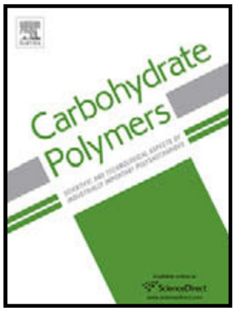

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N-Methylimidazole functionalized carboxymethycellulose-supported Pd catalyst and its applications in Suzuki cross-coupling reaction

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Highlights

- NHC functionalized CMC-supported Pd catalyst was well-designed and synthesized.
- The catalyst exhibited excellent activity and stability in Suzuki cross-coupling reactions.
- A plausible trifunctional catalyst complex was proposed.

Abstract

In this paper，*N*-Methylimidazole functionalized carboxymethylcellulose-supported palladium nanoparticles (CMC-NHC-Pd) was synthesized and characterized by TEM,

SEM, EDX, CP/MAS ^{13}C-NMR, FT-IR, TGA, XRD, and XPS analysis. The prepared nanoparticles can be used as an environmentally-friendly and trifunctional catalyst. The well-designed CMC supported palladium nanoparticles catalyst with polydentate ligands is also stable and efficient for Suzuki cross-coupling reactions under mild conditions through the cooperative interaction of trifunctional capturing sites with palladium, $-COO^-$, -OH and *N*-Methylimidazole. This catalyst can be readily recovered by a few cycles of simple filtration. This work proposes a plausible trifunctional catalyst complex.

Keywords: carboxymethylcellulose, functionalization, palladium nanoparticles, trifunctional catalyst, Suzuki cross-coupling reaction

1. Introduction

Nowadays, in order to cope with the growing demand for green chemistry, the environmentally-sustainable conversion technologies for diverse chemical catalysts have played an essential role in several industrial processes such as chemical production, environmental protection, and energy conversion (Campelo, Luna, Luque, Marinas, & Romero, 2009). Solid supported palladium catalysts (such as polymers, carbons, silica, and clay) that show simple separation and excellent activity in the Suzuki cross-coupling reactions have been considered to be utilized under benign conditions for the synthesis of biaryl compounds (Baran, Inanan, & Menteş, 2016;

Baran, Açıksöz, & Menteş, 2016; Geng, Li, Qi, Fan, Zhou, Chen, et.al. 2016; Baran, Sarginb, Kayab, & Menteş, 2016; Zhang, Wen, Liu, Wang, & Su, 2014; Cassez, Ponchel, Hapiot, & Monflier, 2006; Crudden, Sateesh, & Lewis, 2005; Borja, Monge-Marcet, Pleixats, Parella, Cattoën, & Man, 2012; Baran, Sarginb, Menteş, & Kayab, 2016; Kaur, & Singh, 2015; Varadwaj, Rana, & Parida, 2014； Ghorbani-Vaghei，Hemmati， & Veisi， 2014; Baran, Sarginb, Kayab, Menteş, & Ceter, 2017). Most supports are favored materials with properties such as ease of source, low-cost, reusability and eco-friendliness (Baran, Sarginb, Kayab, & Menteş, 2016; Barana, & Menteş, 2016). The development of easily functionalized supporting materials is beneficial due to the creation of more efficient binding sites through simple surface and structural modifications, which leads to the prevention of metal leaching.

Cellulose and its derivatives are available as versatile solid supports for catalysts because of high tolerance to most solvents, abundance, easy functionalization and biodegradability, thereby providing great potential for application in a wide range of synthesis processes. (An, Long, & Nie, 2017; Wang, Hu, Xue, & Wei, 2014; Yasukawa, Miyamura, & Kobayashi, 2015; Zhou, Wang, Yang, Tang, Sun, & Tang, 2012; Chen, Zhong, Peng, Lin, & Sun, 2014; Hu, Dong, Wu, & Wei, 2016). As one of the cellulose derivatives, carboxymethylcellulose (CMC) is an attractive candidate due to its large specific surface area and high density distribution of carboxyl groups on the surface (Bokias, Mylonas, & Staikos, 2001). These features provide potential opportunities to develop environmentally friendly constituents and new sustainable green chemistries. (Xiao, Lu, Li, & Li, 2015; Zhang, Bacik, Roberts, & Zhao, 2013) However, very few studies have been carried out using functionalized CMC as a support for catalytic applications. Cui et al. prepared a recyclable CMC-supported catalyst and utilized it in Heck coupling reactions (Xu, Xu, Zhang, Zhang, & Cui, 2008). Li et al. used palladium nanoparticles anchored on CMC as a catalyst for Suzuki and Heck reactions (Xiao, Lu, & Li, 2015). Despite these achievements, these catalysts were fabricated via direct deposition of Pd particles onto CMC. Further efforts should be made to exploit more efficient catalysts through the functionalization of carboxymethylcellulose, which is capable of enhancing the binding interaction between metals and CMC in terms of relatively high catalytic efficiency and stability.

Recently, attention has been paid to the *N*-heterocyclic carbenes (NHCs) as ligands which has resulted in several advances in transition-metal-catalyzed reactions (Chatterjee, & Ward, 2016; Lakshmi Kantam, Srinivas, Yadav, Likhar, & Bhargava, 2009; Kantchev, O’Brien, & Organ, 2007; Valente, Calimsiz, Hoi, Mallik, Sayah, & Organ, 2012). NHC ligands are resistant to air oxidation and form a strong bond to the metal center, which is essential to avoid metal leaching during catalytic processes (Karimi, & Akhavan, 2011). Furthermore, complexes with NHCs show higher stability and lower toxicity, thus exhibiting excellent catalytic activities (Lee, Kim, Jun, Kang, Park, & Lee, 2008; Martínez, et al., 2015). We hypothesize combining the excellent characteristics of CMC and *N*-Methylimidazole would be an ideal substrate to immobilize palladium nanoparticles.

