T. Baran / Hacettepe J. Biol. & Chem., 2016, 44 (3), 307-315

New Chitosan-Glyoxal Beads Supported Pd(II) Catalyst: Synthesis, Characterization and Application in Suzuki Coupling Reactions

Yeni Kitosan-Glioksal Küre Destekli Pd(II) Katalizörü: Sentezi, Karakterizasyonu ve Suzuki Kenetlenme Reaksiyonlarindaki Uygulaması

Research Article

Talat Baran
Department of Chemistry, Faculty of Science and Letters, Aksaray University, Aksaray, Turkey.

ABSTRACT

In this paper, a new chitosan bead supported Pd(II) catalyst was prepared and its structure was characterized with FTIR, XRD, TGA, SEM/EDAX and ICP-OES analyses for Suzuki coupling reactions. The catalytic and recyclable performances of the catalyst were explored in the synthesis of biaryl compounds under microwave heating and free solvent media. The catalyst provided good conversion reaction yields and high TON and TOF values with a simple and quick microwave heating procedure. In addition, the recycle tests indicated that the catalyst could be used for up to seven runs under optimum reaction conditions.

Key Words
Coupling reactions, biaryl, reusability, chitosan, Schiff base.

ÖZET

Bu çalışmada, Suzuki çapraz kenetlenme tepkimeleri için yeni bir kitosan boncuk destekli Pd(II) katalizörü hazırlandı ve yapısı FTIR, XRD, TGA, SEM/EDAX ve ICP-OES analizleri ile karakterize edildi. Katalizörün, katalitik ve tekrar kullanılabilirlik performansları mikrodalga ısıtma altında ve çözücüsüz ortamda biaril bileşiklerinin sentezinde araştırıldı. Katalizör basit ve hızlı bir mikrodalga ısıtma yöntemi ileiyi dönüşüm tepkime verimleri ve yüksek TON ve TOF değerleri sağladı. Ayrıca optimum koşullar altında tekrar kullanılabilirlik testleri katalizörün beş çevrime kadar kullanılabileceğini gösterdi.

Anahtar Kelimeler
Kenetleme tepkimeleri, biaril, tekrar kullanılabilirlik, kitosan, Schiff bazı.

Article History: Received: Jun 10, 2016; Revised: Jul 15, 2016; Accepted: Jul 20, 2016; Available Online: Jul 31, 2016.

DOI: 10.15671/HJBC.20164420573

Correspondence to: T. Baran, Department of Chemistry, Faculty of Science and Letters, Aksaray University, Aksaray, Turkey.
Tel: +90 382 288 2142 Fax: +90 382 288 2125 E-Mail: talatbaran_66@hotmail.com

INTRODUCTION

Biaryl compounds are important organic compounds due to their unique chemical and biological properties, and thus they are utilized in pharmacology, medicine and cosmetics [1]. Palladium complexes as catalysts for the synthesis of biaryls have been used widely in homogeneous and heterogeneous systems [2,3]. So far, most of the homogenous palladium catalysts were tested in Suzuki coupling reactions. However, the removal of the homogenous catalysts from the reaction media is not easy and usually affects the recyclable performance of the catalyst [4]. To overcome this problem, natural polymer supported heterogeneous catalysts have been used in recent years [5,6]. As a support material, chitosan which is natural polymer, has superior properties, such as biodegradability, biocompatibility and high metal binding capacity, low cost and environmental friendly material [7,8]. In addition, chitosan has reactive hydroxyl and amino groups, and these groups on the chitosan enable chemical modifications to improve its mechanical strength, solubility, chemical stability and to control hydrophobic, cationic and anionic properties [9,10].

Schiff bases are the most widely used ligands in the field of metal-organic coordination chemistry due to their excellent metal binding ability [11]. Schiff base forms of chitosan are easily produced from the condensation reaction of the free amino group of chitosan with reactive carbonyl groups of ketone or aldehyde [12]. Dialdehyde glyoxal is a cross-linking agent and can react with amine groups of chitosan by forming Schiff bases. Thus this modification increases the metal binding capacity of the chitosan, and so glyoxal cross-linked chitosan Schiff base can provide a better macromolecular ligand for metal ion coordination in catalysts systems.

