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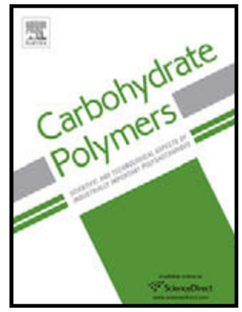

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Cellulose-supported *N*-Heterocyclic Carbene-palladium Catalyst: Synthesis and its applications in the Suzuki Cross-coupling Reaction

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Abstract

A cellulose-supported *N*-methylimidazole-palladium catalyst (Cell-NHC-Pd) was synthesized and used for Suzuki cross-coupling reactions between aryl halides and phenylboronic acids to create the corresponding coupling products in good to excellent yields. Moreover, the catalyst is easily recovered using only a few cycles of simple filtration.

Keywords: Cellulose, *N*-methylimidazole, Palladium, Suzuki cross-coupling reaction

1. Introduction

Palladium-catalyzed Suzuki cross-coupling reactions of aryl halides with arylboronic acids are among the most efficient methods to selectively construct biaryl compounds in organic synthesis (Littke & Fu, 2002; Martin & Buchwald, 2008; Yin & Liebscher, 2007; Old *et al.*, 1998; Zhang et al., 1999; Lemo *et al.*, 2005; Li *et al.*, 2000). To date, Suzuki reactions have been extensively used for the synthesis of natural products, herbicides, pharmaceuticals, and other products (Corbet & Mignani, 2006; Hassan *et al.*, 2002; Suzuki, 1999; Miyaura & Suzuki, 1995; Meijere & Diederich, 2004). Commonly, phosphine ligands are employed to facilitate the corresponding transformations. However, a critical setback for phosphine ligands is the fact that they are toxic and air-sensitive (Birkholz *et al.*, 2009; Fu, 2008). Recently, *N*-heterocyclic carbenes (NHCs) have attracted many chemists' attention as transition metal ligands (Wang *et al.*, 2012; Gao *et al.*, 2012; Fleckenstein *et al.*, 2007) after they were first reported by Herrmann and co-workers (Herrmann *et al.*, 1995; Herrmann *et al.*, 1998). Compared with phosphine ligands, NHCs have the same σ-donor and low π-acceptor ability while they can form stronger bonds with the majority of metals. More importantly, they are air and moisture stable. Nowadays, a wide range of NHC ligands are commercially available which exhibit high activities in various important organic transformations when combined with metallic pre-catalysts (Drge & Glorius, 2010; Dorta *et al.*, 2005; Marion & Nolan, 2008). Despite the significant progress that has been made in the design of these NHC ligands, the desired products are always inevitably contaminated by catalyst residues during these homogeneous reactions (Blaser, 2002; Cole-Hamilton, 2003), which greatly limits the use of NHCs-related organic transformations in industrial applications.

The immobilization of metal catalysts on solid supports has been considered an efficient approach to address the aforementioned issues. Numerous solid supports have been utilized as anchors for NHC and their metal complex such as polystyrene (Kang *et al.*, 2005; Lo & Luo, 2012), polysilylethers (Lázaro *et al.*, 2013) and mesoporous silica (Pozo *et al.*, 2011). However, the progress in the quality of catalysts on solid support has been relatively slow compared to soluble homogeneous complexes because of the deactivation that results from particle aggregation, metal leaching and matrix degradation (Molnár & Papp, 2014). Another major problem is the environmental concern arising from the use of poisonous and often costly materials applied in catalyst synthesis. In this regards, cellulose is an attractive and promising candidate that could be used as an efficient, renewable, and biodegradable support for catalysts (Jamwal *et al.*, 2011). In addition, cellulose is stable in most organic solvents, inexpensive, and has a high surface area. Typically, functional groups present in cellulose backbone participate in bonding with metals. Compared with widely used PS support, cellulose can easily be functionalized due to its abundant hydroxyl groups and can create either soluble or insoluble supports through chemical modification. Cellulose and its derivatives have also been widely used for coatings, optical films, pharmaceuticals, and consumables (Klemm *et al.*, 2005). The use of cellulose as an efficient support for Pd nanoparticles in cross-coupling reactions has also been widely reported (Jamwal *et al.*, 2011; Reddy *et al.*, 2006; Cirtiu *et al.*, 2011; Xu *et al.*, 2008). As demonstrated in a recently accepted review publication (Molnár & Papp, 2014), the most studied catalysts are still cellulose deposited Pd particles. In contrast, the use of immobilized Pd complexes has not been fully exploited. According to the literature, only three examples for such support materials have been synthesized: cellulose-tagged diphenylphosphinate (Du & Li, 2012; Du & Li, 2011; Keshipour *et al.*, 2013), triphenylphosphine (Xu *et al.*, 2014) and ethylenediamine (Zheng *et al.*, 2009). More versatile functionalization techniques should be developed to achieve stable, immobilized cellulose metal complexes, allowing for the improvement of catalytic activities.

