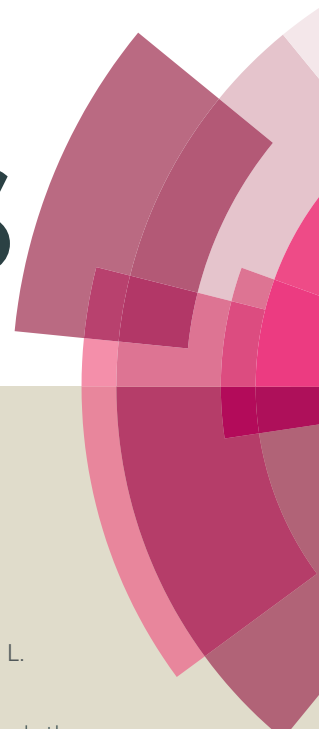


RSC Advances



This article can be cited before page numbers have been issued, to do this please use: C. Wu, X. Peng, L. Zhong, X. Li and R. Sun, *RSC Adv.*, 2016, DOI: 10.1039/C6RA02242A.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Green Synthesis of Palladium Nanoparticles via Branched Polymers: The Bio-Based Nanocomposite for C-C Coupling Reactions

Changyan Wu,^a Xinwen Peng,^{*a} Linxin Zhong,^{*a} Xuehui Li,^b Runcang Sun,^c

^aState Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 381 Wushan Road, Guangzhou 510640, China

^bSchool of Chemistry and Chemical Engineering, South China University of Technology, 381 Wushan Road, Guangzhou 510640, China

^cInstitute of Biomass Chemistry and Utilization, Beijing Forestry University, 35 Tsinghua East Road, Beijing 100083, China

* Corresponding authors. E-mail: fexwpeng@scut.edu.cn (Xinwen Peng) and
lxzhong0611@scut.edu.cn (Linxin Zhong)

Tel.: +86-020-87111735; Fax: +86-020-87111861.

1 ABSTRACT

2 Catalytic process is the key of many chemical industries. In this study, a novel
3 heterogeneous Pd (CMH-Pd (0)) has been prepared by deposition of palladium
4 nanoparticles (Pd NPs) onto the surface of carboxymethyl functionalized
5 hemicelluloses using ethanol as solvent and in situ reducing agent. The as prepared
6 catalyst was characterized by TEM, HR-TEM, XRD, FT-IR, TGA and XPS. The
7 loading level of Pd in the CMH-Pd (0) catalyst was 0.38 mmol g^{-1} . The catalyst
8 showed high catalytic activity and versatility towards Heck coupling reactions under
9 aerobic conditions and could be readily recovered and reused in at least five
10 successive cycles without obvious loss in activity. The catalyst is promising for its
11 renewability, environment benefit, efficient catalytic activity, mild reaction conditions,
12 simple product work-up and easy catalyst recovery.

13

14 *Keywords:* Heterogeneous Pd, Biomass, Hemicelluloses, Carboxymethyl
15 hemicelluloses, Heck reaction, Sustainable chemistry

16

17 Introduction

18 The attribution of the Nobel prizes to the winners who developed cross-coupling
19 catalysis reactions indicates the significance of these pioneering works as a landmark
20 in organic chemistry and their great influence on material science.¹ Since the
21 discovery of these reactions, they have been widely utilized in organic synthesis,
22 especially, palladium occupies a special position of crucial importance in the field of
23 catalysis for different organic transformations.²⁻⁴ Recently, palladium nanoparticle
24 catalysts have been used widely into various C-C coupling reactions.^{5,6} Especially,
25 palladium-catalyzed Heck cross-coupling reaction of aryl halides with olefins is found
26 to be one of the most powerful synthetic methods for the formation of C-C bonds
27 between alkenes and aryl or alkyl halides. These coupling products find good
28 applications as intermediates in the preparation of materials, natural products, and
29 bioactive compounds.⁷ Among the cross-coupling processes, Heck reaction is
30 especially widely used, because of its attractive attributes such as commercial
31 availability, air and water stability and functional-group compatibility, and thus has
32 been widely used in many industrial processes, especially in pharmaceuticals,⁸ fine
33 chemicals,⁹ natural product synthesis,¹⁰ material science,¹¹ bioorganic chemistry¹² and
34 conducting polymers.¹³

35 Traditionally, homogeneous catalyst system such as Pd(OAc)₂ or PdCl₂ was used for
36 Heck reaction. Although, conventional catalytic systems have a series of advantages,
37 the utilization of green, efficient chemistry approaches and reusable catalysts are of
38 great importance in the light of contemporary design of synthetic processes. During

39 Heck reaction, Pd (0) acts as active site to initiate the catalytic cycle, and the catalytic
40 activity depends on the capacity of Pd (0) species to activate the carbon-halogen bond
41 by oxidative addition, which can be further adjusted by the steric and electronic
42 properties of the ligands attached to the nanoparticles. In this regard, phosphine
43 ligands have been extensively utilized because of its effectiveness in stabilizing the Pd
44 (0).¹⁴ However, despite general utility of the phosphine ligands, they are susceptible to
45 oxidation during the reaction, which results in phosphine oxides and “palladium
46 black”, and thus decreasing the catalytic activity. In addition, several other
47 shortcomings such as the pollution of products, tedious work-up, high cost, and
48 difficulty in separation and recovery of the catalyst from the reaction mixture always
49 puzzled researchers.^{2, 10, 15}

50 In order to overcome these drawbacks, many researchers have made great efforts to
51 develop environmentally benign Pd heterogeneous catalysts. Most of the reported
52 supports for catalytic applications are based on various inorganic and organic
53 materials, such as metal oxides,¹⁶ porous silicate,¹⁷ silica materials,¹⁸ clay,¹⁹ zeolites,²⁰
54 ionic liquid,¹⁵ carbon materials²¹ and synthetic polymers.²² However, the synthesis of
55 these supports involves either high temperature calcinations or polymerization of
56 petrochemical and expensive feed stocks. Taking into consideration of all these issues
57 as well as the increasing environmental emphasis on materials and processes,
58 tremendous efforts have been made to develop natural polymers supported catalysts.²³
59 Biopolymers are the most important environment-friendly resources with several
60 interesting features, for example, renewability, high sorption capacity, stability of

61 metal anions, and facile functionalization. Recently, Marzieh et al.²⁴ reported cellulose
62 supported palladium (0) for Heck coupling reactions. Nicola and co-workers²⁵ utilized
63 lignin as support for Heck, Suzuki and Sonogashira cross-coupling reactions in water
64 with satisfactory product yields and selectivity. In addition, the
65 nanopalladium-entrapped several other biopolymers, such as chitosan,¹ alginate,²⁶
66 gelatin,²⁷ starch,²⁸ cyclodextrin²⁹ and DNA³⁰ were fabricated as first successful
67 achievements of such strategy and were further evaluated as the ideal supports for
68 various catalytic applications.