In the present study, we prepared an environmentally-friendly *N*-Methylimidazole-functionalized CMC-supported catalyst (CMC-NHC-Pd) from a green chemistry perspective, which depended on the cooperative interaction of trifunctional capturing sites -COO$^-$, -OH and *N*-Methylimidazole with palladium. By providing more efficient binding sites, the trifunctional catalyst could effectively catalyze Suzuki reactions. In addition, this catalyst can be readily recovered by simple filtration with a few cycles. Finally, the catalytic performance of this catalyst was investigated and a plausible trifunctional catalyst complex was proposed.

2. Experimental section

2.1. Materials

Carboxymethylcellulose (CMC-Na), triethylamine (Et3N), dimethylsulfoxide (DMSO), anhydrous lithium chloride (LiCl), all of which were analytical grade (AR) and purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, P. R. China). Anhydrous ethanol, Dichloromethane (CH_2Cl_2) and Acetone were obtained from Tianjin Jiangtian Chemical Technology Co., Ltd. *N*-Methylimidazole was provided by Sinopharm Chemical Reagent Beijing Co., Ltd and used as received. Dimethylsulfoxide (DMSO) and CH_2Cl_2 were desiccated with CaH_2, distilled under reduced pressure and stored over molecular sieves. All other compounds, unless otherwise stated, were used without further purification. Deionized water was used in the present experiments. CMC tosylate (CMC-OTs) was prepared from CMC-Na as reported in the literature (Orehek, Petek, Dogsa, & Stopar, 2014).

2.2. Instrumentation

Fourier transform infrared (FT-IR) spectra were obtained in KBr pellets with a BIO-RAD FT/IR 3000 spectrophotometer. ^{1}HNMR spectra of samples from Suzuki coupling were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as an internal reference. Transmission electron microscope (TEM) images were observed with a Tecnai G2 F20 TOPCON microscope on samples prepared on Formvar-coated Cu grids. Thermogravity analysis (TGA) curves of catalysts were obtained under nitrogen flow at a sample heating rate of 10°C min^{-1} using a STA 409 PC thermal analyzer (NETZSCH). X-ray Photoelectron Spectroscopy (XPS) measurements were performed on an electron spectrometer PHI1600 ESCA System (Perkin-Elmer). The Pd loading on the carriers was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian 715-ES). The CP/MAS ^{13}C-NMR was measured using a Bruker Advance Ⅲ-600 MHz spectrometer. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) were performed using a Hitachi S-8010 instrument. The X-ray diffraction (XRD) spectra of the samples were recorded on an X-ray diffractometer (D/MAX-2500). Preparative TLC (20 cm×20 cm) was performed on Silica Gel 60 F254.

2.3. Preparation of CMC-NHC-Cl

A mixture of CMC-OTs (5.85 g) and DMSO (150 ml) in a round-bottom 250ml flask was vigorously stirred at 60 °C for 24 h before dissolving CMC-OTs completely with stirring at room temperature. Then, *N*-Methylimidazole (3.28 g, 40.0 mmol) was added to the above solution under inert atmosphere of N_2 and mixed for 12 h at 100 °C under continuous mechanical stirring. After being cooled to room temperature, the mixture was precipitated by adding dropwise to a beaker of acetone and was stirred about 5 h. Next, the mixture was filtered and the white solid product $[CMC\text{-}NHC][OTs]^{-}$ was obtained. Then, the solid product was dissolved in a solution of LiCl (1.69 g, 40.0 mmol) in acetone (50 mL) to use Cl^{-} instead of OTs^{-}. The precipitate (CMC-NHC-Cl) was obtained through filtering. Finally the solid was washed with acetone and was vacuum dried for 24 h at 50 °C to provide the pure product.

2.4. Preparation of CMC-NHC-Pd complex

CMC-NHC-Cl (0.8 g), $Pd(OAc)_2$ (0.08 g, 0.35 mmol) and deionized water (25 ml) were added into a 50 mL flask with a magnetic stirrer for 24 h at 60 °C. After the reaction mixture cooled to room temperature, it was filtered off. Washing with anhydrous alcohol (3 × 25 mL), acetone (3 × 25 mL) and drying at 50 °C under reduced pressure overnight formed a palladium complex (CMC-NHC-Pd) as a dark power.

2.5. General protocol for Heterogeneous Suzuki Cross-Coupling Reaction of aryl halides with arylboronic acids

Under atmospheric conditions, the aryl halide (0.25 mmol), arylboronic acid (0.375 mmol), CMC-NHC-Pd (0.80 mol %), K_2CO_3 (0.5 mmol) and $EtOH/H_2O$ (1:1, v/v, 5.0 mL) were placed in a 25 ml round bottom flask. The solution was magnetically stirred in a pre-heated oil bath at 60 °C for the appropriate time. After completion, the reaction mixture was cooled to room temperature and filtered. The filtrate was then extracted with ethyl acetate (20 ml). The combined organic layer was washed with water , brine three times alternatively and dried over anhydrous Na_2SO_4. The Na_2SO_4 was then filtered off and the filtrate was concentrated under reduced pressure. Finally, the crude product was purified by preparative TLC (eluent: petroleum ether/ethyl acetate, 30/1) to afford the corresponding product.

2.6. Separation of the catalyst and recycling tests

After completion of the reaction, a simple centrifugation process was sufficient to separate the solid catalyst from the products. Then, the catalyst was washed with ethanol and water to remove adsorbed organic substrates and salt respectively. Without drying, the recovered catalyst was directly reused in next run with new portions of reactants.

2.7. Mercury poisoning tests

The model coupling reaction was conducted in the absence of mercury for 1.5 h under optimum conditions (Table 1, entry 1), and the yield of the desired product was 54 %. Next, 300 molar equivalents of mercury, with relation to this catalyst, were added into the reaction mixture after being stirred for another 1.5 h. After the allowed time, the protocol as in Section 2.5 was followed. The yield of the corresponding product (4-methoxybiphenyl) was 52 % after 3 h (Table 1, entry 14).