With all these considerations in mind, in this paper, we present the anchoring of *N*-methylimidazole onto a cellulose backbone as a precursor, followed by coordination with $Pd(OAc)_2$ to prepare a novel cellulose-NHC-palladium catalyst (Cell-NHC-Pd). In addition, we explore its catalytic activity and recycling performance using the Suzuki reaction as an example.

2. Experimental

2.1. Materials

Microcrystalline cellulose AVICEL PH-101 (Microcrystalline cellulose, degree of polymerization = 180) was purchased from Shandong Liaocheng A Hua Pharmaceutical Co., Ltd. (Shandong Province, P.R. China). Triethylamine (Et_3N), anhydrous lithium chloride (LiCl), potassium carbonate (K_2CO_3), dimethylformamide (DMF), all of which are analytical grade (AR), were obtained from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, P.R. China). *N*-methylimidazole was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Acetone was obtained from Tianjin Jiangtian Chemical Technology Co., Ltd. The cellulose, anhydrous lithium chloride, and potassium carbonate were vacuum dried for 48 h at 50 °C, 40 °C and 30 °C respectively, before use. Dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), dichloromethane (CH_2Cl_2) and DMF were desiccated over CaH_2 overnight, then filtered through silica gel; they were then vacuumed distilled and stored in brown bottles with 4A molecular sieves under N_2. Other reagents were only redistilled.

2.2. Instruments

NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ using TMS as an internal standard. The particle sizes of the samples were observed using a Tecnai G2 F20 transmission electron microscope (TEM). The elemental content of palladium was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Jarrell-Ash corporation, ICP-9000 (N+M) instrument. X-ray photoelectron spectrometry (XPS) was conducted using a PHI1600 ESCA System (Perkin-Elmer, United States). The content of sulfur and nitrogen were determined by a Vario Micro cube elemental analyzer. Thermogravimetric analysis (TGA) was measured with a STA 409 PC thermal analyzer (NETZSCH, Germany). Fourier transform infrared spectroscopy (FTIR) analysis was performed on a BIO-RAD FTS3000 IR Spectrum Scanner.

2.3. Preparation of Cell-NHC-Cl

Cellulose *p*-toluenesulfonate (Cell-OTs) was prepared according to methods reported in the literature (Rahn *et al.*, 1996). Cell-OTs (1.91 g, 10.0 mmol) was then added to DMSO (10 mL) in a 25 mL flask, with degree of substitution (DS) of 0.14, and the mixture was stirred for 24 h at 60 °C followed by overnight stirring at room temperature to dissolve the Cell-OTs completely. *N*-methylimidazole (0.86 g, 10.0 mmol) was then added to the reaction mixture under nitrogen and the viscous black mixture was stirred for 12 h at 100 °C. After cooling to room temperature, the mixture was added dropwise into acetone in a beaker and stirred vigorously for approximately 6 h. The reaction mixture was filtered and the resulting

[Cell-NHC][OTs]$^-$ was obtained. [Cell-NHC][OTs]$^-$ was then dissolved in a solution of NaCl (1.15 g, 20.0 mmol) in acetone (10 mL) to replace OTs$^-$ with Cl$^-$. The precipitate (Cell-NHC-Cl) was collected via filtration. The obtained brown powder was vacuum dried for 24 h at 40 °C. The DS of Cell-NHC was 0.08 determined on the base of nitrogen content.

2.4. Preparation of Cell-NHC-Pd complex

Under nitrogen, Cell-NHC-Cl (0.50 g) was added to a solution of $Pd(OAc)_2$ (0.10 g, 0.45 mmol) in DMF (10 mL) and the mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was filtered. The obtained solid black product was washed carefully with distilled water (3×25 mL), absolute ether (2×25 mL) and absolute ethyl alcohol (2×25 mL) successively then dried under reduced pressure at room temperature to give the dark palladium complex (Cell-NHC-Pd).

2.5 General procedure for the Suzuki reaction of aryl halides with arylboronic acids

The aryl halide (0.5 mmol), arylboronic acid (0.75 mmol), Cell-NHC-Pd (0.75 mol%), K_2CO_3 (1 mmol) and DMF : H_2O (1:1) (2.5 mL) were successively added into a 25 mL round bottom flask. The mixture was stirred vigorously at 80 °C for the varying specific length of time based on each different substrate. After reaction completion, the solid catalyst was filtered off. The filtrate was extracted with ethyl acetate (3×5 mL), washed with water and brine three times, and then dried over anhydrous $MgSO_4$. The $MgSO_4$ was then filtered off. After removal of the solvent, the crude product was purified by preparative TLC (eluent: petroleum ether/ethyl acetate, 20/1) to give the desired product and calculate the yield.

