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Carboxymethyl chitosan Schiff base supported heterogeneous palladium(II) catalysts for Suzuki cross-coupling reaction

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ABSTRACT

In this study, two new *O*-carboxymethyl chitosan Schiff bases supported Pd(II) catalyst were synthesized (OCMCS-3aPd and OCMCS-4aPd). The catalysts were characterized with FTIR, TG/DTG, SEM/EDAX, XRD, ICP-OES, UV–vis, magnetic moment and molar conductivity. The catalytic activities of these catalysts were tested in the synthesis of biaryl compounds by Suzuki cross-coupling reactions. Characterizations of the biaryls were performed with GC–MS and ^{1}H NMR. In synthesis of the biaryl compounds in the presence of the Pd(II) catalyst, high selectivity was observed; no homo-coupling byproducts were detected in the spectra. A reusability test demonstrated that the catalysts were highly efficient even after ten run. The mercury poisoning and leaching tests indicated that the catalysts have heterogeneous nature.

1. Introduction

Suzuki cross-coupling reactions are one of the fundamental methods employed in the synthesis of biaryls [1,2]. Palladium is among the transition metals used in Suzuki cross-coupling reactions [3,4]. Pd(II) catalysts have been used in homogenous and heterogeneous systems [5]. Homogenous Pd(II) catalysts produce high yields; however due to the difficulties in separation of the products from the catalyst, researchers prefer heterogeneous catalysts to homogenous ones [6,7].

There have been many recent studies on palladium catalysts supported by solids, such as polystyrene, corn starch, silica and cellulose [8–11]. Biopolymer supported catalysts have gained much attention due to the unique characteristics of the biomaterials; which are nontoxic, biodegradable, renewable and abundant [12–14]. Chitosan is a biomacromolecule that has these properties. This cationic biopolymer is synthesized via alkaline deacetylation of chitin [15]. Additionally, chitosan has an environmentally friendly nature and exhibits high affinity for metal ions due to the NH_2 and OH groups on its chains [12,16–18]. These functional groups also make it possible to modified chitosan (Schiff base, *O*-carboxymethylation) act as suitable ligands for transition metal ions [19–21].

This study aimed to synthesize two new *O*-carboxymethyl chitosan Schiff base supported Pd(II) catalysts. The chemical nature of the compounds were illuminated with FTIR, TG/DTG, SEM/EDAX, XRD, ICP-OES, UV–vis, magnetic moment and molar conductivity. The catalytic activity tests were conducted in reactions of aryl halides with phenyl boronic acid. Suzuki cross-coupling was achieved with high product selectivity and yield.

2. Materials and methods

2.1. Material

Aryl halides, phenyl boronic, palladium chloride, potassium carbonate, sodium chloride, magnesium sulphate, toluene, methanol and Hg(0) obtained from Sigma–Aldrich.

2.2. Physical measurements

The FTIR spectra of samples were performed on PerkinElmer Spectrum 100 FTIR spectrophotometer. Biaryls compounds were analyzed with Agilent GC-7890 A- MS 5975. ^{1}H NMR spectra of the biaryls were recorded on Bruker Avance III 400 MHz spectrometer using Aceton-d$_6$ solvents. TG/DTG curves of catalysts were obtained under a nitrogen atmosphere at a sample heat-

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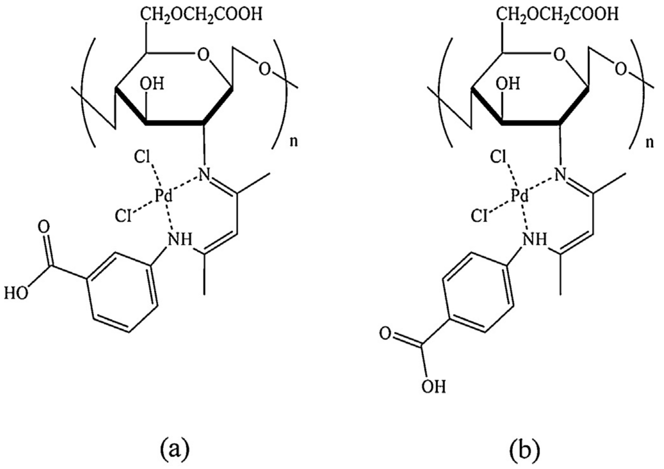
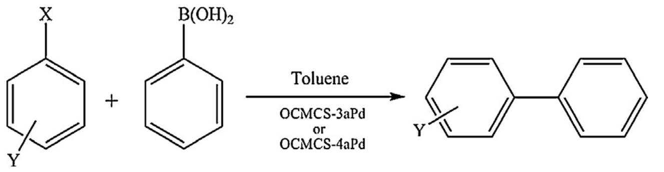


(a) (b)

Fig. 1. Structure of OCMCS-3aPd (a), OCMCS-4aPd (b).



