Palladium(0) nanoparticles encapsulated in diamine-modified glycidyl methacrylate polymer (GMA-CHDA) applied as catalyst of Suzuki–Miyaura cross-coupling reaction†

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Cyclohexyldiamine-modified glycidyl methacrylate polymer (GMA-CHDA) in the form of gel-type beads was used to encapsulate Pd(0) nanoparticles 4–15 nm in diameter and applied as a new, reusable catalyst for the Suzuki–Miyaura cross-coupling reaction of 2- and 4-bromotoluene with phenylboronic acid. It was found that the precatalyst preparation methodology strongly influenced its catalytic activity. The best results (100% yield of the product) were obtained when GMA-CHDA was first treated with hydrazine (reducing agent for Pd(II)) and next with $PdCl_2$ solution. The new catalyst acts heterogeneously, and the post-reaction solution after catalyst separation is not catalytically active, suggesting that there is no leaching.

Introduction

The immobilization of metal catalysts on solid supports has become a valuable tool for the efficient separation of organic products and catalyst recycling. Polymers play a significant role in this area, offering different ways of metal attachment to the polymer matrix *via* covalent or non-covalent bonding, through hydrogen bridges, as well as through ionic, hydrophobic or fluorous interactions.[1,2]

For the purposes of immobilizing catalysts in the form of metal complexes, different polymers have been examined—both soluble (linear, branched and hyperbranched) and insoluble, cross-linked micro- and macroporous, and hybrid materials.[3] Typically, functional groups present in a polymer support participate in bonding with metals. Palladium complexes anchored on polymers with mono- and diphosphines,[4–6] *N*-heterocyclic carbene groups,[7–10] and dendrimers[11,12] have been described. Pd nanoparticles are another kind of attractive catalyst for C–C cross-coupling reactions, including the Suzuki–Miyaura coupling.[13,14] To prevent the eventual aggregation of nanoparticles, polyvinylpyrrolidone (PVP) has been used as a supporting medium.[15] Such a Pd colloid (Pd/PVP) has also been used as a catalyst precursor after immobilization on carbon.[16] Good results in Suzuki couplings, close to those obtained in homogeneous systems, have been reported for Pd nanoparticles supported on a hybrid organic/inorganic material, polyHIPE, functionalized with amine or quaternary ammonium groups.[17] The activity of this catalyst increased when PPh_3 was added; however, some leaching of Pd was observed.[17]

It is also possible to incorporate a Pd precatalyst into a polymeric material during the synthesis of the polymer. This method was applied to the synthesis of an encapsulated Pd catalyst, subsequently commercialized as the Pd EnCat catalyst, used for the Suzuki reaction with a phosphine additive.[18]

Recent progress in the design, preparation and application of polymer-supported Pd complexes is reviewed in ref. 19, where, among other things, the preparation of various supported Pd–phosphine complexes used in carbon–carbon bond forming reactions, such as the Heck reaction, the Suzuki–Miyaura coupling and π-allylic substitution is discussed.

In this work, we report on the application of diamine-modified glycidyl methacrylate resin (GMA-CHDA) as a support for the encapsulation of Pd nanoparticles used in Suzuki–Miyaura cross-coupling. Glycidyl methacrylate polymers, being easily modifiable materials, have been used, for instance, as supports for enzymes[20] and sorbents for chromatography.[21] They can also be utilized for removing metal ions or impurities from solutions[22] and as biomaterials, *e.g.* protein separation and purification agents,[23] and biodegradable hydrogels in drug control release processes.[24]

The polymers under study, with low levels of cross-linking of three-component glycidyl methacrylate terpolymers (GMA resins), were synthesized by the suspension polymerization technique,[25] and were found not only to be good supports for Pd nanoparticles, but also to exhibit interesting swelling characteristics. It was found that the gel-type beads, formed from the mixture of glycidyl methacrylate, styrene and a divinyl monomer (divinylbenzene, mono-, di- or triethyleneglycol dimethacrylates), in the presence of a cyclohexanol/*n*-octanol mixture, were able to enlarge their volume many times over under the influence of thermodynamically favourable (compatible) solvents and return to their initial volume

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when a thermodynamically unfavourable (incompatible) solvent was added.