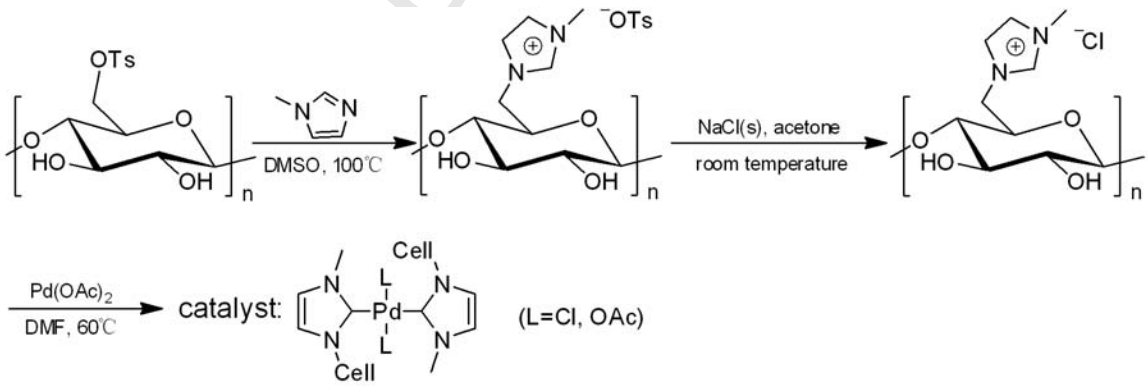
2.6 Separation of the catalyst and recycling tests

After completion of the Suzuki–Miyaura reaction, the liquid phase was removed by centrifugation. The solid catalyst was simply recovered by filtration and washing. Without drying, the recovered catalyst was directly used in next run with new portions of reactants.

3. Results and Discussion

3.1. Synthesis and characterization of Cell-NHC-Pd

Cellulose-supported NHC (Cell-NHC) was synthesized via the nucleophilic substitution of Cell-OTs with *N*-methylimidazole as shown in Scheme 1. The tosylate acted as an effective leaving group, allowing the S_N2 reaction with *N*-methylimidazole to create Cell-NHC-OTs. In order to improve the catalytic activity, OTs^- was exchanged by Cl^- (Kim *et al.*, 2005). The resulting Cell-NHC-Cl was then coordinated with palladium acetate in DMF to give the final catalyst Cell-NHC-Pd complex. The Pd loading was determined to be 0.24 mmol/g by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), which was higher than that of other polymer-supported NHC palladium complex reported in previous literature (Lo & Luo, 2012; Kim *et al.*, 2006).



Scheme 1. Reaction scheme for the formation of catalyst (Cell-NHC-Pd).

The FTIR spectra of cellulose, cellulose derivatives Cell-OTs, Cell-NHC-Cl, and Cell-NHC-Pd are shown in Fig. 1. The bands at 1359 cm^{-1} and 1179 cm^{-1} corresponds to the

O=S asymmetric and symmetric stretching vibration of Cell-OTs, respectively, which are greatly weakened after substitution with *N*-methylimidazole as shown in Fig. 1b-c. Correspondingly, the *N*-methylimidazole graft is visible from appearance of a new band at 1580 cm^{-1}, which corresponds to the stretching vibration of N–sp^2 C bond (Zhao *et al.*, 1995; Kurt *et al.*, 2000). In addition, the absorption in the 1220 cm^{-1} region is interpreted as the vibration of N–sp^3 C bond (Kurt *et al.*, 2000; Rodil *et al.*, 2000). As shown in Fig. 1c-d, the band at 632 cm^{-1} region corresponds to the vibration of the imidazole ring, and the intensity of its absorption is reduced after reaction with palladium acetate, suggesting the formation of the NHC-Pd complex (He & Cai, 2011).

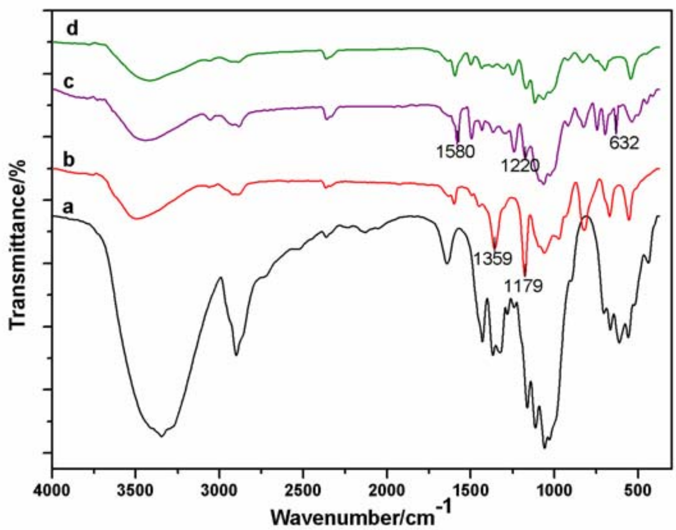


Fig. 1. FT-IR spectra of Cell (a), Cell-OTs (b), Cell-NHC-Cl (c), and Cell-NHC-Pd (d).