In this study, a new glyoxal cross-linked chitosan Schiff base and its Pd(II) catalyst (chitosan bead supported Pd(II) catalyst) were synthesized, and their chemical structures were characterized by FTIR, SEM-EDAX,TG/DTG, XRD and ICP-OES analyses. Then the catalytic activity of the chitosan bead supported Pd(II) catalyst was investigated in the synthesis of biaryl compounds in solvent free media under microwave heating via Suzuki coupling reactions. The glyoxal-chitosan based Pd(II) catalyst indicated good catalytic performance towards Suzuki cross coupling in a short reaction time (5 min). In addition, high TON and TOF values were obtained with 0.025% mol catalyst. The reusability of the glyoxal-chitosan based Pd(II) catalyst was also tested. The test indicated that the catalyst was still active after five cycles. In addition, the biaryl compounds were characterized using GC-MS (Supplementary data).

MATERIALS and METHODS

Synthesis of glyoxal cross-linked chitosan Schiff base

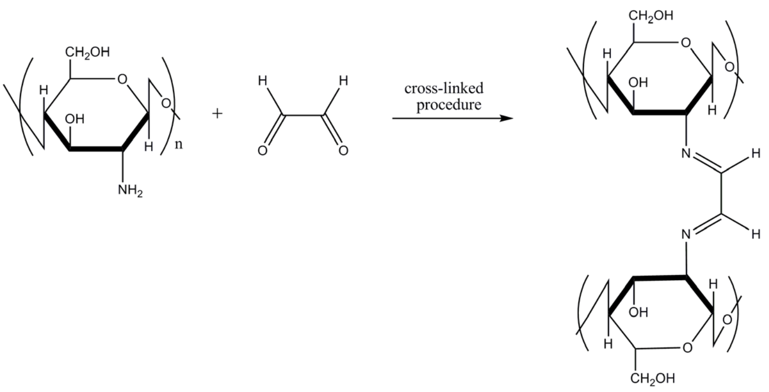
1 g of chitosan was dissolved in an acetic acid solution (50 mL, 2%, w:w). Then the chitosan solution was dropped intoa mixture of ethanol (60 mL), water (40 mL) and NaOH (12 g) to obtained chitosan beads. Subsequently the chitosan beads were filtered out and washed with water to neutrality. To obtain the glyoxal cross-linked beads, the chitosan beads were transferred into a glyoxal-metanol solution (1mL of 40% glyoxal solution and 40 mL metanol) and refluxed for 12 h. Following the reaction time, chitosan beads were filtered and washed with hot metanol to remove the unreacted glyoxal solution and then dried at room temperature.

Synthesis of chitosan bead supported Pd(II) catalyst

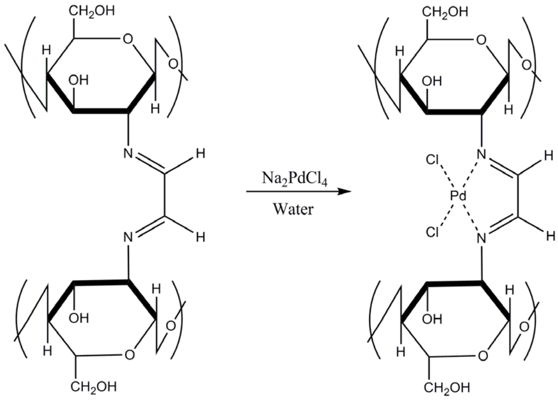
For this, 0.3 g of glyoxal cross-linked chitosan beads were swelled in 30 mL of water and 0.45 g of Na_2PdCl_4 was added to reaction media and stirred at 50ºC for 6h. The brownish chitosan bead supported Pd(II) catalyst was filtered out, rinsed with water and left to dry at room temperature.

General procedure for synthesis of biaryl compounds

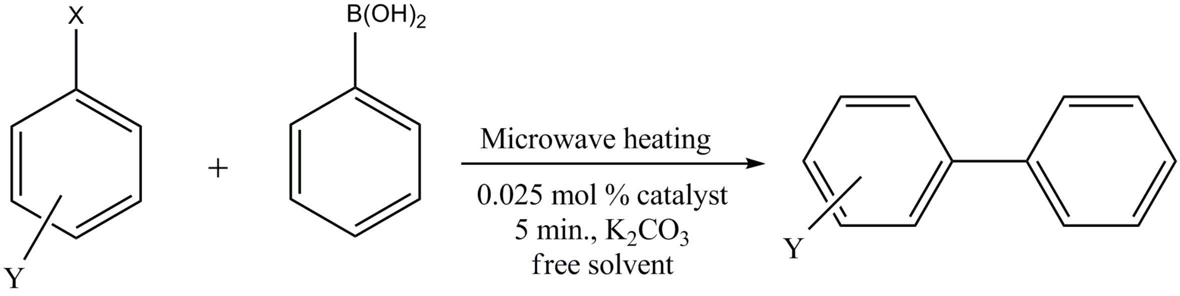
The mixture of phenyl boronic acid (1.87 mmol), aril halide (1.12 mmol), potassium carbonate (3.75 mmol) and chitosan bead supported Pd(II) catalyst (0.025 mol %) was added to a Schlenk tube and heated under microwave irradiation at 50ºC for 5 min. At the end of the reaction time, the mixture was cooled at room temperature and



Scheme 1. Synthesis of glyoxal cross-linked chitosan Schiff base.



