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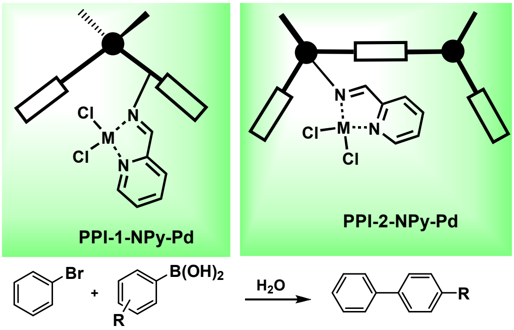
Functionalized porous polyimides have been used as supports for palladium complexes leading to efficient catalysts for the Suzuki cross-coupling of water.



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Palladium-heterogenized Porous Polyimides Materials as Effective and Recyclable Catalysts for reactions in Water

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New functionalized porous polyimides (PPIs-NO_2, PPIs-NH_2, PPIs-NPy) have been synthesized and characterized and the PPI-NPy materials were applied as supports to obtain heterogenized palladium-complexes (PPI-NPy-Pd). The PPI-NPy-Pd hybrid materials have behaved as very efficient heterogeneous catalysts in the Suzuki coupling reaction in water, affording the corresponding cross-coupling products in excellent yields. Furthermore, the catalysts have shown excellent chemical and thermal stability and good recyclability. No evidence of the leaching of Pd from the catalyst during the course of reaction has been observed, suggesting true heterogeneity in our catalytic systems.

Introduction

Heterogeneous catalysts can be prepared by heterogenization of homogeneous counterpart (transition metal complexes, metal salts) over a solid matrix which leads to the formation of solid recyclable molecular catalysts with well-defined active centers. Therefore, the design and development of a suitable support capable of improving the catalyst characteristics by a cooperative effect between the metal complex and the support, is still an important challenge for successful catalysts.[1] In recent decades, many inert solid materials such as mesoporous solids (MCM-41, SBA-15 or related mesoporous silicas),[2] hybrid organic–inorganic structured porous materials,[3] polymers,[4] and coordination polymers[5] as metal–organic frameworks (MOFs),[6] which could originate through the coordination between transition metal centers and chelating organic ligands have been used as supports. Porous organic polymers (POFs) have been developing as very promising functional materials for gas storage, separation and heterogeneous catalysis and sensing, due to their surface area, porosity and chemical stability. For this reason, the interest of using porous organic polymers as transition metal supports remains a challenge of high interest.[7]

A new class of attractive porous materials that are emerged recently is the family of aromatic porous polyimides (PPIs) because they exhibit also large surface areas and interesting properties in gas storage or gas separation.[8] But so far they have not been used for catalytic applications.

The palladium-catalyzed reaction of haloarenes with aryl-boronic acids (Suzuki coupling) is one the most extensively studied organic transformations for the synthesis of biaryl compounds and this reaction is important from both academic and industrial point of views. However, palladium residues are highly polluting because of its difficulty to be removed and recycled and this causes serious problems in large-scale synthesis.[9] To solve these problems, palladium has been attached to different types of supports, such as mesoporous silica supports,[10] activated carbon,[11] zeolites, molecular sieves, metal oxides, metal–organic frameworks (MOFs)[12] and organic polymers[13, 9c] However few examples of porous polymer palladium catalysts can be found. In 2011, Ding et al reported the first porous polyimine Pd catalyst to be used in Suzuki-Miyaura reaction, using *p*-xylene as solvent reaction.[14] Recently palladium has also been anchored to porous polydivinylbenzene and a TpPa-1 matrix and used as catalyst in cross-coupling reactions showing good stabilities in both acidic and alkaline media, high activity and recyclability, but the reactions have to be performed in ethanol, ethanol-water or N-methyl pyrrolidinone.[15] The use of water as solvent has gained special importance in last years due mainly to the economic and environmental advantages, because it is abundant, cheap, nontoxic, noncorrosive, non-flammable and has unique properties in solvating molecules which can improve rate and selectivity of the reactions.[16,13b] Thus, the interest of using water as a solvent in organic reactions is evident because most of the conventional organic solvents are toxic and volatile, particularly chlorinated hydrocarbons which contribute significantly to pollution.[17]

These porous hydrophobic polyimide materials are suitable for functionalization with different transition metal complexes useful as heterogeneous catalysts. Herein, as a preliminary application heterogenized palladium complexes (Fig. 1) were easily prepared by amino functionalization of porous polyimide networks and subsequent incorporation of bidentate nitrogen-binding ligands able to coordinate the metal centre.

These as-synthesized hydrophobic PPI-NPy-Pd(II) materials exhibited outstanding catalytic activity in Suzuki cross-coupling reactions under mild conditions using water as solvent. The effectiveness and recyclability of these hydrophobic catalysts was proved after at least four cycles.

