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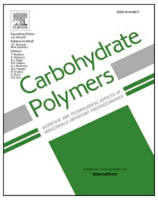

Functionalized chitosan as a novel support for stabilizing palladium in Suzuki reactions

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ABSTRACT

Chitosan is a versatile polysaccharide in different domains due to facile modification and good biodegradability. In this paper, taking advantage of such functional properties, we have developed a stabilizer agent [OCMCS-SB] produced from chitosan, and palladium was successfully immobilized on this designed stabilizer [OCMCS-SB-Pd (II)]. The obtained complex was illuminated by ^{13}C CP-MAS NMR, FT-IR, TGA, XRD, XPS, SEM, TEM and ICP-OES analyses. Due to the interactions of primary hydroxyl groups on chitosan, Schiff base and carboxy groups, the Pd complex showed excellent reactivity (up to 99 %) and stability towards Suzuki reactions in eco-friendly medium. Subsequently, the reusability experiments for OCMCS-SB-Pd(II) formed from chitosan were examined in five consecutive cycles, which showed no appreciable decrease in activity. Furthermore, a reasonably trifunctional complex structure was proposed. The present bio-based system offers a promising approach in utilizing such biopolymers in organic transformations.

1. Introduction

In the past few decades, since the rapidly growing energy consumption and environmental impact concerns, the trend of extensive studies have been dedicated to the eco-sustainable pathway for the demand of green chemistry (De Hoe et al., 2018; Mika, Cséfalvay, & Nemeth, 2018). In this context, several types of solid systems have been explored in the reactions for eliminating ecological contamination, low stability, metal toxicity and recovery barriers associated with the homogeneous catalysts (Thomas et al., 2018). Amongst these reactions, the Suzuki-Miyaura reactions have been poured much interest because of its profound impact and extensive applications in constructing the building blocks over bioactive compounds, advanced materials and pharmaceuticals (Stewart et al., 2016). Although several metal centers are in principle capable of catalyzing this reaction, there is no doubt that the precious palladium catalysts were the protagonist (Biffis, Centomo, Zotto, & Zecca, 2018). Numerous materials have been introduced as solid supports like polymers, carbon nanotubes, zeolite as well as metal oxides for immobilizing Pd catalysts in the synthesis of biaryls for the Suzuki reactions (Hajighorbani & Hekmati, 2016; Salamatmanesh, Heydari, & Nahzomi, 2020; Veisi, Ozturk, Karmakar, Tamoradia, & HemmatiIn, 2020; Wang, Fan, Liu, Li, & Bai, 2020; Xiong et al., 2018; Wang, Liu et al., 2020). In spite of the prominent merits emerging as supporting materials for palladium-based catalysts, their low abundance, toxicity as well as low chemical and mechanical stability would limit their further utilization (Xu et al., 2012; Zhang, Zhong, Xu, & Chen, 2008). On the other hand, the catalyst activity may decrease owing to palladium leaching from the supporting materials (Faria et al., 2014). It is essential that the exploitation for the bio-degradable and bio-derived polymers modification. The functionalized biopolymers are designated as supports, which create more anchoring sites to capture palladium for the preparation of highly efficient catalysts.

Nowadays, biomaterials, which act as acceptable candidate in replacement of petrochemical-based feedstocks, have grabbed considerable study attention. Bio-derived polymers or macromolecules are innoxious and renewable organic polymers including the cell wall of bacteria, plants and some algae. These polymers play an increasingly pivotal role with regards to different fields such as packaging films (Wu, Huang, Li, Xiao, & Wang, 2018), pollutant purification (Elwakeel, Al-Bogami, & Guibal, 2020) and drug delivery (Zhang et al., 2018). Further, the design for bio-derived polymers with interesting intrinsic structure could be a reliable choice in the preparation of heterogeneous novelty catalysts. For example, Li and co-workers (Li, Zhang, & Cai, 2018) immobilized PdNPs on an amphiphilic solid support, which was

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prepared via fluorinated compounds modified cellulose. The catalyst showed excellent catalytic activity and selectivity in the synthesis of 2-methoxy-4-methylphenol under atmospheric hydrogen pressure.

As the most of abundant natural biopolymers second only to cellulose and the *N*-deacetylated derivative of chitin, chitosan (CS) has received growing concerns in the development of different organic transformations (Molnár, 2019). Depending on the presence of reactive $-NH_2$ groups along with $-OH$ groups on the macromolecule backbone, this low-cost and nontoxic biopolymer not only possesses unique affinity for most transition metal species, but also achieves functionalization via various modifications, making it a desirable solid support (Hardy, Hubert, Macquarrie, & Wilson, 2004; Nasir Baig, Vaddula, Gonzalez, & Varma, 2014). For example, Zeng et al. (Zeng, Qi, Yang, Wang, & Zhang, 2014) have reported chitosan directly cross-linked by Pd (II) cation membranes, which was highly efficient in Heck cross-coupling reactions. In another study, a chitosan supported heterogenous catalyst via palladium anchored on the Fe_3O_4/chitosan/pumice hybrid beads was prepared, which exhibited excellent catalytic performance in the synthesis of benzonitriles with $K_4[Fe(CN)_6]$ (Baran, 2020). Accordingly, this advantageous biopolymer is capable of being easily modified and exploited as a matrix to produce the effective heterogeneous catalysts.