As the Suzuki reaction usually requires heating, thermogravimetric analysis (TGA) was performed to evaluate the thermal stability of the cellulose-supported catalyst in air and high temperature. As shown in Fig. 2, TGA of the catalyst system showed high thermal stability with decomposition at around 225 °C in air. The result demonstrated that cellulose was considerably stable in an oxygen-containing atmosphere as a catalyst support in experimental conditions.

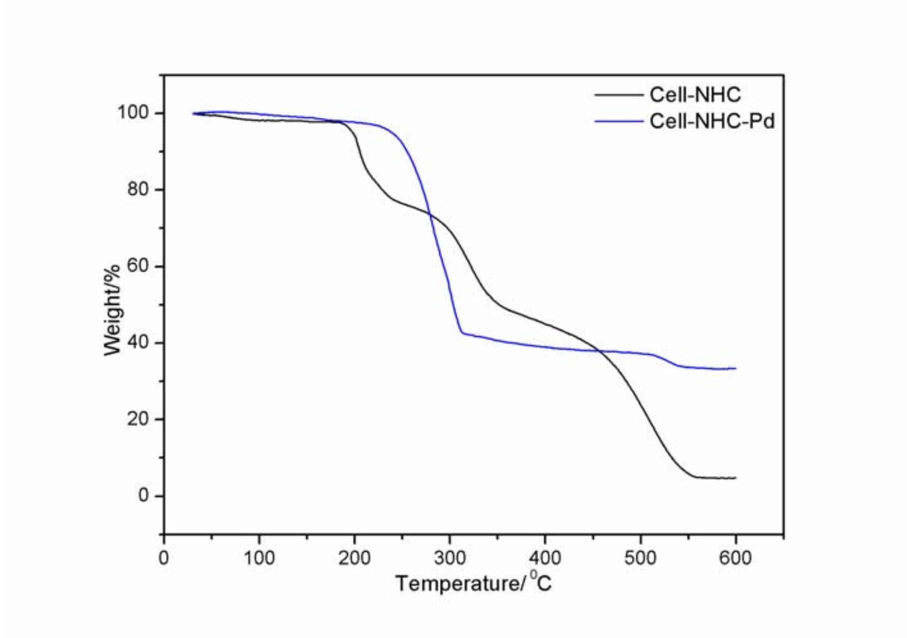
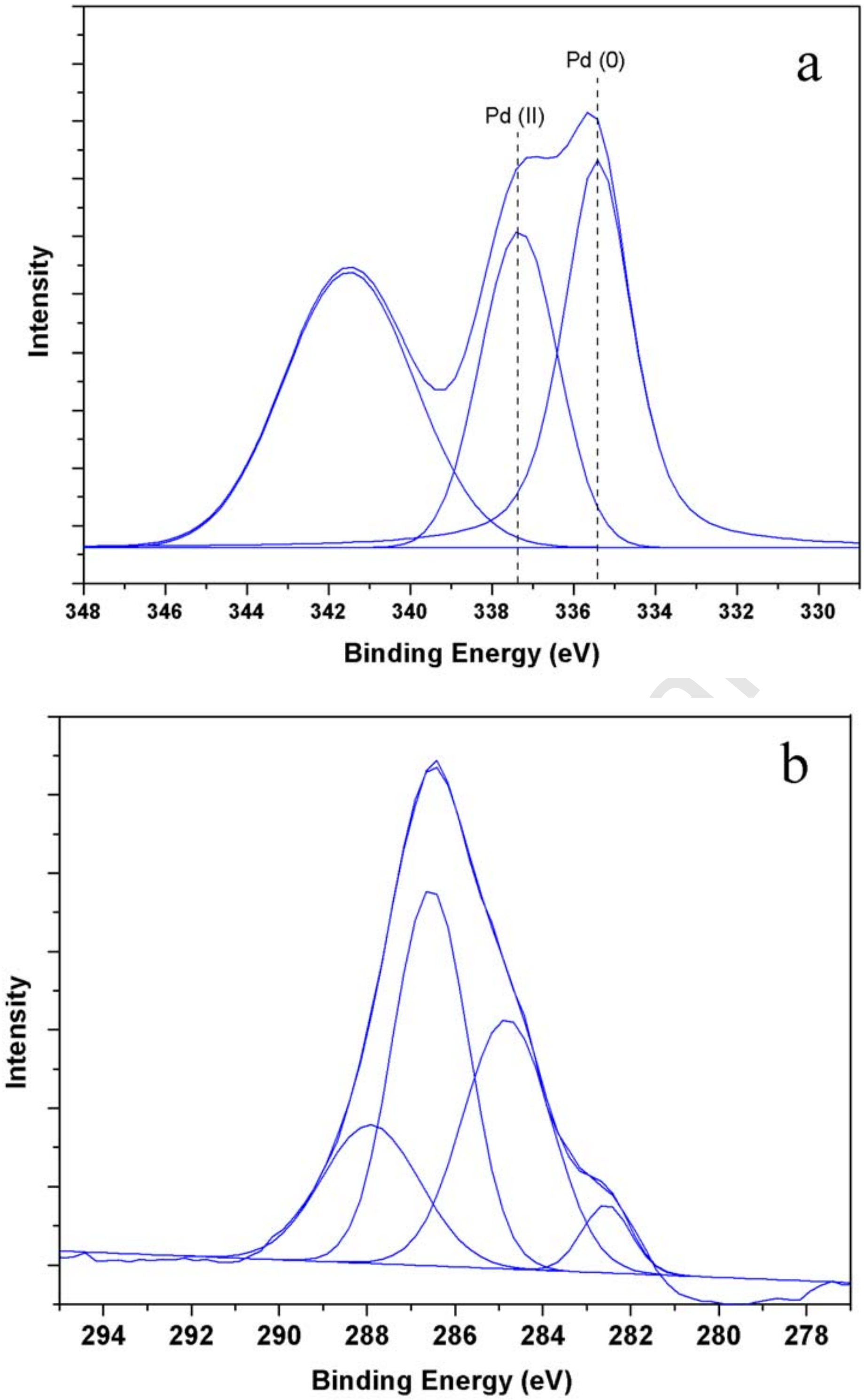