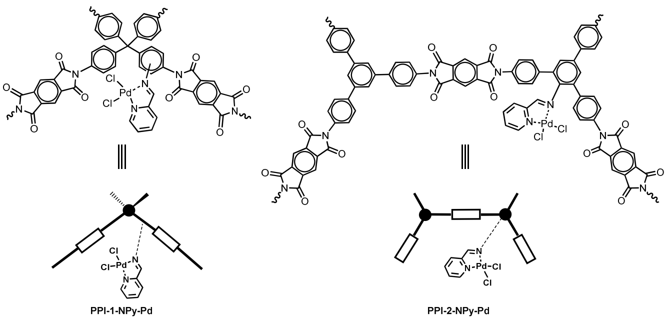


Fig. 1. Structure of the repeat unit and schematic representation of heterogeneous Pd catalysts based on porous polyimides networks.

Results

Amino functionalized porous polyimides

Amino functionalized porous polyimides, PPI-1-NH_2 and PPI-2-NH_2 (Fig. 2) were prepared in two steps from the corresponding porous polyimides networks, PPI-1 and PPI-2. These starting materials were synthetized according to the methods previously reported,[8e,i] by reaction of pyromellitic dianhydride (PMDA) with tetra-(4-aminophenyl)methane (Th)[18] or 1,3,5-tris-(4-aminophenyl)benzene (C_{3v})[19] at 200ºC using *m*-cresol as solvent and quinoline as catalyst. Then, PPI-1 was treated with a mixture of nitric acid and sulphuric acid[20] to yield the nitro-functionalized polyimides **PPI-1-NO_2** and **PPI-2-NO_2**.

Mononitration of 1,3,5-triphenylbenzene yields three isomers with nitro groups located on the central ring (62%) and on the peripheral-rings, in *ortho* and *para* positions (23 and 15% respectively).[21] However, the nitration of **PPI-2** yields a main isomer (**PPI-2-NO_2**) with NO_2 groups located on the central ring of the C3v amine because the *para* positions were occupied and the *ortho* ones were deactivated.

In the next step, the nitro groups were reduced with $SnCl_2{\cdot}2H_2O$ in THF,[22] to yield the corresponding amino functionalized polyimides, **PPI-1-NH_2** and **PPI-2-NH_2**.

The reduction was followed by IR spectroscopy and it was considered finished when the band attributed to the nitro groups at 1530 cm^{-1} disappeared. The other characteristic band of nitro groups at 1350 cm^{-1} was overlapped with the bands of the polyimide skeleton. In the spectra of the amino functionalized polyimides, two new bands emerged, one broad of low intensity at 3500-3300 cm^{-1} and other of higher intensity at 1615 cm^{-1} that were assigned to the presence of –NH_2 groups. As an example, Fig. 3 shows the IR spectra of the amino and nitro functionalized porous polyimides compared with the corresponding starting material **PPI-2**. The thermal stability was evaluated by thermogravimetric analysis (TGA) in air and nitrogen atmosphere (Fig. S1). It can be observed as the weight loss attributed to the nitro groups disappears in the thermograms of amino derivatives (Fig. S1b); PPI-1-NH_2 and PPI-2-NH_2 exhibited lower thermal stability than the starting polyimides (Table 1).

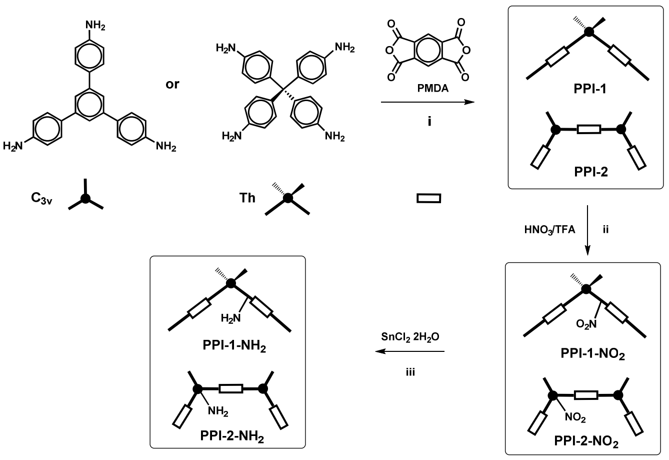


Fig. 2. Synthesis of amino functionalized porous polyimides. i) *m*-cresol/quinoline, 200°C; ii) HNO_3 / H_2SO_4, -10°C iii) $SnCl_2{\cdot}2H_2O$, THF, reflux, 24h