An increase in bead volume indicates that molecules of compatible solvents are able to penetrate deeply into the polymer network and solvate polymer chains. These phenomena facilitate access of potential reagents or other species to essentially all segments of the polymer network.[26] Therefore, we decided to use the selected GMA resin to encapsulate Pd nanoparticles in the polymer network and test the obtained catalysts in Suzuki–Miyaura cross-coupling reactions.

Experimental

Polymer support synthesis

Synthesis of the diamine gel-type polymer support for Pd immobilization was carried out in a two-stage procedure. In the first stage, a mixture of glycidyl methacrylate (GMA; 20 mol%), styrene (S; 77 mol%) and divinylbenzene (DVB, mixture of isomers, ~80%; 3 mol%) was polymerized in suspension, according to a procedure described in ref. 25. The monomers were diluted in a mixed solvent (cyclohexanol/*n*-octanol, 4 : 1 w/w) in a 1 : 1 w/w proportion. Spherical microbeads of the GMA resin were obtained. After being washed and dried under reduced pressure, the beads were sieved and analyzed. A fraction 150–250 μm in diameter was used for further investigations. The epoxy group content in the beads, amounting to ~1.3 mmol g^{-1}, was determined using a modification of Jay's method.[27]

In the second stage, the GMA resin was reacted with a 5-fold excess of *trans*-1,2-diaminocyclohexane (CHDA) in DMF (10 cm^3 per gram of the GMA resin) at 70 °C. The reaction was carried out under argon in thermostatic glass reactors placed on a horizontal shaker. After 20–24 h, the diamine-modified resin, GMA-CHDA, was filtered and washed carefully several times, first with DMF, and then with CH_2Cl_2 and MeOH, and finally dried in a vacuum at 40 °C. Its analysis (Kiejdahl's method) indicated a nitrogen content of ~2 mmol g^{-1}. The nitrogen content was also confirmed by elemental analysis: N, 2.66; C, 79.67; H, 7.91%.

IR (KBr, cm^{-1}): 1730 vs (ν_{CO}), 1604 s (ν_{COO}).

Test of polymer swelling

Swelling of the resin was determined using 2.5 cm^3 syringes equipped with a polypropylene filter. A resin sample of 0.1 g was treated with a selected solvent, and the solvent excess was removed by syringe piston after establishing a swelling equilibrium. The weights of dry and swelled resins were compared to calculate the swelling degree (SD) (Table 1).

Preparation of palladium catalysts (P1, P2, P3)

Catalyst P1. To 0.5 g of GMA-CHDA polymer was added 5 cm^3 of DMF, and the mixture stirred for 20 min. Next, 0.5 cm^3 of the hydrazine solution, prepared by dissolving of 0.2 cm^3 of 80% aqueous hydrazine solution in 10 cm^3 DMF, was added, and the mixture was heated to 60 °C. After temperature stabilization, 5 cm^3 of a $PdCl_2$ solution in DMF, containing 0.00832 g of $PdCl_2$ in 1 cm^3 DMF, was added, and the color of the solution changed to black. The mixture was stirred for 20 min and then filtered. Catalyst P1 was washed three times with DMF, then with MeOH, left for 15 min in MeOH, filtered and dried in a vacuum.

IR (KBr, cm^{-1}): 1730 m (ν_{CO}), 1656 vs (ν_{COO}).