Scheme 2. Synthesis pathway for chitosan bead supported Pd(II) catalyst.



Scheme 3. Synthesis of biarlys compounds.

extracted with a toluene-water solution (2:1) for three times. Then organic phase was dried with $MgSO_4$ to remove water and the biaryl compound was obtained.

RESULTS and DISCUSSION

FTIR analysis

The FTIR spectra of chitosan, glyoxal cross-linked chitosan Schiff base and Pd(II) catalyst are present Figure 1. The FTIR spectra of chitosan has two characteristics peaks at 1650 and 1590 cm^{-1}, respectively, for the stretching of the carbonyl groups of the amide I band and NH_2 bending of the amide II (Figure 1a) [13]. Following the cross-linking procedure (Schiff base formation), the NH_2 bending of chitosan disappeared and a new absorbance band was clearly observed at 1635 cm^{-1}, which was attributed to the stretching of the imine groups (-CH=N) (Figure 1b) [14]. This new peak proved the condensation of chitosan with glyoxal. In addition, other important bands were observed as follows: 3350 (stretching of N-H and OH), 2935 (stretching of C-H) and 1375

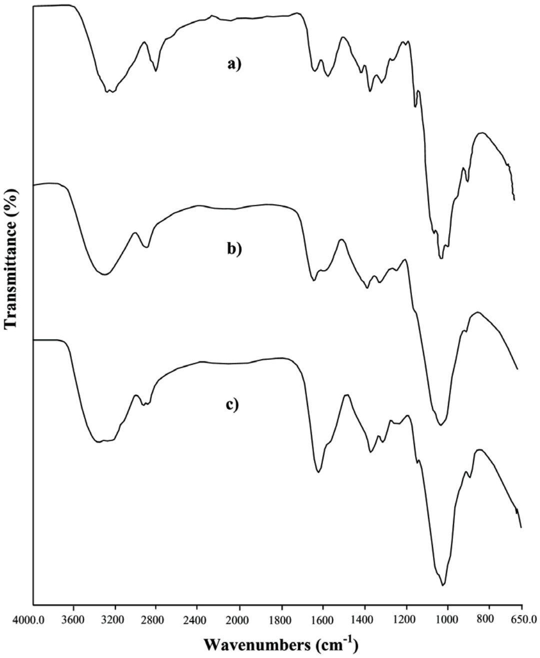


Figure 1. FTIR spectra of a) chitosan b) glyoxal cross-linked chitosan Schiff base c) chitosan bead supported Pd(II) catalyst.

cm^{-1} (stretching of C-N). On the other hand, the stretching of the imine group of the chitosan bead supported Pd(II) catalyst was shifted to a lower frequency compared to its free ligand (1610 cm^{-1}) (Figure 1c). This case can be explained by the coordination of the nitrogen atoms of the glyoxal cross-linked chitosan Schiff base to the palladium ion [15].These findings were in accordance with other chitosan based metal complexes in the literatures [16, 17].

X-Ray Diffraction

In the powder XRD spectra of glyoxal cross-linked chitosan Schiff base and Pd(II) catalyst are present Figure2. It was reported that chitosan has two characteristic sharp peaks at ~10 and 20° [17]. In the diagram of the glyoxal cross-linked chitosan Schiff base, the intensity of these characteristic peaks were weakened and the crystallinity value of chitosan was decreased after the cross-linking procedure (Figure 2a). This important chance can be described by a decrease in the number of $-NH_2$ groups on the polymer chain of the chitosan following the Schiff base modification [18]. In addition, the Pd (II) catalyst was examined with a XRD analysis (Figure 2b). As seen from Figure 2b, the catalyst was more amorphous in nature than its free ligand and chitosan. This amorphous nature showed the coordination of the palladium ion to the chitosan beads [19]. In addition, to determine the crystallinity value of the chitosan, the glyoxal cross-linked chitosan Schiff base and thePd(II) catalyst, the following equation was used [20]:

$$\text{Crystalline index (\%)} = [(I_{110}-I_{am})/I_{110}]\times100 \qquad (1)$$

where I_{110} denotes the maximum intensity at ~ 20° and Iam is the intensity of amorphous diffraction at 16°.