Currently, Schiff bases and their metal complexes have witnessed constant development in catalysis field and other applications *e.g.* antibacterial (Rasool, Hasnain, & Nishat, 2014), liquid crystal materials (Shukla, Rao, & Rakshit, 2003) and semiconductor (Aly & Khalaf, 2000). As a versatile ligand containing HC=N moiety, nontoxic Schiff bases are prepared from the condensation of amino groups with aldehyde or ketone, and retain metal species through excellent electronic properties (Borisova, Reshetova, & Ustynyuk, 2007). Several studies have been reported in literature regarding Schiff bases modified biopolymers for catalytic applications. For instance, Leonhardt and colleagues (Leonhardt et al., 2010) synthesized Schiff bases modified chitosan from salicylaldehyde and 2-pyridinecarboxaldehyde and their palladium complexes were utilized for the preparation of desired products with high yields in Suzuki reactions. While satisfactory results were obtained in above studies, there is still much demand for developing novel Schiff bases modified chitosan. The novel catalysis system could provide more coordination sites with metal in order to enhance stability and prevent metal leaching efficiently. Vanillin (4-Hydroxy-3-methoxybenzaldehyde), an aromatic aldehyde compound, is considered as a commonly used food flavoring agents and is extracted from pods of Vanilla planifolia (Karathanos, Mourtzinos, Yannakopoulou, & Andrikopoulos, 2007). This compound has been extensively employed in many industrial procedures containing food, beverages, perfumes and nutraceuticals (Mourtzinos, Konteles, Kalogeropoulos, & Karathanos, 2009; Sinha, Sharma, & Sharma, 2008). Consequently, the exploitation of Vanillin functionalized chitosan as a novel support for stabilizing palladium is an alternative candidate to explore as polymeric support for future applications.

In light of our interest in the production of polysaccharide supported catalysts (Dong et al., 2020), in this study, we designed and prepared Vanillin functionalized carboxymethylation chitosan as the sustainable substrate to support palladium species for the preparation of Pd complex [OCMCS-SB-Pd(II)] (OCMCS: Vanillin functionalized carboxymethylation chitosan; SB: Schiff Base). The Pd complex was applied for Suzuki-Miyaura reactions in eco-friendly media and the tests indicated that it could effectively catalyze and accelerate the formation of biaryl compounds with high reaction yields under mild condition. Owing to the interaction of trifunctional entrapping sites (Schiff base, hydroxy and carboxy groups) with palladium, higher palladium content and yields were obtained than those of CS-Pd(II) in the Suzuki reaction. In addition, the reusability experiments showed that OCMCS-SB-Pd(II) was reused up to five times with acceptable yields and negligible metal leaching. Also, a reasonably trifunctional complex structure was proposed. Noticeably, this study presents a novel strategy to prepare eco-friendly polysaccharide materials, which are expected to have potential utility in sustainable process.

2. Experimental

2.1. Materials and chemicals

Chitosan (low molecular weight, 80–95 % deacetylated), monochloroacetic acid, acetic acid and methanol were obtained from National Medicine Group Chemical Reagent Co., Ltd. Vanillin was purchased from Aladdin Industrial Corporation. Deionized water was used in this study. Sodium tetrachloropalladate (Na_2PdCl_4) was synthesized according to the literature (Baran, Baran, & Menteş, 2018). All other materials were of analytical grade and directly used as received.

2.2. Instrumentation

Fourier transform infrared (FT-IR) spectra were recorded with a Bruker VERTEX70 spectrometer using KBr pellets. XRD measurements were performed at room temperature on a Rigaku SmartLab-SE X-ray powder diffractometer. TGA experiments were carried out on PerkinElmer thermogravimetric analyzer from 40 °C to 800 °C at a heating rate of 10 °C min^{-1} in air flow. Scanning electron microscopy (SEM) image of the samples was taken using the instrument (Hitachi SU 8010). Transmission electron microscopy (TEM) images were acquired on a Tecnai G2 F30 working at 200 kV. ^1H NMR spectra of Suzuki products were obtained from a Bruker AV-400 MHz instrument in $CDCl_3$ using tetramethylsilane (TMS) as the internal reference. The Solid state ^{13}C CP-MAS NMR spectrum was accumulated on a Bruker Advance III-600 MHz spectrophotometer system. X-ray photoelectron spectroscopy (XPS) detections were collected *via* an AXIS-ULTRA DLD-600W Instrument with Al Kα irradiation. The elemental contents of palladium in the catalysts were determined with a Thermo Scientific ICAP 7200 SERIES inductively coupled plasma-optical emission spectrometry (ICP-OES).

2.3. Preparation of OCMCS-SB

At first, 1.5 g chitosan was dissolved in 2 % acetic acid solution (75 mL; V:V). Next, methanol (60 mL) was added to the chitosan solution and the solution was stirred at 75 °C under N_2 atmosphere for 4 h. Then, the solution of Vanillin (4-Hydroxy-3-methoxybenzaldehyde, 2.685 g, 17.7 mmol), which was dissolved in methanol (25 mL), was added into the reaction mixture. The resulting mixture was refluxed for 12 h overnight. After the addition of the solution of 7.5 g monochloroacetic acid in 10 mL of methanol drop by drop, the mixture was allowed to continue at 60 °C for 5 d. The resultant solid was filtered and washed with methanol and ethanol until the washing fluid got clarified. Finally, the solid was dried under vacuum at 60 °C to give the yellow product (OCMCS-SB).

2.4. Preparation of OCMCS-SB-Pd(II)

OCMCS-SB (0.6 g) was dispersed in 20 mL deionized water at room temperature. After adding the aqueous solution of 0.3 g Na_2PdCl_4 (20 mL), the mixture was reacted at 50 °C for 24 h. Following the completion of reaction, the obtained mixture was cooled down and filtrated. The filtrate was rinsed with deionized water and dried under vacuum at 60 °C to afford the light yellow product [OCMCS-SB-Pd(II)].

