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# Bacteria Cellulose Nanofibers Supported Palladium(0) Nanocomposite and Its Catalysis Evaluation in Heck Reaction

Peipei Zhou, Huanhuan Wang, Jiazhi Yang, Jian Tang, Dongping Sun, and Weihua Tang\*

Key Laboratory of Soft Chemistry and Functional Materials, Ministry of Education, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China

**ABSTRACT:** Bacteria cellulose (BC) nanofibers supported palladium(0) nanocomposites were prepared and fully characterized in terms of morphology, crystallinity, composition, and thermal stability. The as-prepared catalyst was further successfully explored in Heck coupling reaction between aryl halide and styrene or acrylates, with a yield over 86–96% for the first coupling reaction. With coupling yields decreased less than 10% for the fifth reaction cycle, Pd/BC catalyst exhibits great potential as recyclable catalyst for Heck coupling.

## 1. INTRODUCTION

Palladium-catalyzed cross-coupling reactions have been widely used and proved to be an effective means in organic synthesis to build Aryl–Aryl bonds.<sup>1–3</sup> Such reactions have been frequently employed in the synthesis of pharmaceuticals, polymers, and fine chemicals for a great variety of applications.<sup>4</sup> Heck reaction and related chemistry occupy a special place among basic types of palladium (Pd) catalyzed reactions.<sup>3–6</sup> Development of robust, efficient, and cost-effective Pd catalyst is thus the key factor to extend Heck reactions for wide industrial applications.

The separation and recyclability issue facing traditional homogeneous catalyst has attracted great efforts from researchers in various fields of chemistry to develop supported Pd heterogeneous catalysts. For this purpose, two approaches have been developed for supported Pd catalyst by either in situ deposition of Pd nanoparticles (NPs) onto supports or coordinating Pd with pregrafted functional groups on the surface of support.<sup>7</sup> The support employed so far can be carbon materials, metal oxides, porous silicate, molecular sieves, silica materials, synthetic polymers, and biopolymers.<sup>8</sup>

Inspired by the great success of micro/nanocrystalline cellulose as robust support for heterogeneous catalysts<sup>9–11</sup> and our recent research interest in developing bacteria cellulose (BC) related functional materials,<sup>10</sup> it is intriguing for us to explore the applicability of Pd/BC catalyst in various cross-coupling reactions to respond to the current appeal for eco-friendly and sustainable green chemistry. Different from plant cellulose, BC nanofibers are produced from fermentation of *Acetobacter xylinum* from agitated culture. BC boasts a variety of notable properties such as ultrafine nanofiber network structure, high water retention capability, good mechanic properties, and high chemical stability due to its unique specific structure.<sup>11</sup> The ultrafine three-dimension networks endow BC with well-separated nanofibrils (width <100 nm) to create extensive specific area, which is advantageous for BC to function as matrix or support in creating hybrid nanomaterials.<sup>10</sup>

In our previous study, Pd/BC catalyst with 5.29 wt % Pd loading was prepared and its applications were explored for the

catalysis of Suzuki coupling in water, where excellent catalysis performance and recyclability were presented with only 0.05 mol % equiv Pd/BC catalyst used.<sup>12</sup> The objective of this current work is to prepare higher Pd loading Pd/BC catalyst with our reported methodology for the catalysis of Heck coupling reactions. We hereby report the preparation and characterization of the targeted Pd/BC catalyst with higher Pd loading in great detail, and its applicability in Heck reaction is further explored in terms of activity and recyclability.

## 2. EXPERIMENTAL SECTION

**2.1. Preparation of BC Supported Pd Catalyst.** To a suspension of freshly prepared wet BC nanofibers<sup>10</sup> (3 g) in water (50 mL) was added PdCl<sub>2</sub> (0.36 g, 2.06 mmol). The reaction mixture was degassed for 0.5 h before heating up to 140 °C for 5 h with vigorous stirring (1200 rpm) under N<sub>2</sub> atmosphere. To the reaction mixture was then added a solution of potassium borohydride (4 g) in deionized water (50 mL) over 0.5 h. After stirring the mixture solution at 80 °C for another 3 h, the reaction mixture was centrifuged to obtain the crude product. Further five rounds of water washing and centrifuging processes afforded Pd(0)/BC catalyst as black composite.