The crystallinity values of the chitosan, the glyoxal cross-linked chitosan Schiff base and the Pd(II) catalyst were found to be 82, 52 and 18%, respectively. As expected, the chitosan bead supported Pd(II) catalyst has a lower crystallinity index compared with the chitosan and glyoxal cross-linked chitosan Schiff base.

TG/DTG

The decomposition temperatures and thermal stabilities of the glyoxal cross-linked chitosan Schiff base and the Pd(II) catalyst were investigated with TG/DTG measurements and the results are given Figure 3. As shown in Figure 3, the maximum decomposition temperatures (DTG max) of chitosan, glyoxal cross-linked chitosan Schiff base and Pd(II) catalyst were

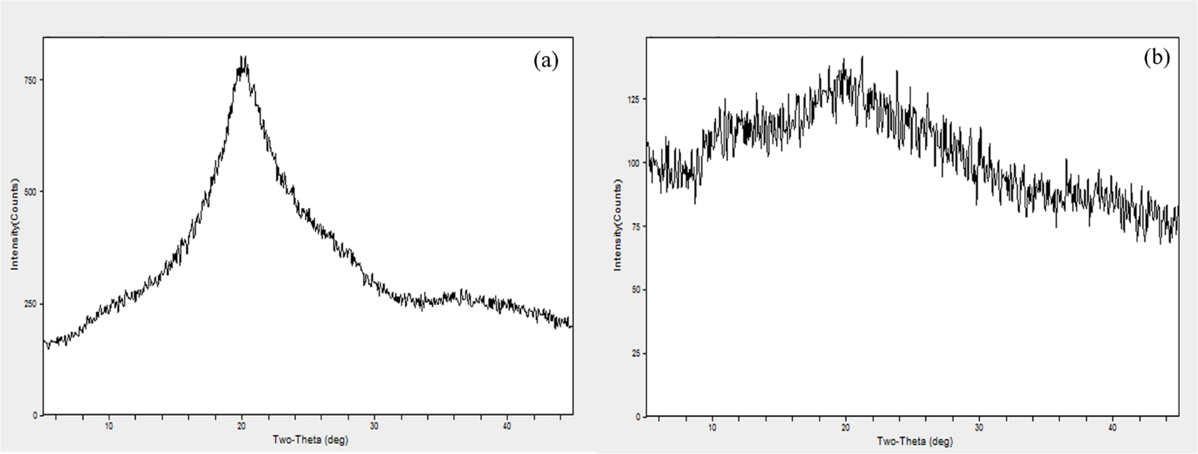


Figure 2. XRD diagram of spectra of a) glyoxal cross-linked chitosan Schiff base b) chitosan bead supported Pd(II) catalyst.