3. Results and Discussion

3.1. Synthesis and characterization of CMC-NHC-Pd

The CMC supported palladium catalyst was designed by the procedure shown in Scheme 1. The precursor CMC-supported NHC (CMC-NHC) was synthesized by the nucleophilic substitution of CMC-OTs with *N*-Methylimidazole. The tosylate group is played an effective leaving group, creating CMC-NHC-OTs via the S_N2 reaction with *N*-Methylimidazole. Next, the OTs^- was replaced with Cl^- to improve the catalytic activity (Wang, Hu, Xue, & Wei, 2014). Finally, the resulting CMC-NHC-Cl was synergized with palladium acetate in water to form the catalyst CMC-NHC-Pd complex. The loading amount of Pd was found to be 4.24 % (determined by ICP-OES), which is higher than the loading amount of other solid supported NHC palladium complexs reported in previous literature (Wang, Xu, Sun, & Song, 2013; Chen, Mao, Qi, Li, Chen, Wang, & Huang, 2016).

CP/MAS ^{13}C-NMR spectrum of CMC-NHC-Cl was depicted in Fig. 1. As shown in Fig. 1, the new signals observed at 126.06 and 127.04 ppm are attributed to the olefinic carbon (C=C). And the signal at 135.73 ppm of carbon atom is assigned to the imine groups (C=N) in *N*-Methylimidazole, indicating the success of grafting

N-Methylimidazole onto the cellulose backbone (Lin, Hsueh, Kanne, Chang, Liu, & Lin, 2013). In addition, the peak at 178.35 ppm belonging to the carbon atom of carboxyl groups (Baran, & Menteş, 2016). Other peaks are obtained from the spectrum as follows: ^{13}C-NMR: 103.29 C(1); 72.89-75.54 C(2), C(3), C(5); 81.21 C(4); 59.60 C(6); 61.80 C(7).

FT-IR spectra of carboxymethylcellulose, carboxymethylcellulose derivatives CMC-OTs, CMC-NHC-Cl, and CMC-NHC-Pd are shown in Fig. S1 (see supplementary data S3). All samples show a broad band at 3440 cm^{-1}, corresponding to the stretching of the -OH group. Two bands around 1196 cm^{-1} and 1337 cm^{-1} are attributed to the asymmetric and symmetric stretching of O=S belonging to CMC-OTs, respectively. The peak at 790 cm^{-1} exhibits the presence of C-H from the benzene ring out–plane flexural vibration in CMC-OTs, which is markedly weakened as shown in Fig. S1(b) and (c), indicating -OTs substituted with *N*-Methylimidazole. After complexation with Pd nanoparticles (Fig. S1d), the intensity of the peak at approximately 1630 cm^{-1} assigned to the asymmetric stretching of -CO_2^- becomes weaker than that of CMC-NHC-Cl (Fig. S1c), indicating the formation of a metal–ligand bond. The characteristic absorption band related to the vibration of the imidazole ring is observed at 1157 cm^{-1}, which is markedly weakened, indicating the occurrence of the palladium complex as depicted in Fig. S1(c) and (d) (Kim, Kim, Shokouhimehr, & Lee, 2005). The absorption peak at 1270 cm^{-1} is ascribed to the vibration of N–*sp*^{3} C bond and the new peak at 1585 cm^{-1} corresponds to the stretching vibration of the N–*sp*^{2} C bond (Rodil, Morrison, Milne, Robertson, Stolojan, & Jayawardane, 2000). Together with ^{13}C-NMR spectrum, the FT-IR spectra suggest that the CMC-NHC-Pd has been synthesized successfully.

Thermogravimetric analysis (TGA) was performed to evaluate the stability of the catalyst. High temperature stability is necessary to utilize the catalyst, because the Suzuki reaction requires heating, and catalysts are required to remain stable in the range of the reaction temperature to ensure catalyst activity and recyclability (Baran, Açıksöz, & Menteş, 2015). The TGA curves in Fig. 2 exhibit the weight loss of CMC-Na (a) occurring at around 260 °C, followed by decomposition. However, the thermal stability of the catalyst (b) is stable up to 205 °C, indicating that the ligands capture Pd nanoparticles successfully (Baran, Açıksöz, & Menteş, 2015). Also, this confirms that the NHC functionalized CMC supported palladium complex is stable at high temperature, indicating that the catalyst is suitable for catalyst systems.

X-ray photoelectron spectroscopy (XPS) was used to confirm the valence state of the Pd nanoparticles on the support surface region. As shown in Fig. 3(a), the Pd3d$_{5/2}$ and Pd3d$_{3/2}$ doublet located at 336.5 and 342.1 eV, respectively, are characteristic of Pd (II) (Reddy, Kumar, Reddy, Sreedhar, & Kantam, 2006). The binding energies at 334.6 and 340.0 eV correspond to Pd3d$_{5/2}$ and Pd3d$_{3/2}$ respectively, are attributed to Pd (0) (Wu, Peng, Zhong, Li, & Sun, 2016). The XPS results indicate that the

CMC-NHC-Pd catalyst contains two Pd species, Pd (II) and Pd (0).

The XPS survey spectra of CMC-NHC-Pd as shown in Fig. 3(b) and 3(c), indicates the binding energies of the C1s and O1s correspond to different components. The C1s spectra can be deconvoluted into five components which appear at 283.7, 284.8, 285.5, 286.2, and 287.7 eV, and are associated with C–OH, C–C, C–N, O–C–O and C=O to Pd bonds, respectively (Ding, Qian, Yu, & An, 2010). Deconvolution of the O1s spectrum of CMC-NHC-Pd results in three peaks located at 531.4, 532.3, and 533 eV in Fig. 3(c), which are attributed to C–O–C, COOH and C−OH, respectively. The intensity of the O1s peak was greater than that of 531.0 eV in CMC-Na, suggesting the coordination of Pd (II), and emergence of Pd (0) (Xu, Xu, Zhang, Zhang, & Cui, 2008). The resolved N 1s (Fig. 3d) XPS spectra shows two nitrogen components that 399 eV (as the low peak) and at 402.8eV (as the high peak), which are assigned to N–*sp*^{2}C and N–*sp*^{3}C bonds (Lahaye, Nanse, Bagreev, & Strelko, 1999). Furthermore, the peaks corresponding to these elements in the XPS spectrum of CMC-NHC-Pd were observed, demonstrating coordination of palladium to the support substrate (see Fig. S2 in Supplementary section). Combining the XPS results with those obtained from FT-IR, it could be speculated that -COO$^-$, -OH and *N*-Methylimidazole on the cellulose backbone capture Pd nanoparticles successfully via covalent bonding, according to the model shown in Scheme 1.