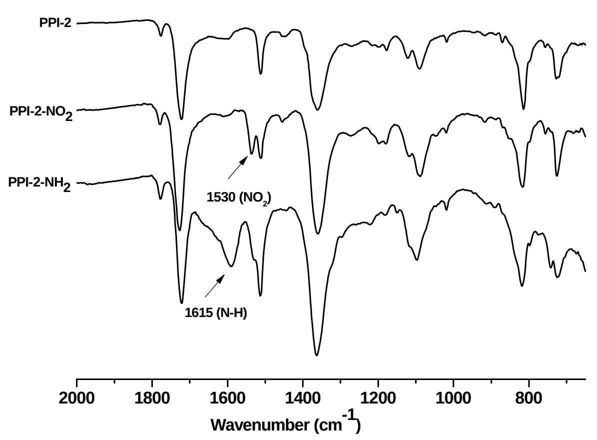


Fig. 3. FT-IR spectra of PPI-2, PPI-2-NO_2 and PPI-2-NH_2

The porosity of the new materials was characterized by nitrogen sorption after heating the samples at 100 ºC. The N_2 isotherms (Fig. S2) were the typical for microporous materials. The porosity parameters obtained are recorded in Table 1 and the pore-size distribution depicted in Fig. S3. The specific surface area of the polyimide **PPI-2** was slightly higher than that of **PPI-1**, which indicated that in this case, the growth of the network has been easier from the monomer with trigonal geometry. The amino-functionalized polyimides showed a considerable decrease of the specific surface areas compared with the starting polyimides. The reduction of the specific surface area after post-functionalization of porous aromatic frameworks (PAFs) has been also reported.[7]

The SEM images of both amino functionalized polyimides (Fig. 4) were similar to those of the precursors and of the nitro derivatives (Fig. S4) displaying the typical morphology of porous cross-linked polymers with spherical structures and agglomerates.

Table 1. Degradation temperatures and porosity parameters of amino functionalized polyimides compared with the starting materials.

Polyimide	Td_{onset}(ºC)	S_{BET} (m^2/g)	Aver. Pore Size (nm)
PPI-1	570	474	3.8
PPI-1-NH_2	405	206	10.3
PPI-2	540	604	5.9
PPI-2-NH_2	410	274	10.8

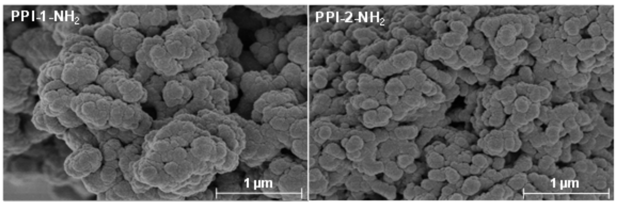


Fig. 4. SEM images of **PPI-1-NH_2** (left) and **PPI-2-NH_2**(right).

Heterogeneous palladium catalysts

The incorporation of palladium on the porous polyimides was carried out in two steps (Fig. 5), following the same strategy used to incorporate rhodium and copper into amino functionalized porous aromatic frameworks (PAFs).[22] Thus, in a first step, the corresponding amino support, **PPI-1-NH_2** or **PPI-2-NH_2**, was reacted with picolinaldehyde to yield the imino pyridine ligands **PPI-1-NPy** and **PPI-2-NPy**. In a second step, these derivatives were reacted with *bis*(benzonitrile) palladium chloride in acetonitrile to obtain the palladium-incorporated heterogenized catalysts **PPI-1-NPy-Pd** and **PPI-2-NPy-Pd**.

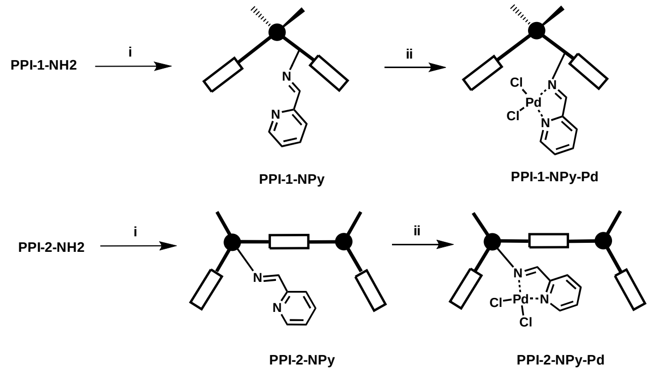


Fig. 5. Synthesis of heterogenized palladium catalysts. i) picolinaldehyde, ethanol, reflux; ii) $PdCl_2(C_6H_5)_2(CN)_2$, acetonitrile.

The analysis by ICP of the palladium content incorporated into the supports revealed that **PPI-2-NPy** ligand showed higher metal binding capacity than **PPI-1-NPy**. Thus, the amount of palladium in **PPI-2-NPy-Pd** was 3.42% while **PPI-1-NPy-Pd** showed 1.76%.

