Carbon-supported statistically distributed polyethyleneimine/palladium (II) complexes as efficient and sustainable Sonogashira catalysts

Antonio Peñas-Sanjuán [a], James A. Anderson [b], Rafael López-Garzón [a], Manuel Pérez-Mendoza [c], Manuel Melguizo [a],[*]

[a] Departamento de Química Inorgánica y Orgánica, Facultad de Ciencias Experimentales, Universidad de Jaén, 23071 Jaén, Spain
[b] Surface Chemistry and Catalysis Group, Dept of Chemistry, University of Aberdeen, AB24 3UE, UK
[c] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

ARTICLE INFO

ABSTRACT

A novel approach toward the obtaining of a Pd (II) carbon-supported catalyst based on a statistical distributed polymer (hyperbranched polyethyleneimine) and its use as a highly efficient and sustainable catalyst for Sonogashira-type coupling reactions is presented. The heterogenous Pd (II)/HBPEI catalyst fabricated through a facile, cost-effective and scalable procedure provides an innovative catalyst structure based on statistical distributed singular catalytic centers with well-defined Pd-Polymer chemical interactions, highly resistant to suffer leaching processes and extensively and homogenously distributed across the whole carbon surface. The catalyst exhibited excellent catalytic and recycling activity for several cross-coupling reactions between different aryl halides and terminal alkynes, free of any undesired by-product and in excellent yields, under air atmosphere, using water as solvent, at moderate temperatures (65 °C) and avoiding the use of phosphine derivatives, Cu(I) as co-catalyst and excess of any of the reactant. Therefore, the reported Pd(II)-HBPEI carbon-supported material can be considered a truly competitive heterogeneous Pd(II) catalyst for large-scale under green chemistry conditions.

1. Introduction

Currently the transition-metal-catalyzed cross-coupling reactions can be considered an essential and important tool in organic synthesis, as was recognized by the 2010 Nobel Prize in Chemistry [1,2]. Among them, the palladium-catalyzed sp^2-sp coupling reaction between aryl or alkenyl halides and acetylenes, known as the Sonogashira coupling [3], is of particular interest due to being one of the most extended and straightforward methods for the preparation of aryl alkynes and conjugated enynes, which have numerous applications in natural product synthesis and material science [4–7].

In the last few years, great efforts have been made toward improving the activity, stability and sustainability of the catalysts in order to overcome the drawbacks related to the catalyst manufacturing and the required cross-coupling reaction conditions, such as: (a) costly catalyst manufacturing processes, (b) poor chemical stability of catalyst under working and recycling conditions, (c) use of high catalyst loading, co-catalysts (usually copper iodide, $ZnCl_2$, $FeCl_3$ or additional strong bases) and excess of reagents in order to reach high yielding conversions

and (d) use of non-sustainable reactions conditions due to need inert atmospheres, prolonged reaction times and organic solvents (typically toluene, THF, DMF or NMP) [8–11]. Consequently, in the last decades several researches have achieved considerable progresses concerning the catalyst activity and stability [12–14] through the development of complex structures based on MOFs [15,16], functionalized halloysites [13,17], magnetic nanoparticles [18] or carbon nitrides [19], as well as, catalyst sustainability by developing heterogeneous catalysts based on polymer-supported phosphines, polymer-supported oxime-based ligands, polymer-supported pyridine ligands, grafted mesoporous silica and carbon-based materials, which have showed activity in pure water [20–23]. However, the low performance of aforementioned catalysts, suffering a progressive drop of yields due to Pd leaching phenomena under reaction working conditions, as well as, the costly catalyst manufacturing process, have limited their practical implementation at industrial scale. Therefore, exploring innovative heterogeneous catalyst with reduced leaching, high stability and long-term recycling, obtained through cost-efficient, facile and scalable procedures, remains challenging [24–31].
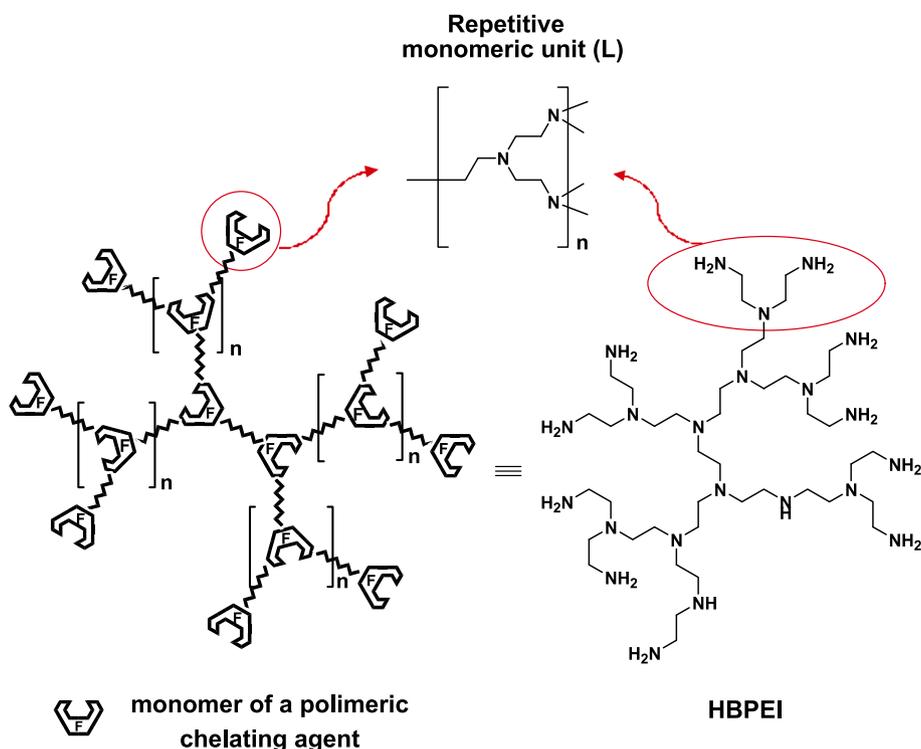
Fig. 1. Polychelatogen structure of hyperbranched polyethyleneimines based on repetitive units (functional unit = L) of triethylenetriamine [-NH(CH$_2$)$_2$] [−(CH$_2$)$_2$NH$_2$] N [−(CH$_2$)$_2$-].

Bearing in mind such challenges, we report the outstanding catalytic properties of a novel and sustainable heterogeneous carbon-supported palladium catalyst (F-HBPEI-Pd) prepared by the complexing of Pd (II) with a defined polychelatogen agent (Fig. 1) [32,33]. The true innovation of the F-HBPEI-Pd catalyst lies in its singular catalytic active centers, based on Pd (II) ions complexed by a statistic-polyaminic polymer (hyperbranched polyethyleneimine, HBPEI), which provides Pd catalytic centers with well-defined Pd-polymer chemical interactions, highly resistant to suffer leaching processes, highly accessible as catalytic centers in aqueous media and extensively and homogenously distributed across the whole carbon surface [32,33]. In this regard, it is worth mentioning that although numerous examples of Pd-based heterogeneous catalysts have been previously reported for Sonogashira coupling reactions, most of them are based on Pd(0) particles or Pd(II) metal ions complexed by molecules with well-defined structures and stoichiometries [34–39], which usually require complex, costly and time-consuming synthetic strategies, while our approach considers HBPEIs complexing units, as singular catalytic centers defined by molecules with a statistical distribution, both in the molecule weights and branches. This innovative approach, in practice, simplifies the development of new catalysts based on polymeric structures with well-known stoichiometries, but random structures, which can be obtained by well-known direct and easily scalable manufacturing processes [32,33,40].

Therefore, the present study provides a breakthrough toward designing efficient heterogeneous catalyst based on a statistic distribution of Pd(II)-complexes formed with statistically well-defined complexing agents. The study revealed that F-HBPEI-Pd is an excellent heterogeneous catalyst for Sonogashira-type coupling reactions under mild, green and cost-effective conditions. Thereby, the reported catalyst proves that the efficiency of a heterogeneous catalyst based on Pd(II)-complexes does not depend on developing complexing units with well-defined structure, as long as the stoichiometry is well-known and the Pd-complexing interactions are strong enough to avoid metal leaching phenomena.

2. Experimental

2.1. General remarks

The reagents were obtained from commercial sources and were used without further purifications. Water was deionized with a Millipore system.

All experiments were analyzed using a Gas Chromatograph (Agilent 6890N) equipped with a mass spectrometric detector (Agilent 5973N Mass Selective Detector) using a Zebron 2B-5MS capillary column (30 m; 250 μm; 0.25 μm). The GS temperature was programmed as follows: Initial temperature 45 °C; Hold time 2 min; Ramp: 2 °C/min until 50 °C where it was held 1 min, then 10 °C/min until 250 °C where it was held for 10 min. Carrier gas He. The MS was operated in electron ionization (EI) mode with the ion source temperature of 230 °C. The standard curves for analytes were prepared by setting the linear dependence between the chromatographic peak area for the given substance and the amount of the substance in the sample introduced into the control-measurement device. Every point was an average from three independent determinations from every standard solution in order to obtain the calibration curves.