Fig. 2. TGA traces of Cell-NHC and Cell-NHC-Pd catalyst under air flow.

XPS spectroscopy was employed to investigate the elemental coordination state of Pd species. As shown in Fig. 3a, the binding energies of $Pd3d_{5/2}$ in the Cell-NHC-Pd catalyst were 335.3 eV and 337.4 eV, respectively (Xu *et al.*, 2008), which revealed that both Pd (0) and Pd (II) were present. Based on previous literature reports (Wu *et al.*, 2013; Xiong *et al.*, 2013), parts of Pd (II) species were likely reduced in the existence of cellulose backbone.


a
Pd (0)
Pd (II)
Intensity
348
346
344
342
340
338
336
334
332
330
Binding Energy (eV)
b
Intensity
294
292
290
288
286
284
282
280
278
Binding Energy (eV)

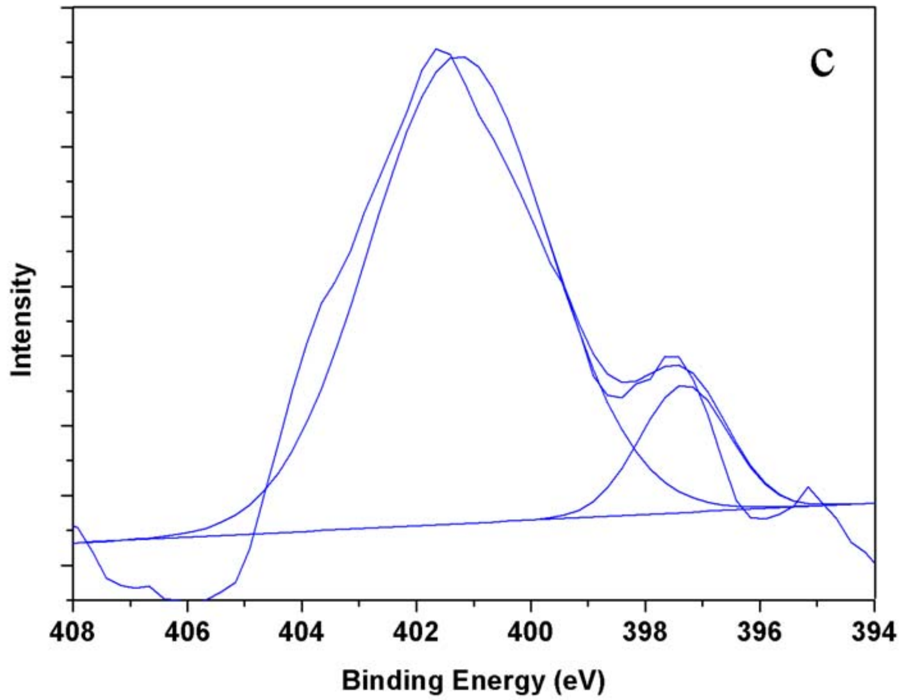


Fig. 3. XPS spectrum of fresh Cell-NHC-Pd catalyst: Pd 3d (a), C 1s (b), N 1s (c).

As shown in Fig. 3b, the status of C in Cell-NHC-Pd can be also explored by XPS analysis of C 1s. The C 1s peak was divided into four components at binding energies of 282.8, 284.8, 286.5 and 288.0 eV, which were attributed to C=C, C–C, C–O and carbene carbon to Pd bonds, respectively (Khabashesku *et al.*, 2000; Mao *et al.*, 2011). Correspondingly, XPS of N 1s (Fig. 3c) showed 401.3 eV as the major peak and 397.4 eV as a minor peak, which were assigned to N–sp^2C and N–sp^3C bonds (Gammon *et al.*, 2003; Li *et al.*, 2009). Combining these results with those obtained from FTIR, it can be speculated that *N*-methylimidazole on cellulose backbone captured the Pd species successfully, as shown by the model in scheme 1.