The specific surface areas of **PPIs-NPy-Pd** significantly decreased (10-30 m^2/g), which could be due to a partial blockage of the pores or interpenetration of the network. The latter behavior has been recently observed in urea-based porous organic frameworks and despite the low surfaces areas (91-113 m^2/g), the palladium catalyst prepared from these materials exhibited high catalytic activity and selectivity in reactions in water.[23]

The SEM images of palladium heterogenized catalysts (Fig. 6) were similar to those of the amino functionalized polyimides, showing the characteristic morphology of porous polymers, despite the apparent loss of porosity observed by BET.

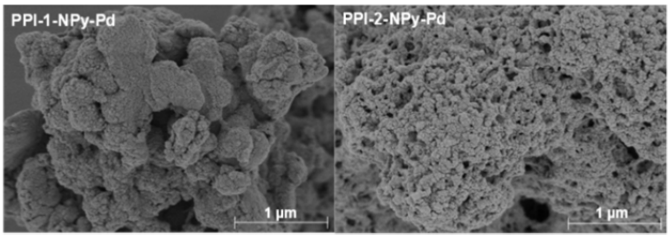


Fig. 6. SEM images of **PPI-1-NPy-Pd** (left) and **PPI-2-NPy-Pd** (right).

The thermal stability of imino pyridine ligands and Pd catalyst was also evaluated by TGA and compared with that of the starting amino functionalized polyimides (Fig. 7). Comparing with the precursors **PPI-1-NH_2** and **PPI-2-NH_2** it can be observed that the bidentate ligand increased the thermal stability around 35-55 ºC. The derivative thermogravimetric curve of **PPI-1-NPy-Pd** showed a main peak accompanied by a shoulder, and a second peak of very low intensity. The thermal degradation of **PPI-2-NPy-Pd** occurred also in two stages at initial decomposition temperatures of 355 and 430 ºC. Thus, as happened with their precursors, the degradation of both palladium catalysts followed different mechanisms. Comparing with **PPI-1-NPy** and **PPI-2-NPy** it should be noticed that palladium decreases the thermal stability around 55 ºC in the case of **PPI-1-NPy-Pd** and 80 ºC for **PPI-1-NPy-Pd** (Fig. S5).

The imino pyridine ligands and palladium heterogenized catalysts were also characterized by ^{13}C-NMR and elemental analysis and compared with the corresponding parent supports **PPI-1-NH_2** and **PPI-2-NH_2**. The spectra of the imino pyridine ligands and palladium catalysts were very similar to those of the starting materials (Fig. S6). Thus, the three spectra showed two signals of low intensity at 165.9 and 141.7 ppm attributed to the carbonyl groups and to the quaternary aromatic carbons respectively and a group of signals of high intensity, between 138 and 125 ppm, characteristic of the rest of aromatic carbons. The signals of the pyridine groups were indistinguishable from these signals. Elemental analysis confirms the functionalization (Table S1).

Reference palladium complex for homogeneous catalysis

For comparative purposes, a palladium complex **NPy-Pd** was prepared following the route depicted in Fig. 7. Thus, 4-tritylaniline, prepared from triphenylmethylchloride, was reacted with picolinaldehyde to obtain quantitatively (*E*)-N-(pyridin-2-ylmethylene)-4-tritylaniline (**NPy**).[7b] Then, NPy was reacted with *bis*(benzonitrile) palladium chloride in acetonitrile to obtain the palladium complex **NPy-Pd**.

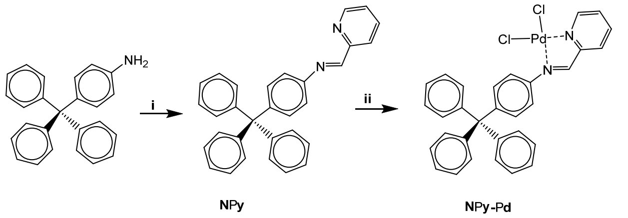
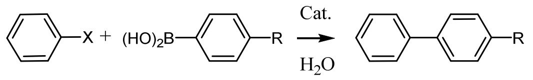


Fig. 7 Synthesis of homogeneous palladium catalyst: i) picolinaldehyde, ethanol, reflux; ii) $PdCl_2(C_6H_5CN)_2$, acetonitrile.

NPy and **NPy-Pd** were characterized by NMR and FTIR spectroscopies. The ^{1}H-NMR (Fig. S7) of both compounds showed a group of signals between 7 and 7.4 ppm, attributed to the aromatic protons of the tetra-phenyl units. The signal corresponding to the proton of the imine group (j) appeared at 8.6 ppm in the **NPy** spectrum whereas in the **NPy-Pd** spectrum this signal was shifted to 8.8 ppm due to the metal coordination. Similar displacement was observed in the signals corresponding to the protons of the pyridine ligands. ^{13}C-NMR (Fig. S8) spectra showed a remarkable displacement of the carbon of the imine bond from 160 to 175 ppm and the carbons *meta* to the nitrogen atoms when the metal was coordinated. Comparing the FT-IR spectra of both compounds (Fig S9) it can be also observed that imine group shifts to lower frequency ($\Delta\nu = 37$ cm^{-1}) when coordination with palladium occurs.