The ^{1}H and ^{13}C NMR spectra were measured with an Avance 400 Bruker spectrometer. The mass spectra were recorded with a TOF Micro-Mass (LCT Premier de Waters) spectrometer equipped with a HPLC (Alliance 2795 de Waters). The leaching of palladium metal was analyzed using an ICP-Ms (Thermo Scientific LTQ-Orbitrap XL).

XPS spectra were acquired on a PHI VersaProbe II, using a monochromatic X-ray source of 1486.6 eV (Al anode) at 47.3 W, with a beam diameter of 200 μm. All XPS spectra were referenced to the C 1s binding energy of 284.8 eV. The spectra were treated with CasaXPS software (version 2.3.23PR1.0, Casa Software Ltd., 2020) for background removal (using Shirley-type integral) and deconvolution with symmetric Lorentzian functions. The survey spectra allowed obtaining the chemical surface composition (at.%) of the samples. The deconvolutions of the high-resolution spectra allowed analyzing the chemical environments of
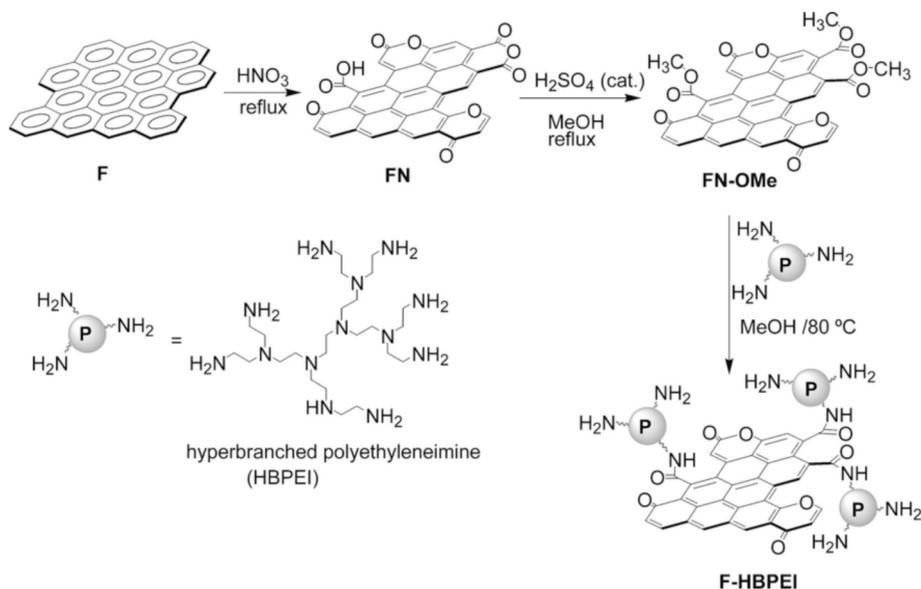
Fig. 2. Preparation of the hybrid material F-HBPEI in three steps from a commercial activated carbon, F.

the surface atoms.

Thermogravimetric analysis (TGA) were carried out in a SHIMADZU mod. TGA-50H under nitrogen atmosphere with a flow of 50 mL/min, in a temperature range of 25 °C and 950 °C with a step of 10 °C/min.

SEM micrographas, EDX mappings and microanalyses were obtained using a CLARA FESEM by TESCAN.

2.1.1. Synthesis of palladium-supported catalyst (F-HBPEI-Pd)

A commercial AC (Filtracarb-SKI 8 × 30, from CPL Carbon Link) was demineralized by successive treatments with concentrated HCl and HF solutions until the ash content was <0.25%. The starting material so obtained, F, was sieved to a particle size in the 1–0.6 mm range. Then, F (1 g) was treated by refluxing with 10 M aqueous HNO$_3$ (50 mL) for 4 h and extensively washed in a soxhlet extractor. The washing was considered complete when, after suspending F in distilled water for 24 h, the conductivity of the suspension was the same as that of the distilled water. Filtration rendered the intermediate oxidized carbon FN. Esterification of FN (1 g) was performed by treatment with a solution of H$_2$SO$_4$ in MeOH (50 mL, 2% v/v) at reflux for 24 h followed by washing with MeOH in a soxhlet extractor for further 24 h, time that ensured complete sulfate washing according to a negative response to qualitative barite test. This produced the FN–OMe material. Finally, a mixture of a HBPEI (M$_n$=600 g/mol, 0.33 g) and the FN–OMe material (1 g) was stirred in MeOH (10 mL) for 12 h at 80 °C in a closed reactor. Subsequently, the sample was washed with MeOH in a soxhlet extractor for 24 h, rendering F-HBPEI [33]. Finally, adsorption of Pd(II) on F-HBPEI (1 g) was conducted at 298 K, using K$_2$PdCl$_4$ in aqueous solutions (1 L, 3 × 10^{-3} M K$_2$PdCl$_4$) at pH 5 and 0.1 M in KCl, obtaining F-HBPEI-Pd as catalyst with 1.72 mmol of Pd(II) per gram of carbon [32].

2.1.2. General procedure for the Sonogashira cross-coupling reaction

A round-bottomed flask was charged with the carbon-supported palladium catalyst (1 mol% of Pd), aryl halide (0.4 mmol), acetylene (0.4 mmol), triethylamine (0.8 mmol) and water (3 mL). The reaction mixture was stirred at 65 °C for 24 h under ambient atmosphere. The reaction mixture was then cooled to room temperature. Subsequently, the catalyst in suspension was collected by filtration and washed with CHCl$_3$ (3 × 10 mL). The combined organic phases were dried (over Na$_2$SO$_4$) and concentrated under vacuum to afford the final product.

2.1.3. Recycling tests

The catalyst collected by filtration and washed with CHCl$_3$ (3 × 10 mL) is dried under vacuum for 24 h at room temperature in order to remove water and solvent residues. Afterwards, the catalyst is used as recycled catalyst in the subsequent Sonogashira reaction.

3. Results and discussion

3.1. Synthesis of F-HBPEI-Pd

The novel palladium-supported catalyst is based on a rigid, non-swelling, chemically inert, porous carbon support, F, and a flexible, water compatible, stable, organic complexant (hyperbranched poly-ethyleneimine, HBPEI) grafted through a three-stepped procedure: i) oxidation, ii) esterification and iii) grafting of the polychelatogen HBPEI to the carbon surface, giving the polychelatogen material, F-HBPEI (Fig. 2).

In the first stage, the F surface was modified by chemical activation using HNO$_3$ to generate carboxylic groups on its surface, since they will be necessary to obtain the carboxamide bonds by reaction with the polyethyleneimine. The oxidation of F results in a significant increase in the oxygen content of sample FN (28.07%) compared to this of the parent carbon F (8.83%). The functional group analysis by temperature-programmed desorption (TPD) and potentiometric titration procedures indicated the generation of a significant amount of carboxylic acids (1.25 mmol/g), anhydrides (1.11 mmol/g) and lactones (0.74 mmol/g) [33]. Then, carboxylic groups were converted into methyl ester by re-action with MeOH and catalytic amounts of H$_2$SO$_4$ (Stage II in Fig. 2). After esterification, the originally unreactive carboxylic acids become suitable to be transformed into amides by reaction with the primary and secondary amino groups of the HBPEI (Stage III in Fig. 2). Thus, the reaction of FN-OMe with HBPEI (M$_n$ = 600) rendered F-HBPEI with an amount of nitrogen around 9%, so that, considering that HBPEI mole-cules with M$_n$ = 600 has an average content of 14 nitrogen atoms, F-HBPEI has an estimated content of HBPEI of 27.5% by weight [33].

Subsequently, F-HBPEI was loaded with Pd(II) by complexation of Pd(II) metal ions in aqueous solution (298 K, [Cl$_4$Pd]$^{2-}$ aqueous solutions at pH 5 and 0.1 M KCl), resulting in the palladium-supported catalyst, F-HBPEI-Pd, with a Pd(II) loading capacity of 1.72 mmol Pd(II) per gram [32].

3.2. Definition of F-HBPEI-Pd catalytic centers

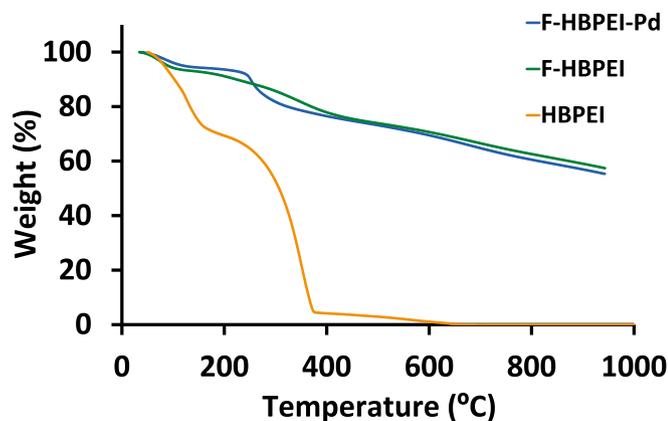The catalytic center interpretation was defined through the

Fig. 3. TGA analysis of HBPEI, F-HBPEI and F-HBPEI-Pd.

complexing properties of HBPEI molecules (integrated in F-HBPEI) toward Pd(II) metal ions. Thus, HBPEI molecules were considered as a composition of repetitive units (functional unit = L) of triethylenetriamine, $[-NH(CH_2)_2]$ $[-(CH_2)_2NH_2]$ N $[-(CH_2)_2-]$ (Fig. 1), which are capable of acting as independent complexing centers with identical behavior [32,40,41]. The analysis of potentiometric titration data obtained for mixtures of Pd(II)/HBPEI and Pd(II)/F-HBPEI systems in water solutions (with 0.1 M KCl as ion strength) indicated the formation of very stable complex species of 1:1 stoichiometry between Pd(II) and the triethylenetriamine subunits, L. Thus, values for the logarithm of the stability constants (logK$_{st}$) of 31.8 and 28.5 were calculated for $[PdL]^{2+}$ and $[Pd_2L_2H]^{5+}$ species, respectively, which are the major species formed in the pH range between 1.0 and 9.0 [32]. On the basis of this data, the analysis of the catalytic activity of F-HBPEI-Pd can be interpreted as a collection of single catalytic centers based on units of triethyleneimine (L) and Pd(II). It is worth noting the relevance of such interpretation, because it allows F-HBPEI-Pd to be considered as a catalyst formed by a statistic polymer loaded with Pd(II), which is structured as a distribution of single complexed-Pd(II) catalytic centers.