The morphology and structure of the palladium particles supported on the carboxymethylcellulose substrate were obtained from transmission electron microscopy (TEM) and are shown in Fig. 4(a). It can be seen that the average diameter of the Pd particles is approximately 6-9 nm and that the nanoparticles are well dispersed in the polymer matrix.

SEM image of CMC-NHC-Pd exhibits that the surface morphology of the catalyst has different morphology and size in comparison with raw material CMC-Na (Fig. S3. a), demonstrating that palladium are coordinated with the ligands (Xiao, Lu, & Li, 2015; Baran, Açıksöz, & Menteş, 2016). Also, EDX spectrum of the palladium complex proves the presence of palladium and other elements such as nitrogen and oxygen. (Fig. S4). It is in accordance with the results of XPS.

The powder XRD diffraction patterns of CMC-Na (a) and CMC-NHC-Pd (b) are shown in Fig. S5. Three weak peaks at 2θ of around 40.2°, 48.8°, and 67.8°, which are corresponding to the crystallographic plane of (111), (200) and (220) reflection of palladium crystalline structure, respectively (Zhou, Wang, Yang, Tang, Sun, & Tang, 2012). The peaks are observed at 2θ of 22.6°, which are assigned to the (200) diffraction planes of cellulose I (Cai, & Kim, 2010), indicating coordination of palladium to the support substrate did not change the crystallographic property of CMC-Na scaffold.

3.2. Applying the catalyst to Suzuki cross-coupling reaction

3.2.1. Evaluation of the catalytic activity

Following the successful preparation of CMC-NHC-Pd, its effectiveness in the Suzuki cross-coupling reaction was investigated. Various parameters such as the amount of catalyst, temperature, solvent, and base in the Suzuki cross-coupling reaction were initially examined using the reaction of *p*-bromoanisole (0.250 mmol, 1.0 equiv) and phenylboronic acid (0.375 mmol, 1.5 equiv) as the model reaction. The data are summarized in Table S1 (see supplementary data S6-S7).

The amount of catalyst plays a significant role in improving the reactivity of this type of coupling reaction. Therefore, a wide range from 0.40 to 2.00 mol % (Table S1, entries 1-5) was utilized in the experiment. The data show that the yield increases from 80 % to 96 % with an increase in the amount of catalyst (Table S1, entries 1-2). However, the yield decreases when the amount of catalyst increases from 0.80 to 2.00 mol % (Table S1, entries 2-5). A level of 0.80 mol % of the catalyst (Table S1, entry2) was identified as the optimal amount to catalyze the reaction. The coupling yield increases from 79% to 94% with an increase of the temperature (Table S1, entries 6 and 7). However, the yield decreases to 78% when the reaction temperature rise up to 80 °C (Table S1, entry 8). Furthermore, among the solvents screened, EtOH : H_2O (1:1) was found to be the most favorable system (Table S1, entry 12), likely owing to the solvent swelling effect on the cellulose matrix. In addition, the effects of organic and inorganic bases such as K_2CO_3, KF, NaOH, t-BuOK, and Et_3N were also tested (Table S1, entries 16-20). Excellent yield of the coupled product was achieved with the usage of K_2CO_3.

Consequently, the optimum reaction conditions were observed in 5 mL of EtOH : H_2O (1:1) at 60 °C using 0.80 mol % of the catalyst (CMC-NHC-Pd) and 0.75 mmol of K_2CO_3 as a base under atomospheric conditions in the reaction of phenylboronic acid (0.375 mmol), and *p*-bromoanisole (0.250 mmol).

A plausible cooperative trifunctional catalyst complex for stabilizing palladium nanoparticles was thus proposed as shown in scheme 2 based on the catalytic performance, ICP results, XPS analysis. The catalytic activity of CMC-NHC-Pd was much higher than that of CMC-Pd (Table S1, entry 2 vs entry 21). Furthermore, the palladium content of CMC-Pd was 2.21 %, which was lower than that of CMC-NHC-Pd (4.24 %). This is most likely attributed to the cooperative interaction of trifunctional capturing sites ($-COO^-$, -OH and *N*-Methylimidazole groups) with palladium as confirmed by CP/MAS ^{13}C-NMR spectrum. *N*-Methylimidazole-functionalized CMC (CMC-NHC-Pd) was able to stabilize the palladium nanoparticles through much stronger bonding interactions between palladium and NHC ligands than CMC-Pd (Levin, Ivry, Diesendruck, & Lemcoff, 2015; Kantchev, O'Brien, & Organ, 2007; Borja, Monge-Marcet, Pleixats, Parella, Cattoën, & Man, 2012). According to the XPS data, carboxyl groups on the surface of CMC were capable of capturing palladium nanoparticles via covalent bonding (Liu, He, Durham, Zhao, & Roberts, 2008). The hydroxyl groups on the backbone of cellulose immobilized Pd nanoparticles efficiently via covalent bonding or hydrogen bonding (Yang, Yu, Fan, Sun, Tang, & Yang, 2011; Wu, Fu, Su, Aslam, Wong, &

Dravid, 2004). Therefore, the catalyst played a trifunctional role to prevent palladium nanoparticles from leaching in the Suzuki reaction (see section 3.2.2) due to the three available binding sites ($-COO^-$, -OH and *N*-Methylimidazole) groups in palladium complexs.