**2.2. Characterization.** Morphology of BC fibers and Pd/BC hybrid nanofibers was observed with TEM (JEM-2100). Crystallinity and the phase composition of samples were characterized by XRD (Bruker D8 ADVANCE). Fourier transform infrared (FT-IR) spectra were collected on Bomen MB154S (FTIR) spectroscopy. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI-5300 X-ray photoelectron spectrometer with an Mg K $\alpha$  excitation source (1253.6 eV). Specific surface area of samples was obtained by BET method using BET instrument (NOVA 1000). Thermogravimetric analyses (TGA) were performed on a Boyuan DTU-2C thermogravimetric analyzer from 50 to 800

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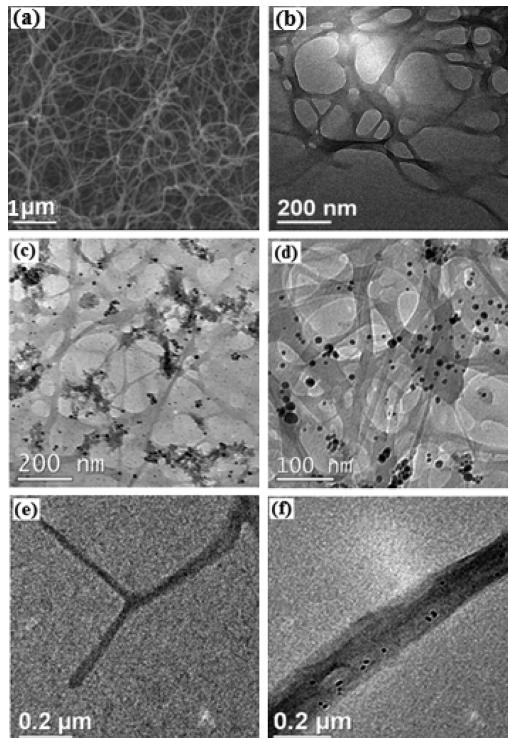
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°C at a heating rate of 10 °C/min<sup>-1</sup> in nitrogen flow. <sup>1</sup>H NMR spectra of samples from Pd/BC catalyzed Heck coupling were recorded on Bruker 500 spectrometer in CDCl<sub>3</sub> unless otherwise specified. Chemical shifts are reported with respect to internal solvent, 7.26 ppm (<sup>1</sup>H, CDCl<sub>3</sub>). Pd leaching after 5-cycle reactions was traced with 3300 DV ICP-AES (Perkin-Elmer Optima).

### 3. RESULTS AND DISCUSSION

**3.1. Characterization of Pd/BC Catalyst.** The freshly prepared BC scaffold is shown as well-separated nanofibers with a diameter of ~40 nm in TEM image (Figure 1a and 1e). The



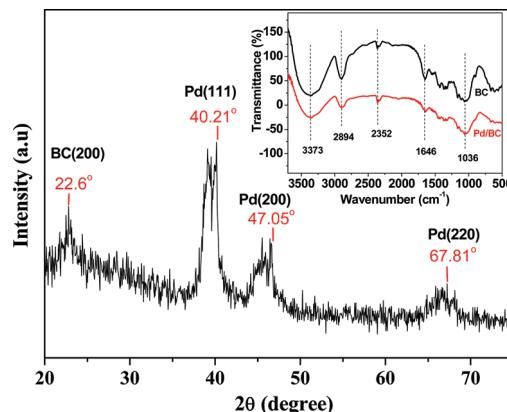
**Figure 1.** SEM image of the dried BC nanofibers (a), TEM images of wet BC nanofibers (b), Pd/BC catalyst after hydrothermal reaction for 1 h (c), the as-prepared Pd/BC catalyst (d), zoomed view of single BC fiber (e), and zoomed view of BC/Pd catalyst on a single BC fiber (f).