3.3. Characterization of catalyst F-HBPEI-Pd

TGA analysis of HBPEI, F-HBPEI, F-HBPEI-Pd revealed a weight loss from room temperature to 200 °C caused by the moisture/bound water present in the materials. Besides, between 200 and 400 °C a weight loss of 13.3% was observed for F-HBPEI, attributed to HBPEI degradation,

and of 16.25% for F-HBPEI-Pd, attributed to the HBPEI and complexes Pd(II)-Chloride degradation, see Fig. 3.

Besides, the surface morphology of F-HBPEI and F-HBPEI-Pd were characterized by scanning electron microscope (SEM), as shown in Fig. 4. The SEM structure of F-HBPEI-Pd showed the presence of palladium nanoparticles (average size 100 nm) on the HBPEI-carbon grafted surface (F-HBPEI). However, the energy dispersive spectroscopy (EDS) image of F-HBPEI-Pd, shown in Fig. 5, clearly revealed the presence of palladium elements uniformly distributed across the whole catalyst surface.

In addition, XPS measurements were performed to determine the catalyst composition and the oxidation state of its Pd loading. Fig. 6 and Table 1 gather the XPS survey spectra (from 0 to 1400 eV binding energy) and quantitative analysis of a sample of F-HBPEI-Pd compared to those of the Pd-free support (F-HBPEI) and that of a catalyst sample after being reused successively four times as catalyst in Sohogashira reactions (F-HBPEI-Pd/AS). Regarding the components of the XPS spectra, for the supporting hybrid material (F-HBPEI), the C 1s region can be deconvoluted into three different components at 284.7, 285.9 and 288.3 eV accounting for 45.0, 43.6 and 11.4%, respectively. That at the lower value of BE is attributed to zerovalent carbon atoms integrated in the solid carbon support. While the significant component at 285.9 eV is mostly produced by the N-bonded saturated carbons provided by the HBPEI units grafted onto the carbon surface. Finally, the smallest component at 288.3 eV is ascribed to caboxamide and carboxylic carbon atoms [42,43]. The same pattern is maintained for C 1s signals in the XPS spectra of palladium-loaded samples, F-HBPEI-Pd, and F-HBPEI-Pd/AS (Fig. 7 and Table 1). The N 1s region in F-HBPEI shows an asymmetric signal that can be deconvoluted into a main component (93.8% of total N) at 399.2 eV originated by the N-amine atoms in the HBPEI units. A second minor component (6.2%) is attributed to the N atoms taking part in caboxamide groups [33]. Complexation of Pd(II) by the HBPEI units, to give F-HBPEI-Pd, results in a general shift of the N 1s photoemission toward a higher value to produce a signal with a single component at 400.7 eV. For the catalytic material (F-HBPEI-Pd), the Pd 3d region is composed of two sets of spin-orbit coupling doublets separated Δ = 5.2–5.3 eV, corresponding to d$_{5/2}$ and d$_{3/2}$ orbitals (Fig. 7). The two sets of doublets have different intensity, so that, the most intense (60.3% of total Pd, made of the signals located at BE values of 338.4 and 343.6 eV for Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$, respectively), is attributable to Pd(II) amino complexes with chloride as counteranions [44,45]. The less intense doublet (39.7% of total Pd) is made of the contributions at BE values of 335.8 and 341.1 eV corresponds to Pd^0 in
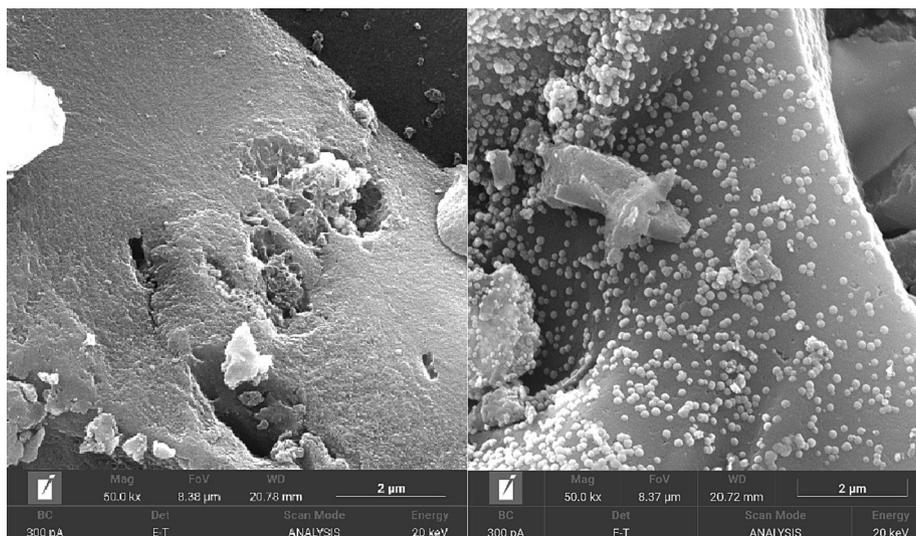

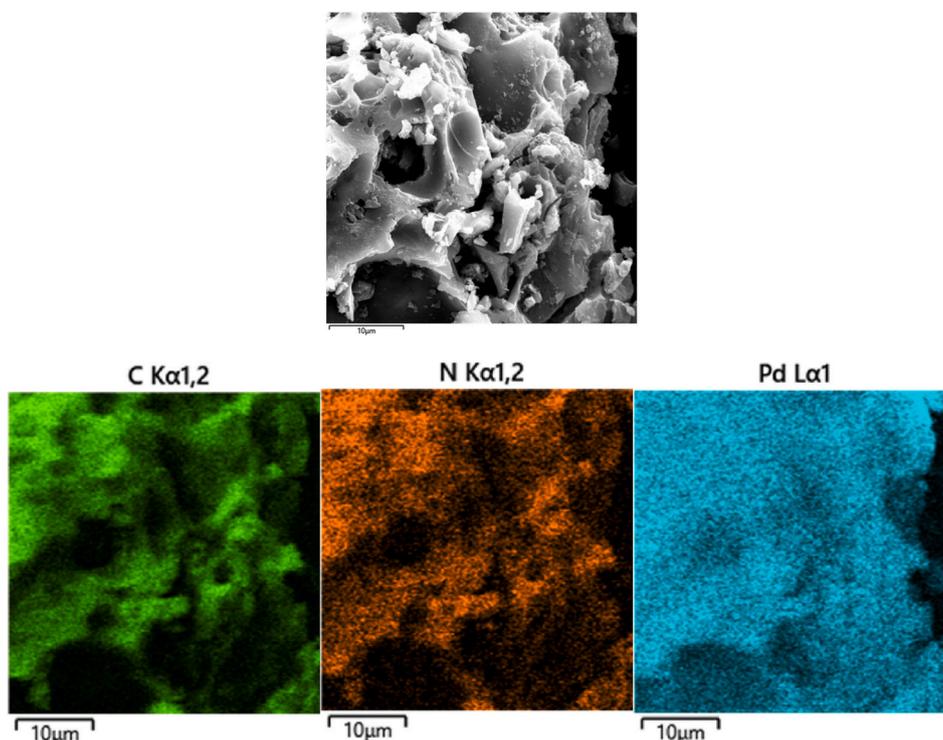**Fig. 4.** SEM images: a) F-HBPEI and b) F-HBPEI-Pd.