Table 1 Swelling characteristics of GMA and GMA-CHDA resins

Solvents	Swelling degree[a]/g g^{-1}	
	GMA resin	GMA-CHDA resin
CH_2Cl_2	3.67	2.56
H_2O after CH_2Cl_2	3.65	2.35
THF	2.30	1.60
H_2O after THF	0.84	0.59
DMF	1.75	1.35
H_2O after DMF	1.70	1.23
N_2H_4[b] after DMF	—	0.52
DMF after N_2H_4[b]	—	0.31
1,4-Dioxane	2.35	2.04
MeCN	0.49	0.42
MeOH	0.54	0.55
Toluene	—	0.47
2-Propanol	—	0.63
2-Propanol–H_2O (1 : 1 v/v)	—	0.65
H_2O	0.75	0.50
Ethylene glycol	0.85	0.66
Ethylene glycol–H_2O (1 : 1 v/v)	—	0.94
CH_2Cl_2–MeOH (1 : 2 v/v)	0.77	1.41
CH_2Cl_2–MeOH (1 : 1 v/v)	1.79	2.02
CH_2Cl_2–MeOH (2 : 1 v/v)	2.70	2.35
THF–H_2O (1 : 1 v/v)	1.29	1.18

[a] Swelling degree was calculated as: SD = $(m_s - m_d)/m_d$; m_s, m_d = weights of the swelled and dry resins, respectively. [b] 64% aqueous solution of N_2H_4.

Catalyst P2. For the preparation of catalyst P2, the same solutions were used as for P1, however $PdCl_2$ was added to the polymer before hydrazine.

0.25 g of GMA-CHDA polymer in 2.5 cm^3 of DMF was heated to 60 °C. In another vessel, to 2.5 cm^3 of the $PdCl_2$ solution in DMF pre-heated to 60 °C, was added 0.5 cm^3 of the hydrazine solution. The resulting black–green solution was stirred for *ca.* 5 min and transferred to the first vessel containing GMA-CHDA; the color changing immediately to black. After stirring for 20 min at 60 °C, catalyst P2 was filtrated, washed three times with DMF, then with MeOH, left for 15 min in MeOH, and then filtered and dried in a vacuum.

IR (KBr, cm^{-1}): 1730 m (ν_{CO}), 1656 vs (ν_{COO}).

Catalyst P3. For the preparation of catalyst P3, the same solutions were used as for P1.

To 0.5 g of GMA-CHDA polymer was added 5 cm^3 of DMF, and the mixture stirred for 20 min. Next, 5 cm^3 of the $PdCl_2$ solution in DMF was added, and the mixture was left stirring for 24 h. The polymer was filtered, washed three times with DMF, dried, transferred to another vessel with 5 cm^3 of DMF and stirred for 20 min. The mixture was then warmed to 60 °C and 0.5 cm^3 of the hydrazine solution added; the color of the polymer changing to black. After 20 min of stirring at 60 °C, catalyst P3 was filtered, washed three times with DMF, then with MeOH, left for 15 min in MeOH, and then filtrated and dried in a vacuum.

IR (KBr, cm^{-1}): 1730 m (ν_{CO}), 1656 vs (ν_{COO}).

In modified procedures regarding the P3 catalyst:

Table 2 Structural data of Pd catalysts (P1, P2, P3 and Pd/PVP) and the yield of 4-methylbiphenyl obtained in Suzuki coupling in ethylene glycol[a]

Catalyst	Pd content (%)		Nanoparticle size from XRD data/nm		Nanoparticle size from TEM data before reaction[g]/nm			
	Before reaction	After reaction	Before reaction	After reaction	Mean (arithmetic)	Variance[d]	Median[e]	Yield of 4-Me-biphenyl (%)
P1[b]	3.5	3.5	4.8	3.3	4.7 (5.2)	2.2 (3.9)	4.6 (4.9)	90
P2	3.5	3.0	5.0	5.2	4.8	1.8	4.5	42
P3	3.5	2.0	15.0	10.6	5.7	4.4	5.4	0–15[f]
Pd/PVP	2.7	—	10.5	—	—	—	—	79