growth process of Pd(0) NPs onto BC fibers from hydrothermal reduction over 1 and 3 h can be understood from the TEM images shown in Figure 1c and 1d, respectively. As shown in Figure 1c, the Pd(0) NPs (~20 nm diameter) were dispersed on BC surface. With the hydrothermal reaction ongoing, single Pd(0) NPs grow in size and more densely Pd(0) NPs were formed as observed in Figure 1d. Some polydisperse Pd(0) NPs were even found to aggregate to form small islands of ~40 nm in dimension. The aggregation of Pd(0) NPs was found to occur after 3 h hydrothermal reaction (Figure 1d and 1f), since no significant change in the morphology of Pd/BC catalyst was found after further elongation of reaction time. The deposition of Pd(0) NPs on BC fiber and certain aggregation of Pd could be clearly observed even by a close look at the TEM images for single BC fibers shown in Figure 1e and 1f.

The Pd loading of the as-prepared Pd(0)/BC catalyst was measured with elemental analysis as reported.<sup>12</sup> The maximum Pd loading on the centrifuged wet Pd/BC was measured to be 8.15 wt % with a BET surface area of 24.8 m<sup>2</sup>/g, which is 7-fold

improved over pristine BC fibers. It is evident that triple feeding of PdCl<sub>2</sub> can increased the Pd loading in Pd(0)/BC catalyst by 54% in comparison to our previous report.<sup>12</sup>

The crystallographic behavior of BC-supported Pd NPs was further investigated by X-ray diffraction (XRD). From the XRD spectra shown in Figure 2, broad peaks are observed at 2θ



**Figure 2.** X-ray diffraction (XRD) patterns of Pd/BC catalyst, with FT-IR spectra of BC fibers and Pd/BC catalyst shown as inset figure.

values of 40.21°, 47.05°, and 67.81°, which are characteristic peaks for Pd(0) and can be assigned to the crystallographic plane of (111), (200) and (220) reflection of Pd crystal. All of the diffraction peaks match well with those of the perfect fcc Pd crystal structure.<sup>13</sup> No extra peaks for Pd are detected in this pattern, indicating clean Pd/BC composites achieved without any impurities. The peaks are observed at 2θ values of 22.6° corresponding to the (200) diffraction planes of cellulose I,<sup>14</sup> indicating the deposition of Pd NPs onto BC nanofibers did not change the crystallographic property of BC scaffold.

As the inset image shows in Figure 2, BC fibers exhibit the characteristic IR peaks including broad band at 3373 cm<sup>-1</sup> attributed to O–H stretching vibration, band at 2894 cm<sup>-1</sup> assigned to aliphatic C–H stretching vibration, and the sharp and steep band at 1036 cm<sup>-1</sup> due to the presence of C–O–C stretching vibrations, agreeing well with those in literature.<sup>14,15</sup> It is worth noting there is a small peak at 1646 cm<sup>-1</sup>, which results from carbonyl functional groups as a result of natural aging of cellulose.<sup>16</sup> Pd/BC catalyst exhibited FT-IR spectra similar to BC scaffold in terms of characteristic peaks and peak intensities, indicating that the adsorption of Pd NPs on BC fibers' surface via physical bonding did not change the original nature of BC nanofibers. This finding agrees well with the above-discussed XRD results.

Further evidence of high crystalline Pd(0) was obtained using X-ray photoelectron spectroscopy (XPS). A comparison of XPS curves for BC and Pd/BC catalyst is shown in Figure 3. The C1s and O1s core levels of BC and Pd/BC catalyst were fitted with different components corresponding to the nature of existing C and O element, according to the binding energy in literature.<sup>9</sup> For C1s, the binding energy of 281.0 eV is assigned for C–H, 283.2 eV for C–OH, 285.0 eV for C=O, and 286.2 eV for O–C–O. Whereas for O1s, the binding energy of 528.6 eV is assigned for C–OH and 531.3 eV for C–O–C.<sup>16</sup>

The perfect match of XPS spectra between Pd/BC catalyst and BC substrate indicated Pd(0) deposited onto BC fibers' surface via physical bonding, which was in good agreement with TEM, XRD, and FT-IR analyses. The Pd 3d spectra,

