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Title: Hemicelluloses supported palladium/xylan nanocomposites containing N and O ligands: highly-performance heterogeneous catalysts for Suzuki reaction



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2	H	ighlights:
3	•	Palladium/xylan heterogeneous catalysts containing N and O
4		ligands were synthesized.
5	•	The prepared catalysts showed excellent catalytic activity with
6		yield up to 100%.
7	٠	The activity of catalysts exhibited no significant loss after
8		recycle for 5 times.
9	•	The reaction conditions are milder, compared with other
10		palladium-based catalysts.
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23	Hemicelluloses supported palladium/xylan nanocomposites
24	containing N and O ligands: highly-performance heterogeneous
25	catalysts for Suzuki reaction
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51 Abstract

Two kinds of xylan/palladium catalysts (PACMX-Pd and EDAX-Pd) were simply fabricated by integrating two N bidentate ligands into the skeleton of oxygen-rich xylan and followed with the in-situ reduction of palladium. The Pd loading in PACMX-Pd and EDAX-Pd nanocomposites was 0.353 mmol/g and 0.302 mmol/g, respectively. The catalysts exhibited an excellent catalytic activity for the Suzuki reaction with a yield of high up to 100% as well as a superior turnover frequency (TOF: 9626 h⁻¹). Moreover, the catalysts showed outstanding stability and could be reused for at least 5 times without significant decrease in activity. Compared with other polymers and non-polymers supported palladium catalysts, the as-prepared biomass-based catalysts possess potential applications in a wide range of organic catalysis.

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80 Keywords: Biomass, Xylan, Palladium, Nanocomposites, Suzuki reaction

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81 **1. Introduction**

Recently, carbon-carbon cross-coupling reactions catalyzed by palladium have 82 attracted enormous interest in synthetic organic chemistry (Hekmati, Bonyasi, 83 84 Javaheri, & Hemmati, 2017; Chen, Engle, Wang, & Yu, 2009). Coupling reactions such as Suzuki (Putta, Sharavath, Sarkar, & Ghosh, 2015), Heck (Ma et al., 2008), 85 and Sonogashira (Gogoi, Dewan, & Bora, 2015) provide a one-step method for 86 synthesizing complex compounds, including pharmaceuticals, herbicides and natural 87 88 products, as well as engineering materials such as conducting polymers, molecular wires, and liquid crystals (Chen et al., 2009). Palladium catalysts, in the form of Pd 89 (II)/Pd (0) complexes or Pd nanoparticles, have been proven to be efficient and 90 irreplaceable catalysts for C-C bond formation reactions (Fortea-Pérez et al., 2015; 91 Narayanan & El-Sayed, 2003). In order to maintain the stability of Pd (II) or Pd (0) 92 and obtain satisfactory yield, homogeneous systems are commonly used. However, 93 palladium is difficult to be separated from the catalysts, leading to undesired residue 94 metals in final products, which is a serious problem in pharmaceutical industry due to 95 the closely regulated level of heavy metals such as Pd in active pharmaceutical 96 intermediates (Zhang et al., 2013; Zhong et al., 2014). 97

Substituting homogeneous catalysts with heterogeneous catalysts is an effective 98 strategy to solve this problem due to the residues can be easily separated by filtration 99 or centrifugation and the catalysts can be reused for several times (Veerakumar, 100 Thanasekaran, Lu, Liu, & Rajagopal, 2017; Crudden, Sateesh, & Lewis, 2005). 101 Supporting homogeneous catalysts on inorganic matters or organic polymers is a 102 typical method to prepare heterogeneous catalysts. Various materials, including 103 sporopollenin (Baran, Sargin, Kaya, Mentes, & Ceter, 2017), ionic liquids 104 (Nikoorazm, Ghorbani-Choghamarani, Noori, & Tahmasbi, 105 2016), zeolite (Baghbanian, Yadollahy, Tajbakhsh, Farhang, & Biparva, 2014), carbon (Zhong et al., 106 2015), silica (Sharma & Gupta, 2015), metal oxides (Amoroso, Colussi, Del Zotto, 107 Llorca, & Trovarelli, 2013; Dumbre, Yadav, Bhargava, & Choudhary, 2013), and 108 polymers (Rangel, Maya, Sanchez, de la Campa, & Iglesias, 2015; Xu, Song, Li, & 109 Tan, 2015) have been employed to support heterogeneous palladium catalysts. 110

However, the heterogeneous Pd catalysts show lower activity and selectivity than their homogeneous counterparts (Choudhary, Nishimura, & Ebitani, 2014), which is due to the Pd leaching from the support and its poor accessibility of the active sites to the reactant (Hekmati, Bonyasi, Javaheri, & Hemmati, 2017). Therefore, designing a highly active and stable palladium heterogeneous catalyst is urgent.