Fig. 5. Elemental mappings images of F-HBPEI-Pd (before Sonogashira cross-coupling reaction).
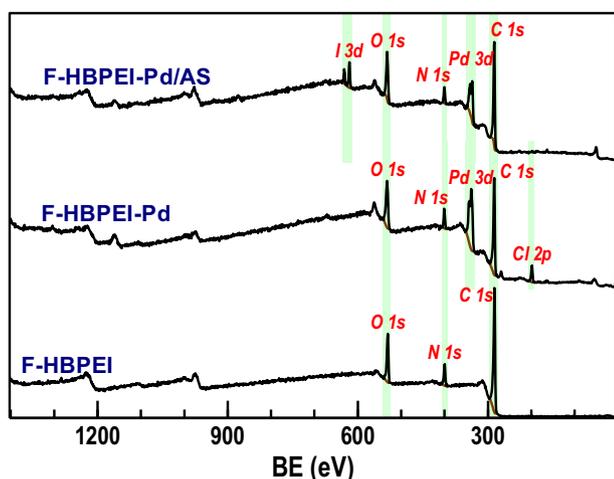

Fig. 6. Qualitative comparison of XPS survey specgra of F-HBPEI, F-HBPEI-Pd and F-HBPEI-Pd/AS. Quantitative data in Table 1.

contact with carbon surface [46,47], likely formed after spontaneous reduction of $PdCl_2$ by reductive action of the carbon support [48].

3.4. Catalytic activity of F-HBPEI-Pd in Sonogashira reaction

In order to explore the catalytic activity of F-HBPEI-Pd, the Sonogashira cross-coupling reaction between iodobenzene (**1a**) and phenylacetylene (**2a**) was selected as a model reaction (Fig. 8). The influence of solvent, amount of catalyst, temperature, time, base and ratio between reagents were analyzed (Table 2).

Under the optimized conditions (water as solvent, 1 mol% of Pd, 16 h at 65 °C, Et_3N as base, and an 1:1:2 ratio between iodobenzene:phenylacetylene:Et_3N), the F-HBPEI-Pd catalyst rendered yields >99% (calculated by GC–MS), which are among the highest values reported for supported heterogeneous catalysts. Interestingly, from such conditions,

Table 1
Binding energy (eV, calibrated to C 1s = 284.8) of XPS signals and percent abundance of elements and synthetic components for samples: a) F-HBPEI; b) F-HBPEI-Pd; c) F-HBPEI-Pd/AS.

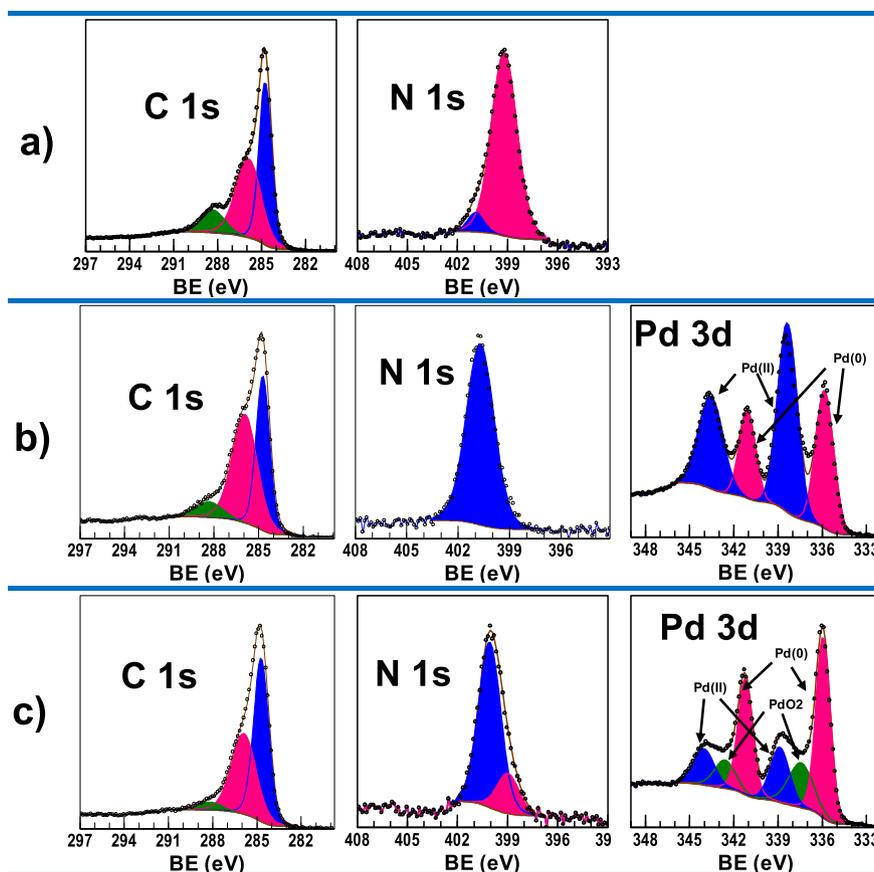|		BE of signals/components and abundance / eV (%)				
		C	N	O	Pd	Other
		[C 1s]	[N 1s]	[O 1s]	[Pd 3d] 3d$_{5/2}$ / 3d$_{3/2}$	[Orbital]
a)	Survey	284.8 (82.1)	399.2 (7.1)	531.2 (10.8)	–	–
	Comps.	284.7 (45.0)	399.2 (93.8)	531.1 (71.0)	- / -	–
		285.9 (43.6)	400.9 (6.2)	533.0 (29.0)		
		288.3 (11.4)				
b)	Survey	284.8 (69.1)	400.7 (6.2)	532.0 (15.1)	338.4 (5.2)	198.4 (4.4) [Cl 2p]
	Comps.	284.7 (39.9)	400.7 (100.0)	531.3 (34.1)	335.8 (25.2) / 341.1(14.5)	
		285.9 (52.1)		532.9 (40.1)	338.4 (37.5) / 343.6 (22.8)	
		288.3 (8.0)		534.9 (25.8)		
c)	Survey	284.8 (75.3)	400.0 (5.7)	532.0 (14.7)	336.0 (3.5)	619.2 (0.8) [I 3d]
	Comps.	284.7 (53.1)	399.0 (19.7)	531.4 (50.1)	335.9 (33.1) / 341.2 (21.9)	
		285.9 (42.9)	400.1 (80.3)	533.0 (40.0)	337.4 (14.1) / 342.6 (7.6)	
		288.2 (4.0)		534.9 (9.9)	338.9 (13.5) / 344.0 (9.7)	

Fig. 7. Selected high-resolution XPS spectral regions with deconvolution in synthetic components for: a) F-HBPEI; b) F-HBPEI-Pd; c) F-HBPEI-Pd/AS. Quantitative data in Table 1.
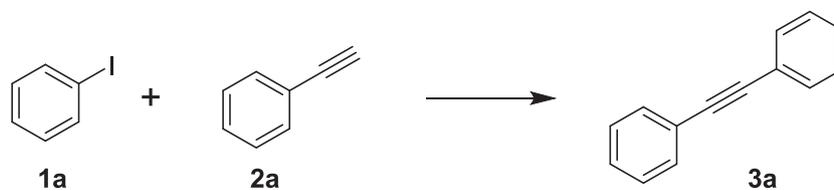

Fig. 8. Model Sonogashira coupling reaction used to optimize experimental conditions according to Table 2.

it is noted that the reaction system is not dependent on the use of excess of reagents, but is clearly dependent on the amount of catalyst and base (entry 7–10, Table 2).

In order to further investigate these interrelationships, several experiments were performed. Firstly, an exhaustive analysis of the material balance on the reaction system was performed by modifying the amount of catalyst (see Table 3). Such experiments showed that at catalyst ratios >5%, the amount of phenylacetylene lost increased (affecting to the reaction yield), which could be attributed to the capacity of the aromatic molecules to be adsorbed onto the surface of activated carbons via pi-pi interactions, so that [49], once they are adsorbed, they cannot react to give the cross-coupling products.

Regarding the base-dependence, two main phenomena were observed: i) an organic base is required to render high reaction yields, and ii) an excess of base is required to obtain high yielding cross-coupling conversions. Both effects were attributed to a mechanism where the base is not exclusively taking part in the reaction mechanism neutralizing protons, from the cross-coupling reaction, but also the base acts as "surfactant agent" that enhance the interaction between the reactants and the catalyst. Indeed, the relevance of hydrophobic effects in

transition-metal-catalyzed processes has been previously reported, noting that such effect often plays a beneficial role when reactions, involving water-insoluble substrates, are performed in water [50,51]. Thus, taking into account the water-media reaction and the hydrophobic nature of both, the carbon-support and reactants, the presence of an amine, with a partial surfactant behavior [52], improves the reactants/catalyst interaction, and consequently, increases the reaction yield (entry 9 and entries 14–17, Table 2).

In the light of the aforementioned results, several cross-coupling reactions were performed using different aryl halides and alkynes under the previously optimized conditions (Fig. 9 and Table 4).

The expected cross-coupling products for different aryl iodides were obtained, not only in excellent yields, but also free of any undesired by-products (Table 4, entry 1, and entries 12–16). Nevertheless, concerning the cross-coupling reaction using aryl chlorides and bromides (Table 4, entry 4–11), the conversion was moderate for bromobenzene (69% at 85 °C) and very low for chlorobenzene (3% at 85 °C), which is in accordance with their lower reactivities. In this respect, additional tests were carried out in order to reach higher chloro- and bromo- coupling reactions, by the addition of CuI as co-catalyst, however, Glaser homo-

Table 2

Sonogashira cross-coupling between iodobenzene y phenylacetylene under different reaction conditions.

