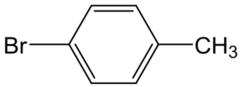
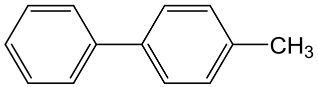
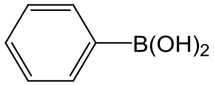
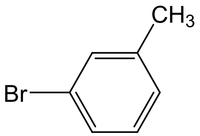
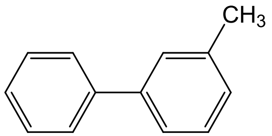
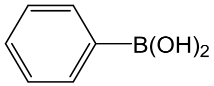
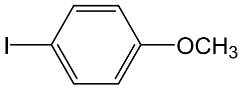
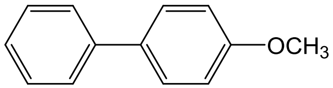
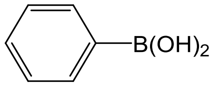
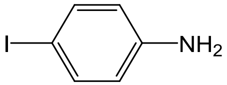
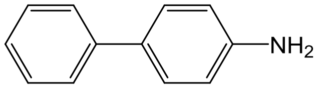
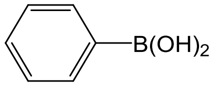
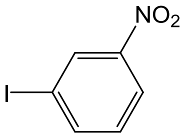
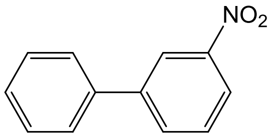
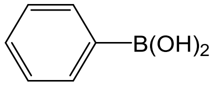
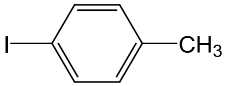
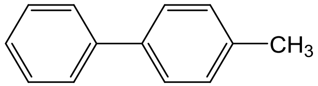
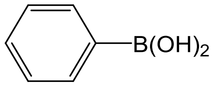
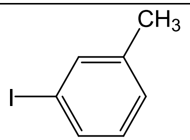
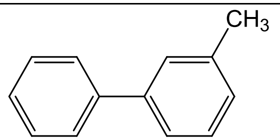


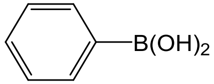
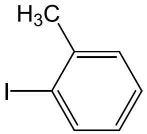
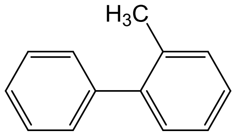
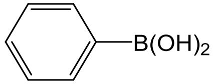
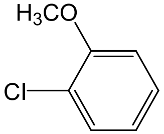
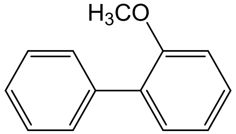
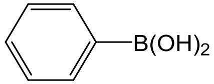
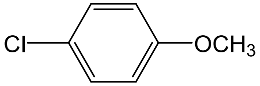
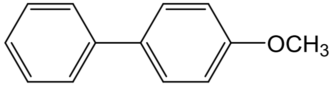
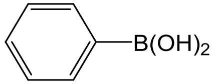
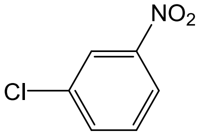
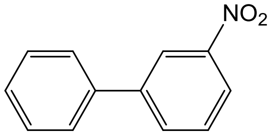
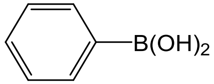
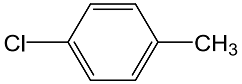
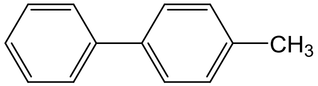
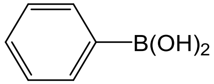
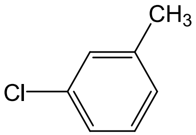
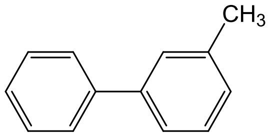
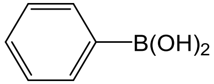
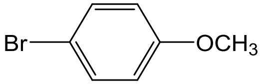
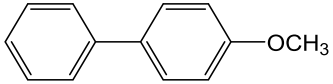
…………………………………..……………Figure 8………...…………..……………….