Tuning the specific composition, morphology and size of catalyst is crucial for the 116 catalytic activity of Pd complex (Julkapli & Bagheri, 2015). In addition, previous 117 studies demonstrated that supports with functional groups containing, oxygen, 118 nitrogen, or sulfur ligands can enhance the stability of Pd nanoparticles, because these 119 heteroatoms have a high affinity towards Pd (II) or Pd (0), thus improving the 120 catalytic activity of their transition metal complexes (Kardanpour et al, 2014; Oliveira, 121 He, Klein Gebbink, & de Jong, 2015; Kostas, Tenchiu, Arbez-Gindre, Psycharis, & 122 Raptopoulou, 2014). Biopolymers, which are a class of organic compounds 123 containing large amounts of O or N or S heteroatom, are considered to be good 124 catalytic materials for their inherent features in chemical composition and chain 125 126 structure. Chitosan-based (containing O and N) palladium (0) catalysts have been confirmed to have excellent catalysis performance in Suzuki coupling reaction 127 (Yilmaz, Baran, & Mentes, 2018; Baran & Mentes, 2017). Cellulose (containing O) 128 was also utilized as a support for palladium (Li et al., 2017). Pd immobilized on lignin 129 (containing O and S) as a catalyst for cross-coupling reactions in water was reported 130 by Coccia etal (Coccia, Tonucci, d'Alessandro, D'Ambrosio, & Bressan, 2013). In 131 addition, alginate (Jouannin et al., 2012), gelatin (Cacchi et al., 2012; Khazaei, 132 Khazaei, & Rahmati, 2015), starch (Khalafi-Nezha & Panahi, 2011), cyclodextrin 133 (Senra et al., 2009) and their derivatives were also employed as supports in catalysis. 134 However, hemicelluloses have been rarely applied in Pd catalytic system and the 135 prepared xylan-palladium nanocomposites can catalyze the Suzuki reactions with 136 equivalent yields in a relatively mild reaction condition. 137

138 Xylan-type hemicellulose has abundant hydroxyl, carbonyl, and aldehyde 139 carboxylic acid groups along the backbone and side chains, and thus it has great 140 potential to stabilize metal particles. Our group successfully prepared Pd/xylan

catalysts by a simple in-situ reduction method for organic synthesis reaction (Chen,
Zhong, Peng, Lin, & Sun, 2014; Chen et al., 2014). 1, 10-phenanthrolin-5-amine and
ethylenediamine have been widely used in transition-metal-catalyzed reactions
(Mandegani et al., 2015; Yang, Li, & Wang, 2011) because they possess high
electron-donating ability, short metal-ligand bond lengths, strong metal-ligand bond
energies, and greater bond dissociation energies (Xu et al., 2015), which are suitable
ligands for palladium particles stabilization.

Herein, novel xylan supported palladium complexes were prepared by grafting N ligands in xylan-type hemicelluloses and then incorporated palladium via in-situ reduction and showed a superior catalytic performance in the Suzuki cross-coupling reactions under moderate condition with a TOF as high as 9626 h⁻¹. Furthermore, both catalysts have excellent recovery and recycle ability. The as-prepared catalysts have a great potential in green chemical catalysis.

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155 2. Materials and Methods

156 *2.1. Materials*

Palladium acetate (Pd(Ac)₂), 1, 10-phenanthrolin-5-amine, ethylenediamine, 157 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC·HCl), hydrochloride 158 N-hydroxysuccinimide (NHS), epichlorohydrin, 1, 8-diazabicyclo [5.4.0] undec-7-ene 159 (DBU), aryl halides, arylboronic acids were purchased from Aladdin Reagent Co., Ltd 160 and were used without further purification. Solvents used for coupling reactions, 161 ethanol (EtOH), methanol (MeOH), acetonitrile, 1,4-dioxane, hexane, tetrahydrofuran 162 (THF) and toluene were purchased from National Medicine Group Chemical Reagent 163 Co., Ltd. Sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium 164 carbonate (K₂CO₃), sodium carbonate (Na₂CO₃), triethylamine (TEA) and other 165 reagents were also commercially available from National Medicine Group Chemical 166 Reagent Co., Ltd. Xylan-type hemicelluloses were prepared according to literature 167 (Peng, Ren, Zhong, & Sun, 2012). The sugar analysis showed sugar composition 168 (relative weight percent): 89.4% xylose, 5.8% arabinose, 1.9% glucose, 0.7% 169 galactose, 1.8% glucuronic acid and 0.6% galactose acid. 170

171 2.2. Synthesis of 1, 10-phenanthrolin-5-amine functionalized carboxymethyl xylan
172 (PACMX)

The typical procedure for the preparation of PACMX was designed as followed. 173 Carboxymethyl xylan was firstly prepared by a similar method as Peng et al (See 174 Supplementary data). Subsequently, carboxymethyl xylan (0.8 mmol) and EDC·HCl 175 (4.0 mmol) were suspended in 12 mL deionized water, the pH was previously 176 adjusted to 5.5. After stirring under low temperature (≤ 20 °C) for 15 min, 4.0 mmol 177 NHS was added to the above solution and the activation stage was maintained for 2 h, 178 followed by the addition of 0.4 mmol 1, 10-phenanthrolin-5-amine which had been 179 dissolved in 8 mL EtOH and the reaction mixture was stirred for 24 h below 20 °C. 180 The obtained solid residual was filtered, thoroughly washed with EtOH and vacuum 181 dried to give PACMX. The typical schematic outline of the preparation of PACMX 182 183 was depicted in Fig. S1a.