2.5. General procedure of Suzuki-Miyaura cross-coupling reaction of aryl halides with aryl boronic acids

In a brief, aryl halide (0.50 mmol), arylboronic acid (0.75 mmol), and K_2CO_3 (1 mmol) were dissolved in the mixture of ethanol (3.0 mL) and water (2.0 mL), followed by addition of OCMCS-SB-Pd(II) catalyst (2 mg, 0.46 mol% Pd, referred to aryl halide). The solution was magnetically stirred at 50 °C for a certain period of time. TLC was adopted for indicating the reaction progress. After completion, the reaction mixture was cooled to room temperature and the yield of products were analyzed with GC analysis.

2.6. *General procedure for the recovery of OCMCS-SB-Pd(II) catalyst*

As the reaction completed, the catalyst was taken out effortlessly by the centrifugation process. Then, the separated catalyst was washed carefully with ethanol and water to extract the adsorbed organic section and salt, respectively. Without further treatment, the washed catalyst was reused for next runs following the afore-mentioned procedure.

3. Results and discussion

3.1. *Synthesis and characterization of OCMCS-SB-Pd(II)*

The synthesis of OCMCS-SB-Pd(II) catalyst was carried out in the route as described in Scheme 1. The modification of CS was obtained via the condensation reaction between CS and Vanillin in the refluxing methanol. Subsequently, the modified CS was treated with mono-chloroacetic acid in methanol, achieving the carboxymethylation of CS (OCMCS-SB). After that, the precursor OCMCS-SB was synergized with Na_2PdCl_4 in water to give the resultant catalyst [OCMCS-SB-Pd(II)]. The content of metal in this catalyst as determined using ICP-OES was found to be 12.25 %, which was higher than the loading amount of other chitosan as the solid material for the Pd catalyst (Anuradha, Kumari, Layek, & Pathak, 2017; Sadjadi, Heravi, & Kazemi, 2018).

The ^{13}C CP-MAS spectrum of OCMCS-SB is illustrated in Fig. 1. In the spectrum, the peak at 149.37 ppm assignable to C=N is observed, indicating that the condensation between CS and Vanillin is accomplished (Bhagarea et al., 2020). In addition, the signal at 176.09 ppm belongs to carbonyl carbon atom, confirming the successful carboxymethylation (Baran, Menteş, & Arslan, 2015). Other signals in the spectrum are presented as follows: ^{13}C NMR: 99.11 C(1); 51.67 C(2); 71.78 C(3); 89.32 C(4); 75.47 C(5); 58.10 C(6); 49.96 C(7); 125.29 C(10); 111.69 C(11); 128.10 C(12); 129.71 C(13); 118.50 C(14); 120.05 C(15); 45.2 C(16).

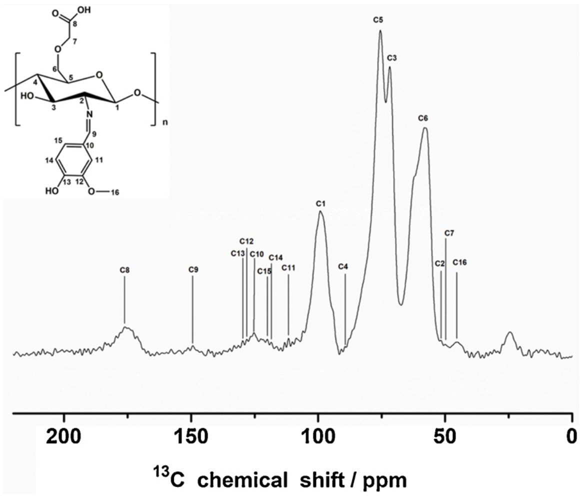
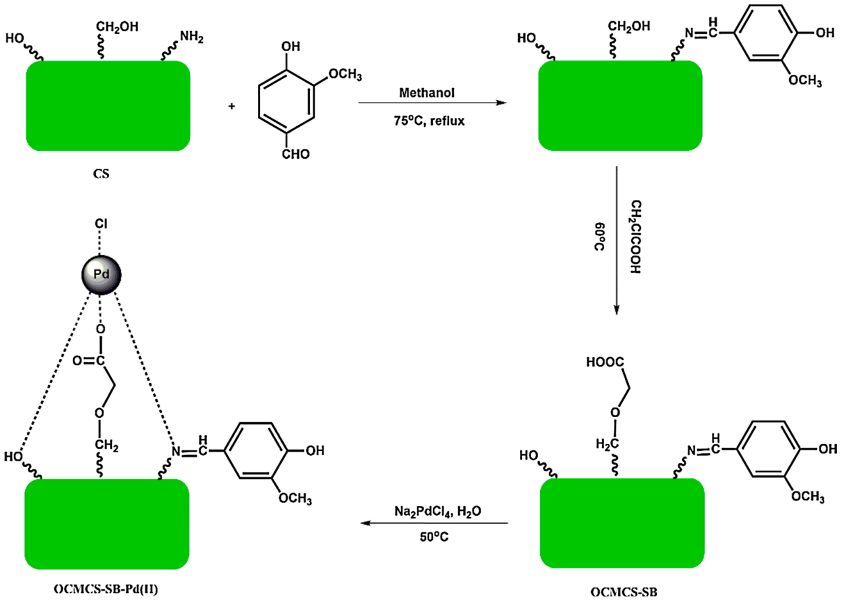


Fig. 1. ^{13}C CP-MAS NMR spectrum of OCMCS-SB.