To explore the applied scope of the catalyst, the optimized protocol was applied to investigate the Suzuki cross-coupling of differently substituted aryl bromides with various phenylboronic acids. It was shown that the CMC-supported catalyst gave the corresponding products in high yield toward most of the substrates in Table 1. When phenylboronic acids were coupled with *p*-bromoanisole, the phenylboronic acids containing activated groups(Table 1, entries 2, 5 and 6) had the higher yields compared to the deactivated groups (Table 1, entries 3-4). The reaction of electron-deficient aryl bromides (4-bromobenzonitrile as a model substrate) with phenylboronic acids reacted smoothly to generate the desired products with high yields within 4.5 h at 60 °C (Table 1, entries 7-11). The sterically hindered affords excellent yield (97 %) in 3.5 h (Table 1, entry 12). Unfortunately, low yield (52 %) was obtained with challenging substrates such as aryl chloride.

3.2.2. Separation of the catalyst and recycling tests

The recyclability of CMC-NHC-Pd was evaluated by utilizing consecutive Suzuki couplings of *p*-bromoanisole with phenylboronic acid as the model reaction. After completion of the first coupling reaction, the catalyst was recovered by centrifugation and extensively washed with anhydrous ethanol and deionized water to remove both organic and inorganic residues. Subsequently, this catalyst was reused directly for new reactions without further manipulation and recycled under the same conditions. The activity of the separated catalyst for four cycles in the Suzuki coupling reaction was depicted in Table 2. A slight decrease in the catalytic activity was observed after the second cycle. However, the yield decreased to 73 % and 65 % during the third and fourth runs, respectively. The amount of Pd present after four consecutive runs was determined to be 4.20 % compared with that of the fresh catalyst 4.24 %. This indicates trace amounts of leaching of the catalyst into the reaction mixture and efficiently preventing the palladium leaching. From the TEM images, the morphology and size of the catalyst after four cycles of reuse exhibits worse dispersion (Fig. 4b). Consequently, it’s concluded that the aggregation of palladium nanoparticles could account for the decrease of catalytic activity as seen in the TEM image of the recovered catalyst in Fig. 4 (Sin, Yi, & Lee, 2010; Wang, Xu, Wang, & Wei, 2015).

Hot filtration experiment were carried out in a similar manner as the general procedure (Table 1, entry 1) for the Suzuki reaction to establish whether the reactions were truly heterogeneous (Lempers, & Sheldon, 1998). The reaction was stopped after 30 min, the immobilized catalyst was separated as depicted above, and the resulted solution was heated for another 4 hours under identical reaction conditions. However, no further reaction was observed after the removal of catalyst from the reaction mixture. In addition, the hot filtrate was analyzed with ICP-OES and negligible amounts of palladium leaching was observed (<0.02%) at the end of the 4th run (Barana, Açıksöz, & Menteş, 2016). These experiments indicate that the Suzuki cross coupling reactions followed a heterogeneous pathway.

Also, SEM image and XPS spectrum of the recovered catalyst after fourth recycles was obtained in Fig. S3. b and Fig. S6 in the supplementary section, respectively. Compared to the SEM micrograph of the fresh catalyst, it appears that the structural of recovered catalyst became slightly aggregated, revealing that the catalytic activity is likely influenced by this change (Baran, Sarginb, Kayab, Menteş, & Ceter, 2017). The XPS result confirms the coordination of the palladium still with the ligands even after 4 runs.

3.2.3. Mercury test

A mercury test was conducted to further confirm the heterogeneous nature of the catalyst since mercury stops the catalytic activity. However, a homogeneous catalyst is not affected by the presence of mercury (Baran, Açıksöz, & Menteş, 2015). Results of the mercury test (Table 1, entry 14) demonstrate that the catalyst is heterogeneous.

In order to evaluate the efficiency of this catalyst, this catalytic system was compared with the previous similarly functionalized catalysts. As illustrated in Table S2, CMC-NHC-Pd catalyst exhibits extensive progress in reaction time and yield. For example, Cell-OPPh$_2$-Pd(0) and Cell-EDA-Pd(0) afforded low yield for the model reaction, although short time was used (Du, & Li, 2011; Zheng, Li, & Zheng, 2009).

Furthermore, a higher yield (96%) was obtained than that of CMC-Pd(II) (90%). The CMC-NHC-Pd catalyst is a promising candidate based on our design concept to make cellulose support have trifunctional capturing sites with palladium.

4. Conclusions

In summary, an environmentally-friendly Pd catalyst (CMC-NHC-Pd) was prepared by anchoring palladium onto carboxymethylcellulose, and was characterized by TEM, FT-IR, TGA and XPS analytical techniques. Due to the cooperative interaction of the trifunctional capturing sites -COO$^-$, -OH and *N*-Methylimidazole, CMC-NHC-Pd displayed higher palladium content and increased yields for the Suzuki cross-coupling reaction than CMC-Pd which was fabricated via Pd nanoparticles directly being deposited on CMC. Furthermore, the three binding sites in the catalyst prevented palladium leaching. Finally, the catalyst could be recycled by simple filtration during the Suzuki cross-coupling reaction.

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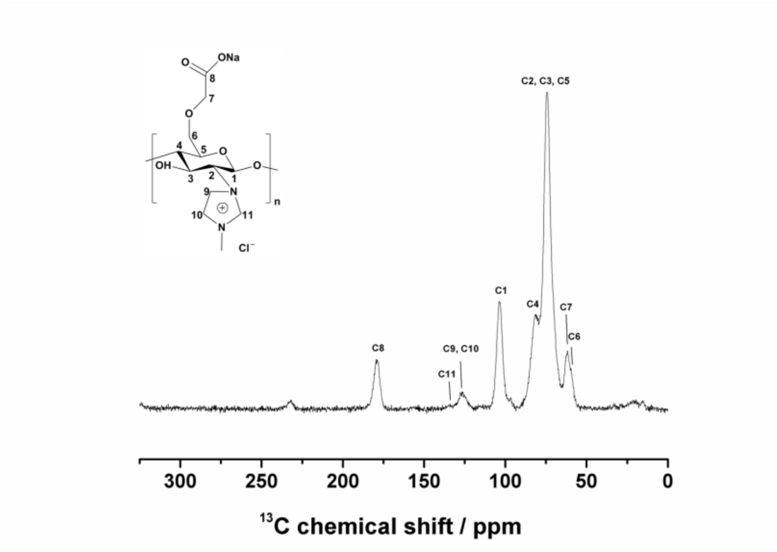