Entry	Reagents [a]	Catalyst (%)	Solvent	Base	Temp. (°C)	Time (h)	Yield (%)[b]
1	1:2:3	5	H_2O	Et_3N	65	24	90
2	1:1:3	5	H_2O	Et_3N	65	24	89
3	1:1:2	5	H_2O	Et_3N	65	24	89
4	1:1:1	5	H_2O	Et_3N	65	24	67
5	1:1:0	5	H_2O	Et_3N	65	24	0
6	1:2:2	10	H_2O	Et_3N	65	24	93
7	1:1:2	10	H_2O	Et_3N	65	24	81
8	1:1:2	3	H_2O	Et_3N	65	24	98
9	1:1:2	1	H_2O	Et_3N	65	24	99
10	1:1:2	0.5	H_2O	Et_3N	65	24	90
11	1:1:1.5	1	H_2O	Et_3N	65	24	71
12	1:1:1	1	H_2O	Et_3N	65	24	61
13	1:1:0	1	H_2O	Et_3N	65	24	0
14	1:1:2	1	H_2O	Piperidine	65	24	90
15	1:1:2	1	H_2O	Pyrrolidine	65	24	80
16	1:1:2	1	H_2O	K_2CO_3	65	24	5
17	1:1:2	1	H_2O	Na_2CO_3	65	24	9
18	1:1:2	1	Ethanol	Et_3N	65	24	6
19	1:1:2	1	THF	Et_3N	65	24	4
20	1:1:2	1	Toluene	Et_3N	65	24	0.6
21	1:1:2	1	H_2O	Et_3N	55	24	98
22	1:1:2	1	H_2O	Et_3N	40	24	83
23	1:1:2	1	H_2O	Et_3N	20	24	32
24	1:1:2	1	H_2O	Et_3N	65	16	98
25	1:1:2	1	H_2O	Et_3N	65	6	95
26	1:1:2	1	H_2O	Et_3N	65	3	68

[a] Molar ratio. Iodobenzene: phenylacetylene: base.
[b] Calculated by GS-MS.

Table 3

Reaction material balance as a function of amount of catalyst employed.

Entry	Catalyst (% mol Pd)	Iodobenzene lost (%)[c]	Phenylacetylene lost (%)[c]	Yield (%)[c]
1[a]	10	6.31	45.13	93
2[b]	10	5.62	18.61	81
3[b]	5	0.12	10.64	89
4[b]	3	1.59	1.59	98
5[b]	1	0.21	0.21	99
6[b]	0.5	0.17	0.17	90

[a] Iodobenzene (0.4 mmol), phenylacetylene (0.8 mmol) and triethylamine (0.8 mmol), H_2O (3 mL) at 65 °C stirring for 24 h.
[b] Iodobenzene (0.4 mmol), phenylacetylene (0.4 mmol) and triethylamine (0.8 mmol), H_2O (3 mL) at 65 °C stirring for 24 h.
[c] Yield determinate by GSMS.

coupling products were obtained instead of Sonogashira cross-coupling products, increasing such effect at higher temperatures, even for iodobenzene [53].

3.5. Recycling tests of F-HBPEI-Pd

Sequential recycling experiments were performed in order to evaluate the catalyst lifespan. F-HBPEI-Pd showed no deactivation after four recycling tests (Table 5). Thus, although the achievement of high yields in a few runs cannot be taken as complete evidence of high recycling potential, high consistent yields, in repeated runs, is an indication of the robust nature of the catalyst, which is a necessary requirement for long-term application. Furthermore, no evidence for leaching of Pd into the reaction medium was detected by ICP-MS, which gives an essential added value to the F-HBPEI-Pd toward real applications.

In addition, for better understanding of the catalyst structure and

1	a	b	c	d	e	f
X	I	Br	Cl	I	I	I
A	CH	CH	CH	CH	N	CH
R^1	H	H	H	CH_3O	H	I

2	a	b	c
R^2	Ph		

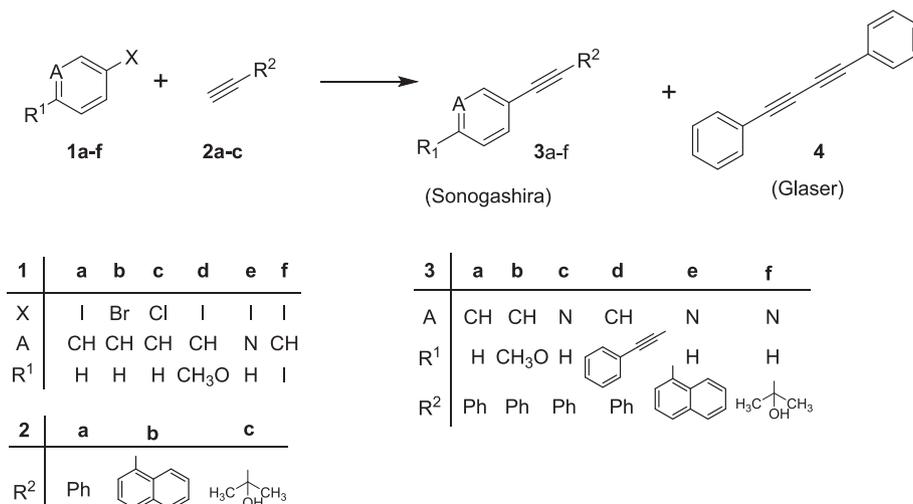| 3	a	b	c	d	e	f
A	CH	CH	N	CH	N	N
R^1	H	CH_3O	H		H	H
R^2	Ph	Ph	Ph	Ph		

Fig. 9. Coupling products of alkyl halides and acetylenes catalyzed by F-HBPEI-Pd (conditions and outcome in Table 4).

Table 4
Cross coupling reactions employing a range of aryl halides and acetylenes.

Entry[a]	Aryl halide[b]	Acetylene[c]	Product[d]	Co-Cat.	T (°C)	Sonogashira (%)[e]	Glaser (%)[e]
1	**1a**	**2a**	**3a**	–	55	99	0
2	**1a**	**2a**	**3a/4**	CuI	55	5	29
3	**1a**	**2a**	**3a/4**	CuI	85	11	37
4	**1b**	**2a**	**3a**	–	55	21	0
5	**1b**	**2a**	**3a**	–	85	69	0
6	**1b**	**2a**	**3a/4**	CuI	55	1.2	21
7	**1b**	**2a**	**4**	CuI	85	0	89
8	**1c**	**2a**	**3a**	–	55	3.1	0
9	**1c**	**2a**	**3a**	–	85	3.4	0
10	**1c**	**2a**	**3a/4**	CuI	55	0.6	22
11	**1c**	**2a**	**4**	CuI	85	0	90
12	**1d**	**2a**	**3b**	–	55	75	0
13	**1e**	**2a**	**3c**	–	55	94	0
14	**1f**	**2a**	**3d**	–	55	96	0
15	**1e**	**2b**	**3e**	–	55	97	0
16	**1e**	**2c**	**3f**	–	55	90	0

[a] Aryl halide (0.4 mmol), acetylene (0.4 mmol), triethylamine (0.8 mmol), F-HBPEI-Pd (1% mol Pd), CuI (1% mol, in case), H_2O (3 mL) at 65 °C stirring for 24 h
[b] **1a**: Iodobenzene; **1b**: Bromobenzene; **1c**: Chlorobenzene; **1d**: 4-Iodoanisole; **1e**: 3-Iodopyridine; **1f**: 1,4-diiodobenzene.
[c] **2a**: Phenylacetylene; **2b**: 1-ethynil-naphtalene; **2c**: 2-methyl-3-butyn-2-ol.
[d] **3a**: diphenylacetylene; **3b**: 1-methoxy-4-(phenylethynyl)benzene; **3c**: 3-(phenylethynyl)pyridine; **3d**: 1,4-bis(phenylethynyl)benzene; **3e**: 3-(naphthalen-1-yle-thynyl)pyridine; **3f**: 2-methyl-4-(pyridin-3-yl)but-3-yn-2-ol; **4**: 1,4-diphenylbutadiyne
[e] Yield determinate by GSMS

Table 5
Recycling experiments.

Recycling test[a]	Yield (%)[b]
1	98.2
2	97.7
3	94.8
4	98.6

[a] Iodobenzene (0.4 mmol), phenylacetylene (0.4 mmol), triethylamine (0.8 mmol), F-HBPEI-Pd (1% mol Pd), H_2O (3 mL) at 65 °C stirring for 24 h.
[b] Yield determinate by GSMS.

composition after performing the Sonogashira cross-coupling reaction, recycled F-HBPEI-Pd catalyst was characterized by SEM and XPS analysis. SEM images and EDX mapping showed a wide presence of palladium elements, which confirm the stability of F-HBPEI-Pd catalyst after reaction (Fig. 10 and Fig. 11). However, XPS measurements revealed a significant change on the nature of the Pd (II) immobilized in F-HBPEI-Pd catalyst, after Sonogashira cross coupling reaction (sample F-HBPEI-Pd/AS). Concerning the elemental composition, some loss of Pd, whose presence in the catalyst drops to 3.5% from the original 5.2%, and a substitution of chlorine by iodide are observed. This replacement is a consequence of the use of aryl iodides as reactants in the catalyzed Sonogashira couplings. Additionally, a change the Pd 3d spectral region (FIG. 7) is also evident. Thus, three pairs of doublets are now observed, with that produced by the Pd(II) amino complexes (at 338.9 and 344.0 eV for Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively) being in minority (23.2%), while that of Pd^0 (at 335.9 and 341 eV, accounting for 55.0%) is the main component. A third doublet, made of signal at BE values of 337.5 and 345.25 eV, also appears in between the other two. It represents a 21.7% of the total Pd 3d signal and is assigned [54] to PdO_2 likely formed under the aerobic and basic conditions employed in the successive reactions and isolation steps.