69 Among various biopolymers, hemicelluloses are heteropolysaccharides with various
70 branches. The units of main chain include xylose, glucose, uronic acid, etc.³¹
71 Hemicelluloses possess many hydroxyl groups, and therefore hemicelluloses can bind
72 and stabilize heavy metal ions.³² In addition, as compared to cellulose, chitosan and
73 other high crystalline biopolymers, hemicelluloses show unique features, for example,
74 controlled surface chemistry, solubility in various solvents. Thus hemicelluloses have
75 great potential to be modified and utilized. Our interest focuses on developing
76 hemicelluloses based functional materials and especially, developing hemicelluloses
77 or their derivatives as the natural ligands for palladium nanoparticle preparation to
78 respond to the current call for environment friendly and sustainable green chemistry.³³
79 Carboxymethyl hemicelluloses (CMH) which have both carboxyl groups and
80 hydroxyl groups are synthesized by hemicelluloses with monochloroacetic acid
81 (MCA), and the reaction scheme is shown in Figure 1. It has been reported that
82 chelating ligands containing O atom result in more stable and efficient Pd catalysts.¹³

83 Thus, CMH can be used as excellent natural ligands for catalysts preparation. In this
84 study, we focused on the preparation of hemicelluloses-based heterogeneous catalyst
85 by the anchoring of palladium on the surface of CMH with O–O ligand interaction,
86 where the oxygen on both hydroxyl groups and carboxy groups acted as ligand and
87 stabilizer for Pd NPs, and its application in Heck cross-coupling reaction. The
88 superiority of physical and chemical structure, convenience for preparation, natural
89 polydentate ligand and minimization of catalysts cost made our ideal catalytic
90 CMH-based nanocomposite exhibit relatively high catalytic efficiency, selectivity and
91 stability in the C-C coupling reactions.

92 **Experimental Section**

93 **Chemicals**

94 All of reagents used including halides, olefins, palladium acetate, MCA and
95 *p*-toluenesulfonic acid were purchased from Aladdin Reagent Co., Ltd., and were used
96 without further purification. N, N-dimethylformamide (DMF), dimethyl sulfoxide
97 (DMSO), ethanol (EtOH), acetonitrile, triethylamine and sodium hydroxide were
98 purchased from National Medicine Group Chemical Reagent Co., Ltd. Hemicelluloses
99 were prepared according to literature.³⁴ The sugar analysis showed the proportion of
100 sugar composition (relative weight percent): 89.4% xylose, 5.80% arabinose, 1.90%
101 glucose, 0.70% galactose, 1.80% glucuronic acid, and 0.60% galactose acid.

102 **Preparation of CMH**

103 The carboxymethylation of hemicelluloses was shown in Figure 1. The typical
104 procedure for the preparation of CMH was according to the literature,³⁵ with slight

105 modifications. The details were shown in supporting information. And six samples
106 were prepared by changing the reaction conditions. (Table S1 in ESI†)

107 **Preparation of CMH-Pd (0)**

108 CMH powder (1.0 g) and palladium acetate (0.1 g) were suspended in 50 mL EtOH,
109 and then Pd (II) in the slurry was reduced by EtOH at 60 °C for 12 h. After the
110 reaction, the black slurry was filtered and washed for several times with ethanol and
111 finally with diethyl ether and dried at 50 °C under vacuum to give the catalyst
112 CMH-Pd (0) with a Pd loading of 0.38 mmol/g calculated by inductively coupled
113 plasma atomic emission spectroscopy (ICP-MS).

114 **Characterizations**

115 Fourier transform infrared spectra (FT-IR) were measured through a Bruker Tensor 27
116 FT-IR spectrometer. The thermal stabilities of CMH and CMH-Pd (0) catalyst were
117 determined by TA Q500 thermo gravimetric analyzer (TGA). The morphologies of the
118 samples were recorded by a JEM-2100 (HR) transmission electron microscopy (TEM)
119 working at 200 kV. The content of palladium in catalyst was determined by
120 TEM-energy dispersive spectrometer (EDS) and ICP-MS using Agilent 7700
121 equipment. X-ray powder diffraction (XRD) patterns were collected using a
122 Bruker-D8 Advance diffractometer with Cu K α radiation ($\lambda=0.154$ nm). X-ray
123 photoelectron spectroscopy/ESCA (XPS) was recorded on Axis Ultra DLD instrument
124 using Al K α radiation ($h\nu=1486.6$ eV) with contaminated C as an internal standard
125 ($C_{1s}=284.6$ eV). $^1\text{H-NMR}$ (600 Hz) and $^{13}\text{C-NMR}$ (150 Hz) spectra were accumulated
126 on a Bruker AVANCE III HD 600 spectrophotometer system.

127 General procedure for Heck coupling reaction

128 A mixture of aryl halide (1.0 mmol), olefin (1.2 mmol), triethylamine (2.0 mmol) and
129 CMH-Pd (0) catalyst (50 mg, 1.9 mol% Pd) were added into a 35 mL pressure tube, 3
130 mL DMF was then added. The mixture was heated and stirred at 120 °C for 6 h. After
131 the reaction was completed, the catalyst was filtrated and washed with ethyl acetate for
132 several times. Before extraction by ethyl acetate for three times, the filtrate was diluted
133 with water and the organic phase was dried over anhydrous Na₂SO₄ and then
134 evaporated under vacuum to obtain crude product. The isolated product was collected,
135 purified by flash column chromatography and characterized by ¹H-NMR and
136 ¹³C-NMR.

137 General procedure for catalyst recovery

138 The catalytic activity of CMH-Pd (0) catalyst was examined after reaction. In a
139 reaction vessel, iodobenzene (1.0 mmol), ethyl acrylate (1.2 mmol), triethylamine (2.0
140 mmol) and CMH-Pd (0) catalyst (50 mg, 1.9 mol% Pd) were mixed in DMF. The
141 mixture was heated and stirred at 120 °C for 6 h. The heterogeneous catalyst was
142 separated by filtration and washed with ethyl acetate for three times, which followed
143 by drying at 70 °C. The catalyst was directly used for the second run, and the same
144 process was repeated for the next run.

145 Heterogeneity test

146 A mixture of iodobenzene (1.0 mmol), ethyl acrylate (1.2 mmol), triethylamine (2.0
147 mmol) and CMH-Pd (0) catalyst (50 mg, 1.9 mol% Pd) were added into a 35 mL
148 pressure tube, 3 mL DMF was then added. The mixture was heated and stirred at 120

149 °C. After 2 h of reaction progress, the catalysts were separated by hot filtration. The
150 filtrate was further reacted under the same conditions for another 4 h. The following
151 process after the Heck reaction was performed by the same procedure mentioned in
152 the general procedure for Heck coupling reaction.