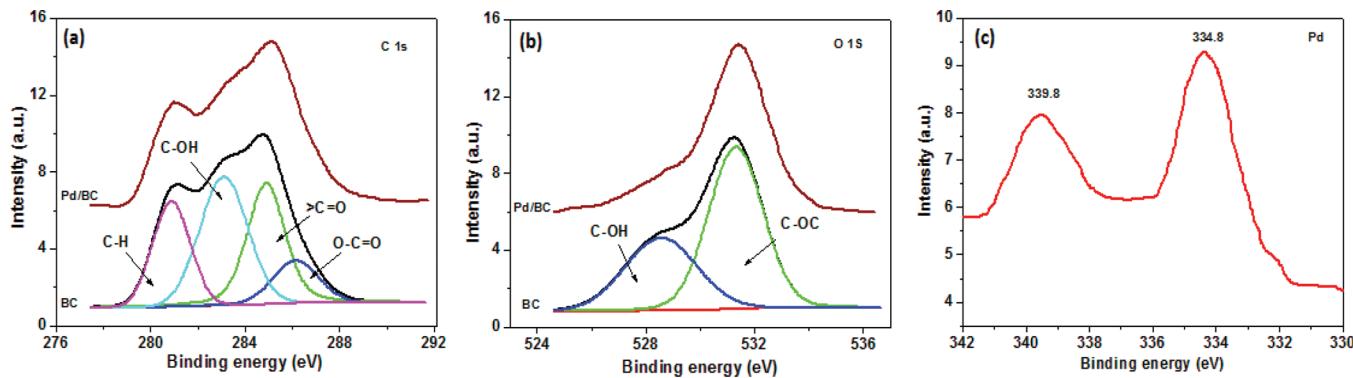


Figure 3. XPS analysis of (a) C 1s, (b) O 1s, and (c) Pd for BC nanofibers and Pd/BC catalyst.

characterized by spin-orbit splitting (Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  components), show binding energies of 334.8 and 339.8 eV, respectively. Both peaks for Pd NPs exhibit perfect match with literature reported states ( $3d_{5/2}$  BE 334.9 eV,  $3d_{3/2}$  BE 340.4 eV) for Pd(0).<sup>9</sup> This was in good agreement with XRD analysis of pure crystal of Pd NPs.

The thermal stability of as-prepared Pd/BC catalysts with Pd loading of 8.15 wt % was studied by thermal gravimetric analysis (TGA) and compared with our previously reported catalyst with 5.29 wt % Pd loading. As shown in Figure 4, Pd/BC

temperatures when heating up over 350 °C and ~3 wt % higher residues remained.

**3.2. Pd/BC Catalyzed Heck Reactions.** With Pd/BC catalyst at hand, its catalysis performance for Heck reaction was evaluated. The reaction protocol including reaction temperature and reaction time was optimized using the model coupling between idobenzene and styrene. As entries 1–7 show in Table 1, the reaction temperature plays an important role in

Table 1. Optimization of Model Heck Reaction with Pd/BC Catalyst<sup>a</sup>

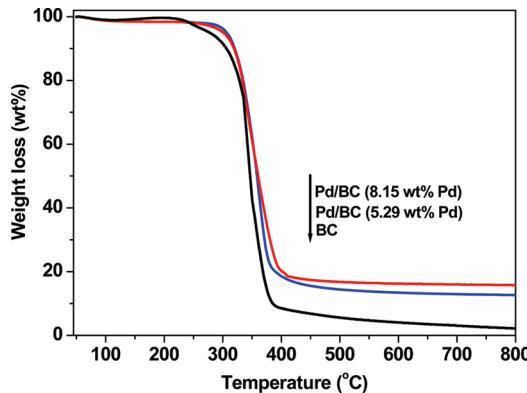
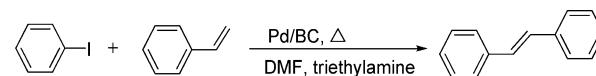


Figure 4. TGA traces of BC nanofibers and Pd/BC catalyst recorded at a heating rate of 20 °C/min under nitrogen flow.