The FT-IR spectra of chitosan and its derivatives containing CS, OCMCS-SB and OCMCS-SB-Pd(II) are presented in Fig. S1. As can be seen from Fig. S1a–c, the broad peaks appeared at 3454 cm^{-1} are allocated to the stretching vibration of amino ($-NH_2$) and hydroxyl ($-OH$) groups on the chitosan backbone. As shown in Fig. S1b, the appearance of peak located at 1634 cm^{-1} can be imputed to imine groups, which indicated the Schiff base reaction occurred. Meanwhile, the bands at 894 and 781 cm^{-1} are related to the vibration of $-CH$ for the aromatic ring. The symmetric stretching of carbonyl groups is observed at 1522 cm^{-1}, confirming the successful carboxymethylation of CS. The absorption peak at 1735 cm^{-1} (Fig. S1b) referred to the C=O stretching of carboxymethyl disappears in Fig. S1c, indicating the coordination of $-COOH$ and Pd ions (Dong, Wu, Chen, & Wei, 2017). Moreover, the imine band shifts from 1634 cm^{-1} to the lower wavelength (1629 cm^{-1}), associating with the binding of Pd ions to the nitrogen atoms of imine groups (Sajjadi et al., 2020). Above all, together with these changes in FT-IR spectra and above ^{13}C-NMR data, it is clearly speculated that the formation of OCMCS-SB-Pd(II), which is dependent on the trifunctional groups (Schiff base, hydroxy and carboxy groups) entrapping palladium.

It is especially significant for designing thermally stable catalysts in the industrial applications that requiring high thermal treatment. The TGA thermograms of CS and OCMCS-SB-Pd(II) samples were undertaken under air atmosphere to determine the thermal stability. As presented in Fig. 2b, the first weight loss (8%) ranging from 40 to 200 °C is due to the exit of adsorbed moisture and the loss of organic solvent molecules



Scheme 1. The schematic route for synthesis of OCMCS-SB-Pd(II).

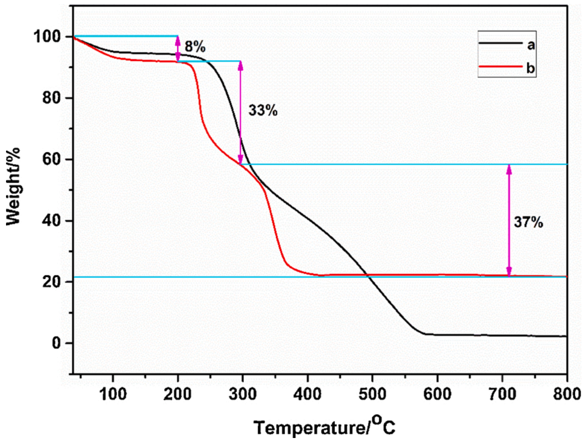


Fig. 2. TGA curves of CS (a) and OCMCS-SB-Pd(II) (b).

physically adsorbed on the surface of the catalyst. The second decomposition (33 %) happens between 200 and 295 °C, which is related to the organic layers anchored onto the matrix surface. The final loss (37 %) around 295–800 °C is associated with the degradation of glycoside bonds chitosan itself, which is in good agreement with previous study (Rangraz, Nemati, & Elhampour, 2018). In addition, the OCMCS-SB-Pd (II) (200 °C) was detected to be thermally less stable than CS (209 °C), which suggests that modification of chitosan including Schiff base functionalization and coordination of palladium are achieved (Antony, Theodore David Manickam, Saravanan, Karuppasamy, & Balakumara, 2013). Therefore, these obtained data confirm this catalyst has good stability in high temperature, implying that the catalyst is acceptable under the following reaction conditions.

The XRD patterns of CS and OCMCS-SB-Pd(II) are given in Fig. 3. As shown in Fig. 3a, the peaks at ∼12° and 20° prove the existence of amorphous chitosan. Nevertheless, the peak at ∼12° disappears, the intensity of the peak at ∼20° decreases and becomes broadening, all of which confirm the successful chemical modification. These features are may be due to the deformation of hydrogen bonds and a reduced number of free amino groups on the backbone, and chitosan becomes more amorphous after synthesis of the Schiff base. The results are in accordance with previously reported work (Anuradha, Layek, Agrahari, & Pathak, 2017). No characteristic peaks of Pd nanoparticles are observed in Fig. 3b, which are probably attributed to palladium existing as Pd(II) in the fresh catalyst (Yang, Ma, & Bian, 2016), and are also confirmed by both TEM and XPS analyses.

X-ray photoelectron spectroscopy (XPS) was employed to further understand the chemical composition and the results are given in Fig. 4. The full survey XPS spectrum of OCMCS-SB-Pd(II) catalyst reveals that each element (C, N, O and Pd) exists in this catalyst, which evidences the formation of the complex (Fig. 4a). In Fig. 4b, two characteristic peaks locate at Pd $3d_{3/2}$ (342.3 eV) and Pd $3d_{5/2}$ (337.1 eV) respectively, which are assigned to the Pd(II) state (Sarkar, Lutfor Rahman, & Yusoff, 2015). Furthermore, in comparison of the binding energy Pd(II) 3d in Na_2PdCl_4 as depicted in Fig. S2 (343.6 eV and 338.2 eV), the shift to the lower peak is observed, which arises from electron-donation of Schiff base, hydroxy and carboxy groups (Li et al., 2012).

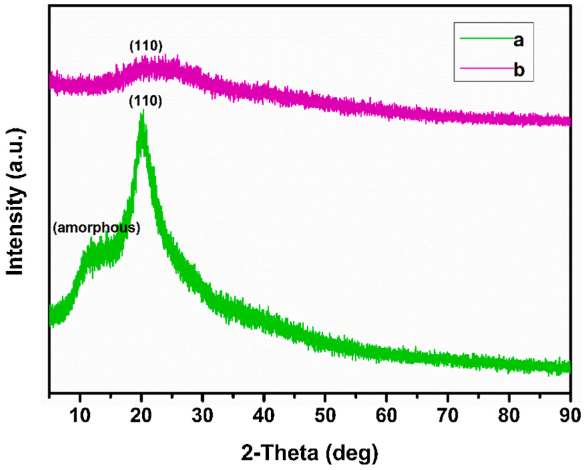


Fig. 3. The X-ray diffraction patterns of CS (a) and OCMCS-SB-Pd(II) (b).