Scheme 1. Chitosan Schiff base supported Pd(II) catalyzed Suzuki coupling reactions.

ing rate of 10 °C min^{-1} using EXSTAR S11 7300. XRD diagrams of the Pd(II) complexes were carried out Rigaku Dmax 2000 system at 40 kV, 30 mA and 2θ with a scan angle from 5° to 50°. The surface morphologies were examined using QUANTA-FEG 250 ESEM. The EDAX spectra of the Pd(II) catalysts were determined by EDAX-Metek. The metal contents of the catalysts were determined with PerkinElmer Optima 2100 DV inductively coupled plasma (ICP) optical emission spectrometer (OES). Electronic spectra of the complexes were obtained with Genesys 10S UV–vis Spectrophotometer. The molar conductivities of the catalysts were measured using tablet op-Digital conductivity meter CD-2005 at 25 °C. Magnetic susceptibilities of the catalysts were performed using Sherwood magnetic susceptibility balance at room temperature.

2.3. Synthesis of Pd(II) complexes (OCMCS-3aPd and OCMCS-4aPd)

First, water soluble of Na_2PdCl_4 was prepared as follows:

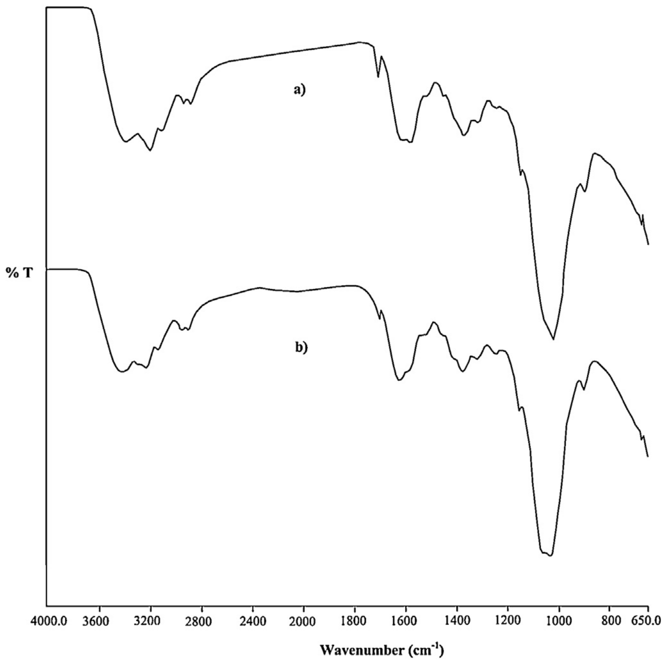


Fig. 2. FTIR spectra of OCMCS-3aPd (a), OCMCS-4aPd (b).

$PdCl_2$ (1.0 g, 5.63 mmol) and NaCl (0.66 g, 11.28 mmol) were dissolved in 100 mL water and stirred over night at room temperature. Upon achieving complete dissolution, water in the medium was evaporated and the product, Na_2PdCl_4, was collected.

The catalysts (OCMCS-3aPd and OCMCS-4aPd) were synthesized following the procedure given below. 0.2 g of the *O*-carboxymethyl chitosan Schiff bases ([OCMCS-3a]·2H_2O and [OCMCS-4a]·2H_2O) were synthesized following the method in our previous study [22] and was dissolved in 10 mL of water at room temperature. Then 0.35 g of Na_2PdCl_4 in 10 mL water was added into the reaction media and stirred for 5 h at 50 °C. After which the mixture was cooled to room temperature, and the yellow–green product was collected. Finally, the product was rinsed with water to remove unreacted reactants. The products (OCMCS-3aPd and OCMCS-4aPd) (Fig. 1) were dried at 50 °C in an oven.

2.4. General procedure for Suzuki coupling

The catalyst, (OCMCS-3aPd or OCMCS-4aPd), 0.04 (% mol), 1.2 mmol aryl halides, 1.87 mmol phenyl boronic acid, 3.75 mmol K_2CO_3 and 6 mL toluene were put into a Schlenk tube and stirred

Table 1
Effect of complexes on Suzuki cross-coupling reaction.