3.6. Comparison with other reported catalysts

Finally, to better illustrate the merits of the F-HBPEI-Pd catalyst, Sonogashira model reaction of phenyl iodide and phenylacetylene was selected to compare the F-HBPEI-Pd activity with other previous reported catalysts. The comparative results presented in Table 6 demonstrate that the present catalyst shows benefits over other PEI-based Pd
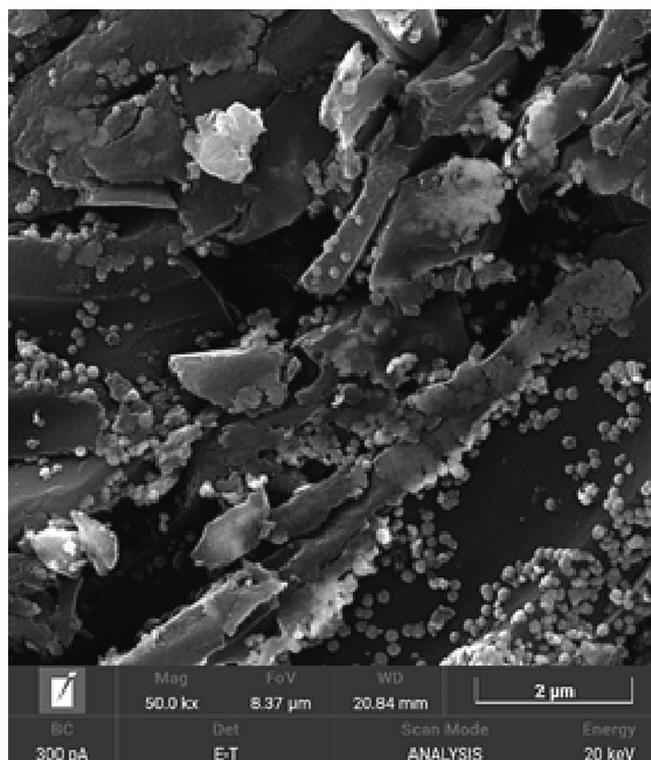
Fig. 10. SEM image of F-HBPEI-Pd-Sonogashira catalyst.

catalysts, in terms of low catalyst loading, mild reaction conditions, short reaction time and excellent yield. Besides, F-HBPEI-Pd, as palladium-supported catalyst has outstanding properties attributed to its preparation and chemical structure, such as: a) easy and cheap preparation; b) chemical stability over a wide range of conditions; c) high mechanical stability; d) water-solvent compatibility; e) well-defined and process-compatible swelling behavior; f) good filterability and g) easy recycling [32].
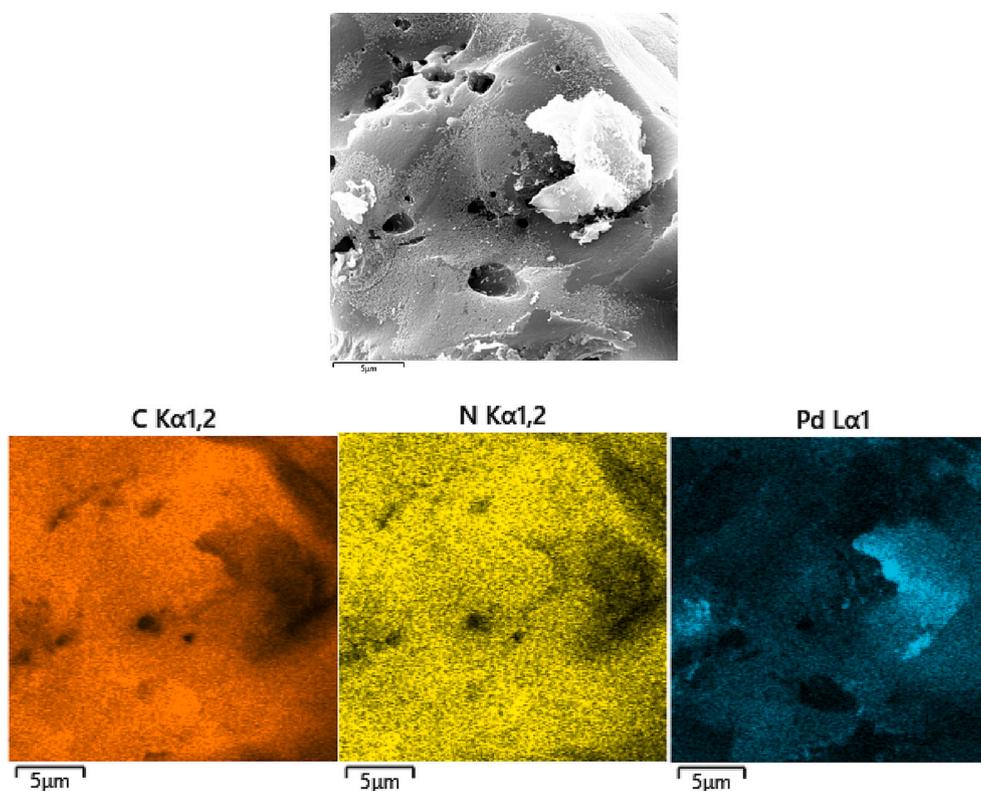
Fig. 11. Elemental mappings images of F-HBPEI-Pd (after Sonogashira cross-coupling reaction).

Table 6

Comparison status of the catalytic behavior of F-HBPEI-Pd.

Entry	Catalyst	Solvent	Base	Temp. (°C)	Time (h)	Atmosphere	Yield (%)	Ref.
1	Pd/NH_2-SiO_2	EG	K_2CO_3	120	1	N_2	98	[55]
2	PEI-(PdCl$_2$/psf)	EtOH	K_2CO_3	80	6	ambient atmosphere	91	[56]
3	Pd/Cu@MCC-PAMAMG2.5-PEI	DMSO	K_2CO_3	80	4	N_2	96	[57]
4	Fe_3O_4/SiO_2/P(GMA-co-EGDMA)–PEI–Pd(0)	DMF	K_2CO_3	120	5	ambient atmosphere	85	[58]
5	PEI-PdNPs	EtOH	K_2CO_3	50	6	N_2	61	[59]
6	AC-PEI-Pd	H_2O	Et$_3$N	65	6	ambient atmosphere	95	Present work

Psf = 2,2′,7,7′-tetra(4-pyridyl)-9, 9′-spirobifluorene; EG = Ethylene glycol; PAMAM = Polyamidoamine; MCC = microcrystalline cellulose; P(GMA-co-EGDMA) = copolymer of ethylene glycol dimethacrylate and glycidyl methacrylate; AC = activated carbon.

4. Conclusions

In summary, a novel and sustainable hybrid material, based on Pd(II) metal ions complexed by HBPEI molecules, covalently grafted onto an activated carbon, has showed excellent properties as a heterogeneous catalyst in Sonogashira cross-coupling reactions. The statistic-polyaminic polymer nature of F-HBPEI-Pd catalyst, provided Pd catalytic centers with well-defined Pd-Polymer chemical interactions, highly resistant to suffer leaching processes, highly accessible as catalytic centers in aqueous media and extensively and homogenously distributed across the whole carbon surface, which evidenced an excellent catalytic activity and high recycling. Besides, the corresponding products of cross-coupling reactions, between aryl iodides and terminal alkynes, were obtained free of any undesired by-product and in excellent yields, under air atmosphere, using water as solvent, at moderate temperatures (65 °C), and avoiding the use of phosphine derivatives, Cu(I) as co-catalyst and excess of any of the reactant, so that, F-HBPEI-Pd can be considered a truly competitive heterogeneous Pd(II) catalyst for large-scale under green chemistry conditions.

CRediT authorship contribution statement

Antonio Peñas-Sanjuán: Conceptualization, Investigation, Formal analysis, Writing - original draft. **James A. Anderson:** Methodology, Investigation, Formal analysis. **Rafael López-Garzón:** Methodology, Investigation, Formal analysis. **Manuel Pérez-Mendoza:** Investigation, Writing - original draft. **Manuel Melguizo:** Conceptualization, Validation, Writing – review & editing.

Declaration of Competing Interest

Rafael Lopez-Garzon reports financial support was provided by Spanish Scientific Research Council. Manuel Melguizo has patent PROCESS FOR OBTAINING CARBON-BASED HYBRID MATERIALS issued to Universidad de Jaen.

Data availability

Data will be made available on request.

Acknowledgments

Appendix A. Structural characterization

Diphenylacetylene (3a).

1H RMN (400 MHz, CDCl$_3$); δ ppm 7.18–7.25 (m, 6H) 7.45–7.51 (m, 4H).