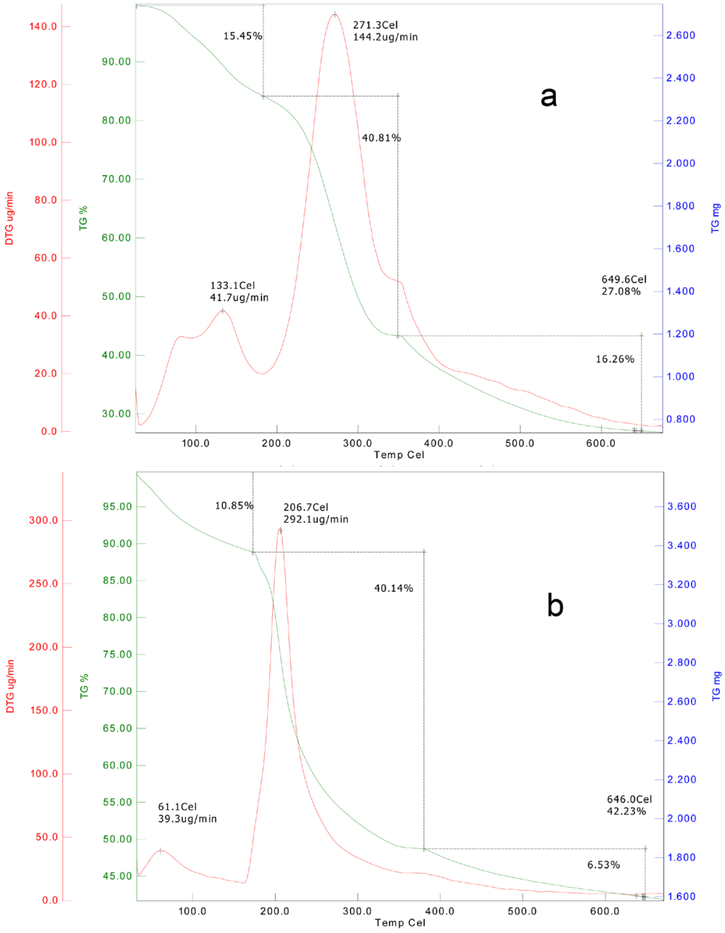


Figure 3. TG/DTG spectra of a) glyoxal cross-linked chitosan Schiff base b) chitosan bead supported Pd(II) catalyst.

determined as 302, 271 and 206°C, respectively. As expected, a lower thermal stability was recorded for the glyoxal cross-linked chitosan Schiff base compared to the chitosan because of the cross linking procedure leading to the deformation of strong hydrogen bonds of the chitosan [21]. In addition, three decomposition steps were observed in the TG/DTG spectrum of the glyoxal cross-linked chitosan Schiff base. The first step was attributed to the removal of water

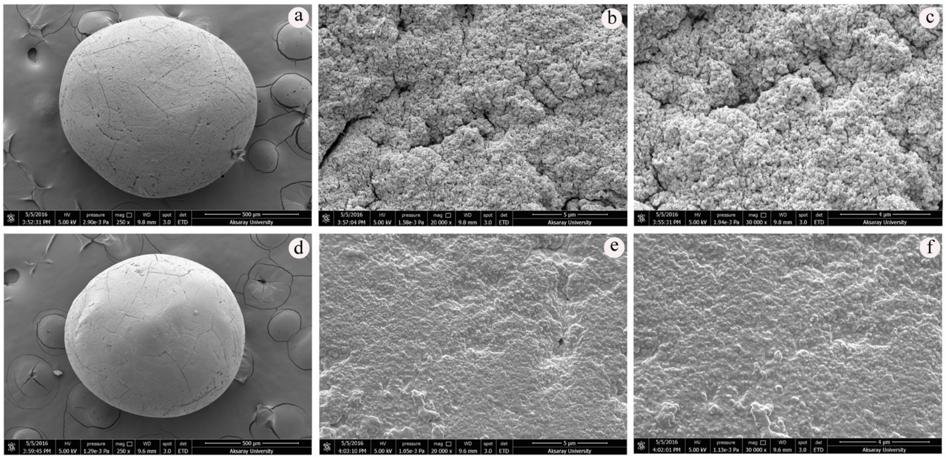


Figure 4. SEM pictures of glyoxal cross-linked chitosan Schiff base (a-c), chitosan bead supported Pd(II) catalyst (d-f).

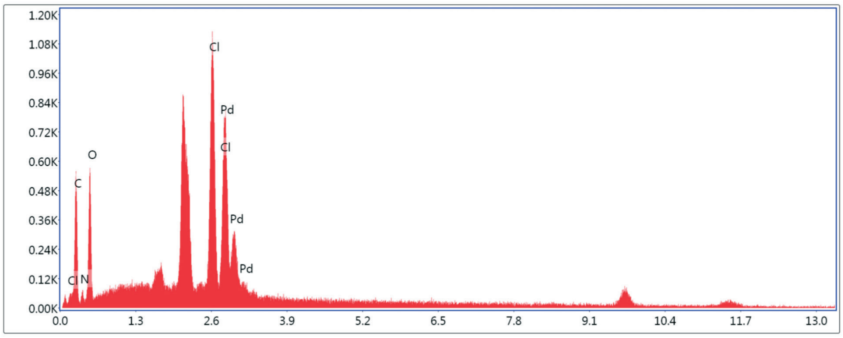


Figure 5. EDAX spectrum of chitosan bead supported Pd(II) catalyst.

