COMMUNICATION

WILEY Applied Organometallic Chemistry

Mesoporous carbon supported ultrasmall palladium particles as highly active catalyst for Suzuki-Miyaura reaction

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Funding information Fondation pour l'ENSCMu A fast and efficient eco-friendly two-step preparation of a palladium-containing mesoporous carbon catalyst (**C1**) from green and readily available carbon precursors (phloroglucinol and glyoxal), a porogen template (pluronic F-127) and PdCl₂ is described. Catalyst **C1** contains ultra-small Pd nanoparticles (1.2 nm) uniformly dispersed in the carbon network and shows an outstanding activity for Suzuki-Miyaura reactions in pure water: extremely low amounts of palladium (10 μ equiv. in most cases) are sufficient to afford almost palladium-free products (containing <0.25 ppm of precious metal without further purification steps).

KEYWORDS

C-C coupling, chemistry in water, mesoporous carbon, palladium nanoparticles, heterogeneous catalysis

1 | INTRODUCTION

The palladium-catalyzed Suzuki-Miyaura coupling is a widely used reaction both in academic and industrial laboratories for the creation of new carbon-carbon bonds.^[1,2] However this coupling presents some drawbacks: 1) palladium is a scarce precious metal; 2) its price increases rapidly (> 28.000 €.kg⁻¹ in October 2018 and > 45.000 \notin .kg⁻¹ in January 2019); 3) residual amounts of palladium contaminates the final products^[3]; 4) cross-couplings are often performed in environmentally-questionable organic solvents. In the two last decades enormous progress has been made in the field of preserving the resources in scarce precious metals with the development of heterogeneous reusable catalysts.^[2] Very recently, the development of palladium catalysts for Suzuki-Miyaura reactions in "green" solvents has suscited huge interest. For example the group of Lipshutz has developed a Suzuki-Miyaura reaction in aqueous nanomicelles using an commercially available

but expensive HandaPhos ligand.^[4] Some of us have also developed a magnetic palladium catalyst supported on a cobalt core covered by a carbon shell bearing diphenylphosphino groups for Suzuki-Miyaura couplings in ethanol.^[5] The group of Grison has also reported an EcoPd catalyst obtained from a plant (Eichhornia crassipes) able to bioconcentrate palladium and its application for Suzuki-Miyaura couplings in glycerol in the presence of 0.1–1 mequiv. of palladium.^[6] The same year, Sarkar et al. have described the preparation of a palladium-containing graphitic carbon nitride (nano-Pd/ gC₃N₄) nanocomposite and its use for Suzuki-Miyaura reactions in water under microwave irradiations using 0.94 mequiv. of supported palladium.^[7] Other groups have reported heterogeneous palladium catalysts supported on silica bearing dimethylamino groups or Nheterocyclic ligands^[8] hydroxyapatite nanospheres,^[9] montmorillonite,^[10] MgO carbon quantum dots,^[11] γ -iron oxide,^[12] imidazolium-functionalized an βcvclodextrin,^[13] urea-based amphiphilic porous organic

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polymers,^[14] an ionic liquid copolymer,^[15] eumelanin,^[16] oak gum.^[17] These catalysts showed an interesting activity for Suzuki-Miyaura reactions in water but most of them are prepared *via* a multi-step synthesis^[8,9] involving toxic and sensitive reagents.^[18]

Mesoporous carbons present some key advantages compared to traditional supports, like high availability and low cost, high specific surface area, well-ordered and interconnected porous structure and good chemical, thermal and mechanical stabilities. Therefore, they have attracted tremendous attention in many fields such as adsorption, catalysis and energy storage.^[19] In addition, the mesoporous carbon has been widely used as supports for metal-based nanoparticles, their unique uniform pore structure and rich surface functionalities allowing to obtain very small and well dispersed supported nanoparticles exhibiting enhanced performances due to the synergetic effects between the two materials.^[20]

In this respect we have recently described direct preparations of mesoporous carbons containing palladium nanoparticles^[21] or palladium/iron nanoalloys^[22] from biosourced precursors for Suzuki-Miyaura reactions in propane-1,2-diol at 140 °C using respectively 0.03 mequiv. and 0.15 mequiv. of supported palladium. More recently we have described a magnetic biosourced mesoporous carbon containing palladium/cobalt nanoalloys and its use for Suzuki-Miyaura reactions in refluxing water requiring however 10 mequiv. of supported palladium.^[2] Despite the efforts undertaken in the last years, the development of efficient and easily accessible palladium catalysts from safe precursors and their use in water with a leaching of only extremely low amounts of palladium is a major but relatively unexplored domain in catalysis. We are therefore pleased to describe herein a novel palladium-containing mesoporous carbon catalyst (C1) ENNEIYMY ET AL.

fulfilling all these requirements. This catalyst has the particularity of containing ultra-small Pd nanoparticles (1.2 nm) which are very homogeneously distributed in the carbon framework providing thus unique catalytic performances for aryl-aryl bond forming reactions in pure water.