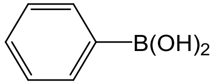
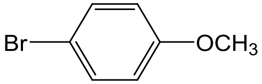
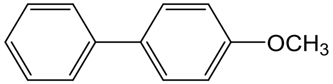
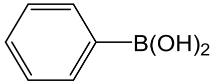
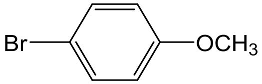
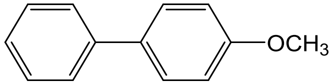
Following the optimum reaction conditions, the catalytic performance of the CL-Sc-Pd catalyst was tested in the the coupling reactions of various aril substrates (20 different substrates) with phenyl boronic acid under microwave heating, and the results are given in Table 2. When the results were examined, the highest conversion yields were obtained with the C-C coupling reaction substrates bearing aril bromides. We recorded substrates containing aril iodides giving higher yields than aril chlorides. In addition, we observed that all coupling reactions in the presence of the withdrawing groups yielded higher reaction conversions than those with the substrates containing the electron-donor groups (Table 2). Moreover, the effects of the substitute groups of the substrates on the yields of the Suzuki coupling reactions were examined, and it was determined to be para>meta >ortho. In addition, the order of the catalytic performance of the substrates (containing aril bromide, aril chloride and aril iodide) was detected as follows: Br > I > Cl. These results may be explained by the size of the halide atoms and the bond dissociation energies. These findings are in accord with the previous literature [1]. TON and TOF values were calculated for all C-C reactions, and the results are listed in Table 2. It can be clearly seen from Table 2, CL-Sc-Pd catalyst gave remarkable TON and TOF values with very small loading of the catalyst and very short time. These high values indicated that the green catalyst can be used efficiently for different coupling reactions. In addition, the catalytic efficiency of CL-Sc-Pd catalyst was tested against different commercial palladium salts with the model reaction under optimum conditions (Table 2). These tests showed that the CL-Sc-Pd catalyst had much higher catalytic activity as well as TON and TOF values than the commercial palladium catalysts. We compared the conventional heating system with microwave heating system on the model reaction (Table 2) and we have found that microwave heating system was more effective than the reflux system. All of the synthesized biaryl compounds were illuminated using the GC/MS and ^{1}H-NMR techniques (please refer to Supplementary data).

Table 2. Effect of the Pd(II) catalyst on C-C coupling reactions

Entry	Boronic acid	Substrate	Product	Reaction Yield (%)	TON	TOF
1				97	19400	194000
2				98	19600	196000
3				99	19800	198000
4				84	16800	168000
5				80	16000	160000
6				90	18000	180000
7				82	16400	164000

8				59	11800	118000
9				53	10600	106000
10				78	15600	156000
11				53	10600	106000
12				68	13600	136000
13				64	12800	128000
14				54	10800	108000

15				32	7000	70000
16				68	13600	136000
17				72	14400	144000
18				60	12000	120000
19				39	7800	78000
20				5	1000	10000
21[a]				39	7800	78000

22[b]				49	9800	98000
23[c]				15	3000	125

Reaction conditions: 1.12 mmol 4-bromoanisole, 1.87 mmol phenyl boronic acid, 3.75 mmol K_2CO_3, $5x10^{-3}$ mol % catalyst, 50 °C, 0.1 h under MW and solvent-free media

a: 1.12 mmol 4-bromoanisole, 1.87 mmol phenyl boronic acid, 3.75 mmol K_2CO_3, $5x10^{-3}$ mol % $PdCl_2$, 50 °C, 0.1 h under MW and solvent-free media

b: 1.12 mmol 4-bromoanisole, 1.87 mmol phenyl boronic acid, 3.75 mmol K_2CO_3, $5x10^{-3}$ mol % Na_2PdCl_4, 50 °C, 0.1 h under MW and solvent-free media

c: Conventional heating method: 1.12 mmol aryl halide, 1.87 mmol phenyl boronic acid, 3.75 mmol K_2CO_3, $5x10^{-3}$ mol % catalyst, 100 °C, 24 h, 5 mL toluene

TON: (turnover number, yield of product/ per mol of Pd).