153 **Results and Discussion**

154 **Characterization of CMH-Pd (0) catalyst**

155 Figure S1a shows the typical absorption frequencies of hemicelluloses at 3431, 2920,
156 1629, 1465, 1250, 1169, 986, and 897 cm^{-1} .³⁵ Compared to the spectra of
157 hemicelluloses, the peak at 1735 cm^{-1} in Figure S1b is ascribed to the carbonyl
158 vibration absorption, and the new bond at 1605 cm^{-1} is attributed to $-\text{COO}^-$ stretching
159 vibration. The band at around 1419 cm^{-1} is assigned to $-\text{CH}_2$ scissoring vibration.³⁵
160 Appearance of these bands suggests that the reaction between hemicelluloses and
161 MCA occurs successfully. Interestingly, the FT-IR spectra of CMH-Pd (0) is similar to
162 that of CMH scaffold in terms of the characteristic peaks, which indicates that the
163 physical bonding exists between Pd NPs and CMH.³⁶

164 The ^1H -NMR spectrums of hemicelluloses and CMH are shown in Figure S2 in ESI†.
165 The major signals at 4.39, 4.00, 3.71, 3.47, 3.29, and 3.21 ppm in Figure S2a are
166 corresponded to the H-1, H-5eq, H-4, H-3, H-5ax, H-2 of non-substituted β -DXyl,
167 respectively.³⁷ In Figure S2b, the new band at 4.52 ppm is ascribed to the substituted
168 carboxymethyl $-\text{CH}_2-$. These observations confirm the occurrence of
169 carboxymethylation of hemicelluloses with MCA. Figure S2c and Figure S2d show
170 the representative ^{13}C -NMR spectra of native hemicelluloses and CMH. The signals at

171 101.69, 76.37, 73.68, 72.72, and 62.98 ppm in Figure S2c are assigned to C-1, C-4,
172 C-3, C-2, and C-5 of the β -D-xylopyranosyl units of hemicelluloses, respectively.
173 Acetyl -CH₃ in xylan gives a signal at 23.28 ppm. The ¹³C-NMR spectrum of CMH
174 shows the new signal at 176.12 ppm, which is assigned to the carboxyl groups. The
175 signal at 69.94 ppm is ascribed to the methylene carbon atoms of carboxymethyl
176 groups.³⁵ In conclusion, the results further indicated the reaction between
177 hemicelluloses and MCA occurred.

178 The structure of CMH-Pd (0) was further studied by means of powder X-ray
179 diffraction (XRD), as shown in Figure 2. The broad peaks of CMH-Pd (0) were
180 observed at $2\theta=40.0^\circ$, 46.1° and 67.5° , corresponding to (111), (200) and (220)
181 crystalline planes of the face-centered cubic (fcc) lattice (PDF-# 46-1043).³⁸

182 Figure 3 displays the XPS spectra of CMH and CMH-Pd (0). Besides O and C
183 elements in CMH, CMH-Pd (0) contains Pd element. The Pd 3d spectrum shows two
184 typical peaks at 334.3 eV and 339.6 eV for 3d_{5/2} and 3d_{3/2}, respectively, which
185 correspond to Pd (0).³⁸ These results well agree with XRD results.

186 Figure 4 showed the TEM images of CMH-Pd (0) before and after catalysis. A typical
187 TEM image of CMH-Pd (0) was shown in Figure 4a, which clearly showed the
188 formation of metallic Pd nanoparticles with size range of 11-19 nm and the average
189 particle size was about 15 and 16 nm. The freshly prepared CMH-Pd (0) particles
190 were homogeneous on the CMH surface. High resolution transmission electron
191 microscopy (HR-TEM) image of an individual Pd nanoparticle showed clear lattice
192 fringes with an interplanar distance of approximately 0.22 nm, corresponding to (111)

193 planes of Pd (Figure 4d). There were clearly numerous crystal forms on the surface of
194 the as-prepared CMH-Pd (0), as indicated by the corresponding electron diffraction
195 pattern form (Figure 4c).³⁹ The element Pd presented in the product was shown in
196 Figure 4e. All of these results clearly confirmed that the palladium complex was
197 immobilized onto xylan molecular chains.

198 Generally, heating is necessary in the Heck cross-coupling reaction. Hence, the
199 thermal stability of CMH-Pd (0) catalyst was studied by TGA. As illustrated in Figure
200 5, compared to CMH, the catalyst exhibited relatively good thermal stability up to 210
201 °C. Weight loss along with exothermic peak occurred when temperature was higher
202 than 210 °C. With the increase of temperature, the decrease of catalyst weight was
203 more obvious. The decomposition of CMH was complete when temperature was
204 raised to 360 °C and the oxide of palladium was remained.²⁴

205 **CMH-Pd (0) catalyzed Heck reaction**

206 The Heck coupling reaction of iodobenzene with ethyl acrylate or styrene was utilized
207 as a model reaction to investigate the catalysis performance of CMH-Pd (0), and the
208 results were listed in Table 1 and Table 2. The results indicated that solvent, catalyst
209 loading, reaction temperature, time and DS of CMH were the key factors that
210 significantly affected the catalytic efficiency of Pd NPs for the formation of C-C
211 bonds. Subsequently, the influence of solvent on the reaction was investigated (Table
212 1, entries 1-5). Solvent screening gave a maximum yield of 74% in DMF (Table 1,
213 entry 1). A relatively high yield of 84% for the cross-coupled direct arylation product
214 could be obtained within 6 h (Entry 16 in Table 1). However, H₂O and CH₃CN

215 resulted in trace amount of product (Entries 4 and 5). The moderate yields (53% and
216 48%) (Entries 2 and 3) indicate that reactions of iodobenzene with ethyl acrylate in
217 EtOH and DMSO were also not effective compared to DMF. The reasons may be
218 explained as follows. On the one hand, CMH could dissolve in H₂O and DMSO, so
219 the structure of CMH-Pd (0) was not stable when the reaction was carried out in H₂O
220 or DMSO. On the other hand, without reflux system, 120 °C was over the boiling
221 points of CH₃CN, EtOH and H₂O, which may not facilitate the reaction. Therefore,
222 DMF was the optimum solvent.

223 In addition, the effect of the catalyst loading on product yield was examined (Table 1,
224 entries 6-10 and 1). When the amount of catalyst was reduced to 12.5 mg (0.48 mol%),
225 a good yield 60% (Table 1, entry 7) was retained, indicating that CMH-Pd (0) was a
226 relatively active catalyst for the direct coupling reactions of aryl halides with olefins.
227 Controlling experiment demonstrated that no reaction could occur in the absence of
228 the CMH-Pd (0) (Entry 6 in Table 1), suggesting that the as-prepared CMH-Pd (0)
229 catalyst actually acted as the real catalyst. The results showed that the optimal catalyst
230 dosage was 1.9 mol%.

231 The optimal reaction temperature was established by monitoring the coupling reaction
232 of iodobenzene with ethyl acrylate as a function of temperature from 60 °C to 140 °C
233 (Table 1, entries 11-14 and 1). The reaction processed successfully and the yield
234 exceeded 60% even at low temperature (80 °C, Table 1, entry 12). The yield of
235 product increased when the reaction temperature was increased from 60 to 120 °C.
236 Due to the side reactions the yield of product decreased slightly when the temperature

237 was raised to 140 °C,²⁴ for further exploration, 120 °C was selected as the optimum
238 temperature.