[a] Reaction conditions: [Pd] = 1% mol, [4-bromotoluene] = 0.172 g, [$BPh(OH)_2$] = 0.184 g, base = Cs_2CO_3, 80 °C, 3 h. [b] The solution that remained after reaction with P1 (catalyst separated) produced 1% of 4-methylbiphenyl. [c] Arithmetic mean $d = \sum n_i d_i / \sum n_i$; n = total number of particles, n_i = number of particles of diameter d_i. [d] Variance $\sigma^2 = (n\sum d_i^2 - \sum d_i^2)/n(n-1)$ (describes the width of the distribution). [e] Size for which there are equal numbers of particles smaller and larger (centre of the nanoparticle size distribution). [f] Different results were obtained with the P3 catalyst obtained by impregnation according to the modified procedures. [g] Parameters of the P1 catalyst after the Suzuki reaction are given in parentheses.

(a) The time of impregnation was prolonged to 5 d (P3a).

(b) After impregnation, the Pd polymer was dried, and the reduction with hydrazine was performed after 3 d (P3b).

(c) After impregnation, the Pd polymer was not separated from the solution, and hydrazine was added to the mixture heated at 65 °C (P3c).

All four types of P3 catalyst (P3, P3a, P3b and P3c) exhibited similar, very low catalytic activities (Table 2).

Pd/PVP (stabilized colloid). Pd colloid stabilized on PVP was prepared according to ref. 28.

To 10 cm^3 of water was added 0.5 g of PVP (M_w = 10 000), and the mixture was stirred 20 min. Next, 0.01 cm^3 of hydrazine hydrate (80%) was added, the mixture stirred for 20 min and warmed to 60 °C. Then, 5 cm^3 of a Pd solution (prepared by dissolving 0.5 g of $PdCl_2$ in 100 cm^3 of water containing 1.5 cm^3 of concentrated HCl) was added. After 15 min of stirring at 60 °C, the colour of the solution changed to dark brown. Evaporation to dryness produced dark Pd/PVP colloid.

TEM measurements

Morphology and microstructure were investigated by TEM (Philips CM-20 SuperTwin operating at 200 kV and providing 0.25 nm resolution). Analyses of TEM images were made with the ImageJ program.[29] Specimens for TEM were prepared by dispersing a powder sample in MeOH and placing a droplet of the suspension onto a copper microscope grid covered with perforated carbon.

The Pd and Cl content in the samples were measured using EDS spectroscopy (Edax PV 9800 spectrometer) in an SEM microscope (Philips SEM 515).

Adsorption of hydrogen

Volumetric adsorption measurements were carried out in conventional glass apparatus. About 0.5 g of the catalyst was taken for each experiment. Prior to the adsorption measurements, the P1 or P3 sample was de-gassed for 30 min at room temperature, then reduced in H_2 (250 Torr) at 120 °C for 1 h and de-gassed at the same temperature for 1 h. This treatment was repeated twice to make sure that the Pd was reduced to its metallic form. According to the literature,[30,31] a temperature of 120 °C is high enough to assure complete reduction of the supported Pd. Finally, the sample was de-gassed at 120 °C for 2 h under a vacuum of 10^{-6} Torr and then cooled down in a vacuum to room temperature. Firstly, the total uptake of hydrogen (adsorption at the Pd surface and absorption in the bulk) was measured at room temperature at pressures ranging from 90 to 180 Torr. An equilibration time of 1 h was allowed for each adsorption point. After evacuating the catalyst sample at 10^{-6} Torr for 30 min at the same temperature, a second isotherm, representing only hydrogen absorbed in the Pd bulk (β-hydride), was measured in the same way.