Catalytic activity

Recently, organic reactions in aqueous media have attracted a great deal of attention because water is benign, cheap, and easily available. The separation of products, however, should be the key consideration when employing water as the solvent for organic reactions. Among the various reactions developed, the Suzuki reaction has strongly benefited from aqueous chemistry.[24] Our objective was the application of hydrophobic **PPI-n-NPy-Pd** polymers as catalysts for Suzuki cross-coupling reaction in pure water (Scheme 1)



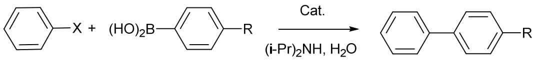
Scheme 1. Suzuki coupling reaction of halobenzenes with boronic acids

Preliminary experiments showed that the model reaction between iodobenzene (1 mmol) and phenyl boronic acid (1.5 mmol) using 1 mmol% of **PPI-1-NPy-Pd** (based on Pd) as the catalyst and excess of K_2CO_3 (2.0 mmol) as the base proceeded smoothly in H_2O at 100 ºC affording the desired biphenyl within 24 h in excellent isolated yield (90%). At this point, we performed a series of experiments in order to optimize the reaction conditions under aerobic condition. Thus, the reaction in the absence of any base resulted in a negligible conversion (Table S2, entry 2). Among a variety of bases that showed satisfactory conversions (e.g., K_2CO_3, K_3PO_4, Et_3N and (i-Pr)$_2$NH) (Table S2, entries 3–5), we chose to proceed with (i-Pr)$_2$NH. In terms of solvent, H_2O afforded the desired product with the highest yield. Other solvent such as xylene resulted in poorer yields (Table S2). At 70 ºC temperature, low amount of coupled product was obtained. Increasing the temperature from 70 to 90 ºC improved significantly the conversion (Table S2). The base-substrate ratio of 2:1 was the best for this catalytic system. Then reactions were carried out at 100 ºC in air using (i-Pr)$_2$NH as base and water as reaction medium. Further, as expected, no product formation was observed in the control experiments in the absence of **PPI-1-NPy-Pd (**Table S2, entry 8)**.** Based on the optimized experimental conditions, we explored the substrate scope using iodo and bromobenzene and different arylboronic acids. The results for Suzuki **PPI-n-NPy-Pd-**catalyzed reactions are summarized in Table 2 and Figures S10 and S11. In general, all the reactions were very clean and the corresponding biaryl products were isolated in good to excellent yields. As expected, iodobenzene was rapidly converted to the corresponding biaryl products with excellent yields (Table 2, entries 1 and 11). The less reactive chlorobenzene displayed a poor conversion. **PPI-2-NPy-Pd** presents a better catalytic activity for Suzuki reaction than **PPI-1-NPy-Pd**. This fact confirms that both amines, C_{3v} and Th yield completely different networks, being the Pd of the C_{3v} derivative more available. The greater accessibility to PPI-2 type network is consistent with the higher metal binding capacity of **PPI-2-NPy** and the higher specific surface areas of the precursors, **PPI-2** and **PPI-NH$_2$**.

Next, to demonstrate versatility of the catalytic system for the Suzuki coupling reaction, we tested 4-substituted boronic acids, bearing either electron-donating or electron-withdrawing groups, such as –OMe, –CHO, –CN, -Me and –NO_2, which provided selectively the corresponding products in good to excellent yields within 0.5-7 h. The (4-cyanophenyl)boronic acid required the longest reaction times (Table 2, entries 7 and 17). Homocoupled product of arylboronic acid was not detected under the reaction conditions.

In order to find out the effect of heterogenization, the activity of the polyimide anchored Pd(II) catalyst (**PPI-1-NPy-Pd**) was compared to that of the homogeneous analogue in the Suzuki coupling reaction. From the results (Table 2) it is seen that the present heterogeneous catalyst is more reactive than the corresponding homogeneous one. The reaction using homogeneous catalyst with bromobenzene and 4-methoxyphenylboronic acid in H_2O medium for 3 h resulted in 43% conversion (Table 2, entry 9), while the analogous heterogeneous reaction was performed successfully with 93% conversion by GC analysis. Reaction with 4-formylphenylboronic affords only 49 % conversion (Table 2, entry 8) and the reaction with (4-cyanophenyl)boronic acid do not occurs. Besides, decomposition of Pd-catalyst was clearly observed. The activity and selectivity of the catalyst was also comparable with other reported heterogeneous (polystyrene-, sepiolite-supported Pd(II)) catalysts[25] for the reaction of aryl halides under aerobic condition.