The corresponding high-resolution C 1s spectrum is shown in Fig. 4c. The binding energy at 289.7, 288.0, 286.7, 285.2 and 283.6 eV can be ascribed to O−C=O, C−OH, C=N, C−C/C=C and C−N/O−C−O, respectively (Balakrishnan, Appunni, & Gopalram, 2020; Luo et al., 2020). In the O 1s region (Fig. 4d), the peaks located at 533.3, 531.8 and 531.2 eV are in accordance with C−OH, −COOH and C−O−C, implying the successful synthesis of modified chitosan (Ignatova et al., 2020). Additionally, two peaks (401.1 and 399.1 eV) in the deconvoluted N 1s spectrum (Fig. 4e) are indexed to C=N and C−N, further illustrating the formation of Schiff base (Alhokbany, Ahamad, Naushad, & Alshehri, 2019). In combination of those data obtained from FT-IR, it can be concluded that the interactions of Schiff base, hydroxy and carboxy groups on the chitosan backbone with palladium via covalent bonding, on the basic of the model depicted in Scheme 1.

As seen from the TEM images of OCMCS-SB-Pd(II) catalyst with different magnifications (Fig. 5a and b), it is obvious that no palladium (0) particles are dispersed on the surface of chitosan, which corresponds well with the XPS results of Pd(II) oxidation state for this catalyst. The SEM analysis of the samples were performed to determine their surface morphologies and the respective images are given in Fig. 6. As displayed in Fig. 6a, CS possesses a smooth surface. As compared to CS, OCMCS-SB (Fig. 6b) appears rough surface, suggesting Schiff base modification is obtained. The change on the surface morphology of OCMCS-SB-Pd(II) catalyst (Fig. 6c) in comparison to CS and OCMCS-SB verifies the coordination of palladium ions with OCMCS-SB (Demetgül, 2012).

3.2. *Catalytic application in Suzuki coupling reactions*

3.2.1. *Assessment of the catalytic efficacy*

The catalytic efficacy of OCMCS-SB-Pd(II) catalyst was estimated in the Suzuki coupling reactions. Bromobenzene and phenylboronic acid were chosen as model reagents. In this model reaction, the effects of the parameters like the amount of catalyst, reaction time, temperature, solvents and base system were studied to detect the optimal reaction conditions (Table S1).

Reaction time and temperature affect the kinetics of Suzuki reaction crucially. The shorter reaction time are desirable for catalysis systems, which decreases labour and operational cost. As illustrated in Table S1, the productivity increased from 53 to 96 % when the reaction time raised from 0.5 to 2 h (Table S1, entries 1–3). Nevertheless, the catalytic performance does not improve greatly though prolonging the time to 3 h (Table S1, entry 4). Furthermore, the yield ranged from 75 to 96 % as the temperature rose from 25 to 50 °C (Table S1, entries 5–6). However, the decrease in reaction yield was observed when the temperature reached 80 and 100 °C (Table S1, entries 7–8). Consequently, 50 °C was selected as the proper temperature at 2 h in model reaction (Table S1, entry 6).

The amount of catalyst is also vital for the reaction, and different amounts of the catalyst were tested. As expected, no product was obtained in the absence of Pd catalyst (Table S1, entry 9). With the increase of the amount of catalyst from 0.12 mol% to 0.46 mol%, the yields have increased apparently from 27 to 96 %, correspondingly, which is probably due to the frequent connection between substrates and much more active sites (Table S1, entries 10–13). In addition, 0.46 mol% of catalyst was enough to push the reaction to completion because of no obvious improvements in catalytic performance with further increasing Pd loading (Table S1, entries 13–15). Therefore, A level of 0.46 mol% of