184 2.3. Synthesis of ethylenediamine functionalized xylan (EDAX)

The representative synthetic procedure for EDAX was illustrated in Fig. S1b. 0.66 185 186 g xylan-type hemicelluloses powder (approximately 5 mmol of xylose) was homo-dispersed evenly in 5.5 mL water and heated to 85 °C with stirring (500 rpm) 187 for 10 min. As the dispersion being cooled down to room temperature, sodium 188 hydroxide (2 mL, 200 g L⁻¹) was added dropwise (20 drops per minute) into the 189 mixture and swollen for 30 min at 85 °C, obtaining alkaline xylan solution. In addition, 190 0.02 mmol ethylenediamine and 0.01 mmol epichlorohydrin were mixed together at 191 room temperature and the reaction progressed violently. After 10 min the alkaline 192 xylan solution was added into the above mixture and stirred at room temperature for 6 193 194 h. The obtained yellow solution was precipitated with EtOH (100 mL) and filtered, then the residue was washed with EtOH and vacuum dried at 60 °C to obtain EDAX. 195

196 2.4. Synthesis of the palladium grafted PACMX and EDAX (PACMX-Pd and197 EDAX-Pd)

0.02 g palladium acetate and 0.2 g PACMX/EDAX were suspended in 10 mL EtOH.
The solution was stirred for 12 h at 60 °C. During the reaction, the Pd (II) was
reduced gradually, and the yellowish solution turned to be deep brown, signifying the

conversion of Pd (II) to Pd (0). After the reaction, the brown colored mixture was
filtrated, washed with EtOH and then vacuum dried at 60 °C to give PACMX-Pd and
EDAX-Pd catalysts. The local structures of palladium/xylan nanocomposites
(PACMX-Pd/EDAX-Pd) were proposed as shown in Fig. S2, and the corresponding
ball and stick model structures were also presented.

206 2.5. Catalytic performance for Suzuki coupling reaction

In a typical procedure, aryl halide (0.5 mmol), arylboronic acid (0.6 mmol), base 207 (1.0 mmol) and catalyst (23 mg PACMX-Pd, containing 1.5 mol% Pd or 4.3 mg 208 EDAX-Pd, containing 0.26 mol% Pd) were added into a 35 mL pressure tube. The 209 solvent (2 mL) was added to disperse the reactants well and the resulting mixture was 210 stirred under air atmosphere. Upon the completion of the reaction, the dispersion was 211 filtered and concentrated under vacuum. The products were purified by flash column 212 chromatography on a silica gel and identified by ¹H NMR and ¹³C NMR 213 spectroscopy. 214

215 2.6. Recycling tests for PACMX-Pd and EDAX-Pd catalysts

216 Recycling tests were performed to check the stability of PACMX-Pd and EDAX-Pd catalysts during the reaction. After the Suzuki reaction of 4-iodoanisole with 217 phenylboronic acid, the catalysts were separated from the reaction mixture by 218 centrifugation. The supernatants were stored and the Pd leaching of catalysts were 219 analysed. The residual catalysts were washed with EtOH, water and vacuum dried 220 overnight. Fresh 4-iodoanisole, phenylboronic acid, K₂CO₃ and reused catalyst were 221 222 added, and then the same reaction was performed under room temperature for 4 h. Each cycle followed the general procedure for Suzuki cross coupling reactions 223 224 mentioned above.

225 2.7. Heterogeneity test

226 23 mg PACMX-Pd (containing 1.5 mol% Pd) or 4.3 mg EDAX-Pd (containing 0.26 227 mol% Pd) was added in a 35 mL pressure tube, which was followed by K_2CO_3 (1.0 228 mmol), 4-iodoanisole (0.5 mmol), and phenylboronic acid (0.6 mmol). Then EtOH (2 229 mL) was added to disperse the reactants and the reaction mixture was performed 230 under room temperature. After 1 h of reaction, the catalysts were separated by

filtration. Subsequently, an additional amount of fresh K₂CO₃ (1.0 mmol) was added

into the filtrate and the system was reacted under the same condition for another 3 h.

233 2.8. *Characterization*

FT-IR spectra of the samples were recorded on a Vector 33 infrared spectrum 234 instrument (Bruker Corporation, Germany). The structures were analyzed by XRD 235 measurements with a Bruker-D8 Advance diffractometer using Cu Ka radiation 236 $(\lambda=0.154 \text{ nm})$. The electronic states of Pd and N were determined by XPS and 237 performed on Thermo Scientific ESCALAB 250 spectrometer system using Al Ka 238 radiation (hv=1486.6 eV) with contaminated C as an internal standard (C 1s=284.6 239 eV). The thermal stabilities of PACMX, EDAX, PACMX-Pd and EDAX-Pd catalysts 240 were confirmed by TGA (TGA Q500, TA). The morphologies of samples were 241 obtained on a JEM-2100 (HR) transmission electron microscopy working at 200 kV. 242 The as-prepared samples were also observed using a scanning electron microscope 243 (Zeiss Merlin, Germany). The Pd content was determined by Z-2000 (Japan) atomic 244 absorption spectrometer (AAS). All ¹H NMR and ¹³C NMR spectra were conducted 245 246 on a 600 MHz Bruker (AVANCE III HD 600) spectrophotometer using CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard. All the spectroscopic data of 247 the products were similar with those reported in the former literature and 248 commercially available. 249