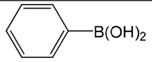
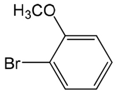
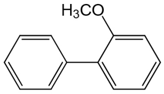
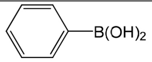
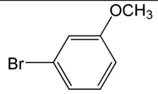
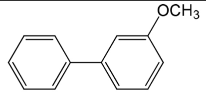
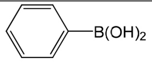
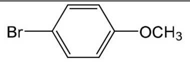
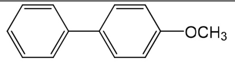
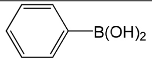
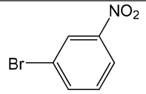
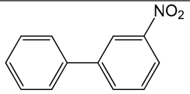
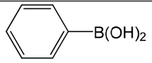
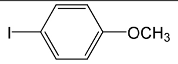
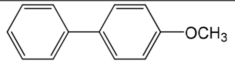
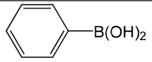
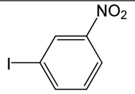
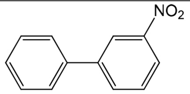
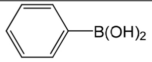
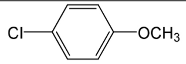
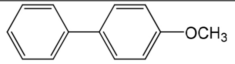
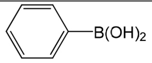
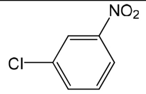
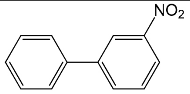
molecules, the second step corresponded to the free chitosan unit and the last step belonged to the decomposition of the cross linked chitosan Schiff base unit. On the other hand, the DTGmax of the Pd(II) catalyst was measured to be 206°C, and a loss of mass in three steps was recorded. The first, second and last steps were caused by the evaporation of water molecules, degradation of free chitosan chain and coordination bonds with palladium ion and condensing of Schiff base units [12]. As a result of the TG/DTG analysis, the order of the thermal stability was determined as glyoxal cross-linked chitosan Schiff base >Pd(II) catalyst.

SEM-EDAX and ICP-OES

The surface properties of the chitosan, the glyoxal cross-linked chitosan Schiff base and the Pd(II) catalyst were investigated with SEM analysis (Figure 4). As seen from Figure 4, the glyoxal cross-linked chitosan Schiff base and the Pd(II) catalyst have spherical formations. This figure demonstrates that chitosan beads were obtained. In addition, SEM images at different magnifications for all compounds are shown in Figure 4. The surface morphologies of the glyoxal cross-linked chitosan Schiff base were completely changed following the chemical modification, while the chitosan had a smooth surface. This significant change was ascribed to the condensation of chitosan with glyoxal [21]. The SEM picture of the chitosan bead supported Pd(II) catalyst clearly shows that the catalyst has a more regular structure than its ligand. This can be explained by thecoordination of the palladium ion with the glyoxal cross-linked chitosan Schiff base [22].

To detect thepresence of the palladium ion, the EDAX spectrum was recorded and is given in Figure 5. The EDAX spectrum confirmed the formation of the Pd(II) catalyst. In addition, to determine the palladium ion content of the chitosan bead supported Pd(II) catalyst, ICP-OES analysis was performed, and the palladium ion content was determined to be 18.5%.

Table 1. Effect of chitosan bead supported Pd(II) catalyst on Suzuki cross-coupling reaction.

Entry	Boronic acid	Substrate	Product	Yield (%)	TON	TOF
1				96	3840	48000
2				93	3720	46500
3				97	3880	48500
4				88	3520	44000
5				73	2920	36500
6				70	2800	35000
7				48	1920	24000
8				52	2080	26000

Reaction conditions: 1.12 mmol aryl halide, 1.87 mmol phenyl boronic acid, 3.75 mmol K_2CO_3, 0.025% mol chitosan bead supported Pd(II) catalyst, 50°C, 5 min under MW.
TON: (turnover number, yield of product/ per mol of Pd).
TOF: (turn over frequency, TON/time of reaction)

Catalytic performance in Suzuki coupling reaction

It has been reported that anumber of reaction factors, such as amount of the catalyst loading, base system, reaction temperature and reaction time, are essential to the catalytic performance of the catalysts for Suzuki cross coupling [23]. Therefore, the coupling reaction of phenyl boronic acid with 4-bromoanisole was chosen as a model reaction, and to determine the optimum reaction conditions, preliminary studies were conducted under microwave heating at 400 W without any organic solvent. The optimum reaction conditions were determined to be catalyst loading: 0.025% mol; base system: K_2CO_3; reaction time: 5 min; and reaction temperature: 50°C under solvent-free conditions. Then, with the optimum reaction parameters, the catalytic performance of the heterogeneous catalyst was examined in C-C reactions between different aryl halides and phenyl boronic acid. As seen from Table 1, all the C-C reactions in the presence of the aryl bromide gave high conversion yields. In addition, aryl halides containing a methoxy group ($-OCH_3$) and electron-donating groups ($-NO_2$) gave good reaction yields. On the other hand, the cross coupling reaction bearing aryl chlorides produced lower reaction yields due to its poor activity [24]. In addition, the TON and TOF values were calculated and are presented in Table 1. As shown from Table 1, exceptionally high TON and TOF values were obtained with lower amounts of catalyst. Considering all the coupling reactions, the chitosan bead supported Pd(II) complex is a good palladium source and it is suitable for use as acatalyst for Suzuki coupling reactions.