Table 2. Suzuki coupling reaction of halobenzenes with various arylboronic acids catalyzed by **PPI-1-NPy-Pd** and **PPI-2-NPy-Pd** complexes.[a]



	Catalyst	mol. (%)[b]	X	R	Yield (%)[c] (h)	TON[d]	TOF (h^{-1})[e]
1	PPI-1-NPy-Pd	0.3	I	H	88 (3)	293	462
2		0.5	Br	H	88 (2)	176	450
3		0.5	Br	OMe	93 (3)	465	96
4		0.4	Br	NO_2	82 (4)	205	125
5		0.4	Br	Me	98 (2)	245	126
6		0.4	Br	COH	85 (1.5)	212	145
7		0.8	Br	CN	93 (5)	116	57
8	NPy-Pd	0.4	Br	COH	49 (2)[f]	105	95
9		0.5	Br	OMe	43 (3)[f]	86	40
10		0.8	Br	CN	4 (5)[f]	6	-
11	PPI-2-NPy-Pd	0.3	I	H	96 (0.5)	319	685
12		0.5	Br	H	100 (0.5)	200	580
13		0.5	Br	OMe	100 (0.5)	200	400
14		0.5	Br	NO_2	85 (3.0)	170	168
15		0.5	Br	Me	100 (1.5)	200	159
16		0.5	Br	CHO	100 (1.5)	200	168
17		0.5	Br	CN	94 (7.0)	188	55

[a] Reaction conditions: arylhalide (1.0 mmol), boronic acid (1.5 mmol), $(i\text{-}Pr)_2NH$ (2.0 mmol), T: 100 ºC, water (1 ml). [b] Based on Pd; [c] Yield determined by GC and GCMS analysis; [d] TON= (mol of product/mol of catalyst); [e] mmol subs./mmol cat. h; [f] Decomposition of catalyst.

For preparative task we have scaled up the reaction with ten times of reagents and catalyst, GC conversion after 30 min was 100% and the final products were isolated with a yield of 85%.

An important point concerning the use of heterogeneous catalyst is its lifetime, particularly for industrial and pharmaceutical applications. To determine whether the catalyst is actually working in a heterogeneous manner, a hot-filtration test was performed in the Suzuki coupling reaction of bromobenzene and 4-methoxyphenylboronic acid (Figure 8). During catalytic reaction, the solid catalyst was separated from the reaction mixture by filtration after 5 min (conversion 10%) and 15 min (conversion 46%); the reaction was carried out for a further 3 h. The gas chromatographic analysis showed no increment in the conversion. Atomic absorption spectrometric analysis of the liquid phase of the reaction mixtures collected by filtration confirms that Pd is absent in the reaction mixture. These results suggested that no leaching of palladium takes place during the reaction and that the catalyst is purely heterogeneous in nature.

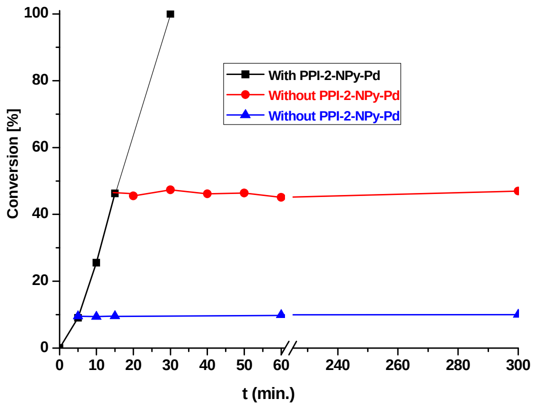


Fig. 8. Hot filtration experiments.

As an important aspect of heterogeneous catalysis, we further studied the recyclability of the catalyst for a model Suzuki reaction. After each run, the catalyst was separated by simple filtration, washed thoroughly with water, and ethyl acetate, and dried at 100 ºC under vacuum for 8 h. The dried catalyst was then reused with a fresh reaction mixture. In spite of a small catalyst deactivation (Fig. 9, Table S4), the results showed a good recyclability of both catalysts, being better for the reaction of iodobenzene with phenylboronic acid (**PPI-1-NPy-Pd**, up to seven runs) than when bromobenzene is the reactant (**PPI-2-NPy-Pd**, Fig. S12, Table S5). In general, the average catalyst productivity and activity were identified in Suzuki reactions (TON 110–465; TOF 55–685 h^{-1}). ICP analysis for the reused **PPI-1-NPy-Pd** (after seven cycles) catalyst reveals that 20 % of Pd was lost, probably due to the washings of catalyst.