250 **3. Results and discussion**

251 3.1. Characterization of PACMX-Pd and EDAX-Pd catalysts

252 PACMX-Pd and EDAX-Pd were prepared by a simple two steps. The synthesis routes of functionalized xylan (PACMX/EDAX) were illustrated in Figure 1. PACMX was 253 254 obtained by the reaction of carboxymethyl xylan and 1, 10-phenanthrolin-5-amine in the presence of EDC·HCl and NHS. EDAX was synthesized by modifying xylan with 255 ethylenediamine and epichlorohydrin under NaOH condition. Subsequently, 256 palladium nanoparticles were supported onto PACMX/EDAX via in-situ reduction of 257 258 Pd(Ac)₂ at room temperature, the solution turned from yellowish to deep brown, indicating the successful reduction of Pd (II) into Pd (0) and simultaneously the 259 coordination of Pd to PACMX/EDAX. As Fig. S2 shown, the palladium was anchored 260

by four nitrogen atoms at the functionalized xylans.

The FT-IR spectra of PACMX, EDAX, PACMX-Pd and EDAX-Pd are shown in 262 Fig. 1. The peak assigned to the C=N stretching vibration of PACMX (Fig. 1c) can be 263 clearly observed at 1645 cm⁻¹ (Govindaiah, Lee, Jung, Lee, & Kim, 2009). After 264 coordination with palladium particles (Fig. 1d), the stretching vibration of C=N group 265 (1645 cm⁻¹) is shifted to 1642 cm⁻¹ due to the nitrogen atom in the benzene ring of 266 PACMX actively participated to give its nonbonding electron pair to the metal 267 particles. As shown in Fig. 1a and 1b, after Pd NPs being immobilized onto the 268 surface of EDAX, a spectral shift for N-H bond in the amino group from 3420 cm⁻¹ to 269 3397 cm⁻¹ is obviously observed. The band at 1640 cm⁻¹ is ascribed to N-H in-plane 270 bending vibration of amide group (Yang, Tan, Wang, & Wang, 2013). After being 271 hydrided with palladium, the peak of N-H in EDAX shifts to 1614 cm⁻¹. All these 272 results indicate that strong ligand bond formed between EDAX and palladium 273 particles. 274



275



277 To further illustrate the interaction between palladium nanoparticles and the carrier,

the oxidation states of the surface elements of PACMX-Pd and EDAX-Pd catalysts

were determined by X-ray photoelectron spectroscopy (XPS) (Fig. 2). The XPS 279 narrow scan of palladium on the surface of PACMX-Pd (Fig. 2c) showed two peaks. 280 281 The binding energy of the doublet peaks at 335.0 eV (Pd $3d_{5/2}$) and 340.3 eV (Pd $3d_{3/2}$) are attributed to Pd (0) state. The peak spliting at 338.1 eV and 342.6 eV corresponds 282 to the characteristic state of Pd (II) (Yang et al., 2013). The difference of N1s binding 283 energies between PACMX and PACMX-Pd was 0.1 eV (Fig. 2d). These results 284 suggest that a coordination bond between palladium and nitrogen was formed in 285 PACMX-Pd. For EDAX-Pd (Fig. 2g), the binding energies at 335.0 eV and 340.3 eV 286 indicate the presence of Pd (0), and Pd (II) split at 338.1 and 343.4 eV (Chen, Zhong, 287 Peng, Lin, & Sun, 2014). The difference of N1s binding energies between EDAX and 288 EDAX-Pd was 1.0 eV (Fig. 2h), which indicates that the strong ligand formed 289 between EDAX and palladium particles. These results are in good agreement with 290 FT-IR spectra. 291







Fig. 2. XPS wide scan of PACMX (a) and PACMX-Pd (b). XPS narrow scan of palladium on
the surface of PACMX (c) and nitrogen in PACMX and PACMX-Pd (d). XPS wide scan of
EDAX (e) and EDAX-Pd (f). XPS narrow scan of palladium on the surface of EDAX (g) and
nitrogen in EDAX and EDAX-Pd (h).

The formation of palladium nanoparticles was also confirmed from the wide angle powder XRD patterns of PACMX-Pd and EDAX-Pd hybrids (Fig. 3). The XRD spectra suggest that PACMX and EDAX are amorphous since no characteristic peak was observed, while a phase in PACMX-Pd and EDAX-Pd was emerged in XRD patterns at $2\theta = 40.0^{\circ}$, 46.1° , and 67.5° , corresponding to (111), (200), and (220) planes of Pd crystal (PDF#46-1043), respectively (Cao, Wu, Su, & Cao, 2015).