239 As shown in Table 2, the DS and M_w of CMH had significant influence on the
240 catalytic activity of the palladium nanocomposites. Hemicelluloses was a kind of ideal
241 support with the yield up to 84%, however, a good yield 90% was obtained when the
242 DS of CMH was up to 0.24. With the increase of DS of CMH, the product yield of
243 Heck reaction was increased, which indicated that carboxy groups have better ability
244 for Pd NPs coordination and stabilization. However, the increase of DS of CMH
245 resulted in the decrease of M_w which might further have great influence on the service
246 life of the CMH-Pd (0).³⁵ Because of the decrease of M_w , the molecular chain and
247 side chains of CMH were broken and shortened, the twisting capacity of CMH
248 molecular chains for Pd NPs stabilization was impaired. Therefore, for further study,
249 DS=0.24 was chose as the typical DS.

250 The reaction scope was also investigated using a range of functionalized aryl halides
251 and olefins under the optimized reaction condition, and the results were summarized
252 in Table 3. In general, all the aryl iodides afforded the corresponding products in good
253 to excellent yields ranging from 90% to 99%. As for different vinyl substrates, such as
254 styrene, acrylic acid, methyl acrylate, ethyl acrylate and *n*-butyl acrylate resulted in
255 high yields (Table 3, entries 4-8). For aryl bromides, the catalyst showed lower
256 activity (Table 3, entries 3, 9, 11, 13, 15). Meanwhile, aryl bromides with
257 electron-withdrawing groups afforded the corresponding products in better yield up to
258 87% and 94% (Table 3, entries 13 and 15). The coupling reactions of aryl chlorides

259 with ethyl acrylate required extended reaction time and the yields of corresponding
260 coupling products were unsatisfactory, because the oxidative-addition of C-Cl bond to
261 catalyst species was usually difficult. Functional groups including methoxyl, methyl,
262 carbonyl and nitril are also tolerated. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of all products
263 were confirmed. The results indicated that CMH-Pd (0) as a novel catalyst was a
264 relatively good choice for Heck coupling reactions.

265 **Reusability of CMH-Pd (0) catalyst**

266 The recyclability of the as-prepared CMH-Pd (0) catalyst was studied by using the
267 reaction between iodobenzene and ethyl acrylate as a model reaction. The catalyst
268 could be recovered by simple filtration. After being washed adequately by EtOH and
269 dried in air, the catalyst could be reused for the next reaction, and the results are listed
270 in Table 4. The yield of the product was decreased from 97% to 89% in the fifth run,
271 and retained nearly 92% of its original reactivity, indicating that CMH stabilized Pd
272 NPs catalyst was highly stable and recyclable. The decreasing activity of the catalyst
273 upon recurrent usage can be explained by the fact that the aggregation of the Pd NPs
274 (Figure 6b). As we all known, Pd NPs are not stable and prone to aggregate because
275 of their large surface cohesion energy. The formation of Pd NPs by reduction of Pd (II)
276 is composed of two steps, that is, the nucleation and the growth of nuclei.⁴⁰ When the
277 initial Pd nuclei is formed, the hydroxyl-groups and carboxyl of CMH participate in
278 controlling growth of Pd nuclei. The strong bonding interaction between CMH and Pd
279 atom prevents individual particle from aggregation, and thus giving well dispersed Pd
280 NPs with small size. After five reaction cycles, the stability of CMH is decreased, thus

281 the interaction between Pd NPs and CMH reduced. In this work, excellent activity and
282 recyclability overcame the reused and environmental problems for homogeneous
283 catalyst. Therefore, the widely available and renewable raw materials, good catalytic
284 properties and reuse performance can significantly decrease the overall cost, and
285 improve the efficiency of the synthetic process for practical applications.

286 **Heterogeneity of the CMH-Pd (0) during the Heck coupling reaction**

287 In order to prove the heterogeneous nature of the CMH-Pd (0) and the absence of Pd
288 leaching, the following reaction conditions were conducted. First, the standard
289 reaction was processed at 120 °C for 2 h (the product yield was 75% checked by
290 column purification of the product), and then CMH-Pd (0) was hot filtrated, the
291 reaction mixture was left stirring at 120 °C for another 4 h. The product yield was
292 only 80%. In another test, after full conversion (6 h, 97% yield), the filtrate was
293 analyzed by ICP-MS, the results showed that the amount of palladium was 0.2 ppm.
294 This indicated that the leakage of Pd NPs during catalytic experiments was negligible
295 and the nature of reaction was heterogeneous.

296 Taking iodobenzene reacting with styrene as an example, we compared the results
297 achieved in this work with other biopolymer-based catalysts supported catalysts for
298 the Heck coupling reaction, and the results are listed in Table 5. As shown in Table 5,
299 CMH-Pd (0) catalyst showed some extensive improvement in reaction conditions,
300 such as reaction time, catalyst dosage and yield. For example, CELL-Pd (0),
301 PdNPs@XH afforded a much longer reaction time and higher dosage of palladium
302 catalysts, although high yield was obtained. In addition, the procedure for the

303 preparation of PNP-SSS is complex and not green, in which thionyl chloride and
304 chloroform were employed during the synthesis reaction, despite the yield was higher
305 than CMH-Pd (0) achieved. Catalysis for the Heck reaction by utilizing renewable
306 CMH-Pd (0) catalyst based on biomass presents an ideal chemical process. The
307 CMH-Pd (0) catalyst is promising for its renewability, environment benefit, efficiently
308 catalytic activity, thus has great potential to be applied into the industry processes.

309 **Conclusion**

310 In summary, CMH-Pd (0) catalyst is a very active and stable bio-based
311 nanocomposite catalyst for the Heck coupling reaction. Furthermore, the catalyst
312 could be easily recovered and reused by simple filtration, which was perfect in terms
313 of cost and environmental sustainability. The catalyst could be reused at least five
314 times without considerable deactivation. Driven by all these advantages, CMH-Pd (0)
315 catalyst will have great potential to be applied in pharmaceutical industry and other
316 environment benign chemical industries.

317 **Associated Content**

318 Details for CMH preparation, FT-IR and ^1H NMR spectra of CMH, spectral data and
319 copies of ^1H and ^{13}C -NMR spectra for the synthesized compounds are shown in
320 supporting information.

321 **Author Information**

322 Corresponding authors. E-mail: fexwpeng@scut.edu.cn (Xinwen Peng) and

323 lxzhong0611@scut.edu.cn (Linxin Zhong).

324 Tel.: +86-010-62336972;

325 Fax: +86-010-62336972.

326 **Notes**

327 The authors declare no competing financial interest.

328 **Acknowledgments**

329 The project is supported by the National Natural Science Foundation of China
330 (21404043, 31430092 and 21336002), Pearl River S&T Nova Program of Guangzhou
331 (2014J2200063), Science and Technology Project of Guangdong Province
332 (2015A010105005), Research Fund for the Doctoral Program of Higher Education
333 (201301721200240), Fundamental Research Funds for the Central Universities.