2 | EXPERIMENTAL

All chemicals were purchased from Sigma-Aldrich and used without any further purification.

2.1 | Preparation of catalyst C1

The catalyst C1 was prepared by a two-step bottom-up approach involving firstly the synthesis of carbon support and then the synthesis of Pd nanoparticles. The general synthesis pathway is illustrated in Scheme 1. The mesoporous carbon support was synthesized by the evaporation induced self-assembly (EISA) route starting from a solution containing a surfactant (Pluronic F-127) and a phenolic resin based on phloroglucinol-glyoxal.[31] Briefly, Pluronic F-127 (3.27 g) and phloroglucinol (1.65 g) were dissolved in 81 mL of ethanol under stirring, followed by the addition of 0.2 g of citric acid and 1.62 ml of glyoxal solution (40% in water). The obtained solution is disposed in several petri dishes and left to evaporate under the fume hood in order to form a polymer film which is removed by mechanical scratching, dried at 80 °C and then pyrolysed at 600 °C under Ar atmosphere. In a second step, the carbon (1.74 g) is impregnated with an anhydrous ethanol solution (10 ml) of tetrachloropalladous acid (H₂PdCl₄), prepared by mixing a proper amount of PdCl₂ (0.066 g) with HCl (37% wt,



SCHEME 1 Preparation of catalyst C1

0.5 ml) at 60 °C. The carbon/Pd-based suspension is stirred under a fume-hood until complete evaporation of the solvent and then is dried at 80 °C for 12 hrs in air followed by thermal reduction under a mixture Ar/H_2 (10% of H_2) at 300 °C for 4 hr.

2.2 | Characterisation of catalyst C1

The crystalline structure of the carbon support and of catalyst C1 was determined by X-ray powder diffraction (XRD) technique with a D8 ADVANCE A25 powder diffractometer (from Bruker) in Bragg-Brentano reflexion geometry $\theta - \theta$. The Pd catalyst dispersion on the carbon support was investigated with a JEOL ARM-200F transmission electron microscope working at 200 kV in STEM (Scanning Transmission Electron Microscopy) mode. The Pd particle size distribution was obtained by ImageJ software by counting ca. 500 particles from several STEM images. The TEM set-up is equipped with an energy dispersive analyzer (EDX) which was used to determine the chemical composition of the materials. The surface chemistry was obtained by X-ray photoelectron spectroscopy (XPS) with a VG Scienta SES 200-2 spectrometer equipped with a monochromatized Al Ka X-ray source (1486.6 eV) and a hemispherical analyzer. The pass energy was 100 eV. The porous characteristics of the catalyst were obtained by N2 sorption isotherms with a Micromeritics ASAP 2020 set-up. The materials were outgassed at 150 °C under vacuum for 12 hr prior to the analyses. The BET specific surface area (SSA) was calculated in the relative pressure range (P/P_0) of 0.05–0.3.

2.3 | General procedure for the synthesis of biaryls 1a-j

Catalyst C1 (10-100 µequiv. of supported Pd) was added to a suspension of aryl bromide (20 mmol, 1 equiv), areneboronic acid (22 mmol, 1.1 equiv.), K₂CO₃ (24 mmol, 1.2 equiv) in H_2O (120 ml). The reaction mixture was refluxed for 10 hr. After cooling to 20 °C, C1 was filtered off using a 0.2 µm PTFE membrane. Ethyl acetate (200 ml) was then added. The organic phase was washed twice with water (50 ml), dried with MgSO₄, filtered and concentrated under vacuum. When necessary the residue was purified by flash-chromatography on silica gel using AcOEt/cyclohexane as eluant. After drying under vacuum (0.1 mbar) pure biaryls were obtained as shown by their ¹H-NMR spectra (CDCl₃, 300 MHz) which were in with the literature (see Supporting accordance information).