Fig. 1. CP/MAS ^{13}C-NMR spectrum of CMC-NHC-Cl

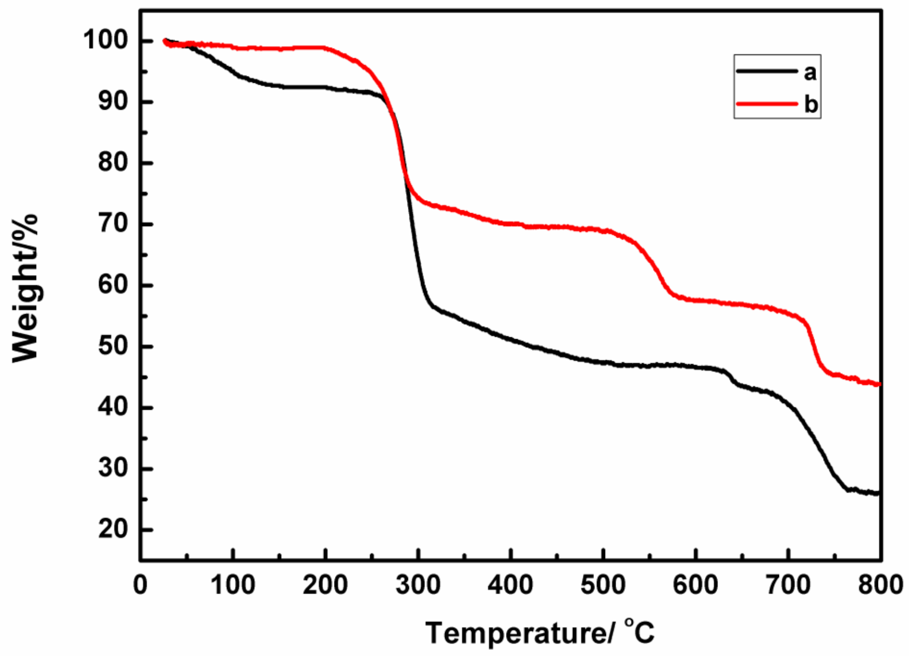
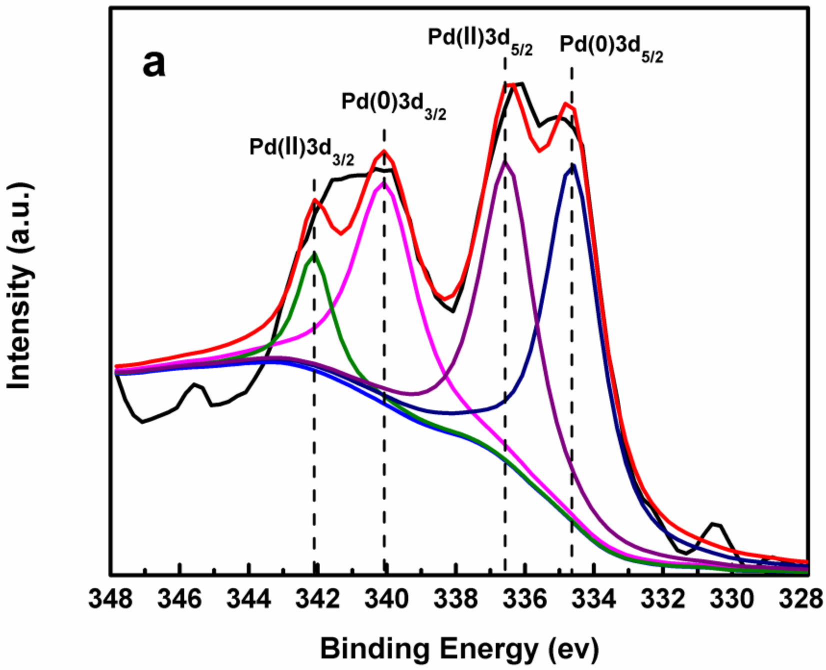
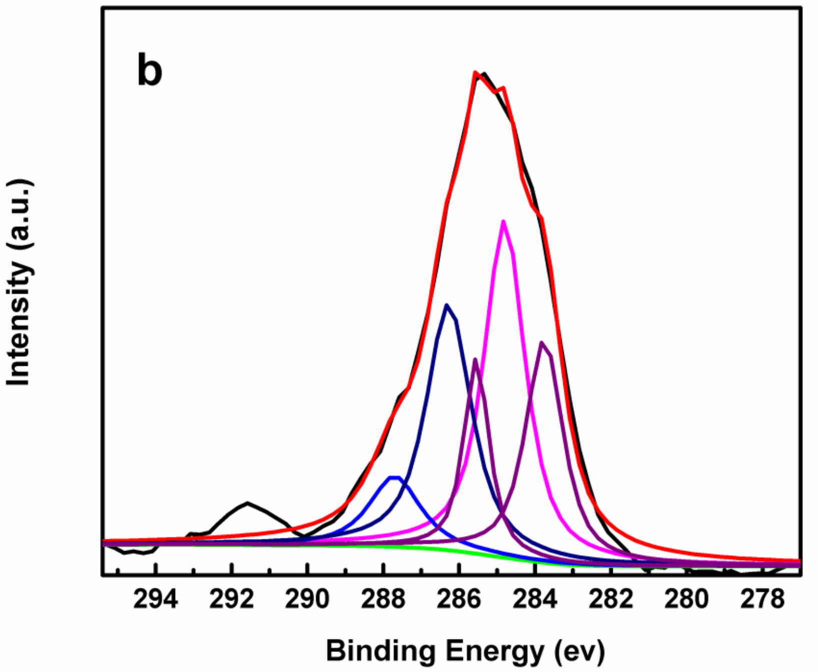
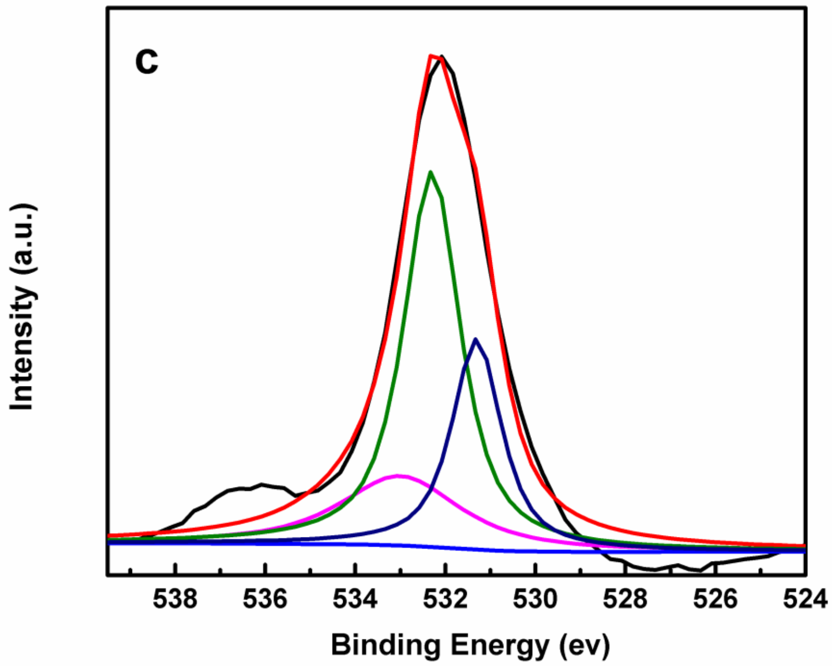


