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Biosourced mesoporous carbon with embedded palladium nanoparticles by a one pot soft-template synthesis: application to Suzuki reactions

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A simple, direct and environmental-friendly one-pot preparation of a palladium-containing mesoporous carbon (Pd@MC) from a cheap, non hazardous and easily accessible biopolymer (tannin) as a carbon precursor, Pluronic® F127 surfactant as a pore structuring agent and a palladium salt is reported. This material has the peculiarity to have palladium nanoparticles entrapped in irregular voids connected to the worm-like mesoporous network limiting palladium leaching while keeping good access to the reactants. It was successfully used as a catalyst for ligand-free Suzuki-Miyaura couplings of aryl bromides in a green solvent (propane-1,2-diol) in the presence of extremely low amounts of supported palladium (usually 30 µequiv). It is noteworthy that almost palladium-free products (containing less than 1.5 µequiv of precious metal) can be obtained. The possibility to reuse the catalyst was also ascertained.

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A Introduction

To face the global warming and limited resource of fossil raw materials, there are needs to develop durable processes while keeping or even improving materials efficiency. In this context, the use of biosourced precursor has regained interest for the preparation of materials possessing well controlled properties adapted to the targeted applications. Biosourced precursors have been used for ages for the preparation of carbonaceous compounds. Currently, one of the largest scale utilization of biosourced carbons is the preparation of activated carbons, which are highly porous and have therefore interesting adsorption properties. They are prepared by carbonization of biosourced precursors followed by a secondary treatment with additives for the activation of the porosity. Nevertheless, these interesting and green materials suffer from a pore size distribution difficult to tailor and not necessarily adapted to specific applications. Therefore, other processes have emerged in order to get a better control of the porosity.¹ According to the porosity desired, particular processes were developed: zeolite-templated carbon²⁻⁸ and carbide-derived carbon⁹ (CDC) for microporous carbons, mesoporous oxides (e.g. SBA-15 or MCM-48 silica) replication for mesoporous carbons¹⁰⁻¹⁴ and reverse opal synthesis for macroporous carbons.¹⁵ With the exception of CDCs' route, these processes rely on the use of a porous hard-template as a mould. It is infiltrated by a carbon precursor, which is then converted to carbon and finally the mould is removed by chemical attack using

concentrated NaOH or HF. Thus, control of the porosity of the carbon is allowed by this inverse replication process since the wall thickness and morphology of the host-template determine the pores size and shape of the replicated carbon. This hard-templating process was widely used for the preparation of carbon materials having ordered array of mesopores starting from organised mesoporous silica. Nevertheless, the preparation of such carbons is long and tedious since it is a multi-step process generating undesirable residues owing to the etching step (i.e.: hazardous HF for SiO₂ dissolution). Another more convenient process was developed more recently^{16,17} for the preparation of ordered mesoporous carbon materials. It was called soft-templating route since it is based on the use of surfactant as soft-matter templating the mesoporosity thanks to a mesostructuration of a carbon precursor resin. By calcination of the resulting resin/surfactant mesophase, the resin is carbonized to carbon while the surfactant is pyrolyzed to gaseous species, creating thus the mesoporosity. Since the carbon precursor is based on phenolic resins that require the use of carcinogenic compounds such as phenol and/or formaldehyde, green processes were developed replacing formaldehyde by glyoxal¹⁸ or using safe biosourced carbon precursors such as fructose¹⁹ in hydrothermal conditions or tannin (condensed) with a simple evaporation²⁰ and/or thermal²¹ induced self-assembly process (denoted EISA and TISA respectively). In the latter case, tannin is a cheap and non hazardous precursor, available on a large scale from the wood industry, which has the ability to self-condense in acidic media;

thus it does not require any carcinogenic cross-linker agent such as formaldehyde for its polymerization.²² Tannins have been largely used for the preparation of carbon materials such as foam,²³ micrometer-size beads,²⁴ carbon doped with nitrogen,²⁵ emulsion-templated porous carbon monoliths,²⁶ xerogels,²⁷ aerogels²⁸ and cryogels.²⁹

Porous carbons of controlled porosity have been largely used as supports for catalysis. These catalysts require the prior preparation of porous carbon materials and their subsequent impregnation with the salt of the metal catalyst; sometimes the salt needs to be further reduced to the metallic state. This impregnation procedure leads to metallic nanoparticles (NPs) located in the pores. This allows a good access to reagents but also possible leaching. A wide range of carbon supports of controlled porosity containing (precious) metallic nanoparticles such as Pt, Pd, Au, Ag, Ni, Co have already been prepared by this impregnation route for catalytic purposes. Palladium catalysts play currently a crucial role in organic chemistry for the versatile creation of carbon-carbon bonds. Suzuki, who obtained the Chemistry Nobel Prize in 2010^{30,31}, has developed one of the most powerful palladium-catalyzed reactions for the formation of aryl-aryl bonds. This coupling finds numerous applications in the fields of pharmaceuticals^{32,33}, OLED materials³⁴, liquid crystals³⁵, metal ligands for catalysis and molecular recognition.³⁶ The Suzuki reaction is traditionally performed by reacting aryl halides with areneboronic acids using a homogeneous (soluble) palladium catalyst in amounts of 10-50 mequiv.^{37,38} Moreover, the Suzuki reaction presents the important drawback that the expensive soluble catalyst is difficult to recover for reuse, whereas palladium is a scarce natural resource which should be preserved. It is important to note that the presence of palladium contaminants in products is unavoidable and problematic in the pharmaceutical field where less than 10 ppm of transition metal contaminants are tolerated^{39,40}. This latter point leads often to tedious and time-consuming purification steps. To overcome these drawbacks some extremely active soluble catalysts have been developed allowing to perform Suzuki reactions with "homeopathic" amounts of precious metal ranging from 0.2-0.5 mequiv.⁴¹ A more widespread strategy consists to use heterogeneous palladium catalysts by encapsulation of the precious metal in a polymer⁴² or by supporting it on polymers,^{43,44} biopolymers^{45,46} or inorganic supports^{47,48} bearing in most cases ligands. These catalysts can be recovered by simple filtration and reused successfully several times with only a low palladium leaching. In this respect, some of us have developed heterogeneous palladium catalysts grafted on polystyrene beads or on magnetic nanoparticles bearing phosphino ligands for carbon-carbon bond forming reactions⁴⁹⁻⁵¹. In most cases the preparation of heterogeneous catalysts requires a tedious multiple step process. Palladium adsorbed on activated carbon (Pd/C) is a widely used heterogeneous catalyst especially for hydrogenation reactions^{52,53}. Several groups have reported its use for Suzuki couplings using generally 10-50 mequiv. of supported palladium^{54,55}. It is noteworthy that the activity of the Pd/C catalyst is often dependent on its commercial source^{56,57} and that decreases of the yields obtained after several reuses are frequently observed owing to the formation and/or growth of palladium aggregates^{58,59}. Moreover, palladium leaching phenomena are