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3 | RESULTS & DISCUSSION

3.1 | Preparation and characterizations of catalyst C1

Catalyst C1 was prepared by a two-step bottom-up synthesis approach (Scheme 1) involving first the synthesis of the carbon porous support and then the formation of Pd nanoparticles in the carbon network. The carbon was obtained by self-assembly of phenolic resin precursors (phloroglucinol-glyoxal) with a pore creating agent (Pluronic F-127) followed by thermal annealing which led to the formation of a porous carbon.^[23] In a second step, the impregnation of this carbon with a Pd-based salt solution followed by thermal reduction (Scheme 1) led to the formation of Pd/Carbon catalyst C1 possessing Pd nanoparticles of a narrowly distributed size and a homogeneous repartition on the carbon surface, as revealed by STEM images (Figure 1a, b). The particle size was surprisingly very small (ca. 1.2 nm) as can be observed in Figure 1c. In our previous reports, the smallest Pd particle sizes obtained were in the range of 2.5-3.0 nm, but other carbon supports and Pd amounts were used which may affect this parameter.^[24]

For instance, the increase in the amount of metal particles generally induces an increase in the particle size.^[25] Herein, the amount of Pd in the carbon network is low (~2.3%) allowing to avoid the particle growth and agglomeration. Moreover, the carbon surface chemistry, i.e., the nature and the amount of functional groups may impact the size and the dispersion of the particles.^[26] Such functional groups improve the wetting behaviour of carbon with the metal salt and may act as active sites to anchor the metal nanoparticles favouring their dispersion. The small size of the nanoparticles could also be observed on XRD patterns (Figure 2a) which show a broad peak at around 41° , which is an overlap of (111)/(200) diffraction peaks of the cubic-face centered structure of Pd and that of (100) peak of graphitic structure (G) of carbon support. It can be noted that in the case of carbon, this peak is shifted towards higher values (43°) compared to catalyst C1, confirming the Pd formation (vertical lines correspond to the theoretical Pd positions extracted from Crystallography Open Database, COD-9013416). The broad peak shape suggested very small nanoparticles and low degree of crystallinility, in line with other work^[27] and in agreement with STEM (Figure 1a, b) and the diffuse diffraction circles observed on the Selected Area Electron Diffraction (SAED) images (in-set Figure 1a). The presence of Pd could be confirmed also by energy dispersive analyses (EDX) as illustrated in Figure S1 (Supporting Information). More insights about the surface chemistry of catalyst C1 were obtained by the XPS technique 4 of 8 WILEY Organometallio



FIGURE 1 HRTEM images of C1 catalyst before (a, b) and after (c, d) 1^{st} catalytic test along with their corresponding particle size distributions: (e) before test and (f) after test. *In-set* of the Figure 1a: SAED image of the C1 material

(Figure 2). The C 1s spectra of carbon support (Figure 2b) shows the presence of a main important peak placed at 284.4 eV corresponding to the C sp² contribution. In addition, oxygen-based functional groups such as ether (C-OR), carbonyl (C=O) and carboxyl (-COOR) are observed as well between 284.9 and 286.0 eV. These functional groups provide a hydrophilic character to carbon which favors the good impregnation with the palladium based solution. The Pd 3d high resolution spectra (Figure 2c) show two main peaks, i.e., Pd $3d_{5/2}$ and Pd $3d_{3/2}$ placed at 335 eV and 340 eV, respectively. Each peak was

deconvoluted into two components, namely metallic palladium, Pd⁰ and palladium oxide, Pd²⁺. The Pd⁰ contribution is predominant compared to that of Pd²⁺ as reflected by the more intense peak of the former one. The presence of a layer of palladium oxide in the surface of Pd nanoparticles is well known to occur due to the small size of the particles which exhibit high reactivity towards oxygen.^[28] The presence of oxygen bonded with Pd can be remarked in the O 1s peak (Figure 2d) as well, however its amount is significantly much lower than the amount of the oxygen bonded with carbon in functional groups.



FIGURE 2 XRD patterns of the carbon support and carbon/Pd catalyst, C1 (a) and XPS high resolution deconvoluted spectra of the C1 catalyst: C 1s core spectra (b), Pd 3d spectra (c) and O 1s core spectra (d)

Catalyst **C1** presented also a developed specific surface area of 785 m²/g, a porous volume of 0.76 cm³/g and had an open 3D porous structure (Figure 1b) formed by micropores (size <2 nm) and mesopores (~5.5 nm) as revealed by the type 4 nitrogen adsorption/desorption isotherm and the pore size distribution (Figure S2, Supporting Information). The size of the whole catalyst was *ca*. 1–2 μ m as shown by TEM (Figure S3, Supporting Information). Such a Pd/carbon hybrid material combining an open carbon porous structure and small Pd nanoparticles allows a good diffusion of the reagents and in addition short diffusion pathways due to the reduced size. The Pd surface to bulk ratio was also increased which may induce significant changes in the performances compared to bulk materials.^[29]

3.2 | Suzuki-Miyaura reactions in the presence of catalyst C.