Fig. 3. XRD patterns of PACMX (a). PACMX-Pd (b). EDAX (c) and EDAX-Pd (d).

The morphologies of PACMX-Pd and EDAX-Pd at a higher resolution TEM were 306 307 recorded. It was shown that the spherical palladium particles with uniform size were homogeneously dispersed on PACMX (Fig. 4a) and EDAX (Fig. 4e). Average sizes 308 for the two catalysts were about 5 nm and 4 nm, respectively. HR-TEM images of 309 individual nanoparticle showed clear lattice fringes with an interplanar distance of 310 approximately 0.22 nm, corresponding to Pd (111) planes (Fig. 4c and 4g) (Cao et al., 311 2015; Maity & Maitra, 2014). The selected area electron diffraction pattern (Fig. 4d 312 and 4h) displayed five diffused rings, which are assigned to the (111), (200), (220), 313 (222), and (311) reflections of face-centered cubic Pd nanoparticles (Maity et al., 314 315 2014), which well agrees with the XRD results. As shown in Fig. 4b and 4f, a slight aggregation was observed in the recycled PACMX-Pd and EDAX-Pd, which could 316 result in the reduced catalytic activity of the Pd nanocatalysts. The SEM images in 317 Supplementary data Fig. S4 showed that both catalysts had coralloid porous as 318 compared to PACMX and EDAX, which is very beneficial for the catalytic reactions. 319 The EDX spectra of PACMX-Pd and EDAX-Pd indicate the presence of metallic Pd 320 signals. 321



322

Fig. 4. TEM images and histogram of the freshly prepared (a) and reused (for five times, b)
PACMX-Pd particles. HR-TEM images and diffraction patterns of the as-prepared PACMX-Pd
particles (c-d). TEM images and histogram of the as-prepared (e) and recycled (for five times, f)
EDAX-Pd particles. HR-TEM images and diffraction patterns of the as-prepared EDAX-Pd
particles (g-h).

Thermal stability of catalysts is also a key factor for its catalytic activity. The 328 thermal behaviors of catalysts were depicted in Fig. S5 by TGA curves. PACMX, 329 EDAX, PACMX-Pd, and EDAX-Pd started to decompose at about 185 °C, indicates 330 the loaded palladium particles didn't significantly affect the initial decomposition 331 temperature. Besides, the remaining weights of PACMX-Pd and EDAX-Pd were 332 higher than those of PACMX and EDAX. These results reveal that the thermal 333 stabilities of PACMX-Pd and EDAX-Pd were suitable for Suzuki catalytic 334 application. 335

336 3.2. Catalytic activities of PACMX-Pd and EDAX-Pd for the Suzuki coupling337 reactions

Suzuki cross coupling reactions were thoroughly performed for testing the catalytic
activities of PACMX-Pd and EDAX-Pd. In the screening experiments, the reaction
conditions, including solvent, base and catalyst loading in PACMX-Pd and EDAX-Pd

were optimized. Firstly, various solvents were examined in the Suzuki coupling 341 reaction of 4-iodoanisole with phenylboronic acid using PACMX-Pd and EDAX-Pd 342 as catalysts and K₂CO₃ as a base. For PACMX-Pd (Table 1, entries 1-8), EtOH, 343 MeOH and CH₃CN gave higher yields of 4-methoxybiphenyl (100%, 97.8%, and 344 100%, respectively), while the reactions in less polar solvents, for example, 1, 345 4-dioxane, hexane, THF and toluene, were less effective (Chen, Zhong, Peng, Lin, & 346 Sun, 2014). PACMX-Pd was not stable in H₂O and therefore the catalytic reaction did 347 not proceed smoothly in aqueous media. For the sake of safety and environmental 348 friendliness, EtOH was chosen as a desirable solvent for the reaction catalyzed by 349 PACMX-Pd, and a remarkable yield of 70% could be achieved even if the reaction 350 just proceeded for 1 h (Table 1, entry 9). EDAX-Pd also showed a good catalytic 351 activity in EtOH and MeOH with yields of high up to 100% (Table 1, entries 10 and 352 11). Compared with PACMX-Pd, EDAX-Pd showed a moderate catalytic activity in 353 H₂O with a yield of 80.3% (Table 1, entry 8 and 17) due to the hydrophilcity of 354 EDAX-Pd. Among various solvents (Table 1, entries 10-17), EtOH was also selected 355 356 as the optimal solvent for EDAX-Pd catalyzed Suzuki coupling reactions, and giving an impressive yield of 59.5% within 1 h (Table 1, entry 18). 357

Table1. Effect of solvent on the Suzuki coupling reaction of 4-iodoanisole with phenylboronic
acid^a.