also usually encountered probably due to a too weak adhesion between palladium NPs and the carbon surface.

Thanks to their high surface areas, large pore sizes, narrow-pore-size distributions, thermal and mechanical stabilities, mesoporous supports are promising for the development of heterogeneous catalysts.⁶⁰ For example, palladium catalysts supported on mesoporous silica SBA-15⁶¹, on functionalized mesoporous silica SBA-15^{62,63} or MCM-41^{64,65}, on PMOs⁶⁶ or on mesocellular foam⁶⁷ have been widely studied.⁶⁸ Some of them were used successfully for Suzuki couplings in the presence of 0.8-10 mequiv of supported palladium. Mesoporous carbons constitute other supports of great interest for the development of palladium-containing heterogeneous catalysts. For instance, they have been used for H₂ storage through H₂ dissociation palladium-based catalytic reaction.^{69,70} These materials were only sparsely studied in fine chemistry for C-C bond forming reactions. For example, colloidal palladium nanoparticles incorporated in mesoporous carbons were prepared by the hard-templating strategy and were successfully used for Suzuki reactions of aryl bromides in aqueous DMF using 0.2 mequiv. of supported palladium⁷¹. More convenient strategies have been used to prepare palladium supported on mesoporous activated carbons obtained from plum stones and oak wood and have been applied to Suzuki reactions but require the use of 16 mequiv. of supported palladium⁷². More recently palladium-containing mesoporous activated carbons presenting a significant amount of phosphorus groups on the carbon surface were prepared by chemical activation of kraft lignin with H₃PO₄ followed by palladium deposition. They have been used successfully for Suzuki reactions in aqueous DMA in the presence of 1 mequiv. of supported palladium⁷³. Finally, one pot syntheses of palladium-containing mesoporous carbons, with or without hard-templates, using a carbon precursor in presence of a palladium salt followed by a carbonization process were also developed but their activity for Suzuki reactions was not determined.⁷⁴⁻⁷⁷ Recently, a mesoporous carbon replicated from SBA-15 mesoporous silica template and containing palladium nanoparticles was tested successfully for Suzuki reactions but 20 mequiv. of supported palladium were required to obtain biaryls in good yields.⁷⁸ It is worth noting that these two last syntheses require an additional step for the silica hard-template removal. To the best of our knowledge, direct preparation of a palladium-containing mesoporous carbon catalyst by a one pot synthesis based on the soft-templating approach has never been reported even if this process was already used for other metallic species such as Pt^{79,80}, NiCo alloy⁸¹, LiFePO₄.⁸² Inspired by our work on the one-step green synthesis of ordered mesoporous carbons using tannin and a soft-templating surfactant,²⁰ we describe herein a facile one-step synthesis of mesoporous carbons containing palladium nanoparticles (Pd@MC Xi) with different palladium contents (0.2, 0.8 and 1.5 wt% for i=1,2 or 3 respectively) and their use for Suzuki couplings under environmental friendly conditions using extremely low amounts of supported palladium (30 μequiv.).

B Experimental

Reagents

All reagents and solvents were obtained from commercial sources and were used without further purification. Tannin was a gift of Silvachimica (Italy) in the form of a fine light brown powder, obtained by spray drying of aqueous wattle (*Acacia mearnsii* formerly *mollissima*, DeWild) bark extracts. Such commercial raw material is sold with a guaranteed content of at least 74% of condensed tannins, and contains generally 80-82% actual phenolic flavonoid materials, 4-6% water, 1% amino acids, the remainder being monomeric and oligomeric carbohydrates, originating from hemicelluloses. Pluronic F127 (Sigma Aldrich) is a low cost triblock copolymer of average formula (PEO)₁₀₆(PPO)₇₀(PEO)₁₀₆.