Performing the Suzuki-Miyaura coupling in EtOH or in EtOH/ H_2O mixtures afforded **1a** in almost quantitative yields (Table 1, entries 1–3). Gratifyingly using only water

as the solvent gave **1a** in 99% yield (entry 4). Decreasing the reaction time from 20 hr to 10 hr resulted in the obtention of **1a** in still an excellent 98% yield (entry 5). Noteworthily replacing water by usual organic solvents (DMF, ACN, toluene) gave only traces of **1a** (entries 6– 8). Finally performing the cross-coupling with 4chloroacetophenone was unsuccessful even in the presence of 1 mequiv. of supported palladium and only traces of **1a** were obtained.

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A hot filtration test was then performed to determine the nature of the catalysis. After 2 hr of reaction between 4-bromoacetophenone and benzeneboronic acid under the optimized conditions of entry 5 (yield at that point: 64%) the catalyst was filtered off and the filtrate was refluxed for another 8 hr (yield at that point: 74%). Soluble palladium entities seem therefore to play only a minor role in this coupling. The amount of residual palladium present in product **1a** after coupling was then determined after complete mineralization of the crude mixture. It was found that only *ca*. < 0.9% of the initial amount of supported palladium used was present. Even if palladium was entirely found in the final product after work-up, it represents less than 0.25 ppm (wt/wt) of palladium in 6 of 8 WILEY-Organometallic

the final product. Therefore almost palladium-free products can be obtained without tedious purification steps. In addition after one use no significant changes were observed by TEM and the Pd nanoparticles conserve a small 1.3 nm size (Figure 1c,d,f). It is noteworthy that catalyst **C1** can be stored for several months without particular precautions and no loss of efficiency was observed (Table 1).

Various biaryls were then prepared (Table 2) under the optimized reaction conditions (Table 1, entry 5). Coupling 4-bromoacetophenone with different areneboronic acids led the corresponding biaryls in good yields (entries 1-5). Reacting benzeneboronic acid with aryl bromides bearing electro-attracting or electron-donating groups afforded also the desired biaryls (entries 6-10). However it is noteworthy that some couplings, in particular those involing more hindered substrates, required the use of a larger amount of supported palladium to proceed satisfactorily (entries 4, 9, 10). Finally the cross-couplings of 3thiopheneboronic acid with 4-bromoacetophenone and of benzeneboronic acid with 3-bromopyridine were unsuccessful even in the presence of 50 µequiv. of supported palladium, the desired products being obtained in <20% yields.

TABLE 1	Optimization	of the	reaction	conditior
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	•		
0 Br + B(OH)2	$\frac{\text{C1 (10 } \mu \text{equiv. Pd)}}{\text{K}_2\text{CO}_3, \text{ Solvent}}$		
Entry ^a	Solvent	Conditions	Yield ^b
1	EtOH	Reflux, 20 hr	98%
2	EtOH/H ₂ O 95: 5	Reflux, 20 hr	99%
3	EtOH/H ₂ O 50: 50	Reflux, 20 hr	97%
4	H ₂ O	Reflux, 20 hr	99%
5	H_2O	Reflux, 10 hr	98% ^{c,d}
6	H ₂ O	50 °C, 20 hr	41%
7	DMF	100 °C, 20 hr	< 5%
8	ACN	Reflux, 20 hr	< 5%
9	Toluene	100 °C, 20 hr	< 5%

^aReactions performed in the presence of 4-bromoacetophenone (1.0 equiv.), benzeneboronic acid (1.1 equiv.), K_2CO_3 (1.2 equiv.) and catalyst **C1** (10 μ equiv. of supported Pd).

^bYields calculated by ¹H-NMR of the crude reaction mixture.

^cIsolated yield: 97%.

^dYield after refluxing the reaction mixture for 2 hr: 64%.