Entry	*X*	*Y*	Yield (%)		TON	
			OCMCS-3aPd	OCMCS-4aPd	OCMCS-3aPd	OCMCS-4aPd
1	Br	3-OCH$_3$	94	95	2350	2375
2	Br	4-OCH$_3$	97	98	2425	2450
3	Br	3-CH$_3$	37	29	925	725
4	Br	3-NH$_2$	75	92	1875	2300
5	Br	4-NH$_2$	70	90	1458	2250
6	Br	4-NO$_2$	98	88	2450	1833
7	Br	4-CN	94	84	2350	2100
8	I	4-CH$_3$	51	39	1275	975
9	Cl	3-OCH$_3$	6	5	150	125
10	Cl	4-CH$_3$	2	3	50	75
11[a]	Br	4-OCH$_3$	55	58	1375	1450

Reaction conditions: 1.12 mmol of aryl halide, 1.87 mmol of phenyl boronic acid, 3.75 mmol of K_2CO_3, 0.04 mol% catalyst, 6 mL of toluene, 100 °C, 48 h.
TON: (turnover number, yield of product/per mole of Pd).
[a] In the presence of excess Hg (Hg:Pd = 300:1).

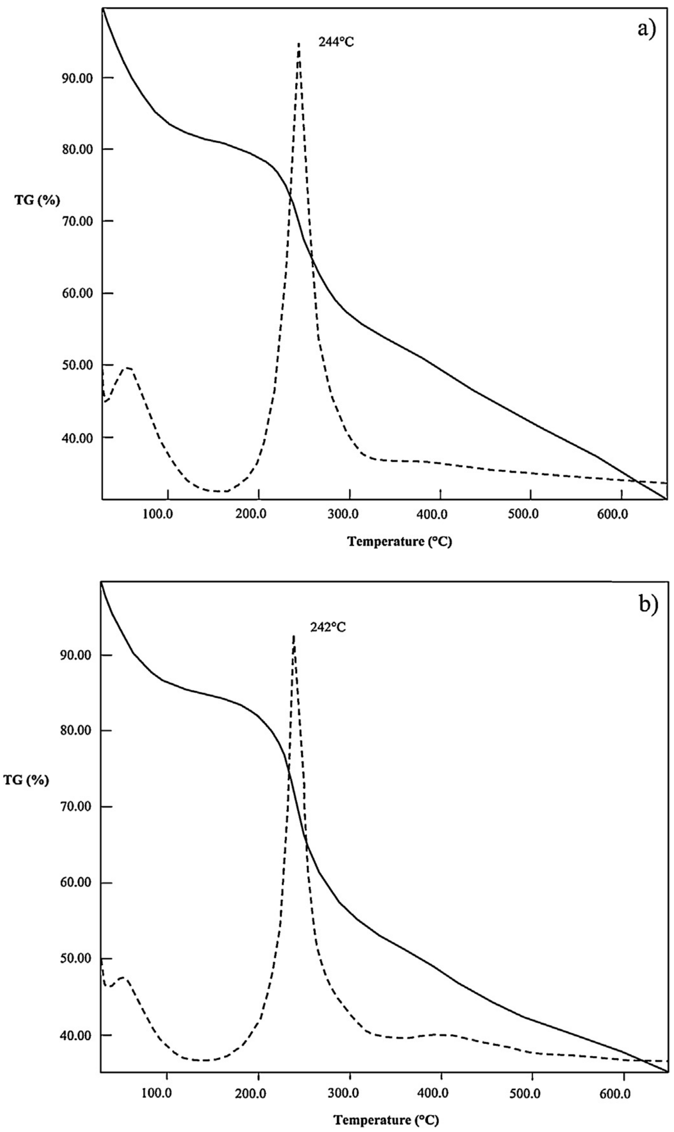


Fig. 3. TG/DTG spectra of OCMCS-3aPd (a), OCMCS-4aPd (b).

at 100 °C for 48 h (Scheme 1). Reaction was followed by TLC. Then the reaction media was allowed to cool at room temperature. The mixture was extracted with 10 mL of water and the aqueous and organic phases were separated in a separatory funnel. The extraction was repeated three times. $MgSO_4$ was added into the organic phase to ensure complete water removal. The products were analyzed and characterized with GC–MS and ^1H NMR.