13C RMN (100 MHz, CDCl$_3$); δ ppm 89.47, 123.40, 128.26, 128.35, 134.62.

HRMS (EI): m/z calcd for C$_{14}$H$_{10}$: 178.2292; found: 178.2290.

1-methoxy-4-(phenylethynyl)benzene (3b).

1H RMN (400 MHz, CDCl$_3$); δ ppm 3.84 (s, 3H) 6.83–6.96 (m, 2H) 7.29–7.40 (m, 3H) 7.44–7.62 (m, 4H) [60].

13C RMN (100 MHz, CDCl3); δ ppm 55.26, 88.05, 89.36, 113.98, 115.37, 123.59, 127.90, 128.28, 131.42, 133.03, 159.61 [60].

HRMS (EI): m/z calcd for C$_{15}$H$_{12}$O: 208.0888; found: 208.0881.

3-(phenylethynyl)pyridine (3c).

1H RMN (400 MHz, CDCl$_3$); δ ppm 7.28–7.32 (m, 1H) 7.33–7.42 (m, 3H) 7.47–7.63 (m, 2H) 7.81 (dt, $J = 7.91$, 1.94 Hz, 1H) 8.55 (dd, $J = 4.96$, 1.65 Hz, 1H) 8.78 (dd, $J = 2.07$, 0.62 Hz, 1H) [61].

13C RMN (100 MHz, CDCl$_3$); δ ppm 85.90, 92.60, 120.43, 122.50, 122.96, 128.40, 128.76, 131.65, 138.36, 148.52, 152.23 [61].

HRMS (EI): m/z calcd for C$_{13}$H$_9$N: 179.0735; found: 179.0733.

1,4-bis(phenylethynyl)benzene (3d).

1H RMN (400 MHz, CDCl$_3$); 6.95–7.82 (m, 14H) [62].

13C RMN (100 MHz, CDCl$_3$); δ ppm 89.10, 91.23, 123.04, 123.10, 128.38, 128.45, 131.52, 131.62 [62].

HRMS (EI): m/z calcd for C$_{22}$H$_{14}$: 278.1096; found: 278.1091.

3-(naphthalen-1-ylethynyl)pyridine (3e).

1H RMN (400 MHz, CDCl$_3$); δ ppm 7.30 (ddd, $J = 7.86$, 4.86, 0.93 Hz, 1H) 7.46 (dd, $J = 8.27$, 7.24 Hz, 1H) 7.55 (dd, $J = 8.17$, 1.34 Hz, 1H) 7.60 (dd, $J = 8.27$, 1.45 Hz, 1H) 7.78 (dd, $J = 7.24$, 1.24 Hz, 1H) 7.82–7.94 (m, 3H) 8.35–8.45 (m, 1H) 8.57 (dd, $J = 4.86$, 1.76 Hz, 1H) 8.88 (dd, $J = 2.07$, 0.83 Hz, 1H) [63].

13C RMN (100 MHz, CDCl$_3$); δ ppm 90.76, 90.86, 120.12, 120.61, 123.10, 125.25, 125.99, 126.58, 127.01, 128.41, 129.36, 130.75, 133.14, 133.20, 138.44, 148.67, 152.27 [63].

HRMS (EI): m/z calcd for C$_{17}$H$_{11}$N: 229.0891; found: 229.0892.

2-methyl-4-(pyridin-3-yl)but-3-yn-2-ol (3f).

1H RMN (400 MHz, CDCl$_3$); δ ppm 1.63 (s, 6H) 7.26 (s, 1H) 7.70 (s, 1H) 8.49 (s, 1H) 8.74 (dd, $J = 2.07$, 0.83 Hz, 1H) [64].

13C RMN (100 MHz, CDCl$_3$); δ ppm 31.38, 65.09, 78.40, 98.24, 120.31, 123.15, 138.85, 148.14, 152.03 [64].

HRMS (EI): m/z calcd for C$_{10}$H$_{11}$NO: 161.0841; found: 161.0835.

1,4-diphenylbutadiyne (4).

1H RMN (400 MHz, CDCl$_3$); δ ppm 7.26–7.31 (m, 4H) 7–32-7.34 (m, 2H) 7.45–7.50 (m, 4H) [65].

13C RMN (100 MHz, CDCl$_3$); δ ppm 73.93, 81.70, 121.60, 128.42, 129.22, 132.44 [66].

HRMS (EI): m/z calcd for C$_{16}$H$_{10}$: 202.2506; found: 202.2503.

References

[1] A. Molnár, Chem. Rev. 111 (2011) 2251–2320, https://doi.org/10.1021/cr100355b.

[2] F. Mohajer, M.M. Heravi, V. Zadsirjana, N. Poormohammada, RSC Adv. 11 (2021) 6885–6925, https://doi.org/10.1039/D0RA10575A.

[3] K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 16 (1975) 4467–4470, https://doi.org/10.1016/S0040-4039(00)91094-3.

[4] I. Paterson, R.D.M. Davies, R. Marquez, Angew. Chem. Int. Ed. 40 (2001) 603–607, https://doi.org/10.1002/1521-3773(20010202)40:3<603::AID-ANIE603>3.0.CO;2-O.

[5] S. Tabassum, A.F. Zahoor, S. Ahmad, R. Noreen, S.G. Khan, H. Ahmad, Mol. Divers. 26 (2022) 647–689, https://doi.org/10.1007/s11030-021-10195-6.

[6] I. Kanwal, A. Mujahid, N. Rasool, K. Rizwan, A. Malik, G. Ahmad, S.A.A. Shah, U. Rashid, N.M. Nasir, Catalysts 10 (2020) 443, https://doi.org/10.3390/catal10040443.

[7] R.B. Prince, L. Brunsveld, E.W. Meijer, J.S. Moore, Angew. Chem. Int. Ed. 39 (2000) 228–230, https://doi.org/10.1002/(SICI)1521-3773(20000103)39:1<228::AID-ANIE228>3.0.CO;2-B.

[8] M.A. Andrade, Luisa M.D.R.S. Martins, Molecules 25 (2020) 5506, https://doi.org/10.3390/molecules25235506.

[9] R. Chinchilla, C. Nájera, Chem. Rev. 107 (2007) 874–922, https://doi.org/10.1021/cr050992x.

[10] I. Błaszczyk, A.M. Trzeciak, J.J. Ziółkowski, Catal. Lett. 133 (2009) 262–266, https://doi.org/10.1007/s10562-009-0181-y.

[11] T. Suzuka, Y. Okada, K. Ooshiro, Y. Uozumi, Tetrahedron 66 (2010) 1064–1069, https://doi.org/10.1016/j.tet.2009.11.011.

[12] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772–3789, https://doi.org/10.1002/1521-3773(20001103)39:21<3772::AID-ANIE3772>3.0.CO;2-5.

[13] S. Sadjadi, Appl. Organometal. Chem. 32 (2018), e4211, https://doi.org/10.1002/aoc.4211.

[14] S. Sadjadi, M.M. Heravi, M. Raja, Carbohydr. Polym. 185 (2018) 48–55, https://doi.org/10.1016/j.carbpol.2018.01.020.

[15] M. Najafi, H. Alinezhad, S. Ghasemi, E. Yeganeh-Salman, J. Organomet. Chem. 980-981 (2022), 122497, https://doi.org/10.1016/j.jorganchem.2022.122497.

[16] F. Khosravi, M. Gholinejad, J.M. Sansano, R. Luque, Mol. Catal. 522 (2022), 112199, https://doi.org/10.1016/j.mcat.2022.112199.

[17] M. Daraie, M.M. Heravi, Y. Rangra, Z. Besharati, Sci. Rep. 11 (2021) 6223, https://doi.org/10.1038/s41598-021-85821-2.

[18] M. Gholinejad, A. Neshat, F. Zareh, C. Nájera, M. Razeghi, A. Khoshnood, Appl. Catal. A Gen. 525 (2016) 31–40, https://doi.org/10.1016/j.apcata.2016.06.041.

[19] E. Kalay, Synth. Commun. 52 (2022) 1290–1305, https://doi.org/10.1080/00397911.2022.2084416.

[20] J. Soni, A. Sethiya, N. Sahiba, S. Agarwal, Appl. Organomet. Chem. 35 (2021), e6162, https://doi.org/10.1002/aoc.6162.

[21] M. Lamblin, L. Nassar-Hardy, J.C. Hierso, E. Fouquet, F.X. Felpin, Adv. Synth. Catal. 352 (2010) 33–79, https://doi.org/10.1002/adsc.200900765.

[22] M. Zhao, Y. Wu, J.P. Cao, Appl. Organometal. Chem. 34 (2020), e5539, https://doi.org/10.1002/aoc.5539.

[23] A. Rajmane, S. Jadhav, A. Kumbhar, J. Organomet. Chem. 957 (2022), 122147, https://doi.org/10.1016/j.jorganchem.2021.122147.

[24] C.A. McNamara, M.J. Dixon, M. Bradley, Chem. Rev. 102 (2002) 3275–3300, https://doi.org/10.1021/cr0103571.

[25] Z. Zhao, J. Wang, X. Zhang, T. Lin, J. Ren, W. Pang, Tetrahedron Lett. 100 (2022), 153849, https://doi.org/10.1016/j.tetlet.2022.153849.