Surface morphology of the cellulose fibers was investigated with transmission electron microscopy (TEM). TEM images (Fig. 4) revealed the presence of palladium nanoparticles of about 9 nm in size, which proved the excellent dispersion of palladium sites on the surface of cellulose.

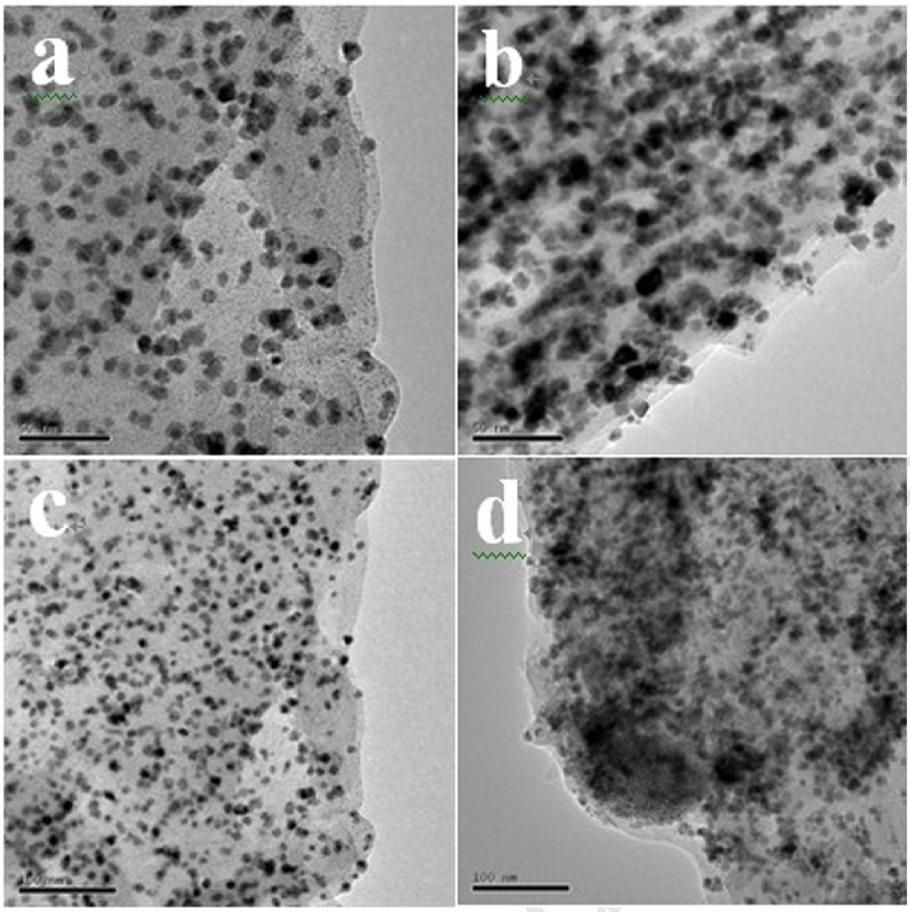


Fig. 4. TEM images of the fresh Cell-NHC-Pd (a and c) and recovered (b and d).

3.2. Applying the catalyst to Suzuki cross-coupling reactions

3.2.1 Evaluation of its catalytic activity

Initial examination was carried out using *p*-bromoanisole (0.250 mmol, 1.0 equiv) and phenylboronic acid (0.375 mmol, 1.5 equiv) as a model reaction in the presence of Cell-NHC-Pd. Several variables such as the amount of catalyst, temperature, solvent and base were screened to optimize the reaction conditions. Results were summarized in Table 1.

As shown in Table 1, the product yield increased with the increase of the amount of catalyst (Table 1, entries 1-3). However, the yield decreased when the amount of catalyst increased from 0.75 to 1.25 mol% (Table 1, entries 3-5). Therefore, 0.75 mol% of the catalyst (Table 1, entry 3) was sufficient to efficiently catalyze the reaction. The coupling yield increased slightly from 60 °C to 80 °C (Table 1, entries 6 and 7). However, the yield decreased when the temperature rose to 100 °C (Table 1, entry 8). We tried a variety of solvent systems, going from pure water (Table 1, entry 12) to a mixture of an organic solvent with water. The organic solvents tried were dimethylformamide (DMF), dimethylacetamide (DMAc) and Ethanol (EtOH) (Table 1, entries 6-11, 13-17). Results showed that DMF : H_2O (1:1) was the most favorable system. Using potassium carbonate and potassium *tert*-butoxide (Table 1, entries 7 and 16) both gave excellent yields. However, due to the hygroscopic nature of potassium *tert*-butoxide and considering its higher cost, we opted for potassium carbonate. When we increased the amount of K_2CO_3 to 3 equivalents, the yield rose to 98% (Table 1, entry 13).