Preparation of Pd@MC Xi- catalysts

The direct synthesis of the palladium-containing mesoporous carbon catalyst (Pd@MC) was inspired from our recent work on the preparation of ordered mesoporous carbon from a biosourced carbon precursor (tannin).²⁰ PdCl₂ (4 mg for **X1**, 20 mg for **X2** and 40 mg for **X3**) was dissolved in concentrated HCl (24.5 wt%, 1.4 mL) then 96% ethanol (5.7 mL) and water (3 mL) were added. Tannin (1.1g) and Pluronic F127 (1.1 g) were dissolved in that solution which was stirred for one hour at room temperature and disposed into four petri dishes in order to have a thin layer of liquid that was left to evaporate at room temperature overnight. The dishes were then placed in an oven (130 °C) overnight. The resulting solid is then scratched and carbonized under an inert atmosphere (Argon, 7 L/h) at 400 °C for 18 min (heating rate 5 °C/min). The recovered compound (~500 mg) is crushed by hand to a fine black carbon powder. The resulting catalysts are labeled Pd@MC Xi (i=1,2 or 3) where **X1**, **X2** and **X3** correspond respectively to 0.2, 0.8 and 1.5 wt% of palladium.

Characterization of Pd@MC catalysts

The Pd@MC catalysts were characterized by X-Ray diffraction (XRD), N₂ physisorption at 77K and Transmission Electronic Microscopy (TEM) to get information on their textural and structural properties. X-ray diffractograms were collected with a X'Pert MPD PANalytical with Cu K α radiation ($\lambda = 0.154$ nm). The materials were observed by classical High Resolution Transmission Electron Microscopy using a Philips CM200 microscope which has a point-to-point resolution of 0.3 nm. In order to localize precisely the palladium NP within the MC matrix, 3D-TEM tomography were acquired by means of a spherical aberration (Cs) probe corrected JEOL 2100F transmission electron microscope with a field emission gun operating at 200 kV. Before observation, the powdered material was suspended in ethanol by sonication and several droplets were deposited onto a cooper grid covered by a carbon holey membrane. Acquisitions of the tilt series were performed using a high tilt sample holder from the GATAN Company, the images tilt series were acquired with angles ranging from +70 to -70 degree, with projections taken every 2° according to Saxton schema. The acquisition of the 98 TEM tilt series images was achieved with cooled CCD detector (2048 x 2048 pixels with a

pixel size of 0.4 nm). The images were first roughly aligned using a cross-correlation algorithm, a refinement of this initial alignment and a precise determination of the tilt axis direction were then obtained using the IMOD software where the centers of several palladium nanoparticles from the analyzed group were used as fiducial markers⁸³. The volume reconstructions have been computed using an iterative approach consisting of a simultaneous algebraic reconstruction technique implemented using the TOMO3D software⁸⁴, the number of iterations not exceeding 20. Visualization and quantitative analysis of the final volumes were carried out using ImageJ software.

N₂ physisorption at 77 K was done on the ASAP 2420 of Micromeritics. The specific surface area, the pore volumes and the pore size distribution were calculated with the software provided with the apparatus considering the DFT method with slit-like pore geometry.

General procedure for the determination of the palladium content of Pd@MC Xi

Concentrated H₂SO₄ (3 mL) was added to a sample of Pd@MC Xi (i=1 to 3) (ca. 1 mg, precisely weighted). The mixture was brought to reflux in a fume hood. After cooling to 100 °C, fuming HNO₃ (2 mL) was then added and the heating resumed until disappearance of nitric fumes, complete evaporation of HNO₃ and beginning of the reflux of the remaining H₂SO₄. After cooling to 100 °C, fuming HNO₃ (2 mL) was then added, the mixture was heated until evaporation of HNO₃ and of most of the H₂SO₄. Concentrated HNO₃ (3 mL) and concentrated HCl (3 mL) were successively added and the mixture heated until evaporation of the acids. The residue was then dissolved in H₂O (25 mL) and the amount of palladium present in this mixture was determined by complexation following a procedure described in the literature. Two independent experiments were performed and the average value retained⁸⁵.

Suzuki reactions

Pd@MC **X1** (1.8 mg, 0.03 mequiv. of supported palladium) was added to a solution of aryl bromide (1 mmol, 1 equiv), areneboronic acid (1.1 mmol, 1.1 equiv), Na₂CO₃ (1.2 mmol, 127.2 mg, 1.2 equiv) in propane-1,2-diol (2 mL) containing 5% of H₂O (0.1 mL). The reaction mixture was heated at 140 °C for 4 h. After cooling to 20 °C, **X1** was filtered on a polytetrafluoroethylene Whatman membrane (0.2 μ m) and the Pd@MC catalyst was washed with AcOEt (3x15 mL). The combined organic phase was then washed with H₂O (25 mL), dried with MgSO₄, filtered and concentrated under vacuum. 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 (400 MHz instrument in CDCl₃) in accordance with the literature.

Determination of the palladium leached in the reaction medium during the Suzuki reaction

After Suzuki reaction, the Pd@MC **X1** was filtered off and washed with AcOEt (3x15 mL). The combined organic phase was evaporated under vacuum. Concentrated H₂SO₄ (5 mL) was added to the residue and heated to 100 °C in a fume hood.

Fuming HNO₃ (5 mL) was then slowly added and the heating resumed until disappearance of the nitric fumes, complete evaporation of HNO₃ and beginning of the reflux of the remaining H₂SO₄. After cooling to 100 °C, fuming HNO₃ (5 mL) was then slowly added, the mixture was heated until evaporation of HNO₃ and this process was repeated twice, the heating of the sample in acids during, as a whole, 15–20 min. Most of the H₂SO₄ was then boiled off, concentrated HNO₃ (3 mL) and concentrated HCl (3 mL) were successively added and the mixture heated until evaporation of the acids. The residue was then dissolved in H₂O (25 mL) and the amount of palladium present in this mixture was determined by complexation following a procedure described in the literature. Two independent experiments were performed and the average value retained.