2.5. Mercury poisoning experiments

Mercury poisoning test were conducted with the model reaction in the optimum conditions (Table 1, entry 2). The model reaction (4-bromoanisole with phenyl boronic acid) was done for 24 h without adding mercury. Yields for catalysts OCMCS-4aPd and OCMCS-3aPd are 60, 56%, respectively. Then, 300 molar equivalents of mercury, relative to the Pd catalyst, was added in to the reaction medium and stirred for another 24 h. After the allowed time the procedure as in Section 2.4 was followed. The expected products (4-methoxy biphenyl) were obtained with lower yields after 48 h. Yields for OCMCS-4aPd and OCMCS-3aPd are 58, 55%, respectively.

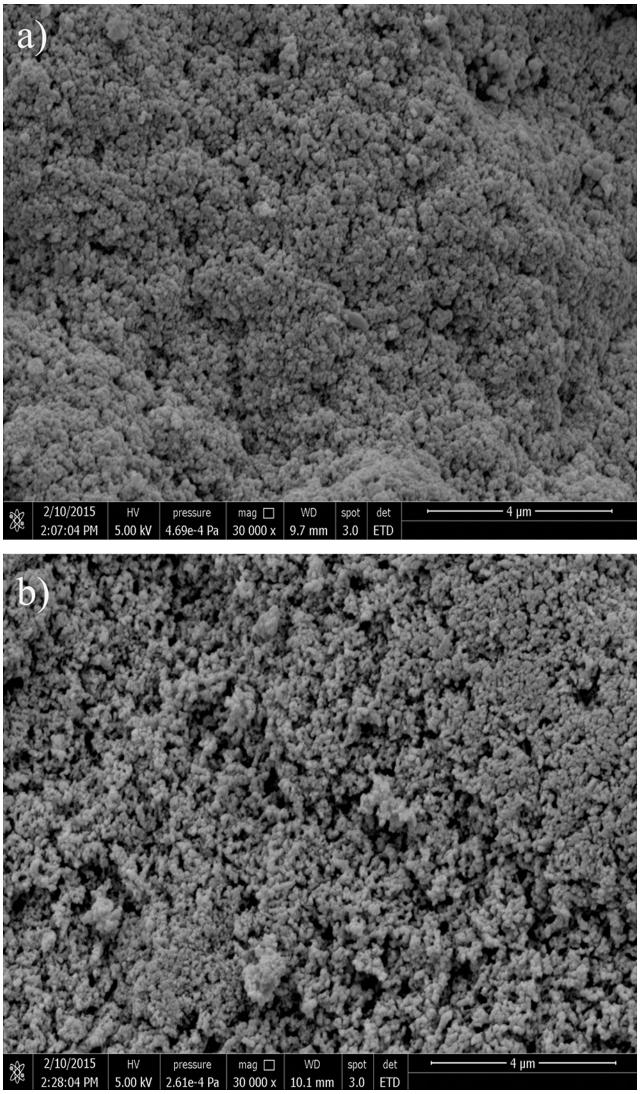


Fig. 4. Scanning electron microscopy pictures of OCMCS-3aPd (a), OCMCS-4aPd (b).

3. Results and discussion

3.1. FTIR spectra

The imine stretching bands of [OCMCS-3a]·$2H_2O$ and [OCMCS-4a]·$2H_2O$ were observed at 1625 and 1635 cm^{-1} in our previous study [22]. In the FTIR spectra of the catalysts, these bands were shifted to lower wavenumbers (OCMCS-3aPd: 1614 cm^{-1} and OCMCS-4aPd: 1618 cm^{-1}) (Fig. 2), which indicated that palladium ions were coordinated with the ligands via nitrogen atoms [23]. Furthermore, the bands at 1729 cm^{-1} (OCMCS-3aPd) and 1728 cm^{-1} (OCMCS-4aPd) can be attributed to the C=O stretching of carboxymethyl groups [22]. The other bands observed in the spectra of OCMCS-3aPd and OCMCS-4aPd were as follows; —NH and —OH stretching: 3349, 3351 cm^{-1}, —CH stretching: 2935, 2929 cm^{-1}, —C—N stretching: 1364, 1371 cm^{-1} (Fig. 2).