TOF: (turn over frequency, TON/time of reaction)

4.3. Recyclability of CL-Sc-Pd catalyst

The recyclability of the catalyst was explored on a model C-C reaction, and the recyclability of the catalyst as well as the TON and TOF values for each run are presented in Table 3. At the end of the longevity tests, the catalyst showed activity up to 8th cycle without loss of its activity. In addition, as seen from Table 3, excellent TON and TOF values were recorded with short reaction time and small catalyst loading. To determine the changes in the chemical structure of the catalyst following the eighth cycle, SEM and FTIR analyses were performed and the results are presented in the Supplementary data. These analyses showed that CL-Sc-Pd catalyst maintained its chemical structure after the longevity tests.

Table 3. Reusability of CL-Sc-Pd

Suzuki C-C reaction			
The number of cycle	**Reaction yield (%)**	**TON**	**TOF**
1st	99	19800	198000
2nd	95	19000	190000
3rd	83	16600	166000
4th	83	16000	160000
5th	73	14600	146000
6th	72	14400	144000
7th	72	14400	144000
8th	71	14200	142000

Reaction conditions: 1.12 mmol 4-bromoanisole, 1.87 mmol phenyl boronic acid, 3.75 mmol base, $5x10^{-3}$ % mol catalyst, 50 °C, 0.1 h under MW and solvent-free media

5. Conclusion

In conclusion, a new green Pd(II) catalyst was designed and characterized by FTIR, TG/DTG, SEM-EDAX, XRD, ICP-OES and magnetic moment analyses. Then, the catalytic performance of the catalyst was tested against 20 coupling reactions using a fast and simple microwave heating technique. The longevity of the activity of the CL-St-Pd catalyst was done. In addition, the activity of the catalyst was tested against commercial palladium salts. To prove the efficiency of the microwave irradiation, the model coupling reaction was also performed using conventional heating systems. As shown by all of the tests performed, the green CL-St-Pd catalyst had excellent TON (19,800) and TOF (198,000) values, catalytic activity and selectivity in the presence of a low amount of the catalyst under mild conditions for a very fast reaction time. As a result, this paper demonstrated that the new green catalyst and green microwave technique could be used with different catalytic systems. Finally, this catalyst is superior to the other catalysts because of its unique properties, such as high thermal stability, ease of removal by filtration from the reaction media, usability under an oxygen atmosphere, long life time and provision of high product yields with a very small catalyst loading.

Justification for publication

How the content of the manuscript relates to the *Aims and Scope of the Journal*:

In this study we synthesized an green cellulose Schiff base supported Pd(II) catalyst. The catalytic activity tests of this green catalyst were conducted in green synthesis of biaryl compounds under mild conditions. The method involved a very short-time microwave irradiation at low temperature in absence of any chemical solvents (e.g., 6 min treatment in microwave oven at 400W at 50°C). Considering these aspects of the catalyst and the test technique employed in the study, we believe that this study is suitable for the journal *Applied Catalysis A: General.*

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Figure and Scheme Captions

Fig.1. FT-IR spectra of a) CL b) CL-NH_2 c) CL-Sc d) CL-Sc-Pd catalyst

Fig.2. Color test of CL-NH_2

Fig.3. TG/DTG spectra of a) CL b) CL-NH_2 c) CL-Sc d) CL-Sc-Pd catalyst

Fig.4. SEM images of a) CL b) CL-NH_2 c) CL-Sc d) CL-Sc-Pd catalyst

Fig. 5. EDAX spectra of a) CL-NH_2 b) CL-Sc-Pd catalyst

Fig. 6. XRD diagram of a) CL b) CL-NH_2 c) CL-Sc d) CL-Sc-Pd catalyst

Fig. 7. The effect of catalyst loading on Suzuki coupling reaction

Fig. 8. The effect of reaction time on Suzuki coupling reaction

Scheme 1. Design of green CL-Sc-Pd catalyst