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C Results and discussion

Preparation of Pd@MC Xi (i=1, 2 or 3) catalysts

Thanks to the one-pot soft-templating process, a mesoporous carbon embedding palladium nanoparticles (NP) within its mesostructure was obtained directly from a mixture of tannin (the carbon precursor), an amphiphilic triblock copolymer named Pluronic F127 ((PEO)₁₀₆(PPO)₇₀(PEO)₁₀₆) being the pore structuring agent and a palladium salt. The procedure is detailed in the experimental section. The mechanism, based on the EISA or TISA process, is yet not fully understood. The wattle condensed tannins used are generally composed of two up to eleven monomeric flavonoid units and are therefore low molecular weight biopolymers ranging typically from 500 to 3500 g/mol. These polyphenolic compounds could develop an attractive interaction with the hydrophilic part of the amphiphilic triblock copolymer F127 (PEO groups) either *via* H bonds or by a coulombic interaction mediated *via* Cl⁻ anions (S⁺ClO⁺ interaction where S⁺ is a protonated PEO surfactant group and O⁺ is a protonated phenolic group)⁸⁶. As shown schematically in Fig. 1, when the dissolved mixture of tannin, F127 and palladium salt is dried and heated to 130 °C (EISA and TISA process), composites micelles are formed and self-assemble together to yield a (disordered) mesophase. Thanks to the complexing properties of tannin, a good dispersion of Pd²⁺ through the mesophase is expected. During its carbonization, tannin is converted to carbon, Pluronic F127 is pyrolyzed creating thus the mesoporosity and Pd²⁺ is reduced to Pd⁰.

This one-pot process does not require a subsequent impregnation of Pd²⁺ into the carbon matrix and reduction of Pd²⁺ in hydrogen gas, or a chemical etching for the hard-template removal as performed usually for palladium catalysts. The resulting materials displayed a peculiar mesostructure and interesting properties that were evidenced by different techniques.

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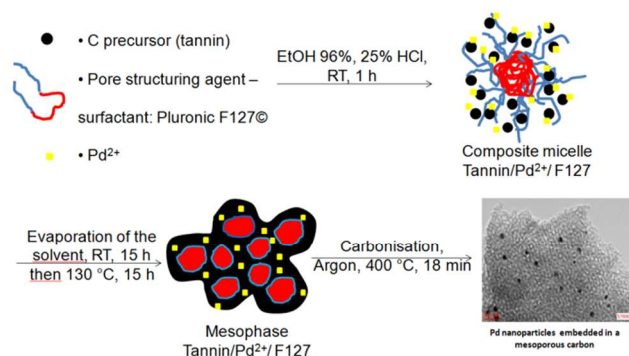


Fig. 1 Schematic representation of the one-pot evaporation or thermally induced self-assembly process for the preparation of palladium nanoparticles embedded in a worm-like mesoporous carbon Pd@MC materials.

Characterizations of Pd@MC catalysts

First, the formation of metallic palladium was confirmed by XRD (see Fig. 2). The reduction of Pd²⁺ could be due either to the reducing properties of tannin as shown with tannin extracted from green tea and Au salt⁸⁷ and/or by carbothermal reduction during the carbonization step. The absence of interstitial carbon in palladium (PdC_x phase) that may significantly deactivate the catalyst⁸⁸ was checked by the determination of the f.c.c palladium cell parameter (0.390 ± 0.01 nm) that was very close to the one of pure palladium phase (0.389 nm –ICDD n° 00-046-1043). The excellent catalytic performance of these materials confirmed the absence of such PdC_x phase on palladium NPs' surface. The broad peak around 22° corresponds to the poorly graphitized carbon matrix due to its low temperature of carbonization (400 °C).

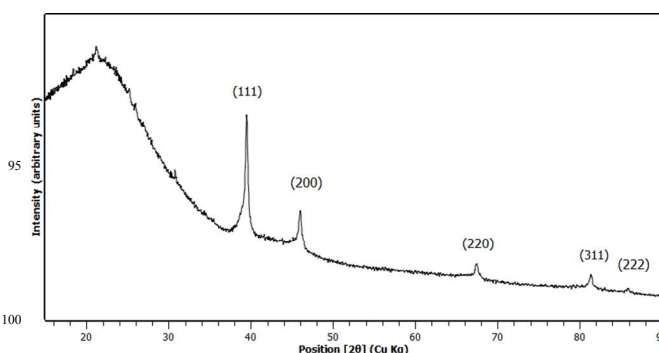


Fig. 2 XRD diffraction pattern of Pd@MC X2 (0.8 wt% palladium) obtained after carbonization of the tannin/Pd²⁺/surfactant mesophase at 400 °C in Ar atmosphere. The indexed peaks correspond to metallic f.c.c. palladium phase (ICDD 00-046-1043).

The nanoparticulate nature of palladium was proved by TEM where particles of size ranging from 7 to 70 nm and averaging around 25 nm were observed (Fig. 3). The worm-like or locally ordered carbon mesoporosity was also clearly evidenced (compared Fig. 3a and 3b).