334 **Abbreviations**

335 CMH, carboxymethyl hemicelluloses; Pd NPs, palladium nanoparticles; MCA,
336 monochloroacetic acid; DMF, N,N-dimethylformamide; DMSO, dimethyl sulfoxide;
337 EtOH, ethanol; CMH-Pd (0), carboxymethyl hemicelluloses with Pd (0) catalyst;
338 FT-IR, fourier transform infrared spectra; TGA, thermal gravimetric analysis; TEM,
339 transmission electron microscopy; HR-TEM, high resolution transmission electron
340 microscopy; XRD, X-ray powder diffraction; EDS, TEM-energy dispersive
341 spectrometer; FT-IR, fourier transform infrared spectra; TGA, thermo gravimetric
342 analyzer; XPS, X-ray photoelectron spectroscopy/ESCA; ICP-MS, inductively
343 coupled plasma mass spectrometry.

344

345 **References**

- 346 1. S. Frindy, A. Primo, M. Lahcini, M. Bousmina, H. Garcia and A. El Kadib,
347 *Green Chem.*, 2015, **17**, 1893-1898.
- 348 2. J. D. Senra, L. F. B. Malta, A. L. F. Souza, L. C. S. Aguiar and O. A. C.
349 Antunes, *Adv. Synth. Catal.*, 2008, **350**, 2551-2558.
- 350 3. D. Astruc, F. Lu and J. R. Aranzaes, *Angew Chem Int Edit*, 2005, **44**,
351 7852-7872.
- 352 4. S. Paul, M. M. Islam and S. M. Islam, *Rsc Adv.*, 2015, **5**, 42193-42221.
- 353 5. H. Veisi, R. Ghorbani-Vaghei, S. Hemmati, M. H. Aliani and T. Ozturk, *Appl.*
354 *Organomet. Chem.*, 2015, **29**, 26-32.
- 355 6. S. M. McAfee, J. S. J. McCahill, C. M. Macaulay, A. D. Hendsbee and G. C.
356 Welch, *RSC Adv.*, 2015, **5**, 26097-26106.
- 357 7. C. Shen, H. Y. Shen, M. Yang, C. C. Xia and P. F. Zhang, *Green Chem.*, 2015,
358 **17**, 225-230.
- 359 8. D. Schils, F. Stappers, G. Solberghe, R. V. Heck, M. Coppens, D. V. D. Heuvel,
360 P. V. D. Donck, T. Callewaert, F. Meeussen, E. D. Bie, K. Eersels and E.
361 Schouteden, *Org. Process Res. Dev.*, 2008, **12**, 530-536.
- 362 9. K. Deplanche, J. A. Bennett, I. P. Mikheenko, J. Omajali, A. S. Wells, R. E.
363 Meadows, J. Wood and L. E. Macaskie, *Appl. Catal. B: Environ.*, 2014, **147**,
364 651-665.
- 365 10. X. M. Ma, Y. X. Zhou, J. C. Zhang, A. L. Zhu, T. Jiang and B. X. Han, *Green*
366 *Chem.*, 2008, **10**, 59-66.

- 367 11. L. F. Tietze, G. Kettschau, U. Heuschert and G. Nordmann, *Chem. Eur. J.*, 2001,
368 7, 368-373.
- 369 12. A. Haberli and C. J. Leumann, *Org. Lett.*, 2001, **3**, 489-492.
- 370 13. F. R. Fortea-Pérez, I. Schlegel, M. Julve, D. Armentano, G. De Munno and
371 S.-E. Stiriba, *J. Organomet. Chem.*, 2013, **743**, 102-108.
- 372 14. K. Saikia, B. Deb, B. J. Borah, P. P. Sarmah and D. K. Dutta, *J. Organomet.*
373 *Chem.*, 2012, **696**, 4293-4297.
- 374 15. Y. Wang, J. Luo and Z. Liu, *J. Organomet. Chem.*, 2013, **739**, 1-5.
- 375 16. M. Hosseini-Sarvari, Z. Razmi and M. M. Doroodmand, *Appl. Catal., A:*
376 *General*, 2014, **475**, 477-486.
- 377 17. C. M. Crudden, M. Sateesh and R. Lewis, *J. Am. Chem. Soc.*, 2005, **127**,
378 10045-10050.
- 379 18. G. Borja, A. Monge-Marcet, R. Pleixats, T. Parella, X. Cattoën and M. Wong
380 Chi Man, *Eur. J. Org. Chem.*, 2012, **2012**, 3625-3635.
- 381 19. M. L. Kantam, K. B. S. Kumar, P. Srinivas and B. Sreedhar, *Adv. Synth. Catal.*,
382 2007, **349**, 1141-1149.
- 383 20. N. Ren, Y. Yang, Y. Zhang, Q. Wang and Y. Tang, *J. Catal.*, 2007, **246**,
384 215-222.
- 385 21. H. Yoon, S. Ko and J. Jang, *Chem. Commun.*, 2007, 1468-1470.
- 386 22. C. Desmarets, R. Omar-Amrani, A. Walcarius, J. Lambert, B. Champagne, Y.
387 Fort and R. Schneider, *Tetrahedron*, 2008, **64**, 372-381.
- 388 23. K. R. Reddy, N. S. Kumar, P. S. Reddy, B. Sreedhar and M. L. Kantam, *J Mol*

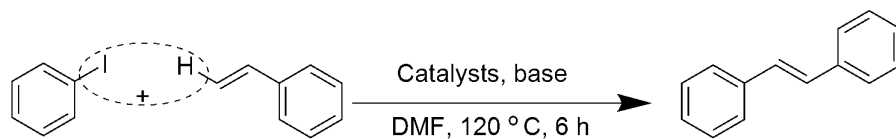
- 389 *Catal a-Chem*, 2006, **252**, 12-16.
- 390 24. M. Reayat, R. K. Blundell, J. E. Camp, D. A. Walsh and W. Thielemans, *ACS*
391 *Sustainable Chem. Eng.*, 2014, **2**, 1241-1250.
- 392 25. F. Coccia, L. Tonucci, N. d'Alessandro, P. D'Ambrosio and M. Bressan, *Inorg.*
393 *Chim. Acta*, 2013, **399**, 12-18.
- 394 26. C. Jouannin, C. Vincent, I. Dez, A. C. Gaumont, T. Vincent and E. Guibal,
395 *Nano. Mater.*, 2012, **2**, 31-53.
- 396 27. S. Cacchi, E. Caponetti, M. A. Casadei, A. Di Giulio, G. Fabrizi, G. Forte, A.
397 Goggiamani, S. Moreno, P. Paolicelli, F. Petrucci, A. Prastaro and M. L.
398 Saladino, *Green Chem.*, 2012, **14**, 317-320.
- 399 28. A. Khalafi-Nezhad and F. Panahi, *Green Chem.*, 2011, **13**, 2408-2415.
- 400 29. A. Khalafi-Nezhad and F. Panahi, *ACS Sustainable Chem. Eng.*, 2014, **2**,
401 1177-1186.
- 402 30. K. G. Qu, L. Wu, J. S. Ren and X. G. Qu, *Acs Appl Mater Inter*, 2012, **4**,
403 5001-5009.
- 404 31. H. Peng, N. Wang, J. S. Zhang and Z. P. Yu, *Adv. Mater. Res.*, 2011, **311-313**,
405 149-154.
- 406 32. Y. Q. Luo, S. Q. Shen, J. W. Luo, X. Y. Wang and R. C. Sun, *Nanoscale*, 2015,
407 **7**, 690-700.
- 408 33. W. Chen, L. X. Zhong, X. W. Peng, J. H. Lin and R. C. Sun, *Cellulose*, 2013,
409 **21**, 125-137.
- 410 34. X. W. Peng, J. L. Ren, L. X. Zhong and R. C. Sun, *J. Agric. Food Chem.*, 2012,