Fig. 2. TGA curves of CMC-Na (a) and CMC-NHC-Pd catalyst (b).


a
Pd(II)3d$_{3/2}$
Pd(0)3d$_{3/2}$
Pd(II)3d$_{5/2}$
Pd(0)3d$_{5/2}$
Intensity (a.u.)
348
346
344
342
340
338
336
334
332
330
328
Binding Energy (ev)


b
Intensity (a.u.)
294
292
290
288
286
284
282
280
278
Binding Energy (ev)



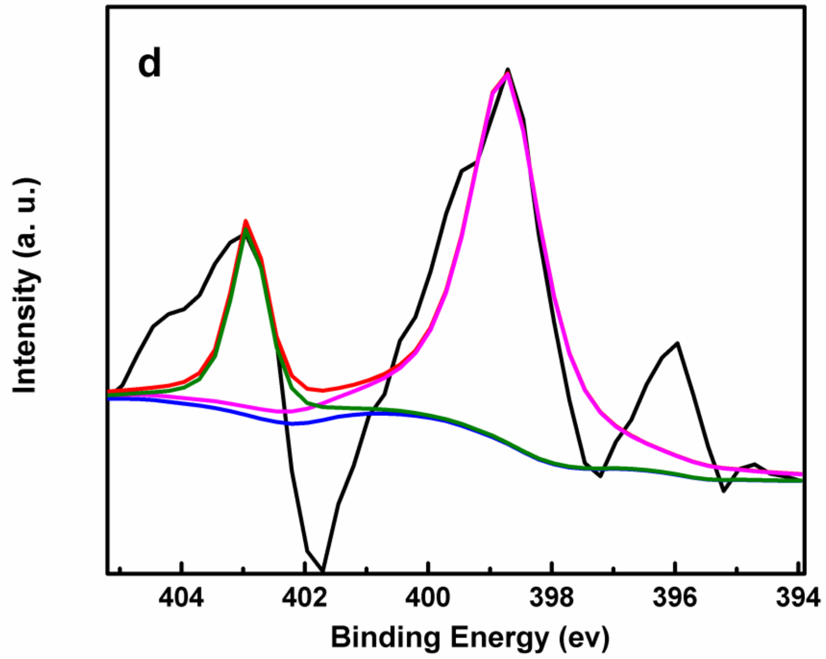


Fig. 3. XPS spectrum of the fresh CMC-NHC-Pd catalyst: Pd 3d (a), C 1s (b), O 1s (c), N 1s (d).