Table 2. Reusability performance of chitosan bead supported Pd(II) catalyst.

Suzuki C-C reaction			
The number of cycle	**Yield (%)**	**TON**	**TOF**
1 st	97	3880	48500
2 nd	82	3280	41000
3 rd	73	2920	36500
4 th	58	2320	29000
5 th	45	1800	22500

Reaction conditions: 1.12 mmol 4-bromoanisole, 1.87 mmol phenyl boronic acid, 3.75 mmol base, 0.025% mol chitosan bead supported Pd(II) catalyst, 50°C, 5 min under MW.

Reusability potential of chitosan bead supported Pd(II) catalyst

The reusability test of the chitosan bead supported Pd(II) catalyst was studied with a model coupling reaction under optimum reaction parameters, and the results are summarized in Table 2. After the C-C coupling reaction (first run), the catalyst was filtered and washed with hot water and methanol to reactive the catalyst [25] and the same process was carried out for each run. At the end of the recycle tests, the chitosan bead supported Pd(II) catalyst had been used for five runs. The reusability test showed the long life time potential of the catalyst, so it is suitable for different industrial operations.

CONCLUSION

In this paper, firstly, a new glyoxal cross-linked chitosan Schiff base was prepared as a support material for palladium catalyzed Suzuki cross coupling reactions. Then a chitosan bead supported Pd(II) complex was synthesized and characterized by FTIR, XRD, TGA, SEM/EDAX and ICP-OES analysis techniques. The catalytic performance of the catalyst was explored for the synthesis of biaryls using a fast, safe and simple microwave heating method without solvent. The catalyst showed high catalytic activity in different coupling reactions and it is capable of being reused for up to five cycles. In summary, the significant advantages of the chitosan bead supported Pd(II) catalyst are high thermal stability, high selectivity, long life time and easy removal of the reaction media compared to other natural polymer supported catalysts. These outstanding properties show that the chitosan bead supported Pd(II) complex is a suitable catalyst for different catalytic systems.

References

1. A.-R. Hajipour, F. Rafiee, Dimeric ortho-palladated complex of 2,3-dimethoxybenzaldehyde oxime catalyzed Suzuki-Miyaura cross-coupling reaction under microwave irradiation, J. Iran. Chem. Soc., 12 (2015) 1177-1181.
2. B.C.E. Makhubela, A. Jardine, G.S. Smith, Pd nanosized particles supported on chitosan and 6-deoxy-6-amino chitosan as recyclable catalysts for Suzuki–Miyaura and Heck cross-coupling reactions, Appl. Catal. A-Gen., 393 (2011) 231-241.
3. P. Cotugno, M. Casiello, A. Nacci, P. Mastrorilli, M.M. Dell'Anna, A. Monopoli, Suzuki coupling of iodo and bromoarenes catalyzed by chitosan-supported Pd-nanoparticles in ionic liquids, J. Organomet. Chem., 752 (2014) 1-5.
4. Y. Chang, Y. Lv, F. Lu, F. Zha, Z. Lei, Efficient allylic oxidation of cyclohexene with oxygen catalyzed by chloromethylated polystyrene supported tridentate Schiff-base complexes, J. Mol. Catal. A-Chem., 320 (2010) 56-61.
5. P. Puthiaraj, W.-S. Ahn, Highly active palladium nanoparticles immobilized on NH2-MIL-125 as efficient and recyclable catalysts for Suzuki–Miyaura cross coupling reaction, Catal. Commun., 65 (2015) 91-95.
6. X. Wang, P. Hu, F. Xue, Y. Wei, Cellulose-supported N-heterocyclic carbene-palladium catalyst: Synthesis and its applications in the Suzuki cross-coupling reaction, Carbohyd. Polym., 114 (2014) 476-483.
7. Y. Xiang, Q. Zhang, J. Si, J. Du, H. Guo, T. Zhang, Characterization and catalytic kinetics studies of N-cetyl-O-sulfate chitosan multinuclear copper complex as an artificial hydrolase, J. Mol. Catal. A-Chem., 322 (2010) 33-38.
8. İ. Uslu, H. Çelikkan, O. Atakol, M.L. Aksu, Preparation of PVA/chitosan doped with boron composite fibers and their characterization, Hacettepe J. Biol. & Chem., 36 (2008) 117-122.
9. D. de Britto, O.B.G. Assis, A novel method for obtaining a quaternary salt of chitosan, Carbohyd. Polym., 69 (2007) 305-310.
10. L.S. Guinesi, É.T.G. Cavalheiro, Influence of some reactional parameters on the substitution degree of biopolymeric Schiff bases prepared from chitosan and salicylaldehyde, Carbohyd. Polym., 65 (2006) 557-561.