- 411 **60**, 1695-1702.
- 412 35. X. W. Peng, J. L. Ren, L. X. Zhong, X. F. Cao and R. C. Sun, *J. Agric. Food*
413 *Chem.*, 2011, **59**, 570-576.
- 414 36. W. Chen, L. X. Zhong, X. W. Peng, K. Wang, Z. F. Chen and R. C. Sun, *Catal.*
415 *Sci. Technol.*, 2014, **4**, 1426-1435.
- 416 37. Y. Habibi and M. R. Vignon, *Carbohydr. Res.*, 2005, **340**, 1431-1436.
- 417 38. P. Zhou, H. Wang, J. Yang, J. Tang, D. Sun and W. Tang, *Ind. Eng. Chem. Res.*,
418 2012, **51**, 5743-5748.
- 419 39. M. N. Cao, D. S. Wu, W. P. Su and R. Cao, *J. Catal.*, 2015, **321**, 62-69.
- 420 40. H. Wu, C. Wu, Q. He, X. Liao and B. Shi, *Mater. Sci. Eng.: C*, 2010, **30**,
421 770-776.

Table 1. Optimization of the Heck reaction conditions^a.

Entry	Catalyst (mg)/DS=1.77	Solvent	Temp (°C)	Time (h)	Yield (%) ^b
1	50	DMF	120	8	74
2	50	EtOH	120	8	53
3	50	DMSO	120	8	48
4	20	CH ₃ CN	120	8	8
5	50	H ₂ O	120	8	4
6	0	DMF	120	8	trace
7	12.5	DMF	120	8	60
8	25	DMF	120	8	67
9	75	DMF	120	8	73
10	100	DMF	120	8	74
11	50	DMF	60	8	16
12	50	DMF	80	8	65
13	50	DMF	100	8	67
14	50	DMF	140	8	64
15	50	DMF	120	4	83
16	50	DMF	120	6	84
17	50	DMF	120	10	75
18	50	DMF	120	12	71

^a Reaction conditions: 1.0 mmol iodobenzene, 1.2 mmol ethyl acrylate, 2.0 mmol triethylamine, 3 mL Solvent. ^b Isolated yield was based on the iodobenzene.

Table 2. Optimization of the DS of CMH for Heck reaction^a.

Entry	DS	M_w	Temp (°C)	Time (h)	Yield (%) ^b
1	0	283410	120	6	84
2	0.055	177080	120	6	56
3	0.082	148100	120	6	59
4	0.0534	183250	120	6	54
5	0.109	113650	120	6	62
6	0.177	82727	120	6	77
7	0.24	51383	120	6	90

^a Reaction conditions: 1.0 mmol iodobenzene, 1.2 mmol styrene, 2.0 mmol triethylamine, 3 mL DMF. ^b Isolated yield was based on the iodobenzene.

Table 3. Heck reactions of aryl halides with olefins^a.

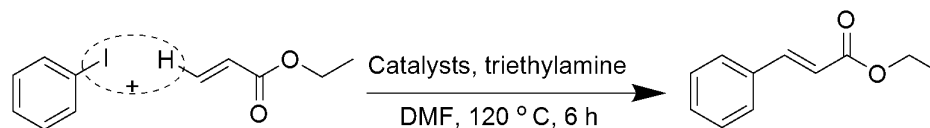
Entry	R ₁	X	R ₂	Yield/% ^b	Product
1	H	I		97	3a
2	H	I		90	3b
3	H	Br		32	3a
4	<i>p</i> -CH ₃ O	I		91	3c
5	<i>p</i> -CH ₃ O	I		95	3d
6	<i>p</i> -CH ₃ O	I		96	3e
7	<i>p</i> -CH ₃ O	I		96	3f
8	<i>p</i> -CH ₃ O	I		92	3g
9	<i>p</i> -CH ₃ O	Br		34	3c
10	<i>p</i> -CH ₃	I		96	3h
11	<i>p</i> -CH ₃	Br		31	3h
12	<i>p</i> -CH ₃ CO	I		94	3i
13	<i>p</i> -CH ₃ CO	Br		87	3i
14	<i>p</i> -NO ₂	I		99	3j
15	<i>p</i> -NO ₂	Br		94	3j
16 ^c	<i>p</i> -NO ₂	Cl		63	3i
17 ^c	<i>p</i> -CH ₃ CO	Cl		55	3j
18 ^c	<i>p</i> -CH ₃ O	Cl		12	3c



Entry	R ₁	X	R ₂	Yield/% ^b	Product
19 ^c	<i>p</i> -CH ₃	Cl		trace	3h

^a Reaction conditions: 1.0 mmol aryl halide, 1.2 mmol olefin, 2.0 mmol triethylamine, 50 mg CMH-Pd (0) (1.9 mol% Pd), 3 mL DMF, 120 °C, 6 h. ^b Isolated yield. ^c At 120 °C for 24 h.

423

Table 4. Successive Heck reaction using recovered catalysts^a.

Entry	Catalyst	Solvent	Temp (°C)	Yield (%) ^b
1	H-Pd (50 mg)	DMF	120	97
2	H-Pd 1st reuse	DMF	120	95
3	H-Pd 2nd reuse	DMF	120	95
4	H-Pd 3rd reuse	DMF	120	90
5	H-Pd 4th reuse	DMF	120	87
6	CMH-Pd (50mg)	DMF	120	97
7	CMH-Pd 1st reuse	DMF	120	96
8	CMH-Pd 2nd reuse	DMF	120	96
9	CMH-Pd 3rd reuse	DMF	120	94
10	CMH-Pd 4th reuse	DMF	120	89

^a Reaction conditions: 1.0 mmol iodobenzene, 1.2 mmol ethyl acrylate, 2.0 mmol triethylamine, 3 mL DMF at 120 °C for 6 h. ^b Isolated yield was based on the iodobenzene.