To eliminate all doubts concerning the location of the Pd NPs within the carbon mesostructure, a tomographic TEM analysis was conducted for several representative fragments of Pd@MC

sample X3. Herein we present the results concerning a fragment with a worm-like structure displayed in Figure 4a in classical TEM mode. The size of Pd particles within the studied zone range from 7 to 25 nm and size of the carbon support pores is around 12 nm. The analyses of the reconstructed volume show that the particles observed on the 0° tilt image (Fig 4a) are located at different thicknesses on the fragment volume (Fig 4b to 4d). Furthermore, these analyses highlight also that the palladium particles are surrounded by a large porosity around them with a 30 nm and 25 nm pore diameter whereas the other pores of the support had a diameter around 12 nm in the area without palladium particles. This feature is confirmed by another tomographic TEM analysis reported in the supporting information part. This peculiar nanostructuration could explain the very good retention of the palladium NPs in the carbon support during the use of this catalyst in Suzuki reactions (*vide infra*). Indeed, palladium NPs are bigger than the mesopores; they have a diameter of ca. 25 nm according to TEM for large observed domains compared to around 10 nm for the mesopores. They are therefore trapped in the large voids of the matrix and cannot be lost in the solvent through the mesoporous network. This release could only happen when NPs are located in the mesopores and have similar or smaller size than the mesopores as is usually encountered by conventional infiltration

of NPs or salt during a post-synthesis treatment of a porous support. This highlights the interest of the one pot soft-templating process for catalytic applications. Beside this interesting aspect, the original nanostructuration observed here has also the advantage of maintaining a high accessibility of palladium NPs to the reagents thanks to the presence of the mesopores network around the voids surrounding palladium NPs. Moreover, these large voids allow a complete access of reagents to the palladium surface with a resulting high efficiency for catalytic reaction (see below).

At the difference of our previous work²⁰ where more ordered mesoporous carbon were obtained, here the mesostructure appears not so well organized even if an hexagonal arrangement of mesopores was observed locally (Fig. 3b). This difference of nanostructuration could be attributed to the slight different characteristics of tannin's batches used between the two studies but also to the variability of the materials' properties obtained for similar synthesis (see N₂ adsorption/desorption isotherms in the supplementary information part). Nevertheless, the ordering of the porosity is not a compulsory requirement for the applications in catalysis.

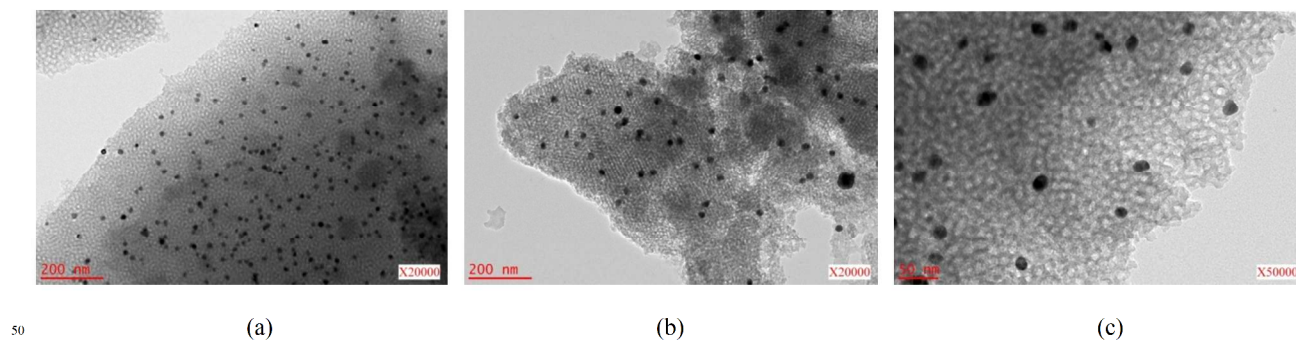


Fig. 3 TEM micrographs of Pd@MC X3 samples showing the palladium nanoparticles and the carbon mesoporosity within zones having (a) a worm-like structure or (b) an ordered structure; (c) the average particles size is around 25 nm (c).

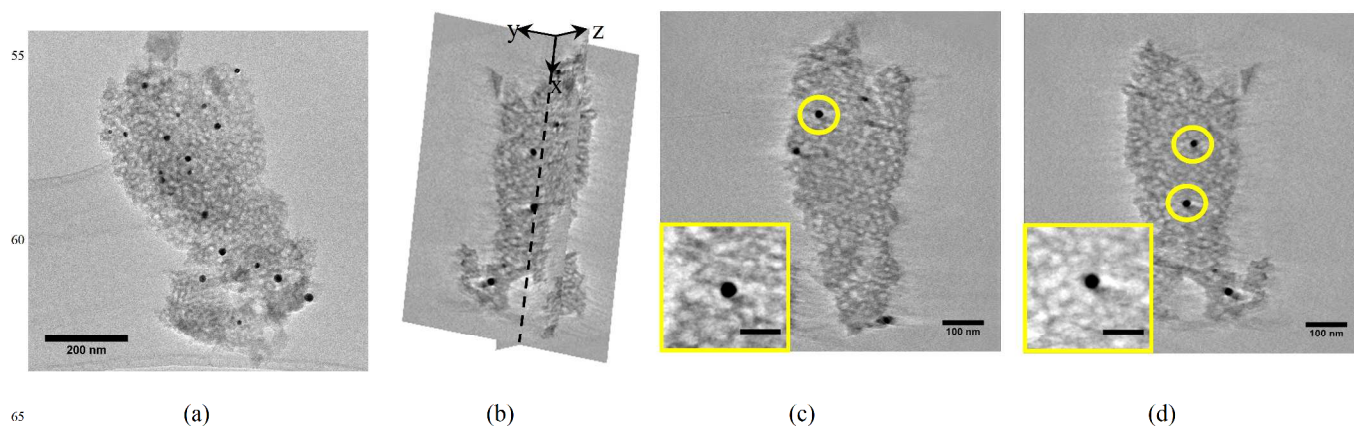


Fig. 4. 3D analysis by electron tomography of Pd@MC fragment with a worm-like structure: a) TEM image at 0° tilt from the tilt series; b) to d) representative slices extracted from the reconstruction volume. The intersection of two slices highlights the location of Pd NPs within the large porosity generated around B). For a better illustration of this behavior, some of the nanoparticles that are present in the chosen slices are encircled and showed in the insets in figures c) and d), the scale for the insets is 50 nm.