Entry	Catalyst	Solvent	Yield ^b /%
1	PACMX-Pd	EtOH	100
2	PACMX-Pd	MeOH	97.8
3	PACMX-Pd	CH ₃ CN	100
4	PACMX-Pd	1,4-dioxane	63
5	PACMX-Pd	hexane	49.5
6	PACMX-Pd	THF	47.2
7	PACMX-Pd	toluene	43.5
8	PACMX-Pd	H_2O	16.3

9	PACMX-Pd	EtOH ^c	70
10	EDAX-Pd	EtOH	100
11	EDAX-Pd	MeOH	100
12	EDAX-Pd	CH ₃ CN	65.3
13	EDAX-Pd	1,4-dioxane	15.5
14	EDAX-Pd	hexane	84.5
15	EDAX-Pd	THF	37.8
16	EDAX-Pd	toluene	87
17	EDAX-Pd	H ₂ O	80.3
18	EDAX-Pd	EtOH ^d	59.5

^aReaction conditions: 4-iodoanisole (0.5 mmol), phenylboronic acid (0.6 mmol), K₂CO₃ (1 mmol),
PACMX-Pd (23 mg, containing 1.5 mol% Pd), EDAX-Pd (4.3 mg, containing 0.26 mol% Pd),
solvent (2 mL), at room temperature, 4 h. ^bIsolated yields (each experiment was repeated for 3 times, and the final isolated yield was the average of 3 similar yields). ^{c, d}1 h.

For screening desirable bases, the Suzuki reactions with various bases were 364 evaluated in EtOH at room temperature. As shown in Table 2, both PACMX-Pd and 365 EDAX-Pd didn't proceed well with organic bases such as TEA and DBU (Table 2, 366 entry 4-5 and 9-10). However, the inorganic bases (Table 2, entries 1-3 and 6-8) 367 generally exhibited high efficiencies in the Suzuki coupling reaction of 4-iodoanisole 368 with phenylboronic acid. Among the bases, K₂CO₃ showed the highest yield of 100%. 369 Consequently, the following reactions were carried out using EtOH as a solvent and 370 371 K_2CO_3 as a base to examine the effect of the Pd loading on the product yield (Table 3). As for PACMX-Pd, the yield was enhanced from 60% to 100% as the Pd content 372 increased from 0.2 mol% to 1.5 mol%, while it remained almost unchanged after 373 improved the dosage of Pd loading (Table 3, entries 1-6). In terms of EDAX-Pd, the 374 yield was up to 100% when the Pd content reached to 0.26 mol% and being constant 375 with further increasing the Pd loading (Table 3, entries 8-13). These results imply that 376 PACMX-Pd and EDAX-Pd with less palladium exhibited excellent catalytic activity 377 towards Suzuki reaction and the optimal Pd loading for PACMX-Pd and EDAX-Pd 378

- was 1.5 mol% and 0.26 mol%, respectively. Control experiments indicated that there
- 380 was no product acquired in the absence of Pd (Table 3, entries 7 and 14), suggesting
- that PACMX-Pd and EDAX-Pd could act as highly effective catalysts. In addition, the
- pure palladium acetate was also used for the reaction (Table 3, entry 15), and it was
- found that $Pd(OAc)_2$ was not as effective as PACMX-Pd and EDAX-Pd.

Entry	Catalyst	Base	Yield ^b /%	
1	PACMX-Pd	K ₂ CO ₃	100	
2	PACMX-Pd	Na ₂ CO ₃	50.1	
3	PACMX-Pd	КОН	80	
4	PACMX-Pd	TEA	26	
5	PACMX-Pd	DBU	28	
6	EDAX-Pd	K ₂ CO ₃	100	
7	EDAX-Pd	Na ₂ CO ₃	67.5	
8	EDAX-Pd	КОН	52.8	
9	EDAX-Pd	TEA	47.3	
10	EDAX-Pd	DBU	56.8	

Table 2. Effect of base on the Suzuki coupling reaction of 4-iodoanisole with phenylboronic acid^a.

^aReaction conditions: 4-iodoanisole (0.5 mmol), phenylboronic acid (0.6 mmol), various bases (1
mmol), PACMX-Pd (23 mg, containing 1.5 mol% Pd), EDAX-Pd (4.3 mg, containing 0.26 mol%
Pd), EtOH (2 mL), at room temperature, 4 h. ^bIsolated yields (each experiment was repeated for 3
times, and the final isolated yield was the average of 3 similar yields).

391	Table 3. Effect of Pd loading	on the Suzuki	coupling reaction o	of 4-iodoanisole with	henylboronic
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392 acid^a.

Entry	Catalyst	Pd/mol%	Yield ^b /%	
1	PACMX-Pd	0.2	60	
2	PACMX-Pd	0.26	69	
3	PACMX-Pd	0.50	62	
4	PACMX-Pd	1.0	69	
5	PACMX-Pd	1.5	100	
6	PACMX-Pd	2.0	100	
7	PACMX-Pd	0	0	
8	EDAX-Pd	0.2	84	
9	EDAX-Pd	0.26	100	
10	EDAX-Pd	0.50	100	
11	EDAX-Pd	1.0	100	
12	EDAX-Pd	1.5	100	
13	EDAX-Pd	2.0	100	
14	EDAX-Pd	0	0	
15	Pd(OAc) ₂	3.38	90.1	

^aReaction conditions: 4-iodoanisole (0.5 mmol), phenylboronic acid (0.6 mmol), K₂CO₃ (1 mmol).
EtOH (2 mL), at room temperature, 4 h. ^bIsolated yields (each experiment was repeated for 3 times, and the final isolated yield was the average of 3 similar yields).