424

425

426

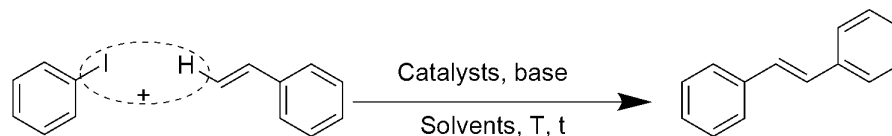
427

428

429

430

431

Table 5. Catalytic performance of different Pd-based catalysts in the Heck reaction.

Entry	Catalyst	Solvent	T (°C)	t (h)	Catalyst Dosage (mol%)	Yield (%)	Ref.
1	HPCD/Pd/CaCO ₃ ^a	H ₂ O/DMF	110	24	1	80	2
2	CELL-Pd(0) ^b	DMF	120	12	2.3	100	23
3	PNP-SSS ^c	H ₂ O	reflux	1.5	1.2	95	28
4	PdNPs@XH ^d	CH ₃ CN	90	8	2	92	35
5	Pd/BC ^e	DMF	120	8	0.1	87	37
6	CMC-Pd (II)	DMF	120	6	0.9	69	This work
7	H-Pd (0)	DMF	120	6	1.7	84	This work
8	CMH-Pd (0)	DMF	120	6	1.9	90	This work

^a Palladium on calcium carbonate combined to 2-hydroxypropyl- α -cyclodextrins. ^b Cellulose supported Pd(0). ^c Pd nanoparticles supported on silica-starch substrate. ^d Xylan-type hemicellulose supported Pd (0). ^e Bacteria cellulose nanofibers supported Pd (0).

432

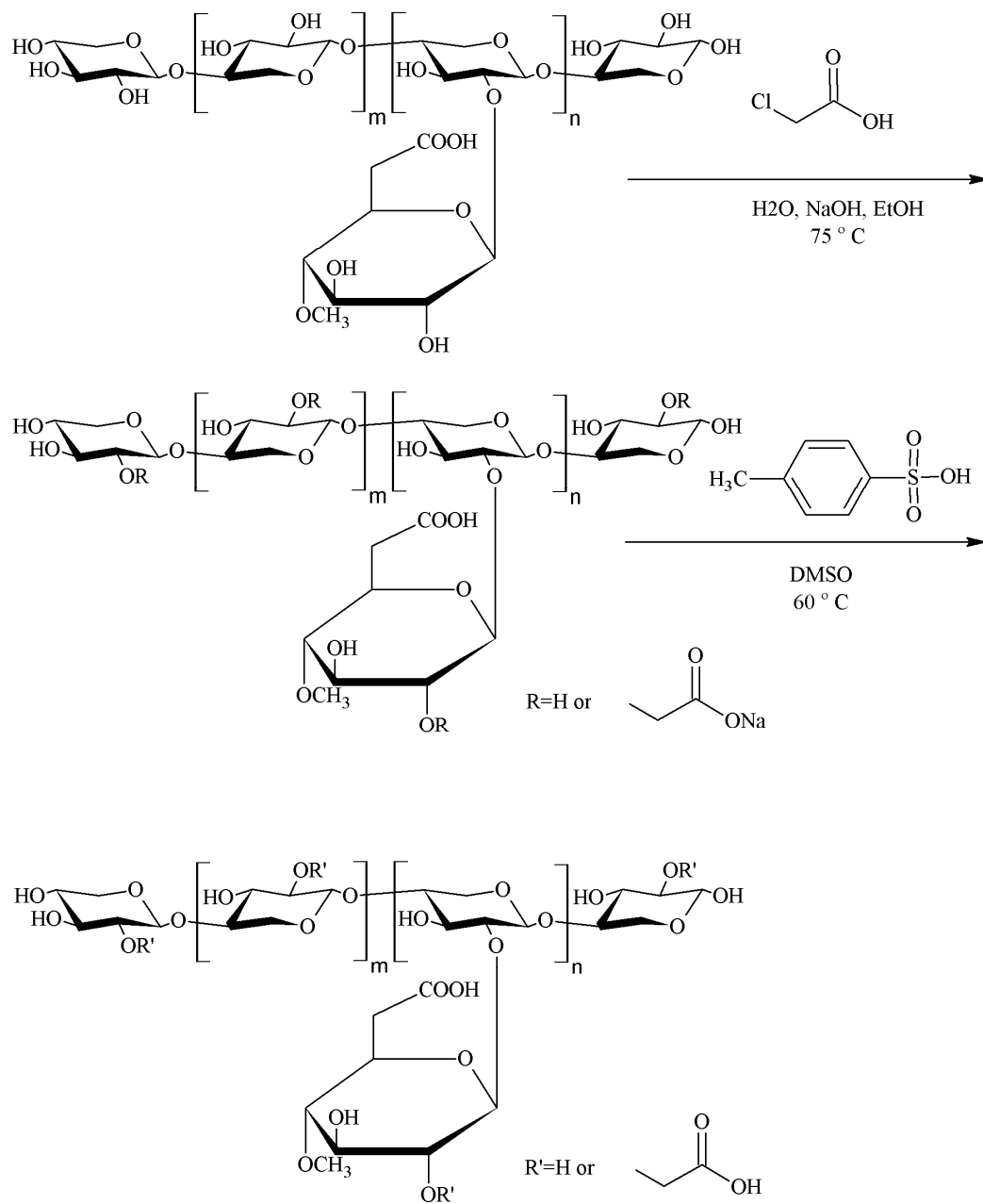


Figure 1. Schematic illustration for the preparation of CMH.

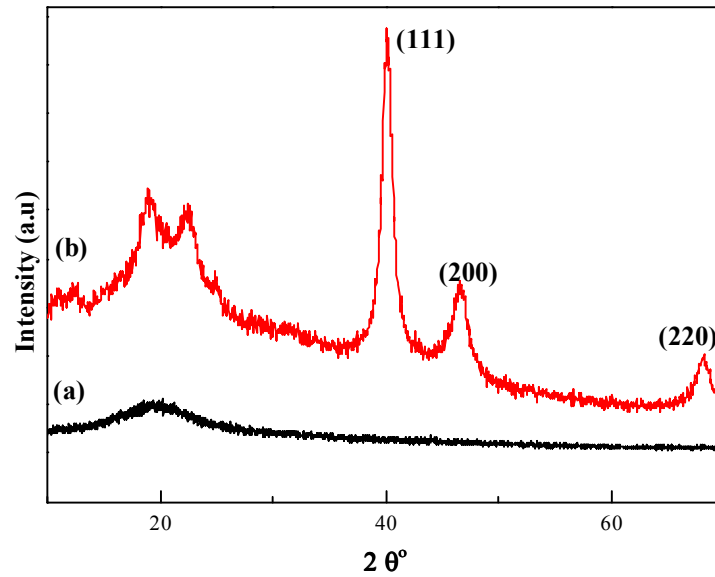


Figure 2. XRD diffraction patterns of (a) CMH and (b) CMH-Pd (0) catalyst.