TABLE 2Syntheses of biaryls

	r			
+	Catalyst	$C1 \xrightarrow{R^1}$		
B(O	H) ₂ K_2CO_3 , H	H ₂ O, \ 0 h	/ \/ 1a-j	
$R^2 \frac{\Pi}{\Pi}$				
Entry ^a	R ¹	R ²	Pd (µequiv.)	Yield ^b
1	4-Ac	Н	10	97 (1a)
2	4-Ac	4-Me	10	99 (1b)
3	4-Ac	3-Me	10	96 (1c)
4	4-Ac	2-Me	50	68 ^c (1d)
5	4-Ac	4-OMe	50	97 ^d (1e)
6	4-CO ₂ Et	Н	10	96 (1f)
7	4-CN	Н	10	68 (1 g)
8	4-Me	Н	10	92 (1 h)
9	3-Me	Н	100	80 ^e (1i)
10	2-Me	Н	100	49 ^e (1j)

^aReactions performed in the presence of an aryl bromide (1.0 equiv.), an areneboronic acid (1.1 equiv.), K_2CO_3 (1.2 equiv.) and catalyst C1.

^bIsolated yield.

 $^{c}\mbox{Yield}$ using 10 $\mu\mbox{equiv.}$ of supported Pd: < 10%.

^dYield using 10 µequiv. of supported Pd: 27%.

 $^{e}\mbox{Yield}$ using 10 $\mu\mbox{equiv.}$ of supported Pd: < 10%.

The activity of **C1** was then compared to that of other heterogeneous catalysts reported in the literature for Suzuki-Miyaura reactions in water (Table 3). Catalyst **C1** is one of the most active in terms of amount of supported palladium necessary and turn over frequency (TOF). It is noteworthy that **C1** exhibits also the smallest palladium NPs sizes. 5. The author should give rational reason about

TABLE 3 Comparative study of reusable palladium-catalysts forSuzuki-Miyaura reactions in water

Entry	Catalyst, additives	Pd mequiv	PdNP nm	TOF h ⁻¹
1	C1	0.01	1.2	10000
2 ^[7]	nano-Pd/gC ₃ N ₄	0.94	15	11000
3 ^[10]	PdNPs@acid-treated montmorillonite	0.7	<10	60
48a	Pd@SiO ₂ -NMe ₂	5	2–7	140
5 ^[15]	PdNPs@ionic copolymer, TBAB	0.1	2-5	4950
6 ^[13]	Pd@β-cyclodextrine	5	-	400
7 ^[17]	PdNPs@oak gum	3	5-7	60
$8^{[11]}$	Pd@MgO-CQD ^a	3	2–6	150
9 ^[16]	Pd NPs@Eum ^b	0.5	2-3	1000

^aCQD: carbon quantum dots.

^bEum: eumelanin support.

the enhanced catalysis. Both the hydrophilic nature of the mesoporous carbon and the easily accessible ultrasmall Pd nanoparticles may explain the very high activity of catalyst **C1** for Suzuki-Miyaura couplings in water.

4 | CONCLUSION

In conclusion, a "green" and efficient preparation of a palladium-containing mesoporous carbon catalyst **C1** was described. Catalyst **C1** was characterized using various techniques (STEM, HRD, EDX and XPS) proving the presence of ultra-small Pd nanoparticles (1.2 nm) homogeneously dispersed in a 3D open mesoporous hydrophilic carbon framework. Catalyst **C1** allows Suzuki-Miyaura reactions in water in the presence of ppm amounts of supported palladium (10 μ equiv. in most cases). It is noteworthy that **C1** is biosourced and represents so far one of the most active heterogeneous catalyst for Suzuki-Miyaura reactions in water leading to almost palladium-free products after reaction. Further studies are underway in our group to determine the synthetic potential of **C1** for other C-C couplings and reductions.

ACKNOWLEDGMENTS

We are grateful to the Fondation pour l'Ecole Nationale Supérieure de Chimie de Mulhouse for a doctoral grant and generous financial support to M. Enneiymy, to J. Coulleray and B. Rety for helpful technical assistance, to Dr. L. Vidal for TEM, to Dr. J.-M. Le Meins for the XRD and P. Fioux for the XPS analyses via IS2M technical platform.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article. **How to cite this article:** Enneiymy M, Le Drian C, Ghimbeu CM, Becht J-M. Mesoporous carbon supported ultrasmall palladium particles as highly active catalyst for Suzuki-Miyaura reaction. *Appl Organometal Chem.* 2019;e5104. <u>https://doi.org/10.1002/aoc.5104</u>