3.2. TG-DTG analysis

The maximum thermal decomposition temperature (DTG_{max}) of the modified chitosan is supposed to be lower than that of pristine chitosan due to the deformation of hydrogen bonds and the degree of the crystallinity index of chitosan [24,25]. The DTG_{max} values of OCMCS-3aPd and OCMCS-4aPd were recorded to be 244 °C

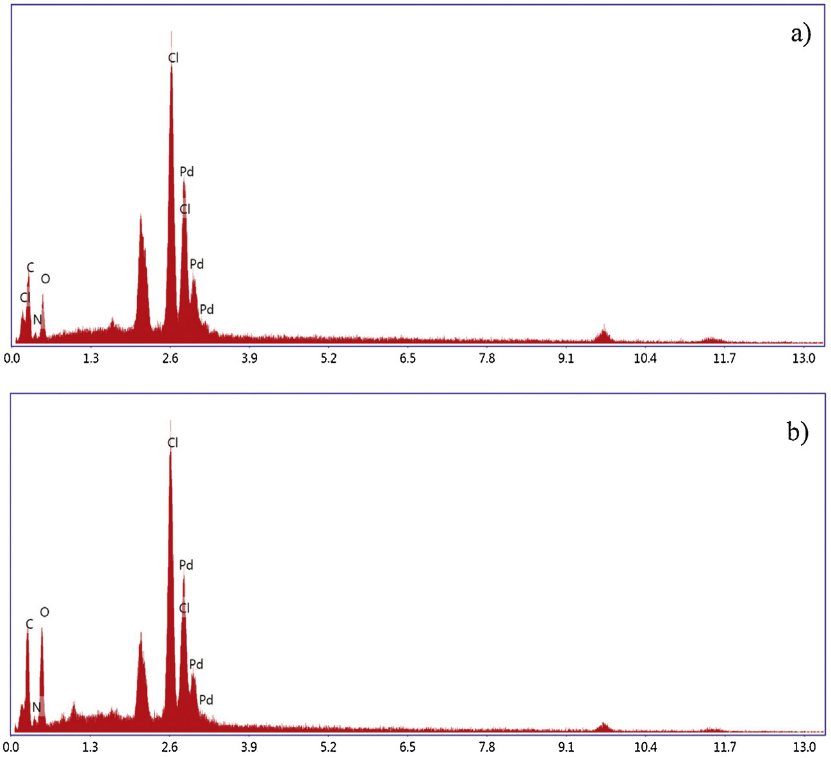


Fig. 5. SEM/EDAX spectra of OCMCS-3aPd (a), OCMCS-4aPd (b).

and 242 °C (Fig. 3), respectively. When compared to chitosan, the reduction in the thermal stability of the catalysts demonstrated the coordination of the metal ions with the ligands. Since C–C coupling reactions are carried out at high temperatures, catalysts are required to remain stable in the range of the reaction temperature to ensure catalyst activity and recyclability [26]. We observed that the catalysts were thermally stable at high temperature, which indicates that the catalysts are suitable for C–C coupling reactions.

3.3. SEM–EDAX

SEM images of OCMCS-3aPd and OCMCS-4aPd exhibited that the surface morphologies of the catalysts were completely different from those of the ligands and chitosan; the catalysts had more regular stacked structure (Fig. 4). These observations demonstrated that palladium ions coordinated with the ligands [27]. Additionally, to confirm the presence of the metal ions, EDAX spectra of the catalysts were recorded. The spectra proved the presence of the palladium and chloride ions that had already been coordinated to the palladium (Fig. 5).

3.4. XRD

When chitosan is modified, its thermal stability and crystallinity are subject to reduce because of the deformation of hydrogen bonds [28,29]. When compared to the chitosan, in the XRD patterns of the catalysts, decreases in the crystallinity values peak intensity and peak broadening were observed (Fig. 6). These findings demonstrated that palladium ions were coordinated with the ligands. The crystallinity values of the catalysts were determined to be [OCMCS-3aPd > OCMCS-4aPd] using the following equation[30].

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

I_{110} is the maximum intensity at $\sim 20^{\circ} I_{\text{am}}$ is the intensity of amorphous diffraction at 16°.