444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469

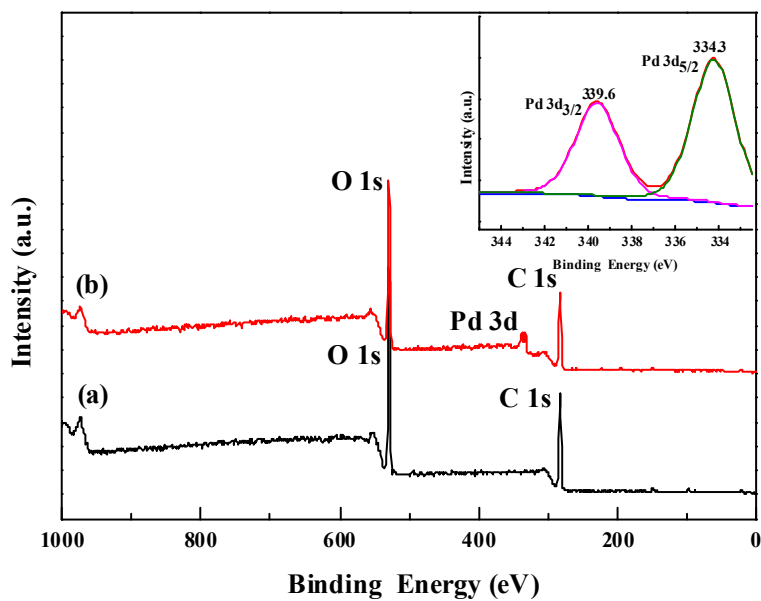


Figure 3. XPS spectra of (a) CMH and (b) CMH-Pd (0) catalyst.

470

471

472

473

474

475

476

477

478

479

480

481

482

483

484

485

486

487

488

489

490

491

492

493

494 zzz

495

496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522

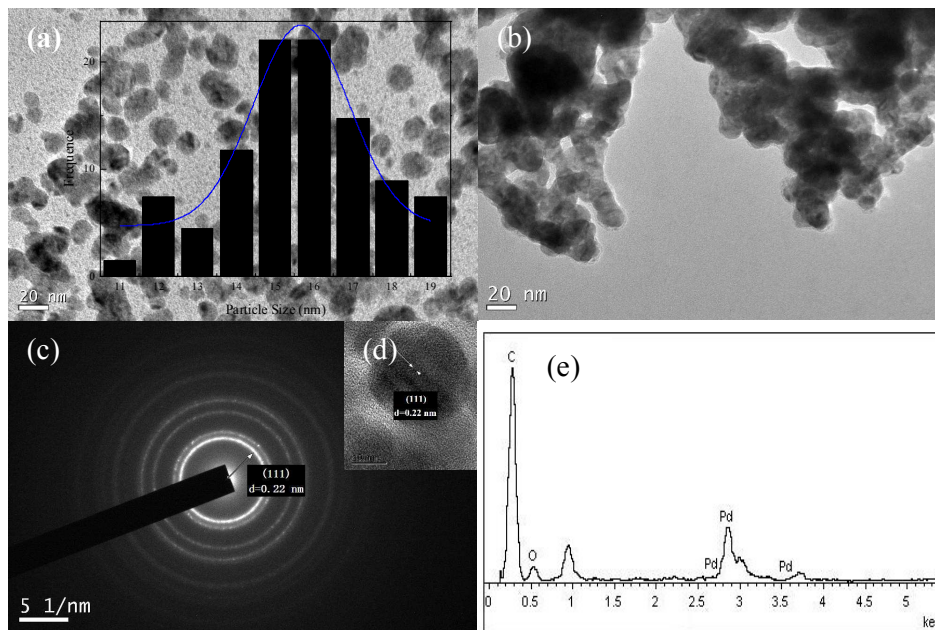
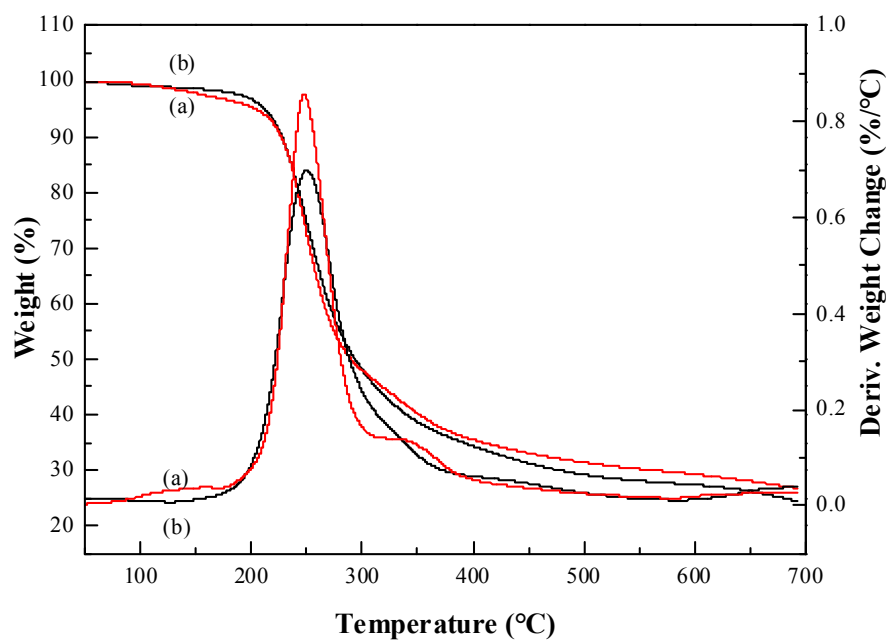


Figure 4. (a) TEM images and histogram of the as-prepared fresh CMH-Pd (0) catalyst, (b) TEM images of CMH-Pd (0) after five cycles of Heck reaction, (c) Electron diffraction pattern from the metallic Pd nanoparticles, (d) HRTEM image of CMH-Pd (0) catalyst and (e) EDS spectrum of CMH-Pd (0) catalyst.



523

524

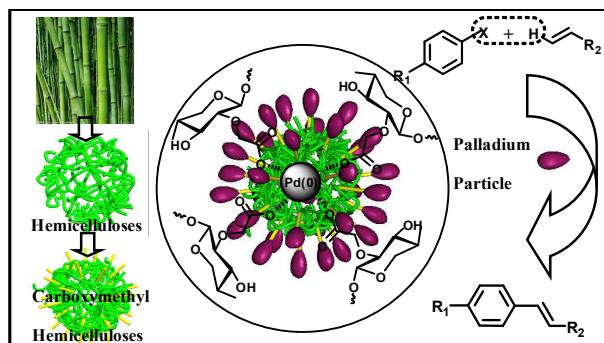
525 **Figure 5.** TGA traces of (a) CMH and (b) CMH-Pd (0) catalyst recorded at heating rate of
526 15.00 °C/min under nitrogen flow.

527

528

529

Graphic Abstract



530

531 Renewable and sustainable CMH was the natural ligand for CMH-Pd (0)

532 nanocomposite which was as an efficient and recyclable catalyst for Heck Reaction.