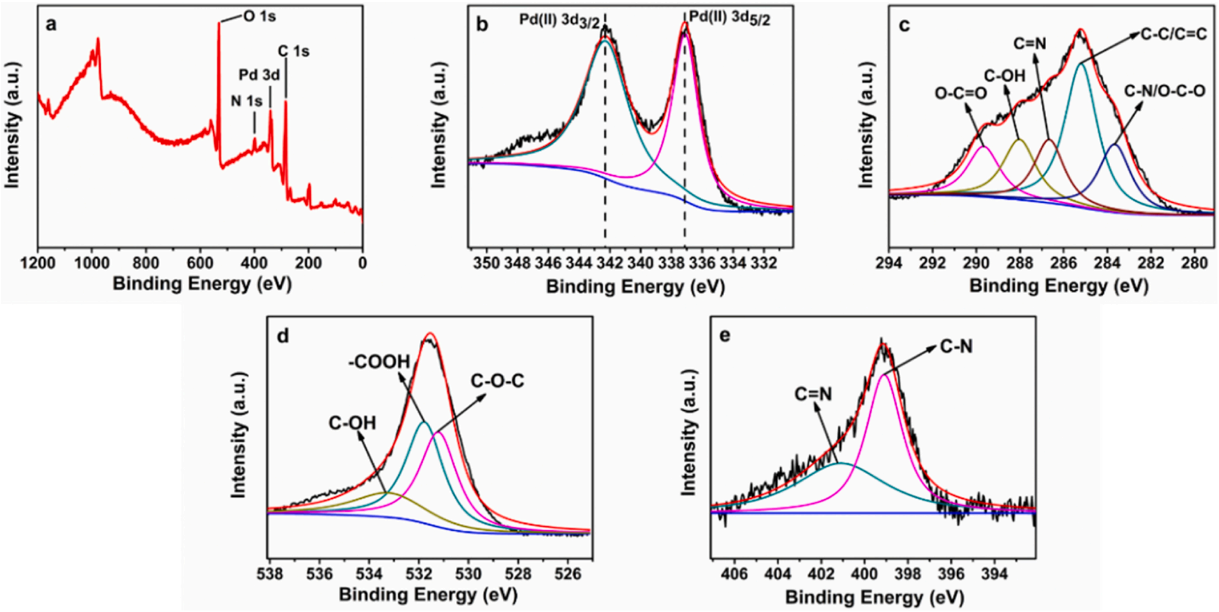


Fig. 4. Full XPS spectrum (a) and high-resolution of XPS survey spectra for OCMCS-SB-Pd(II): Pd 3d (b), C 1s (c), O 1s (d), N 1s (e).

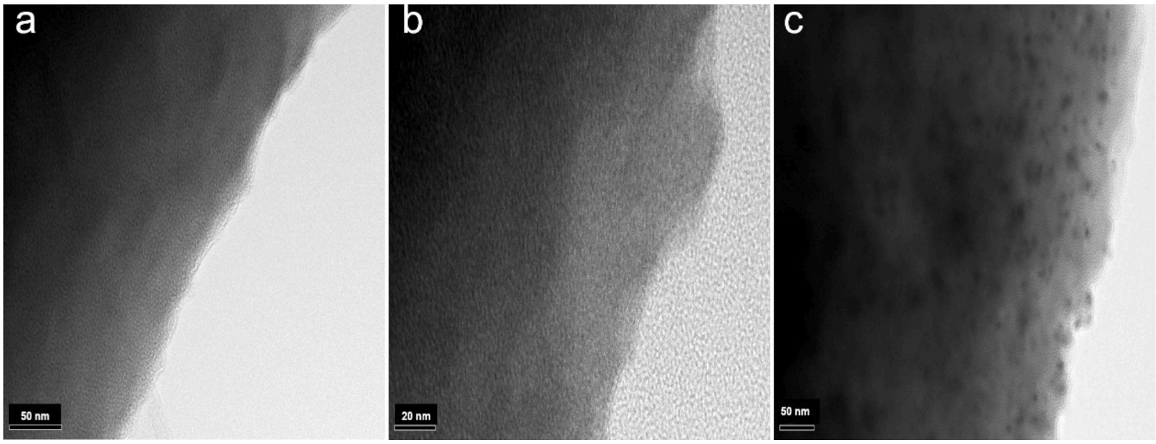


Fig. 5. TEM images of fresh OCMCS-SB-Pd(II) with different magnifications (a and b) and recovered OCMCS-SB-Pd(II) after the 5th cycle (c).

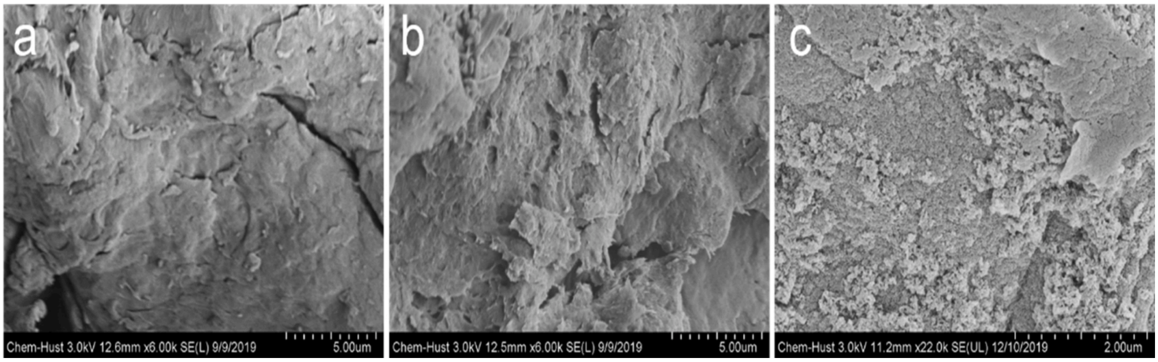


Fig. 6. SEM images of CS (a), OCMCS-SB (b) and fresh OCMCS-SB-Pd(II) (c).

catalyst (Table S1, entry 2) was identified as the optimal amount to catalyze this reaction.

The catalytic activity and reaction rate were profoundly influenced by the solvents (Table S1, entries 16–26). For conventional solvents, a mixture of EtOH and H_2O (3:2) proved to be the most favorable medium which proceeded in highest yields, probably because of the higher solubility of phenylboronic acid and sodium carbonate in the solvents. Since bases play important roles in the catalytic mechanism, high efficiency and low cost for the base are demanded. Various bases including inorganic and organic bases were explored (Table S1, entries 27–35).

The results indicated that K_2CO_3 was found to be more appropriate for the reaction.

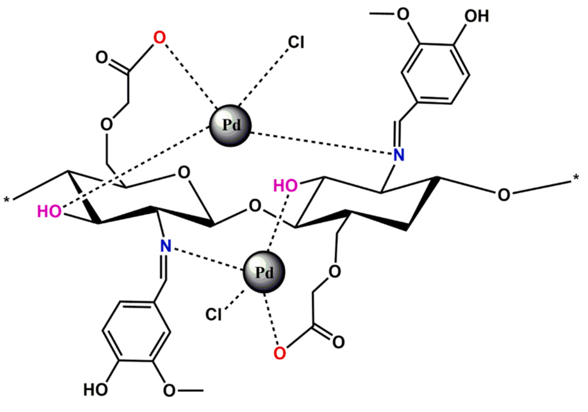
Based on the optimal results, the best result was obtained when the reaction was conducted in the presence of 0.46 mol% Pd catalyst with K_2CO_3 serving as base in EtOH/H_2O (3:2) at 50 °C for 2.0 h to give best yield for the corresponding products.