3.5. Electronic spectra (UV–vis)

In an earlier study [22], benzene π–π^* and (C=N) n–π^* transitions of the ligands ([OCMCS-3a]·$2H_2O$: 286 and 313 nm; [OCMCS-4a]·$2H_2O$: 266 and 305 nm) were reported. With complexation of the palladium ions, these transitions were shifted to higher wavelengths. The shifting confirmed the coordination of palladium ions via nitrogen atoms of the ligands [29]. In addition, we observed two new weak d–d transitions at 360–450 nm (OCMCS-3aPd) and 365–470 nm (OCMCS-4aPd). These bands were attributed to $^1A_{1g} \rightarrow {}^1E_{1g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions. These transitions demonstrated that the geometry of the complexes was square planar [31,32].

3.6. Molar conductivity, magnetic properties and ICP-OES

To define the geometry of the complexes, molar conductivity and magnetic moment measurements were performed. The molar conductivities were determined to be 19 Ω^{-1} cm^2 mol^{-1} (OCMCS-3aPd) and 15 Ω^{-1} cm^2 mol^{-1} (OCMCS-4aPd). These low values showed the nonconductivity of the complexes. Magnetic moment measurements revealed that the complexes had diamagnetic properties. These findings supported the square planar geometry of the complexes that had d^8 system [31,33]. The metal content of the complexes (% mass) were determined with ICP-OES (OCMCS-3aPd: 13.02% and OCMCS-4aPd: 15.63%).

3.7. Catalysis of the Suzuki reaction

In the palladium catalyzed Suzuki C–C coupling reactions, the type and amount of the catalyst, reaction time, base system and temperature are important parameters. To optimize the reaction

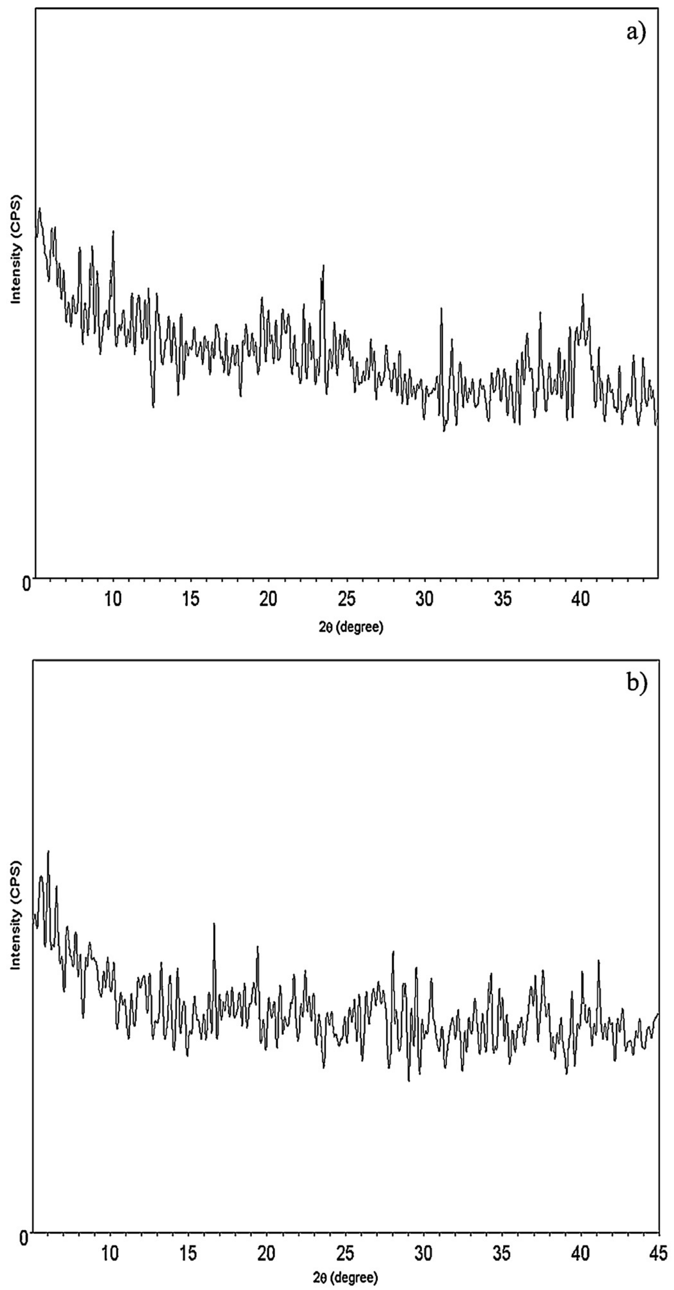


Fig. 6. XRD patterns of OCMCS-3aPd (a), OCMCS-4aPd (b).

conditions (see Fig. S1-S3 and Table S1, S2 in Supplementary data), the reaction of 4-bromoanisole with phenyl boronic acid was preferred as a model reaction. The studies revealed the optimum conditions in the presence of the catalysts; amount of catalyst: 0.04% mol, temperature: 100 °C, base system: K_2CO_3 and reaction time: 48 h (see Fig. S1-S3 and Table S1, S2 in Supplementary data).