The substrate scope of this Suzuki reaction between various aryl halides and arylboronic acids was investigated under the optimized reaction condition, and the results were summarized in Tables 4 and 5. For the both catalysts, electron-deficient aryl halides and electron-rich phenylboronic acid afforded higher coupling yields up

to 100%, especially aryl iodides containing methoxyl, nitro and ether group could 400 smoothly reacted with phenylboronic acid (Table 4 and 5, entries 6, 8, and 11). 401 However, deactivated aryl chlorides did not give good yields in the coupling reactions 402 with phenylboronic acid (Tables 4 and 5, entries 5 and 10). Moreover, arylboronic 403 acids with either electro-withdrawing or electro-donating groups on the phenyl ring 404 was reacted with iodobenzene (Table 4 and 5, entries 1, 13 and 14), the yields of the 405 products were good to excellent. It was reported that electron-rich ligands promoted 406 407 the oxidative addition that is a crucial step for enhancing the catalytic activity of palladium catalyst in Suzuki coupling reaction (Cho et al., 2014). As a consequence, 408 the high catalytic activities of PACMX-Pd and EDAX-Pd can be attributed to their 409 electron-rich N bidentate ligand. Moreover, the TOF values were recorded up to 1540 410 h⁻¹ for PACMX-Pd, and the corresponding values were observed as high as 9626 h⁻¹ 411 for EDAX-Pd (Luconi et al., 2018; Dong, Wu, Chen, & Wei, 2017). 412

413

Received and the second s

R_1 R_2 R_2		$)_2 \mathbf{B} - \mathbf{R}_2$	$\xrightarrow{\text{PACMXPd}, K_2\text{CO}_3(1 \text{ eq.})} R_1 R_2$			
			EtOH, Room tempera	ture, Air		
aryl hali 0.5 ec	ides].	boronic acid 0.6 eq.			biphenyls	
Entry	Х	R ₁	R ₂	Time/h	Yield ^b /%	TOF (h ⁻¹)
1	Ι	Н	Н	8	92.6	713
2	Br	Н	Н	12	49.2	252
3	Ι	CH ₃	Н	8	60.5	466
4	Br	CH ₃	Н	12	16.2	83
5	Cl	CH ₃	Н	24	trace	trace
6	Ι	OCH ₃	н	4	100	1540
7	Br	OCH ₃	Н	8	48.9	376
8	Ι	O=CCH ₃	Н	4	100	1540
9	Br	O=CCH ₃	Н	4	100	1540
10	Cl	O=CCH ₃	Н	8	24.5	189
11	Ι	NO ₂	Н	4	96.3	1483
12	Br	NO ₂	Н	4	82.2	1266
13	Ι	Н	OCH ₃	4	91.4	1407
14	Ι	Н	O=CCH ₃	8	71.1	547

414 Table 4. The Suzuki coupling reactions of aryl halides and arylboronic acids catalyzed by

415 PACMX-Pd^a.

^aReaction conditions: aryl halide (0.5 mmol), arylboronic acid (0.6 mmol), K₂CO₃ (1 mmol),
PACMX-Pd (23 mg, containing 1.5 mol% Pd), EtOH (2 mL), at room temperature. ^bIsolated
yields (each experiment was repeated for 3 times, and the final isolated yield was the average of 3
similar yields). TOF: turnover frequency ((yield of product / per mol of Pd)/time of reaction)

R1-	$\rightarrow \frac{1}{1}X + (OH)_2$	\mathbf{B}	EDAX·Pd, K_2CO_3 (1	eq.) R 1	\mathbb{R}	
	'	'	EtOH, Room tempera	ture, Air		
aryl hali 0.5 ec	des].	boronic acid 0.6 eq.			biphenyls	
Entry	Х	R ₁	R ₂	Time/h	Yield ^b /%	TOF (h ⁻¹)
1	Ι	Н	Н	8	70.3	3384
2	Br	Н	Н	12	70.7	2269
3	Ι	CH ₃	Н	24	69.2	1110
4	Br	CH ₃	Н	24	68.6	1100
5	Cl	CH ₃	Н	24	trace	trace
6	Ι	OCH ₃	Н	4	100	9626
7	Br	OCH ₃	Н	8	57	2743
8	Ι	O=CCH ₃	Н	4	100	9626
9	Br	O=CCH ₃	Н	4	100	9626
10	C1	O=CCH ₃	Н	12	trace	trace
11	Ι	NO ₂	Н	4	100	9626
12	Br	NO_2	Н	4	80.7	7768
13	I	Н	OCH ₃	4	81.4	7835
14	I	Н	O=CCH ₃	8	76	3658

420 **Table 5.** The Suzuki coupling reactions of aryl halides and arylboronic acids catalyzed with

421 EDAX-Pd^a.

422 ^aReaction conditions: aryl halide (0.5 mmol), arylboronic acid (0.6 mmol), K₂CO₃ (1 mmol),

423 EDAX-Pd (4.3 mg, containing 0.26 mol% Pd), EtOH (2 mL), at room temperature. ^bIsolated yield

424 (each experiment was repeated for 3 times, and the final isolated yield was the average of 3 similar

425 yields). TOF: turnover frequency ((yield of product / per mol of Pd)/time of reaction)

426 We compared the results achieved in this work with those catalyzed by other

427 catalysts reported recently for the Suzuki coupling reactions, and the results were
428 listed in Supplementary data Table S1. Our catalysts showed superiority to some
429 degree, such as lower reaction temperature, shorter reaction time, and higher yield.