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The isotherms of the three studied Pd@MC samples displayed similar features that are close to those of mesoporous carbons prepared without Pd²⁺ (see supporting information). No clear structural evolution of the mesostructured Pd@MC Xi samples could be related to Pd²⁺ content, therefore only one of them is presented and discussed here (see Fig. 5a). Isotherms are composed of type I and IV components characteristic of the presence of micropores (uptake for low pressure $P/P^0 < 0.1$) and mesopores (uptake at higher pressure and presence of a hysteresis) respectively. The former porosity is related to the carbonization process and is located in the carbon walls whereas the second arises from the surfactant pyrolysis during the heat-treatment of the F127/tannin mesophase.²⁰ Their different contributions to the textural properties were determined by the DFT method. The pore size distribution (PSD) calculated by this method is in agreement with the shape of the isotherms (Fig. 5b). Micropores, with a size below 2 nm are evidenced. The minima around 1 nm does not seem to have an experimental validity and could be rather attributed to an artifact due to the calculation.⁸⁹ The mesopores are rather broadly distributed with a maximum around 10 nm. This data is in agreement with TEM tomography where pore sizes around 12 nm were measured. The calculated micro- and mesopore volumes are around 0.10 and 0.35 cm³/g respectively and the surface area is around 330 m²/g.

Applications of Pd@MC X1 and X2 for Suzuki reactions

The reaction conditions were optimized by using 4-bromoacetophenone and benzenboronic acid as model substrates in the presence of Na₂CO₃. Firstly, the Suzuki coupling was performed in the presence of a MC (prepared according to ref.²⁰) that contained no palladium nanoparticles. No reaction was observed and 4-bromoacetophenone was recovered unchanged. Then, the activities of Pd@MC X1 or X2 containing respectively 0.2% and 0.8% of supported palladium were determined (Table 1).

The initial experiments were performed in the presence of 0.5 mequiv of supported palladium using Pd@MC X2. Performing the Suzuki cross-coupling in toluene, MeCN or DMSO was unsuccessful (entries 1-3). The desired biaryl was obtained in moderate yields using DMAC or DMF (entries 4-5). Then, we focused our attention on the use of green solvents. Using EtOH or H₂O as solvent afforded **1a** respectively in low 22% and 9% yields (entries 6-7). Gratifyingly, much improved results were obtained by performing the reaction in propane-1,2-diol since **1a** was obtained in 94% yield at 100 °C in the presence of 0.5 mequiv. of supported palladium (entry 8) and even in 95% yield by using only 0.03 mequiv. of supported palladium and heating the reaction mixture at 140 °C (entries 9-10). In conditions of Table 1, entry 10 we replaced Na₂CO₃ by other bases (Li₂CO₃, K₂CO₃, Cs₂CO₃, NaOAc.3H₂O and NaOH) and comparable

yields were obtained. Slightly improved results were obtained by using **X1** instead of **X2** and **1a** was obtained in almost quantitative yield in the presence of only 0.03 mequiv. of supported palladium (entry 11). It is important to note that the amount of supported palladium required here is extremely low compared to the amount traditionally used both in homogeneous or heterogeneous catalysis for Suzuki couplings.^{37,90} For practical reasons, we decided to use Pd@MC **X1** to pursue our study. Then, we determined the amount of palladium lost in the crude mixture at the end of the reaction (according to table 1, entry 11 but using 50 times the amount of reagents). For this purpose, after reaction, the catalyst was filtered off and the crude mixture mineralized (for further details see the Experimental Section). It turned out that ca. 5% of the initial amount of supported palladium are present in the crude mixture. This amount represents only 1.5 μequiv of the obtained biaryl, showing that almost palladium-free products can be obtained.

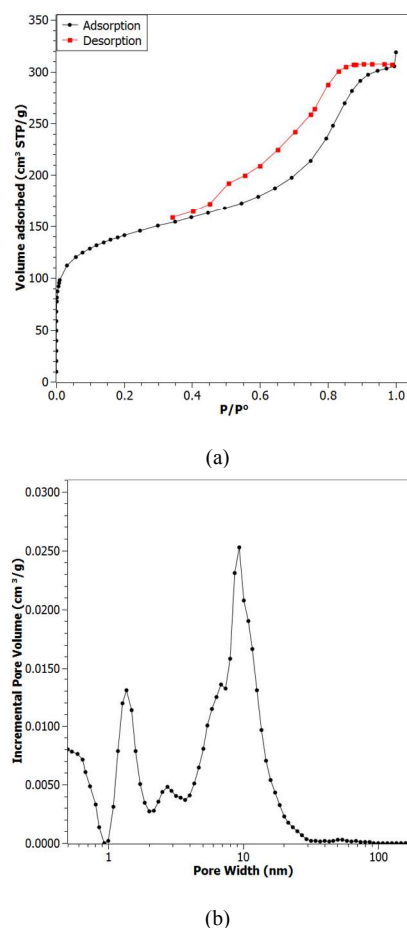
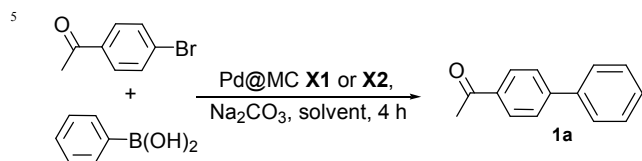


Fig. 5 (a) N₂ adsorption/desorption isotherms of sample Pd@MC X3 measured at 77K; (b) and corresponding pore size distribution determined by the DFT method considering a slit-like pore geometry.