Under the optimum conditions, the catalytic activity was tested in Suzuki coupling reaction of aryl halides with phenyl boronic acid. These findings are presented in Table 1. An evaluation of the Suzuki coupling reactions demonstrated that the reactions with aryl bromide (entries 1–7) had a high yield with the exception of the entry 3. Also, when aryl iodides were compared with aryl chlorides, it was observed that the aryl iodides had higher yields (entry 8). The differentiation observed in the reaction yield can be accounted for by the bond dissociation energies and the size of the halide atoms [14]. In an earlier study by Makhubela et al. (2011), the authors reported higher yields for aryl bromide in the C–C coupling reactions of chitosan Schiff bases supported palladium catalyst. On the other hand, lower yields were recorded for the reactions with aryl chlorides (entries 9 and 10). This can be attributed to the poor reactivity of aryl chlorides [34]. Furthermore, the catalysts were more efficient in the reactions of compounds with electron withdrawing groups (entries 6 and 7). Turnover numbers (TON) were calculated [35] for all the products and listed in Table 1. ^{1}H NMR and GC–MS spectra of synthesis of the biaryl compounds are given in the Supplementary section (Fig. S4-S17).

Table 2
Recycling of OCMCS-3aPd and OCMCS-4aPd.

Yield (%)		
The number of cycle	OCMCS-3aPd	OCMCS-4aPd
1st	97	98
2nd	98	98
3rd	96	95
4th	94	94
5th	92	91
6th	91	90
7th	86	89
8th	82	87
9th	79	80
10th	73	75

Reaction conditions: 1.12 mmol of 4-bromoanisole, 1.87 mmol of phenyl boronic acid, 3.75 mmol of K_2CO_3, 0.04 mol% catalyst, 6 mL of toluene, 100 °C, 48 h.

3.8. *Reusability test of catalyst*

The reusability of the catalysts was tested and the findings are given in Table 2. Upon achieving C–C coupling reactions, the catalysts were removed from the reaction media with filtration and the filtrate was rinsed with water and hot methanol to ensure the catalytic activity of the catalysts. The recycling reactions were carried out under the optimum conditions; it was observed that the catalyst retained their activity even after ten run. After 10th run, we observed that yield decrease to 75% (OCMCS-4aPd) and 73% (OCMCS-3aPd). Also at the end of the 10th run, hot filtrate was analyzed with ICP-OES and very low palladium leaching was observed (<1%). The leaching test indicated that the catalysts have heterogeneous nature.

3.9. *Mercury poisoning tests*

It is already known that if addition of mercury stops the catalytic activity, then the reaction mechanism is said to be heterogeneous. If not, it is concluded that the reaction mechanism has a homogenous nature [36–38]. The mercury poisoning tests showed that the reaction mechanism follows a heterogeneous pathway (Table 1, entry 11).

4. Conclusion

In this study, two new *O*-carboxymethyl chitosan Schiff base supported heterogeneous Pd(II) catalysts were synthesized. The mode of bonding (FTIR), thermal stability (TG/DTG), surface morphology (SEM/EDAX), crystallinity index (XRD) and metal content (ICP-OES) of the catalysts were investigated. Moreover, to define the geometry of the catalysts, UV–vis, magnetic moment and molar conductivity measurements were performed. The catalytic activity was tested for the first time in the synthesis of biaryls and the products were characterized with GC–MS and ^{1}H NMR. The selectivity of the catalysts was high in Suzuki coupling reactions. There reusability studies showed that the catalysts retained their activity after ten run. Leaching studies observed that very low leaching of Pd (<%1) and mercury test indicated that these catalysts have heterogeneous nature. In conclusion, the advantages of these catalysts include (1) their ease of separation from the reaction medium, (2) having oxygen insensitivity, (3) stability at high temperatures, (4) long life time and (5) achieving high TON values with small amount of catalysts. These catalysts can be used in both industrial operations and pharmaceutical applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2015.06.008

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