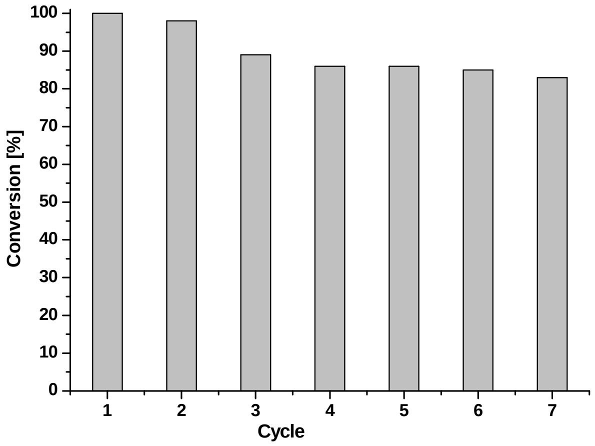


Fig. 9. Recycling experiments for Suzuki reaction between iodobenzene and phenylboronic acid.

The chemical structure of the catalysts was checked after the recycling by IR spectroscopy and WAXS (Fig. S13 and S14). No differences were found between the materials before and after recycling which indicated that chemical structure was maintained after the catalysis. By TGA (Figure 10) a slight reduction in the thermal stability (around 10-15ºC) was observed after recycling.

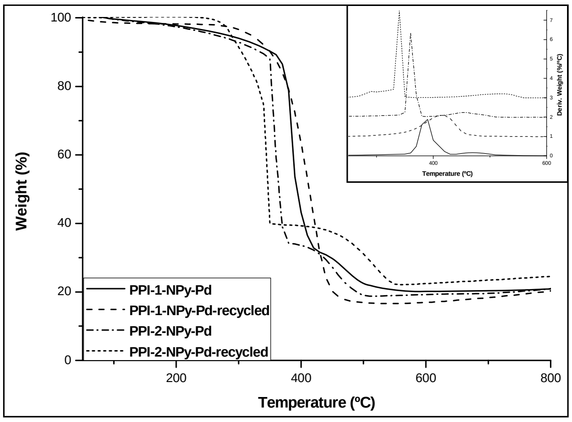


Fig. 10. TGA and DTG (Vertically shifted) of PPI-1-NPy-Pd, PPI-2-NPy and the corresponding recycled catalysts.

Experimental

Materials

The syntheses of *tetra*(4-aminophenyl)methane (Th) and 1,3,5-tris(4-aminophenyl)benzene (C_{3v}) were carried out according to methods reported.[18,19] Pyromellitic dianhydride (PMDA) (Aldrich) was purified by sublimation. 2-Pyridinecarboxaldehyde (Aldrich), dichloro*bis*(benzonitrile) palladium (Aldrich), ethanol (Prolabo), *m*-cresol (Aldrich) and acetonitrile (Aldrich) were used without purification.

Porous polyimides (PPI-*n*)

General procedure: Porous polyimides were obtained by condensation reaction of aromatic amines (Th or C_{3v}) and pyromellitic dianhydride using m-cresol as a solvent and quinoline as catalyst.[20,8i]
The products were characterized by elemental analysis, ATR-FTIR, solid ^{13}C-NMR, TGA and SEM. The specific surface area and pore size were determined by BET.

Amino functionalized porous polyimides (PPI-*n*-NH_2)

Synthesis of PPI-n-NO_2, general procedure: In a 50 mL flask equipped with magnetic stirring containing PPI-*n* (1 mmol) H_2SO_4 (20 mL), and then HNO_3 (1 mmol) were added at -10 °C and the mixture was stirred for 2 h at that temperature. Then, the reaction mixture was added into ice-water. The solid was filtered and washed with THF and diethyl ether and finally dried at 100 °C/1 h under vacuum.
Synthesis of PPI-n-NH_2, general procedure: A 50 mL flask equipped with magnetic stirring and condenser, was charged with PPI-*n*-NO_2 (1mmol), THF and $SnCl_2.2H_2O$ (13 mmol). Then the mixture was heated to reflux for 24 hours. The solid was filtered and washed with 0.05 M HCl, water, 0.05 M NaOH, water, THF and diethyl ether. Finally, the product was dried at 100 °C/1 hour under vacuum.
PPI-*n*-NO_2 and PPI-*n*-NH_2 were characterized by elemental analysis, ATR-FTIR, solid ^{13}C-NMR, TGA and SEM. The specific surface area and pore size were determined by BET.

Imino pyridine ligands (PPI-*n*-NPy)

General procedure: In a 250 mL flask equipped with mechanical stirring and condenser, 200 mg of **PPI-*n*-NH_2** and 100 mL of ethanol were added. To this suspension was added 0.11 mg (1.05 mmol) of 2-pyridinecarboxaldehyde and 1 drop of formic acid. The mixture was heated to reflux for 48 hours. The solid was filtered and washed with ethanol, dichloromethane and ether and dried at 100 °C/1 h. The ligands were characterized by elemental analysis, ATR-FTIR, solid ^{13}C-NMR, WAXS, SEM and TGA.