On the basic of the results from the catalytic performance, ICP and XPS analysis, we proposed a reasonably trifunctional complex structure as shown in Scheme 2. In the presence of CS-Pd(II) catalyst, the model reaction was performed. Compared with those of OCMCS-SB-Pd(II) (12.25 % and 96 %) (Table S1, entry 3), weaken catalytic activity and lower Pd content (10.02 % and 79 %) were observed (Table S1, entry 36), revealing the capturing sites (Schiff base, hydroxy and carboxy moieties) with palladium, which was also demonstrated by solid state ^{13}CNMR spectrum. Dependent on higher affinity to palladium with Schiff base and carboxy groups than direct coordination, OCMCS-SB-Pd (II) was able to entrap palladium more tightly via covalent bond (Liu, He, Durham, Zhao, & Roberts, 2008). Moreover, the hydroxy groups coordinated the metal by covalent bond (Calò et al., 2004). Eventually, this trifunctional palladium complex can prevent palladium leaching effectually (see Section 3.2.2), which is attributed to the three available binding sites (Schiff base, hydroxy and carboxy groups).

Having established the optimal conditions for this reaction, we investigated the applicability of the Suzuki reaction with different aryl halides and arylboronic acids. As presented in Table 1, most reactions underwent smoothly to afford the corresponding biphenyls in moderate to excellent yields (up to 99 %). For bromoanisole (Table 1, entries 5–7), the highest yield was obtained (98 %) when the methoxy group was at the para position (Table 1, entry 7), followed by the meta and ortho positions (Table 1, entries 6 and 5), indicating the position of substituted groups could affect the yield of products. As expected, the phenylboronic acids containing EWG (electron withdrawing groups) afforded the desired biaryls in notably lower yields (Table 1, entries 9–10), with exception of *o*-fluorophenylboronic acid (Table 1, entry 8) which gave the biaryl product in excellent yield in only 3 h of reaction time. Owing to poorer tendency of C-Cl bond in oxidative addition, aryl chlorides afforded inferior results than their iodo or bromo analogues (Table 1, entry 18 vs entries 1 and 17) and the yield was very low though prolonging the reaction time (Littke & Fu, 2002).

3.2.2. Separation and reusability of OCMCS-SB-Pd(II)

Considering economic and ecological demands, the assessment of the recycling capability for OCMCS-SB-Pd(II) was performed in the coupling reaction of bromobenzene with phenylboronic acid under the best reaction conditions. After completion in each cycle, the catalyst was separated by simple centrifugation and then was washed with anhydrous ethanol and deionized water, respectively. Next, the catalyst was reused for the next cycle in the same reaction. As can be seen from Table 2, the catalyst still produced 80 % yield of the corresponding biaryl even after the 5th cycle. Compared to the fresh catalyst (12.25 %), the ICP analysis revealed that the palladium content was 12.18 %. In addition, the recycling experiments of CS-Pd(II) were performed and these results were presented in Table S2 (See Supplementary data S6). In comparison of CS-Pd(II) (Table S2), the OCMCS-Sb-Pd(II) catalyst could be reused five cycles and had not significantly lost its activity, while the former catalyst could be reused three cycles and the catalytic activity of CS-Pd(II) decreased from 67 to 47 %. These results demonstrated that the advantage of vanillin functionalized CS, which is necessary for the stabilization. It is reasonable to believe that the electrostatic interaction of palladium with binding sites (Schiff base, hydroxy and carboxy groups) is strong enough for holding metal ions, thus immobilizing palladium effectually with high stability. Moreover, partial agglomeration was observed from TEM image after recycling, which might result in the slight loss of the yield (Fig. 5c) (Narayanan & El-Sayed, 2003; Wang, Shen, Zou, & He, 2005). Overall, the Schiff base functionalized chitosan catalyst might be an excellently potential candidate for reusable catalyst in Suzuki coupling reaction.



Scheme 2. Reasonably trifunctional complex structure of OCMCS-SB-Pd(II).

FT-IR analysis was conducted for the recycled catalyst to investigate the changes in the chemical structure after five cycles (Fig. S3). It was observed that the chemical structure was maintained during successive reactions. Moreover, as shown for the SEM image of the recovered catalyst in Fig. S4, there was a light change in the morphology, which might account for the slight decrease of catalytic performance.

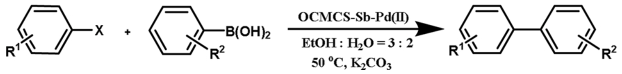
In order to determine whether or not there is leaching out of palladium from the Pd catalyst, the hot filtration test was performed (Heidari, Hekmati, & Veisi, 2017). After proceeding the model reaction for 0.5 h, the catalyst was quickly filtered at hot condition and the filtrate was stirred for further 3 h. In final, no significant increase for the yield of isolated product was observed. In addition, the palladium leaching determined by ICP analysis was insignificant (<0.6 %) after the 5th cycle.