11. N. Çolak, V. Kuşçu, Spectroscopic properties of 2,2′-[thiobis(p-phenylene nitrilo methylidyne)] bis(4-chloro/bromo/methyl/nitro/methoxy) phenol, Hacettepe J. Biol. & Chem., 40 (2012) 213–218.
12. T. Baran, A. Menteş, Highly efficient Suzuki cross-coupling reaction of biomaterial supported catalyst derived from glyoxal and chitosan, J. Organomet. Chem., 803 (2016) 30-38.
13. T. Peng, K.D. Yao, C. Yuan, M.F.A. Goosen, Structural-Changes of Ph-Sensitive Chitosan Polyether Hydrogels in Different Ph Solution, J. Polym. Sci. Pol. Chem., 32 (1994) 591-596.
14. T. Baran, A. Menteş, H. Arslan, Synthesis and characterization of water soluble O-carboxymethyl chitosan Schiff bases and Cu(II) complexes, Int. J. Biol. Macromol., 72 (2015) 94-103.
15. T.D. Thangadurai, S.K. Ihm, Chiral Schiff base ruthenium(III) complexes: Synthesis, characterisation, catalytic and antibacterial studies, J. Ind. Eng. Chem., 9 (2003) 563-568.
16. C. Demetgül, S. Serin, Synthesis and characterization of a new vic-dioxime derivative of chitosan and its transition metal complexes, Carbohyd. Polym., 72 (2008) 506-512.
17. N.A. Anan, S.M. Hassan, E.M. Saad, I.S. Butler, S.I. Mostafa, Preparation, characterization and pH-metric measurements of 4-hydroxysalicylidenechitosan Schiff-base complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ru(III), Rh(III), Pd(II) and Au(III), Carbohyd. Res., 346 (2011) 775-793.
18. W. Li-xia, W. Zi-wei, W. Guo-song, L. Xiao-dong, R. Jian-guo, Catalytic performance of chitosan-Schiff base supported Pd/Co bimetallic catalyst for acrylamide with phenyl halide, Polym. Advan. Technol., 21 (2010) 244-249.
19. T. Baran, E. Açıksöz, A. Menteş, Highly efficient, quick and green synthesis of biarlys with chitosan supported catalyst using microwave irradiation in the absence of solvent, Carbohyd. Polym., 142 (2016) 189-198.
20. Y.Q. Zhang, C.H. Xue, Y. Xue, R.C. Gao, X.L. Zhang, Determination of the degree of deacetylation of chitin and chitosan by X-ray powder diffraction, Carbohyd. Res., 340 (2005) 1914-1917.
21. R. Antony, S.T. David, K. Saravanan, K. Karuppasamy, S. Balakumar, Synthesis, spectrochemical characterisation and catalytic activity of transition metal complexes derived from Schiff base modified chitosan, Spectrochim. Acta A., 103 (2013) 423-430.
22. C. Demetgul, Synthesis of the ketimine of chitosan and 4,6-diacetylresorcinol, and study of the catalase-like activity of its copper chelate, Carbohyd. Polym., 89 (2012) 354-361.
23. N. Liu, C. Liu, Z. Jin, Green synthesis of fluorinated biaryl derivatives via thermoregulated ligand/palladium-catalyzed Suzuki reaction, J. Organomet. Chem., 696 (2011) 2641-2647.
24. A.F. Littke, C.Y. Dai, G.C. Fu, Versatile catalysts for the Suzuki cross-coupling of arylboronic acids with aryl and vinyl halides and triflates under mild conditions, J. Am. Chem. Soc., 122 (2000) 4020-4028.
25. S.E.S. Leonhardt, A. Stolle, B. Ondruschka, G. Cravotto, C.D. Leo, K.D. Jandt, T.F. Keller, Chitosan as a support for heterogeneous Pd catalysts in liquid phase catalysis, Appl. Catal. A Gen., 379 (2010) 30-37.