Table 1 Optimization of the reaction conditions. Reactions performed using 4-bromoacetophenone (1 mmol, 1 equiv.), benzenboronic acid (1.2 mmol, 1.2 equiv.), Na₂CO₃ (1.2 mmol, 1.2 equiv.) and Pd@MC catalyst **X1** or **X2** in the indicated solvent (2 mL).



Entry	Pd@MC (mequiv.)	Solvent	Temperature (°C)	Yield (%) ^a
1	X2 (0.5 mequiv.)	Toluene ^b	100	Traces
2	X2 (0.5 mequiv.)	MeCN ^b	Reflux	No reaction
3	X2 (0.5 mequiv.)	DMSO ^b	100	No reaction
4	X2 (0.5 mequiv.)	DMAC ^b	100	35
5	X2 (0.5 mequiv.)	DMF ^b	100	46
6	X2 (0.5 mequiv.)	EtOH 96%	Reflux	22
7	X2 (0.5 mequiv.)	H ₂ O	Reflux	9
8	X2 (0.5 mequiv.)	Propane-1,2-diol ^b	100	94
9	X2 (0.03 mequiv.)	Propane-1,2-diol ^b	100	Traces
10	X2 (0.03 mequiv.)	Propane-1,2-diol ^b	140	95
11	X1 (0.03 mequiv.)	Propane-1,2-diol ^b	140	99 (98) ^c
12	X1 (0.01 mequiv.)	Propane-1,2-diol ^b	140	8

^a Calculated yields by ¹H-NMR of the crude reaction mixture. ^b Reactions performed in the presence of 5% of H₂O. ^c Isolated yield after flash-chromatography of the crude reaction mixture on silica gel.

The initial experiments were performed in the presence of 0.5 mequiv of supported palladium using Pd@MC **X2**. Performing the Suzuki cross-coupling in toluene, MeCN or DMSO was unsuccessful (entries 1-3). The desired biaryl was obtained in moderate yields using DMAC or DMF (entries 4-5). Then, we focused our attention on the use of green solvents. Using EtOH or H₂O as solvent afforded **1a** respectively in low 22% and 9% yields (entries 6-7). Gratifyingly, much improved results were obtained by performing the reaction in propane-1,2-diol since **1a** was obtained in 94% yield at 100 °C in the presence of 0.5 mequiv. of supported palladium (entry 8) and even in 95% yield by using only 0.03 mequiv. of supported palladium and heating the reaction mixture at 140 °C (entries 9-10). In conditions of Table 1, entry 10 we replaced Na₂CO₃ by other bases (Li₂CO₃, K₂CO₃, Cs₂CO₃, NaOAc.3H₂O and NaOH) and comparable yields were obtained. Slightly improved results were obtained by using **X1** instead of **X2** and **1a** was obtained in almost quantitative yield in the presence of only 0.03 mequiv. of supported palladium (entry 11). It is important to note that the amount of supported palladium required here is extremely low compared to the amount traditionally used both in homogeneous or heterogeneous catalysis for Suzuki couplings.^{37,90} For practical reasons, we decided to use Pd@MC **X1** to pursue our study. Then, we determined the amount of palladium lost in the crude mixture at the end of the reaction (according to table 1, entry 11 but using 50 times the amount of reagents). For this purpose, after reaction, the catalyst was filtered off and the crude mixture mineralized (for further details see the Experimental Section). It turned out that ca. 5% of the initial amount of supported palladium are present in the crude mixture. This amount represents only 1.5 μequiv of the obtained biaryl, showing that almost palladium-free products can be obtained.

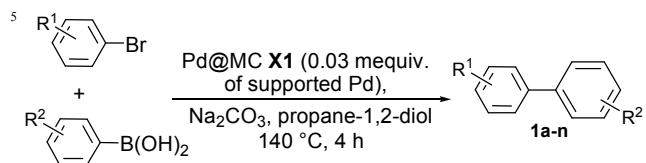
The homogeneous or heterogeneous nature of the catalysis was then determined.⁹¹ For this purpose, the catalyst **X1** was filtered off after 1 h 30 of reaction under the conditions of Table 1, entry 11. The yield at that point was 86 %. After heating the filtrate for another 2 h 30 at 140 °C no further increase in the yield was observed. Therefore we concluded that soluble palladium entities play no role in this coupling. In our previous experiences of Suzuki couplings the soluble palladium entities play no role in catalysis since the reaction stopped after filtration of the heterogeneous catalyst.⁴⁹⁻⁵¹ In contrary dissolution-redeposition of palladium entities during Heck reactions are frequently observed.^{49,91} An intermediate situation was found during Sonogashira reactions where palladium entities play a moderate role.⁴⁹

The Suzuki couplings of benzenboronic acid with arylbromides bearing various electron-attracting or electron-donating groups afforded the desired biaryls in yields ranging from 70% to 99% (entries 1-6). Noteworthy, no biaryl was obtained by reacting benzenboronic acid with 4-bromobenzonitrile or 1-bromo-4-chlorobenzene. Replacing 4-bromoacetophenone by 4-chloroacetophenone was also unsuccessful even in the presence of 2 mequiv of supported palladium and the starting materials were recovered unchanged. Interestingly, the sterically more hindered 1-bromo-2-isopropylbenzene was also reacted successfully with benzenboronic acid in a good 70% yield (entry 6). The use of catalyst **X1** was also extended to Suzuki reactions of various areneboronic acids with 93%-97% yields (entries 7-9). Noteworthy, the coupling of 4-bromoacetophenone with the sterically hindered 2-methylbenzenboronic acid afforded the corresponding biaryl in 93% yield, but required the use of 0.3 mequiv. of supported palladium (entry 8). Finally, 2-bromonaphthalene was also successfully reacted with benzenboronic acid in 91% yield (in conditions of Table 2).