BC catalysts exhibited better thermal stabilities than BC scaffold, indicating a 20 °C higher decomposition temperature (5% weight loss) around 320 °C. The TGA trace of BC nanofiber features (i) a first slow weight loss (~1.5%) corresponding to the elimination of ordered water around BC fibers via hydrogen bonding in the samples at ~104 °C,<sup>10</sup> (ii) a second weight loss (~74%) between 167 to 356 °C involving the removal of small molecular fragments such as O–H and CH<sub>2</sub>–OH groups during this rapid degradation process,<sup>10</sup> and (iii) a third process attributed to the decomposition of cellulose backbone.<sup>18</sup> Pd/BC catalyst presented a three-stage degradation profile similar to BC scaffold but with lower weight loss at the same temperature range due to the presence of Pd. It is noted that Pd/BC catalysts exhibited almost 10% higher weight remained for the residues than BC scaffold. A close look at the TGA traces of Pd/BC catalysts with different Pd loadings shows that the catalyst with 8.15 wt % Pd loading presented slightly higher thermal stability in terms of lower weight losses at certain



entry	temperature (°C)	yield (%)	entry	time (h)	yield (%)
1	80	80	8	2	73
2	90	84	9	4	82
3	100	86	10	6	89
4	110	94	11	8	97
5	120	97	12	10	97
6	130	95	13	12	98
7	140	95	14	14	99

<sup>a</sup>Reaction conditions: iodobenzene (5.0 mmol), styrene (6.0 mmol), triethylamine (5 mmol), DMF (15 mL), Pd/BC (0.1 mol %), N<sub>2</sub> atmosphere; 8 h for entries 1–7; 120 °C for entries 8–14.

the Pd/BC catalyzed Heck coupling, with the maximum conversion reaching 120 °C. Entries 8–14 in Table 1 show the influence of reaction time on the mode coupling. The coupling yield is found to increase with reaction time, with the optimum yield (97%) reaching for 8 h. The yield of this model Heck reaction is comparable to the yield of 68%,<sup>19</sup> 75%,<sup>20</sup> and 87%<sup>21</sup> achieved with reported Pd catalysts.

With the optimized reaction temperature and reaction time at hand, we extended this methodology to 4 acryl acetates (Table 2, entries 2–5) and more challenging coupling with arylbromide (Table 2, entries 6–10). The general protocol for Heck coupling is described as follows: Aryl halide (1 equiv), styrene or acrylate (1.2 equiv), base (1 equiv), and DMF (15 mL) were added to a 50-mL round-bottom flask. After adding Pd/BC (0.1 mol %) catalyst, the reaction was stirred at 120 °C for 8 h. After cooling to room temperature, the reaction mixture was subjected to filtration. Pd/BC catalyst was filtered off and washed with ethyl acetate (3 × 30 mL) and then deionized water (3 × 30 mL) for recycling. The collected filtrate was extracted with ethyl acetate and washed with water. After drying the extract with anhydrous MgSO<sub>4</sub>, the organic solvent was

**Table 2.** Heck Reaction with Pd/BC Catalyst for up to 5 Cycles<sup>a</sup>

Entry	X	R	Product	Cycle (yield %)			
				1	2	3	5
1	I	Ph		87	85	82	80
2	I	COOCH <sub>3</sub>		94	92	86	83
3	I	COOC <sub>2</sub> H <sub>5</sub>		91	89	85	82
4	I	COO <sup>n</sup> C <sub>4</sub> H <sub>9</sub>		96	94	89	87
5	I	COO <sup>t</sup> C <sub>4</sub> H <sub>9</sub>		95	92	88	84
6	Br	Ph		86	84	82	79
7	Br	COOCH <sub>3</sub>		87	85	81	80
8	Br	COOC <sub>2</sub> H <sub>5</sub>		86	83	82	80
9	Br	COO <sup>n</sup> C <sub>4</sub> H <sub>9</sub>		89	86	84	83
10	Br	COO <sup>t</sup> C <sub>4</sub> H <sub>9</sub>		88	85	83	82

<sup>a</sup>0.1 mol % Pd/BC catalyst, 1 equiv. triethylamine, DMF, 120 °C, 8 h.