430 *3.3. Recyclability of PACMX-Pd and EDAX-Pd*

The recyclability of the catalysts was examined for the Suzuki reaction between 431 4-iodoanisole and phenylboronic acid under standard condition with 23 mg 432 PACMX-Pd (containing 1.5 mol% Pd) and 4.3 mg EDAX-Pd (containing 0.26 mol% 433 434 Pd), and the results were shown in Fig. 8. After the completion of the first cycle (100% yield), the catalysts were recovered by centrifugation and then vacuum dried. 435 The recovered catalysts were directly used for the second run under the same reaction 436 conditions. The yield of the product was decreased to 87.9% for PACMX-Pd catalysis 437 in the fifth run, indicating that PACMX stabilized Pd NPs was highly stable and 438 recyclable. However, it yielded only 57.4% in the fifth run for EDAX-Pd. The results 439 indicate that the rigid ligand modified xylan (PACMX) is superior to the flexible 440 ligand modified one (EDAX). Furthermore, the AAS measurement revealed that the 441 442 loss concentration of Pd was less than 1 ppm after being used for five times, demonstrating PACMX and EDAX could act as good substrates to stabilize Pd NPs 443 and the Pd leaching was negligible. According to the TEM analysis, the Pd 444 nanocatalysts appeared a slight aggregation in the 5th cycle (especially the EDAX-Pd). 445 Hence, the reduced catalytic activity in recycling can ascribed to the agglomeration of 446 Pd nanocatalysts. 447



448



450 *3.4. Heterogeneity of PACMX-Pd and EDAX-Pd*

451 In order to explore the heterogeneity of the catalysts, the following experiments were conducted. After the typical Suzuki reactions proceeding for 1 h, the catalyst 452 was quickly filtered off and the filtrate along with the fresh base was stirred for 453 another 3 h at room temperature. Within 1 h of the reaction, the product yield was 454 70% and 59.5% for PACMX-Pd and EDAX-Pd (Table 1, entries 9 and 18), 455 respectively. However, the yield increased by only 1% and 3% for PACMX-Pd and 456 EDAX-Pd in the following 3 h, indicating the reaction was inefficient in the absence 457 of catalysts. Therefore, we can conclude that the catalysts were heterogeneous and 458 459 efficient for the Suzuki reactions.

460

461 **4. Conclusions**

In summary, we synthesized N bidentate ligand functionalized xylan supported palladium composites and applied as heterogeneous catalysts for catalyzing Suzuki cross-coupling reaction. The palladium/xylan heterogeneous catalysts showed unique features, such as the good usability under air atmosphere, ease of separation,

providing high yield of products with a small amount of catalysts and no Pd leaching 466 was occurred during the catalytic reaction. A series of aryl halides were effectively 467 coupled with arylboronic acid under room temperature by the catalysis of PACMX-Pd 468 and EDAX-Pd, and giving excellent TOF values up to 9626 h⁻¹. Additionally, the 469 catalysts can be reused for five times without considerable deactivation and the high 470 stability of PACMX or EDAX indicating their potential for grafting various metal 471 species as catalytic active centers for a wide range of metal-catalyzed reactions. The 472 473 xylan-based complex may also open the pathway for other organic catalysis reactions in which Pd NPs are involved. 474

475

476 Abbreviations

PACMX, 1, 10-phenanthrolin-5-amine functionalized carboxymethyl xylan; 477 PACMX-Pd, palladium grafted PACMX; EDAX, ethylenediamine functionalized 478 xylan; EDAX-Pd, palladium grafted EDAX; Pd NPs, palladium nanoparticles; 479 EDC • HCl, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride; NHS, 480 N-hydroxysuccinimide; DBU, 1, 8-diazabicyclo [5.4.0] undec-7-ene; EtOH, ethanol; 481 MeOH, methanol; THF, tetrahydrofuran; NaOH, sodium hydroxide; KOH, potassium 482 483 hydroxide; K₂CO₃, potassium carbonate; Na₂CO₃, sodium carbonate; TEA, triethylamine; FT-IR, fourier transform infrared spectra; XRD, X-ray powder 484 diffraction; XPS, X-ray photoelectron spectroscopy; TGA, thermal gravimetric 485 analysis; TEM, transmission electron microscopy; HR-TEM, high resolution 486 transmission electron microscopy; AAS, atomic absorption spectrometer; NMR, 487 nuclear magnetic resonance spectra; SEM, scanning electron microscope; EDX, 488 energy dispersive X-ray spectroscopy. 489

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