Next we determined the possibility to reuse Pd@MC **X1**. For practical reasons we chose the coupling between 4-bromoacetophenone and 2-methylbenzenboronic acid that requires 0.3 mequiv. of supported palladium (Table 3). After reaction **X1** was recovered from the reaction mixture by filtration, washed, dried and reused in another coupling. It turned out that **X1** can be used more than five times with no significant yield decrease.

Next the activity of catalyst **X1** was compared to that of commercially available Pd/C for the Suzuki coupling of 4-bromoacetophenone and benzenboronic acid (conditions of Table 1, entry 11). We found that Pd/C afforded also quantitatively the biaryl. Finally we determined the TON and TOF of catalyst **X1** for the Suzuki reaction between 4-bromoacetophenone and benzenboronic acid (according to conditions of Table 1, entry 11). These values were compared with other reported catalysts (Table 4). We concluded that catalyst **X1** presents higher TON and TOF than most of these catalysts.

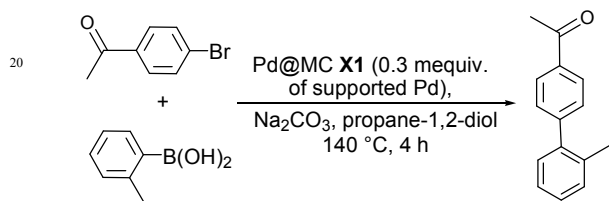
Table 2 Syntheses of biaryls. Reactions performed using aryl iodide (1 mmol, 1 equiv.), areneboronic acid (1.2 mmol, 1.2 equiv.), Na₂CO₃ (1.2 mmol, 1.2 equiv.) and Pd@MC catalyst **X1** (0.03 mequiv. of supported palladium) in propane-1,2-diol (2 mL) containing 5% of H₂O.



Entry	R ¹	R ²	Yield (%) ^a
1	4-Ac	H	98 (1a)
2	4-OMe	H	96 (1b)
3	4-Me	H	95 (1c)
4	3-Me	H	98 (1d)
5	2-Me	H	99 (1e)
6	2-iPr	H	70 (1f)
7	4-Ac	4-Me	97 (1g)
8	4-Ac	2-Me	< 10 (93) ^b (1h)
9	4-Ac	4-OMe	93 (1i)

^a Isolated yields after flash-chromatography of the crude reaction mixture on silica gel. ^b Reactions performed in the presence of 0.3 mequiv. of supported palladium.

Table 3 Reuse of catalyst Pd@MC **X1**. Reactions performed using 4-bromoacetophenone (1 mmol, 1 equiv.), 2-methylbenzeneboronic acid (1.2 mmol, 1.2 equiv.), Na₂CO₃ (1.2 mmol, 1.2 equiv.) and Pd@MC catalyst **X1** (0.3 mequiv. of supported palladium) in propane-1,2-diol (2 mL) containing 5% of H₂O.



Run	1	2	3	4	5
Yield ^a	98	97	95	98	98

^a Isolated yields after flash-chromatography of the crude reaction mixture on silica gel.

Table 4 Comparison TONs and TOFs of Suzuki reactions catalyzed by various palladium catalysts.

Entry	Catalyst	Temperature (°C)	TON	TOF (h ⁻¹)
1	X1	140	33000	8250
2 ^[92]	HAP-Pd(0)	100	139	23
3 ^[92]	Pd/IL	120	970	970
4 ^[92]	Pd-salt	90	4250	1062
5 ^[92]	Pd-G3-p3	80	85000	2125
6 ^[93]	PI Pd	110	9480	132
7 ^[94]	Pd ²⁺ sepiolite	100	4150	819

^a The couplings have been performed in the presence of various catalysts and solvents at different temperatures (the comparison is limited to representative Pd catalysts used for Suzuki couplings of 4-bromoacetophenone and benzeneboronic acid).

D Conclusions

Numerous heterogeneous palladium catalysts supported on organic or inorganic supports bearing various ligands have been described in the literature. They are traditionally prepared in several steps that can be tedious in some cases. Among known heterogeneous ligand-free catalysts, palladium-containing mesoporous carbons have raised many interests. However, they are generally prepared in several steps and require the use of hazardous and toxic chemicals. Herein, we have reported an efficient and easy direct preparation of mesoporous carbons containing palladium nanoparticles using a biosourced carbon precursor under environmental-friendly conditions. Noteworthy, we have shown that versatile Suzuki couplings could be performed efficiently in a green solvent using only 30 μequiv of supported palladium (Pd@MC **X1**). The determination of the TON and TOF showed that catalyst **X1** presents an excellent activity compared to other heterogeneous catalysts. Moreover, the peculiar mesostructure of the material with palladium nanoparticles embedded in large irregular voids connected to the worm-like mesoporous network could limit the leaching of palladium nanoparticles. Indeed, extremely low palladium amounts (< 1.5 μequiv of product) were found in the reaction mixture after Suzuki coupling. Therefore, almost palladium-free products can easily be obtained avoiding therefore tedious and time-consuming purification steps. The green chemistry principles are therefore respected for the preparation of the catalyst and for its application to the synthesis of biaryls. Other studies are underway in our group to modify chemically the tannin precursor to extend the use of Pd@MC to other C-C (Mizoroki-Heck or Sonogashira couplings) or C-N bond forming reactions.

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[†] Electronic Supplementary Information (ESI) available: NMR spectra of the Suzuki reaction products. See DOI: 10.1039/b000000x/

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Tannin-based mesoporous carbons embedding palladium nanoparticles synthesized by a one pot soft-template route present excellent catalytic activity for Suzuki reactions.