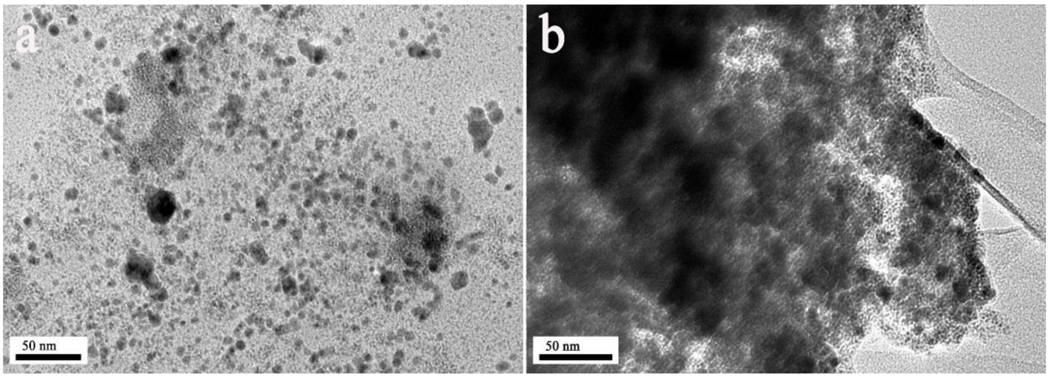
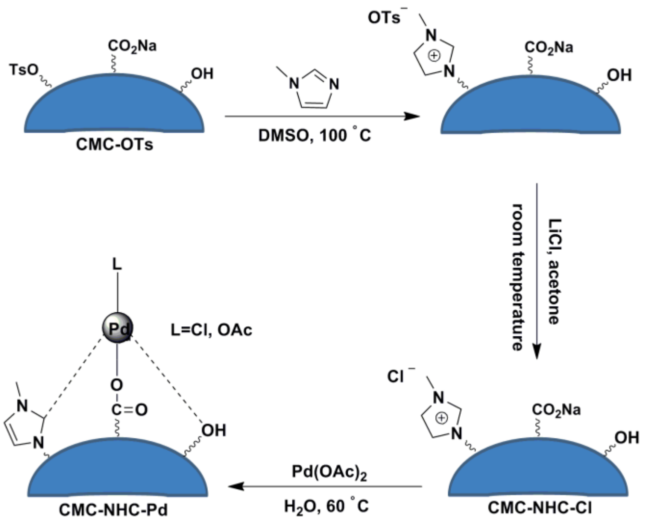
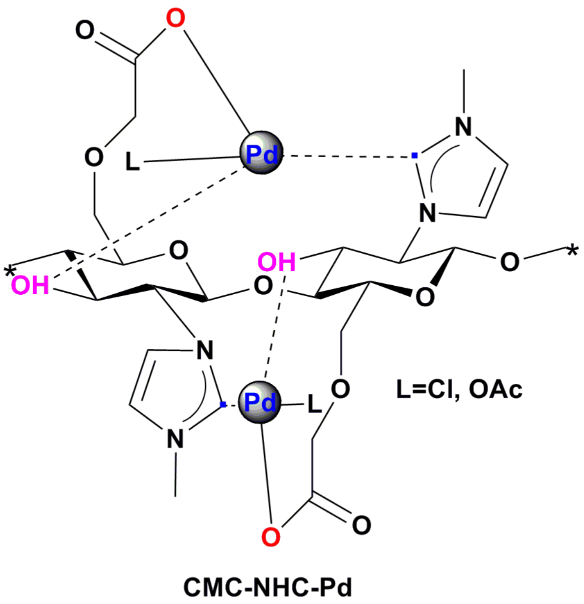


Fig. 4. TEM images of fresh CMC-NHC-Pd catalyst (a) and recovered catalyst (b).

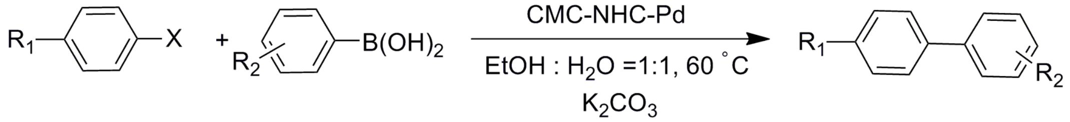


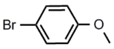
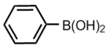
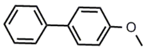
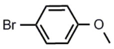
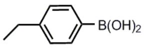
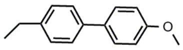
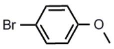
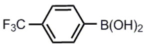
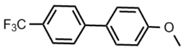
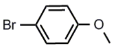
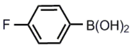
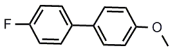
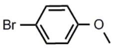
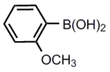
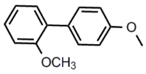
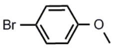
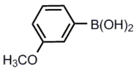
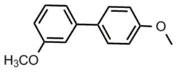
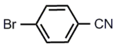
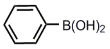
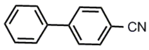
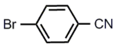
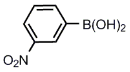
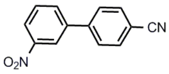
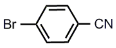
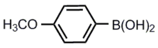
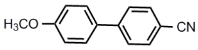
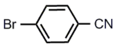
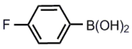
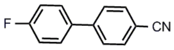
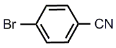
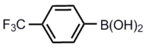
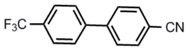
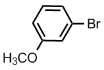
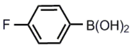
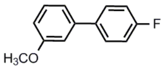
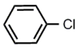
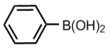
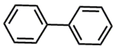
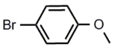
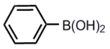
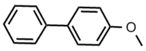
Scheme 1. Synthetic pathway for formation of the CMC-NHC-Pd catalyst.



Scheme 2. Plausible catalyst structure of CMC-NHC-Pd.

Table 1 Suzuki coupling reactions of aryl halides with Phenylboronic acids.



Entry[a]	Aryl halide	Phenylboronic acid	Product	Time (h)[b]	Yield (%)[c]	TON[d]	TOF[d]
1				3	96	120	40
2				4.5	96	124	28
3				5	73	92	18
4				5	85	115	23
5				1.5	90	114	76
6				1.5	94	117	78
7				3	94	118	39
8				4.5	89	113	25
9				4	95	126	32
10				3	91	114	38
11				2	98	123	62
12				3.5	97	122	35
13				5	52	65	13
14[e]				3	52	68	23

[a] Reaction conditions unless specified otherwise: aryl halides (0.250 mmol), phenylboronic acids (0.375 mmol), K_2CO_3 (0.75 mmol), CMC-NHC-Pd (0.80 mol %), 5 mL of EtOH : H_2O (1:1), under 60 °C in air.

[b] Detected by TLC.

[c] Isolated yield after purification.

[d] TON: (turnover number, yield of product/per mol of Pd). TOF: (turn over frequency, TON/time of reaction)(Baran, & Menteş, 2016).

[e] In the presence of excess Hg (Hg : Pd = 300:1).

Table 2 Recyclability of the CMC-NHC-Pd with Suzuki cross-coupling reactions [a].

Recycle	1st	2nd	3rd	4th
Time (h) [b]	3	3	3.5	4
Yield (%) [c]	88	79	73	65

[a] Reaction conditions: *p*-bromoanisole (0.250 mmol), phenylboronic acids (0.375 mmol), K_2CO_3 (0.75 mmol), CMC-NHC-Pd (0.80 mol %), 5 mL of EtOH : H_2O (1:1), under 60 °C in air.

[b] Detected by TLC.

[c] Isolated yield after purification.