Table 1

Cell-NHC-Pd catalyzed Suzuki cross-coupling reaction.

Entry [a]	Amount of catalyst (mol%)	Temperature (°C)	Solvent	Base	Yield (%) [b]
1	0.25	80	DMF : H_2O (1:1)	K_2CO_3	79
2	0.50	80	DMF : H_2O (1:1)	K_2CO_3	85
3	0.75	80	DMF : H_2O (1:1)	K_2CO_3	94
4	1.00	80	DMF : H_2O (1:1)	K_2CO_3	92
5	1.25	80	DMF : H_2O (1:1)	K_2CO_3	85

6	0.75	60	DMF : H_2O (1:1)	K_2CO_3	89
7	0.75	80	DMF : H_2O (1:1)	K_2CO_3	93
8	0.75	100	DMF : H_2O (1:1)	K_2CO_3	84
9	0.75	80	DMAc : H_2O (1:1)	K_2CO_3	91
10	0.75	80	DMF : H_2O (1:3)	K_2CO_3	76
11	0.75	80	EtOH : H_2O (1:1)	K_2CO_3	86
12	0.75	80	H_2O	K_2CO_3	22
13 [c]	0.75	80	DMF : H_2O (1:1)	K_2CO_3	98
14	0.75	80	DMF : H_2O (1:1)	Cs_2CO_3	88
15	0.75	80	DMF : H_2O (1:1)	K_3PO_4	90
16	0.75	80	DMF : H_2O (1:1)	*t*-BuOK	92
17	0.75	80	DMF : H_2O (1:1)	Et_3N	52

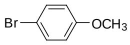
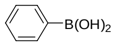
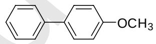
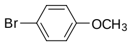
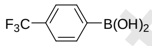
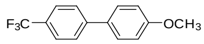
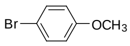
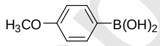
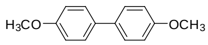
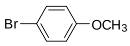
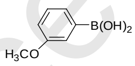
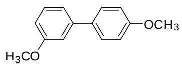
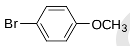
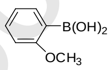
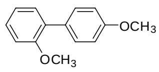
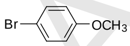
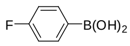
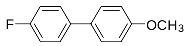
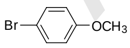
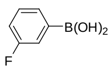
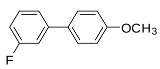
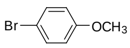
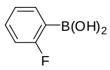
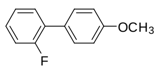
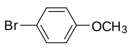
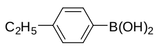
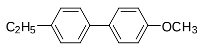
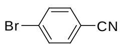
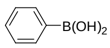
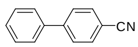
[a] Reaction conditions: 4-bromoanisole (0.250 mmol), phenylboronic acid (0.375 mmol), base (0.5 mmol), solvent (2.5 mL), heating in air for 2 h, detected by TLC. [b] Isolated yield. [c] K_2CO_3 was used for 3 equiv (0.75 mmol).

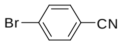
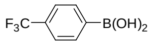
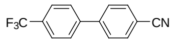
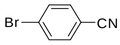
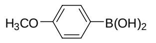
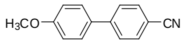
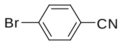
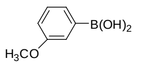
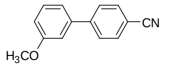
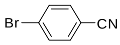
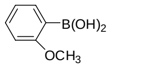
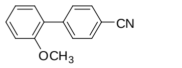
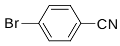
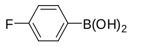
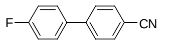
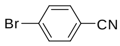
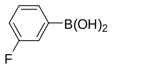
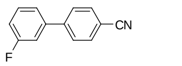
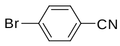
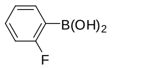
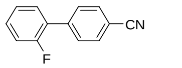
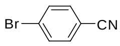
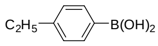
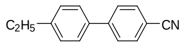
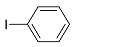
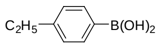
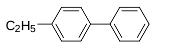
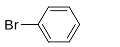
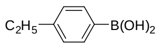
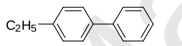
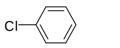
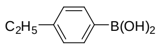
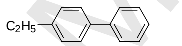
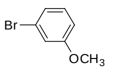
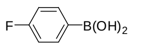
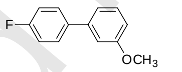
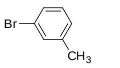
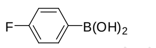
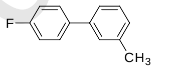
Overall, the optimized conditions were as follows: phenylboronic acid (0.375 mmol), 4-bromoanisole (0.250 mmol), catalyst (0.75 mol%), K_2CO_3 (0.75 mmol) in DMF : H_2O (1:1) (2.5 mL) at 80 °C under air.