[26] A. Dewan, M. Sarmah, P. Bharali, A.J. Thakur, P.K. Boruah, M.R. Das, U. Bora, ACS Sustain. Chem. Eng. 9 (2021) 954–966, https://doi.org/10.1021/acssuschemeng.0c08315.

[27] V. Polshettiwar, C. Len, A. Fihri, Coord. Chem. Rev. 253 (2009) 2599–2626, https://doi.org/10.1016/j.ccr.2009.06.001.

[28] Z. Xu, J. Xu, W. Zheng, Y. Li, Cellulose 29 (2022) 2159–2173, https://doi.org/10.1007/s10570-022-04459-z.

[29] X. Wang, L. Sun, M. Wang, G. Maestri, M. Malacria, X. Liu, Y. Wang, L. Wu, Eur. J. Org. Chem. (2022), e202200009, https://doi.org/10.1002/ejoc.202200009.

[30] M. Savastano, P. Arranz-Mascarós, M.P. Clares, R. Cuesta, M.L. Godino-Salido, L. Guijarro, M.D. Gutiérrez-Valero, M. Inclán, A. Bianchi, E. García-España, R. López-Garzón, Molecules 24 (2019) 2714, https://doi.org/10.3390/molecules24152714.

[31] G. Wang, P. Hao, Y. Chang, Q. Zhang, W. Liu, B. Duan, H. Zhana, S. Bia, Nanoscale 14 (2022) 2256–2265, https://doi.org/10.1039/D1NR07640J.

[32] A. Peñas-Sanjuán, R. López-Garzón, J. López-Garzón, M. Pérez-Mendoza, M. Melguizo, Carbon 50 (2012) 2350–2352, https://doi.org/10.1016/j.carbon.2012.01.022.

[33] A. Peñas-Sanjuán, R. López-Garzón, M. Domingo-García, F.J. López-Garzón, M. Melguizo, M. Pérez-Mendoza, Carbon 50 (2012) 3977–3986, https://doi.org/10.1016/j.carbon.2012.04.003.

[34] M. Gholinejad, Z. Naghshbandi, C. Nájera, ChemCatChem. 11 (2019) 1792–1823, https://doi.org/10.1002/cctc.201802101.

[35] M. Baghayeri, H. Alinezhad, M. Tarahomi, M. Fayazi, M. Ghanei-Motlagh, B. Maleki, Appl. Surf. Sci. 478 (2019) 87–93, https://doi.org/10.1016/j.apsusc.2019.01.201.

[36] S.S. Karbasaki, G. Bagherzade, B. Maleki, M. Ghanic, J. Taiwan Inst. Chem. Eng. 118 (2021) 342–354, https://doi.org/10.1016/j.jtice.2020.12.025.

[37] S. Peiman, R. Baharfar, B. Maleki, Materials Today Communications 26 (2021), 101759, https://doi.org/10.1016/j.mtcomm.2020.101759.

[38] B. Maleki, F. Jafari-Soghieh, H. Alinezhad, M. Ghani, A. Jamshidi, High Performance Polymers 34 (2022) 768–777, https://doi.org/10.1177/09540083221108956.

[39] M. Tarahomi, H. Alinezhad, B. Maleki, Appl Organometal Chem 33 (2019), e5203, https://doi.org/10.1002/aoc.5203.

[40] A.E. Martell, R.M. Smith, R.J. Motekaitis, NIST Standard Reference Data, 2003.

[41] N.V. Jarvis, J.M. Wagener, Talanta 42 (1995) 219–226, https://doi.org/10.1016/0039-9140(94)00231-G.

[42] N. Pollock, G. Fowler, L.J. Twyman, S.L. McArthur, Chem. Commun. (2007) 2482–2484, https://doi.org/10.1039/B701550J.

[43] F. Morales-Lara, M. Domingo-García, R. López-Garzón, M. Luz Godino-Salido, A. Peñas-Sanjuán, F.J. López-Garzón, M. Pérez-Mendoza, M. Melguizo, Sci.,

Technol, Adv. Mater. 17 (2016) 541–553, https://doi.org/10.1080/14686996.2016.1221728.

[44] M. Yamashita, I. Murase, T. Ito, Y. Wada, T. Mitani, I. Ikemoto, Bull. Chem. Soc. Jpn. 58 (1985) 2336–2339, https://doi.org/10.1246/bcsj.58.2336.

[45] G.A. Shafeev, J.-M. Themlin, L. Bellard, W. Marine, A. Cros, J. Vac. Sci. Technol. A 14 (1996) 319–326, https://doi.org/10.1116/1.579895.

[46] J.C. Bertolini, P. Delichere, B.C. Khanra, J. Massardier, C. Noupa, B. Tardy, Catal. Letters. 6 (1990) 215–223, https://doi.org/10.1007/BF00774723.

[47] S. Wang, G. Jiang, Z. Yang, L. Mu, T. Ji, X. Lu, J. Zhu, A.C.S. Sustain, Chem. Eng. 10 (2022) 13750–13758, https://doi.org/10.1021/acssuschemeng.2c03906.

[48] V. Tsakova, ACS Omega. 7 (2022) 3158–3166, https://doi.org/10.1021/acsomega.1c06225.

[49] L.R. Radovic, I.F. Silva, J. Ume, J.A. Menéndez, C.A. Leon y Leon, A.W. Scaroni, Carbon 35 (1997) 1339–1348, https://doi.org/10.1016/S0008-6223(97)00072-9.

[50] A. Boffi, S. Cacchi, P. Ceci, R. Cirilli, G. Fabrizi, A. Prastaro, S. Niembro, A. Shafir, A. Vallribera, ChemCatChem 3 (2011) 347–353, https://doi.org/10.1002/cctc.201000260.

[51] M. Cai, Q. Xu, J. Sha, J. Mol. Catal. A Chem. 272 (2007) 293–297, https://doi.org/10.1016/j.molcata.2007.03.055.

[52] H. El-Sharkawy, Catal. Commun. 8 (2007) 855–860, https://doi.org/10.1016/j.catcom.2006.09.013.

[53] P. Siemsen, R.C. Livingston, F. Diederich, Angew. Chem. Int. Ed. 39 (2000) 2632–2657, https://doi.org/10.1002/1521-3773(20000804)39:15<2632::AID-ANIE2632>3.0.CO;2-F.

[54] H. Ali, F.K. Kanodarwala, I. Majeed, J.A. Stride, M.A. Nadeem, A.C.S. Appl, Mater. Interfaces. 8 (2016) 32581–32590, https://doi.org/10.1021/acsami.6b09645.

[55] V. Pitchaimani, V. Murugesan, L. Kuang-Lieh, R. Seenivasan, Appl. Catal. A Gen. 455 (2013) 247–260, https://doi.org/10.1016/j.apcata.2013.01.021.

[56] J. Zhang, T. Li, X. Zhao, Y. Zhao, F. Li, X. Li, J. Colloid Interface Sci. 463 (2016) 13–21, https://doi.org/10.1016/j.jcis.2015.10.035.

[57] X. Fan, D. Lin, Z. Xu, Y. Li, Colloids Surf. A Physicochem. Eng. Asp. 648 (2022), 129206, https://doi.org/10.1016/j.colsurfa.2022.129206.

[58] W. Li, X. Jia, B. Zhang, L. Tian, X. Li, H. Zhangab, Q. Zhang, New J. Chem. 39 (2015) 2925, https://doi.org/10.1039/C4NJ02117G.

[59] S. Santra, P. Ranjan, S.K. Mandal, P. Kr, Ghorai, Inorg. Chim. Acta 372 (2011) 47–52, https://doi.org/10.1016/j.ica.2011.01.056.

[60] C. Nájera, J. Gil-Moltó, S. Karlström, L.R. Falvello, Org. Lett. 5 (2003) 1451–1454, https://doi.org/10.1021/ol0341849.

[61] J. Cheng, Y. Sun, F. Wang, M. Guo, J.-H. Xu, Y. Pan, Z. Zhang, J. Org. Chem. 69 (2004) 5428–5432, https://doi.org/10.1021/jo049379o.

[62] B. Liang, M. Dai, J. Chen, Z. Yang, J. Org. Chem. 70 (2005) 391–393, https://doi.org/10.1021/jo048599z.

[63] J. Moon, M. Jeong, H. Nam, J. Ju, J.H. Moon, H.M. Jung, S. Lee, Org. Lett. 10 (2008) 945–948, https://doi.org/10.1021/ol703130y.

[64] T.Z. Nagy, A. Csámpai, A. Kotschy, Tetrahedron 61 (2005) 9767–9774, https://doi.org/10.1016/j.tet.2005.06.072.

[65] A.S. Batsanov, J.C. Collings, I.J.S. Fairlamb, J.P. Holland, J.A.K. Howard, Z. Lin, T.B. Marder, A.C. Parsons, R.M. Ward, J. Zhu, J. Org. Chem. 70 (2005) 703–706, https://doi.org/10.1021/jo048428u.

[66] Y. Rubin, C.B. Knobler, F. Diederich, J. Am. Chem. Soc. 112 (1990) 1607–1617, https://doi.org/10.1021/ja00160a047.