removed by evaporation. The crude solid was recrystallized with petroleum ether to afford the corresponding coupling product. The chemical structures of coupling products were confirmed with <sup>1</sup>H NMR and FT-IR measurement, with data agreeing well with literature.<sup>19–21</sup>

For the coupling of iodobenzene with acrylates (Table 2, entries 2–5), excellent yields (91–96%) were achieved for the first cycle coupling. And ~2% higher yields were obtained for entries 2–5 when compared with our previous attempts of 3.5 h reactions under the same conditions.<sup>12</sup> For entry 2, the yield of 94% is outstanding compared to the reported yield of 80% from microcrystalline cellulose supported Pd catalyst.<sup>9</sup> This conversion is also comparable to the literature-reported 86%,<sup>20</sup> 89%,<sup>22</sup> 82%,<sup>22</sup> 93%,<sup>23</sup> 96%,<sup>24</sup> and 91%<sup>25</sup> achieved from carbon or silica supported Pd catalysts. The coupling yield of 91% (entry 3) is comparable to those reported yields of 82%,<sup>20</sup> 92%,<sup>26</sup> and 95%.<sup>24</sup> Similarly, the coupling for iodobenzene and butyl acrylate (entry 4) is efficient with Pd/BC, indicated by its excellent yield comparable to the yields of 93%,<sup>26</sup> 99%,<sup>27</sup> 95%,<sup>19,28</sup> and 98%<sup>29</sup> in literature from carbon/silica supported Pd catalysts.

The couplings with less reactive bromobenzene exhibited slightly lower yield in comparison to iodobenzene. Nevertheless, good yields ranging from 86% to 89% were achieved for the first-cycle coupling. For coupling of bromobenzene with styrene (entry 6), the yield of 86% is very good when compared with 62%,<sup>21</sup> 96%,<sup>30</sup> 92%,<sup>31</sup> 74%,<sup>32</sup> and 56%<sup>33</sup> in literature with different Pd(0) catalyst. The coupling with methyl acrylate by Pd/BC (entry 7) is more efficient when compared with the reported yields of 33%<sup>26</sup> and 60%<sup>33</sup> with other Pd catalyst. The couplings with ethyl acrylate (entry 8) and propyl acrylate (entry 9) via Pd/BC afforded slightly lower yield compared to

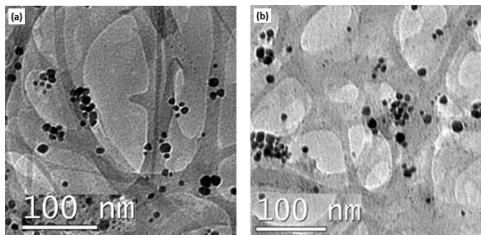
the highest yield of 92%.<sup>30</sup> The couplings with propyl acrylate (entry 9) are good when compared to its yields of 98%,<sup>31</sup> 75%,<sup>33</sup> 77%,<sup>34</sup> and 36%<sup>35</sup> in literature.

The above-mentioned methodology was further extended to couplings with chrolobenzene. Due to its less reactive nature than bromo- and iodobenzene, lower conversions ranging from 75% to 82% were observed for the couplings with same substrates entries 1–5 in Table 2.