To extend the scope of the heterogeneous reaction, the Suzuki cross-coupling reaction of aryl halides with various phenylboronic acids were examined as shown in Table 2. Most of the aryl bromides were converted to the corresponding biaryls with good to excellent yields in reasonable reaction times. Coupling of 4-bromoanisole with sterically hindered phenylboronic acids proceeded with different yields (Table 2, entries 3-5 and 6-8). The reaction of electron-deficient aryl bromides (4-bromobenzonitrile as a model substrate) with phenylboronic acid occurred smoothly to afford the biaryls with excellent yields within 4 h at 80 °C (Table 2, entries 10-18). However, the reaction between benzene halides and 4-ethylphenylboronic acid was sluggish and gave only small amounts of products even with prolonged reaction times (Table 2, entries 19-21). The reaction of electron-deficient bromobenzene with 4-fluorine phenylboronic acid went smoothly. On the other hand, the reaction of electron-rich bromobenzene with 4-fluorine phenylboronic acid was not successful, with a yield of only 10%.

Table 2

Suzuki Cross-coupling Reaction of Aryl halide with Phenylboronic acids[a].

Entry	Aryl halide	Phenylboronic acid	Product	Time (h)[b]	Yield (%)[c]
1				2.0	97
2				4.5	78
3				1.5	85
4				1.5	80
5				1.5	66
6				5.0	91
7				5.0	81
8				5.0	45
9				5.0	93
10				2.0	99

11				1.5	80
12				4.0	99
13				4.0	97
14				1.5	95
15				2.0	96
16				2.0	95
17				2.6	83
18				2.3	98
19				4.0	61
20				4.0	53
21				4.0	33
22				3.5	76
23				6.0	10

[a] Unless otherwise specified, all the reactions were carried out using aryl halides (0.250 mmol), phenylboronic acids (0.375 mmol), K_2CO_3 (0.75 mmol), Cell-NHC-Pd (0.75 mol%), DMF : H_2O (1:1) (2.5 mL), under 80 °C in air. [b] Detected by TLC. [c] Isolated yield.

3.2.2 Separation of the catalyst and recycling tests.

The recyclability of the Cell-NHC-Pd catalyst was also investigated in the Suzuki cross-coupling reaction of 4-bromoanisole with phenylboronic acid. After the reaction, the liquid phase was removed by centrifugation and the catalyst was washed with ethyl acetate. The catalyst was then used in the four additional reactions and the catalytic activity for the five consecutive cycles was shown in Table 3. For the second and third reactions, only a minor loss of catalytic activity was observed compared to the initial run. However, the reaction at the 4th and 5th recycled runs gave the products in 60% and 58% yields, respectively. In addition, the filtrate resulting from the reaction mixture had no catalytic activity under identical conditions. The total amount of palladium leaching after the 5th cycle was 1.2% as detected by ICP-AES analysis (The amount of palladium is 2.55% before reaction and 2.52% after 5 cycles). Therefore, the decrease of activity may be due to the aggregation of palladium nanoparticles during the reaction as shown in TEM images of Fig. 4 (Narayanan & El-Sayed, 2003; Hu & Liu, 2005; Sin *et al.*, 2010).

Table 3
Reusability of the Cell-NHC-Pd in Suzuki cross-coupling reaction[a].

Recycle	1st	2nd	3rd	4th	5th
Time (h) [b]	2.6	3	3	3.5	4
Yield (%) [c]	91	85	79	60	58

[a] The reactions conditions: 4-bromoanisole (0.250 mmol), phenylboronic acid (0.375 mmol), K_2CO_3 (0.75 mmol), Cell-NHC-Pd (0.75 mol%), DMF : H_2O (1:1) (2.5 mL), under 80 °C in air. [b] Detected by TLC. [c] Isolated yield.

4. Conclusions

In conclusion, cellulose-supported *N*-methylimidazole was prepared by the nucleophilic substitution reaction of *N*-methylimidazole with cellulose tosylate. The success of the grafting of *N*-methylimidazole onto the cellulose backbone was confirmed by FT-IR and XPS analysis. Cellulose-supported *N*-methylimidazole was then coordinated with $Pd(OAc)_2$ in DMF to give the final cellulose-tagged *N*-methylimidazole palladium complex, which showed high thermal ability from TG analysis. Nanopalladiums sites on the surface of the cellulose support were very well distributed, as demonstrated by TEM images. Moreover, this catalyst efficiently catalyzed Suzuki cross-coupling reactions and gave the corresponding products in good to excellent yields. Of particular note is that the Cell-NHC-Pd catalyst can be recycled by simple filtration following a Suzuki cross-coupling reaction. Further applications of cellulose-based *N*-methylimidazole in other organic reactions are currently being investigated in our laboratory.

Acknowledgment

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Highlights:

- NHC ligand was introduced onto cellulose backbone to explore an avenue for polysaccharide-based catalysts.
- Cellulose-supported NHC-Pd complex can efficiently promote Suzuki coupling reactions.
- Catalysts can be recovered by easy filtration and can be used several times.