Heterogeneous palladium catalysts (PPI-*n*-NPy-Pd)

General procedure: A 50 mL flask equipped with mechanical stirring and condenser was charged with 100 mg of PPI-*n*-NPy, 50 mg (0.130 mmol) of dichloro*bis*(benzonitrile) palladium and 30 mL of acetonitrile. Then the mixture was heated to reflux for 4.5 h. The solid was filtered and washed with acetonitrile and finally dried at 100 °C/1 h. The catalysts were characterized by elemental analysis, ICP, ATR-FTIR, solid ^{13}C-NMR, BET, WAXS, SEM and TGA.

Synthesis of N-pyridin-2-ylmethylene-4-trimethylaniline (NPy): In a flask containing activated molecular sieve (4Å) was added 4-tritilaniline (0.50 g, 1.50 mmol), 100 ml of absolute ethanol, 2-pyridinecarboxaldehyde (0.18 g, 1.64 mmol) and one drop of formic acid. The mixture was heated to reflux for 24 h. After this time, the molecular sieve was filtered and washed with ethyl acetate. The mixture of solvents was evaporated under reduced pressure to obtain a pale pink solid. This crude was recrystallized from heptane to give a white crystalline solid. Yield 0.62 g (99 %). FTIR (cm^{-1}) 1632 (C=N). ^{1}H-NMR (400 MHz, DMSO-d_6): 8.72 (d, 1 H), 8.63 (s, 1 H), 8.14 (d, 1 H), 7.95 (td, 1 H), 7.53 (m, 1 H), 7.4-7.0 (m, 19 H) ; ^{13}C-NMR (100 MHz, DMSO-d_6): δ (ppm) 160.97, 154.40, 150.06, 148.28, 146.68, 145.44, 137.43, 131.78, 130.82, 128.15, 126.42, 126.01, 121.54, 120.97, 64.60. HR-MS calculated for $C_{31}H_{24}N_2$ 424.53, found [M$^+$] 424.40.

Synthesis of homogeneous complex (NPy-Pd): To a 50 mL flask equipped with mechanical stirring and condenser were charged 50.00 mg of NPy (1.178 mmol), 45.17 mg (1.178 mmol) of dichloro*bis*(benzonitrile) palladium and 30 ml of acetonitrile. Then, the system was heated to refluxing temperature for 4.5 h. The reaction mixture was concentrated to leave a yellow solid. The solid was washed with *n*-pentane and filtered. Yield 60.0 mg (84.6 %). FTIR (cm^{-1}): 1595 (C=N). ^{1}H-NMR (400 MHz, DMSO-d_6): 9.06 (d, 1 H), 8.78 (s, 1 H), 8.38 (td, 1 H), 8.17 (d, 1 H), 7.93 (m, 1 H), 7.4-7.0 (m, 19 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ (ppm) 173.06, 156.24, 150.50, 147.28, 146.50, 145.25, 141.73, 130.89, 135.59, 129.90, 129.51, 128.32, 126.66, 123.84, 64.84. HR-MS calculated for $C_{31}H_{24}N_2PdCl_2$ 601.85, found [M$^+$] 602.1.

General experimental procedure for Suzuki cross-coupling reaction in water medium.

The reactions were carried out in a micro reaction vessel (5 mL). A mixture of aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), diisopropyl amine (2 mmol), H_2O (2-3 ml) and **PPI-n-**

NPy-Pd catalyst (1.4-0.3 mol %) was stirred at 100 ºC under air. To study the progress of the reaction, aliquots were taken from the reaction mixtures at different times, extracted with ethyl acetate and quantified by GC-MS analysis.

Recycling experiments

Once the reaction was completed, the heterogenized **PPI-n-NPy-Pd** complex was recovered by washing with ethyl acetate and water, with stirring, for 1 day. Then, the catalyst was centrifuged and dried in an oven at 100 °C.

Conclusions

In summary, we have reported the preparation of new functionalized porous polyimides (PPIs) with two different 2D and tetrahedral topologies with high specific surfaces and thermal and chemical stabilities. These new materials have been used as effective supports for heterogeneous palladium complexes which were efficiently used as catalysts for Suzuki cross-coupling reactions in water medium under aerobic conditions. The catalysts show not only high catalytic activity, but also offer many practical advantages such as oxygen insensitivity, thermal stability, and fair recyclability. The excellent catalytic performance in water medium and the easy preparation and separation of the catalyst make them good recyclable heterogeneous catalytic systems in water and a useful alternative to other heterogeneous palladium catalysts.

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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