The coupling products were structurally confirmed, with characterization data listed as follows: Product a: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.53 (d, 4H, J = 7.5 Hz), 7.37–7.40 (d, 4H, J = 7.5 Hz), 7.26–7.30 (d, 2H, J = 7.5 Hz), 7.14 (s, 2H); FT-IR (KBr, cm<sup>-1</sup>) 3075 (C—H), 1690, 1631, 1578, 1494 (benzene ring, C=C), 1650(C=C); b: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.69 (d, 1H, J = 16 Hz), 7.52–7.54 (m, 2H), 7.38–7.40 (m, 4H) 6.43 (d, 1H, J = 16 Hz), 3.81 (s, 3H); FT-IR (KBr, cm<sup>-1</sup>) 3076, 2988 (C—H), 1717 (C=O), 1691, 1604, 1572, 1522 (benzene ring, C=C), 1651 (C=C), 1453 (C—H), 1103(C—O); c: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.67 (d, 1H, J = 16 Hz), 7.51–7.53 (m, 2H), 7.37–7.39 (m, 3H), 6.43 (d, 1H, J = 16 Hz), 4.26–4.27 (m, 2H), 1.34 (m, 3H); FT-IR (KBr, cm<sup>-1</sup>) 3078, 1986 (C—H), 1718 (C=O), 1694, 1601, 1574, 1523 (benzene ring, C=C), 1652 (C=C), 1451 (C—H), 1102 (C—O); d: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.71–7.75 (d, 2H, J = 16 Hz), 7.56–7.58 (m, 2H), 7.41–7.43 (m, 3H), 6.47 (d, 1H, J = 16 Hz), 4.24–4.27 (m, 2H), 1.71–1.75 (m, 2H), 1.42–1.51 (m, 2H), 1.02 (s, 3H, J = 7.5 Hz); FT-IR (KBr, cm<sup>-1</sup>) 3077, 1987 (C—H), 1719 (C=O), 1693, 1602, 1573, 1524 (benzene ring, C=C), 1653 (C=C), 1452 (C—H), 1101 (C—O); e: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.68 (d, 1H, J = 16 Hz), 7.52–7.53 (m, 2H), 7.37–7.38 (m, 3H), 6.44 (d, 1H, J = 16 Hz), 4.00 (d, 2H, J = 7 Hz), 2.00–2.03 (m, 1H), 0.98 (d, 6H, J = 7 Hz); FT-IR (KBr, cm<sup>-1</sup>) 3075, 2985 (C—H), 1716 (C=O), 1695, 1600, 1575, 1525 (benzene ring, C=C), 1650 (C=C), 1450 (C—H), 1100 (C—O).

For practical applications of Pd/BC catalyst, its lifetime and level of reusability are very important considerations.<sup>36</sup> To clarify this issue, we established a set of experiments for all couplings listed in Table 2 using the recycled Pd/BC catalyst. After the completion of the first coupling reaction, the catalyst was recovered by filtration and subsequent washing with ethyl acetate and deionized water for reuse. A new reaction was then performed with fresh reactants and the recycled catalyst under the same conditions. The as-prepared Pd/BC catalyst could be used at least 3 times with the catalysis efficiency decreased only ~6%. Even for five reaction cycles, the catalysis performance of Pd/BC dropped no more than 10% (entry 8). This behavior may be attributed to slightly declined quality of Pd/BC catalyst (Figure 5b), where larger island domains were observed due to higher aggregation of polydisperse Pd NPs after 5-cycle reaction.

Metal leaching was another concern for supported heterogeneous catalyst. In our current study, Pd leaching was studied by ICP-AES analysis of Pd/BC catalyst before and after the fifth reaction cycle.<sup>12</sup> The Pd concentration was found to be 8.12% after the 5-cycle reaction. No Pd metal was detected in the final coupling product, indicating the possible Pd loss in workup process. The negligible Pd leaching is probably due to the protection from the ordered water layers covering around BC fibers via H-bonding.<sup>10</sup>



**Figure 5.** TEM image of as-prepared Pd/BC catalyst (a) and catalyst after 5-cycle reaction (b).

#### 4. CONCLUSIONS

In summary, BC nanofibers supported Pd catalyst has been prepared by facile hydrothermal reduction. The Pd/BC catalyst has been successfully characterized using various analytical techniques. The results showed that Pd NPs were deposited onto BC nanofibers via physical coating, where the crystalline structures of both Pd and BC remained unchanged after deposition of Pd NPs. The catalysis results indicated Pd/BC catalyst was a highly efficient and recyclable catalyst for standard Heck coupling reaction. The robust catalyst can be recycled as least 5 times, with the coupling yields maintaining ~90%. Extension of this catalyst to more coupling with aryl chlorides, as well as the measurement of adhesion strength between Pd NPs and BC nanofibers, are in progress and will be reported in due time.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

\*E-mail: whtang@mail.njust.edu.cn

##### Notes

The authors declare no competing financial interest.

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