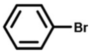
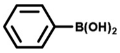
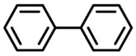
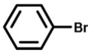
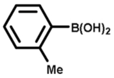
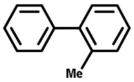
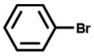
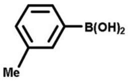
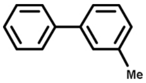
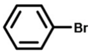
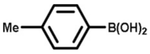
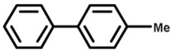
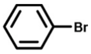
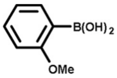
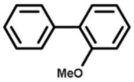
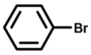
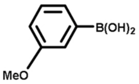
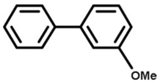
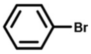
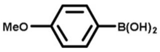
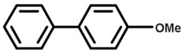
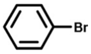
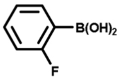
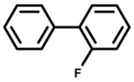
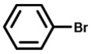
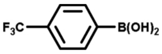
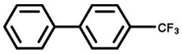
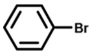
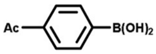
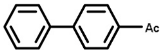
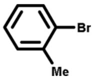
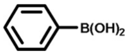
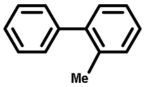
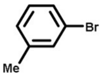
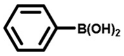
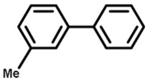
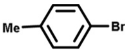
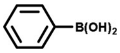
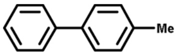
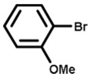
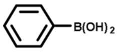
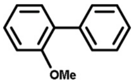
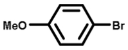
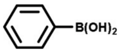
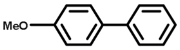
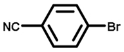
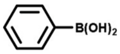
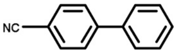
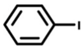
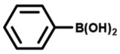
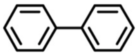
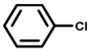
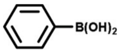
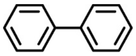
For the purpose of identifying the worthiness of present catalysis system, the catalytic performance of this system was compared to that of earlier studies in the Suzuki coupling reaction and the results are given in Table S3 (See Supplementary data S7) (Cotugno et al., 2014; Hasan, 2020; Jadhav, Kumbhar, & Salunkhe, 2015; Naghipour & Fakhri, 2016; Peng et al., 2016; Sedghi, Heidari, Shahmohamadi, Zarshenas, & Varma, 2019; Sin, Yi, & Lee, 2010). Although each of these systems has its own advantages, some of them often suffer from some defects including utilization of organic solvents, long reaction times and lower yield. The as-synthesized Pd complex [OCMCS-SB-Pd(II)] is noticeably comparable in terms of utilization of green medium, low reaction temperatures, short reaction time as well as high yield of the desired product, and these merits make this developed methodology a valuable tool. Consequently, it can be accomplished that the catalyst is a promising candidate as our concept, making chitosan as a support possessing trifunctional securing sites with palladium.

4. Conclusions

In conclusion, we have designed and prepared Schiff base functionalized chitosan as a novel stabilizer agent for palladium [OCMCS-SB-Pd (II)]. This chitosan supported Pd complex proves to be efficient for Suzuki coupling reactions. Due to the interactions of binding sites (Schiff base, hydroxy and carboxy groups) with palladium, higher palladium content (12.25 % vs 10.02 %) and catalytic activity (96 % vs 79 %) are obtained for OCMCS-SB-Pd(II) than those of CS-Pd(II), which is directly fabricated via depositing palladium onto pristine chitosan. The OCMCS-SB-Pd(II) produced from chitosan possesses another advantages including short reaction time, cost-effective, high palladium loading and use of aqueous ethanol instead of toxic solvents such as DMF in addition to high stability in this catalytic process. The coupling reactions catalyzed by this Pd complex displays an acceptable decline in catalytic activity after the 5th cycle with trace metal leaching (<0.6 %). This study provides a polysaccharide supported catalyst for the synthesis of

Table 1
OCMCS-SB-Pd(II) catalyzed Suzuki coupling reactions of aryl halides and arylboronic acids.



Entry [a]	Aryl halide	Arylboronic acid	Product	Time (h)[b]	Yield (%) [c]
1				2	96
2				2	90
3				2	93
4				2	95
5				2	76
6				2	84
7				1.5	98
8				3	98
9				2.5	40
10				2	48
11				3	96
12				2	99
13				2	98
14				2.5	97
15				2	99
16				1.5	95
17				1.5	99
18				3.5	25

[a] Reaction conditions: aryl halides (0.50 mmol), arylboronic acids (0.75 mmol), K_2CO_3 (1.0 mmol), OCMCS-SB-Pd(II) (0.46 mol%), $EtOH/H_2O = 3:2$ (5 mL), at 50 °C in air.

[b] Detected by TLC.

[c] Yield was determined by GC using n-dodecane as an internal standard.

Table 2
Recyclability test of OCMCS-SB-Pd(II) in Suzuki coupling reaction.

Recycle [a]	1st	2nd	3rd	4th	5th
Time (h) [b]	2	2	2.5	3	4
Yield (%) [c]	94	90	84	81	80

[a] Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), K_2CO_3 (1.0 mmol), OCMCS-SB-Pd(II) (0.46 mol% Pd), $EtOH/H_2O = 3:2$ (5 mL), at 50 °C for available time in air.

[b] Detected by TLC.

[c] Yield was determined by GC using n-dodecane as an internal standard.

biaryl compounds within the framework of green chemistry and may be extendable to a range of other important catalytic applications in the long run.

CRediT authorship contribution statement

Yahao Dong: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing - original draft, Writing - review & editing. **Jiajun Bi:** Investigation, Formal analysis, Writing - review & editing. **Shujun Ming:** Validation, Writing - review & editing. **Shoute Zhang:** Formal analysis, Writing - review & editing. **Dajian Zhu:** Writing - review & editing. **Di Meng:** Writing - review & editing. **Tao Li:**

Supervision, Conceptualization, Methodology, Writing - review & editing, Project administration, Funding acquisition.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.carbpol.2021.117815.

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