Suzuki–Miyaura reaction (Scheme 3)

To a carefully deoxygenated Schlenk tube (40 cm^3) in an N_2 atmosphere was added 0.031 g of P1, P2 or P3 catalyst (containing *ca.* 1 mg Pd), 1.5 mmol of phenylboronic acid, 2 mmol of base, 1 mmol of 4-bromotoluene or 2-bromotoluene, and 5 cm^3 of solvent (usually ethylene glycol). The Schlenk tube was placed in an oil bath and heated for 3 h with magnetic stirring. After the reaction was complete, the reaction mixture was cooled down to room temperature and 0.075 cm^3 of dodecane was added as an internal standard. The reaction product was extracted with three portions of hexane (4, 3 and 3 cm^3, respectively). The combined extracts (10 cm^3) were analyzed by GC-MS.

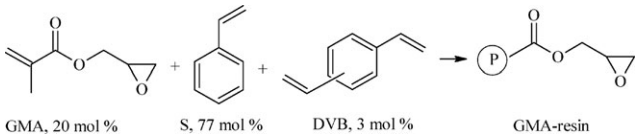
In recycling experiments, the reaction products were extracted from the reaction mixture by the above-described procedure, and the portions of all the new reactants were added to the post-reaction residue.

Results and discussion

Synthesis and properties of GMA resin

Divinylbenzene glycidyl methacrylate resin (GMA) was obtained as a result of the suspension polymerization of a mixture of glycidyl methacrylate, styrene and divinylbenzene (Scheme 1). The resin, containing ~1.3 mmol of epoxy groups g^{-1} was then treated with an excess of a 1,2-diamine (ethylenediamine (EDA) or *trans*-1,2-diaminocyclohexane (CHDA)) in DMF to obtain a diamine-modified polymer (Scheme 2).[32]

An interesting property of GMA resin is its remarkable swelling in CH_2Cl_2, THF, DMF and 1,4-dioxane solvents, but



Scheme 1 Copolymerisation of glycidyl methacrylate—formation of GMA resin.

not in water, MeOH or MeCN.[25] The introduction of diamine into the polymer network decreases the swelling degree (Table 1); however, it remains quite high when appropriate (compatible) solvents are used. Furthermore, the resin retains a good swelling ability in mixed solvents, such as mixtures of THF/water and CH_2Cl_2/MeOH. Consequently, by changing the proportion of the compatible and the uncompatible solvent, the bead volume can be controlled, which makes it possible to encapsulate Pd colloid particles in a network of polymer-bound diamines.

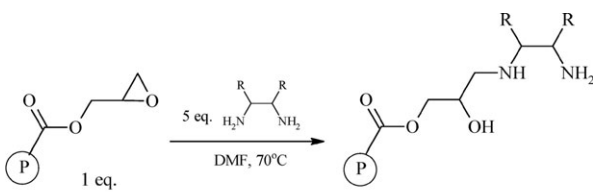
Since the nature of the solvent may be important for the effective attachment of Pd to the polymer, several experiments with different solvents were performed to check the effective replacement of one solvent by another one. These experiments showed that water as solvent cannot substitute CH_2Cl_2 or DMF in the polymer but effectively replaces THF.

The swelling of the polymer with an aqueous solution of hydrazine (64%) (used as a reducing agent for Pd(II) in the catalyst synthesis procedure) was also tested and found to differ considerably compared to pure water. Although hydrazine itself does not swell the polymer, it interacts with the polymer strongly enough to diminish the swelling properties of DMF. The polymer treated first with DMF and next with the same amount of an aqueous solution of hydrazine gave SD = 0.52 g g^{-1}, which means that DMF molecules were dislodged from the polymer by the water-containing hydrazine. Conversely, when the polymer was first treated with the hydrazine solution and then with DMF, a swelling parameter SD = 0.31 g g^{-1} was obtained, which indicates that entry of DMF into the polymer was blocked.

Characterization of supported palladium catalysts (P1, P2, P3)

The first experiments with Pd(0) nanoparticle immobilization on GMA resin were not successful because only a very small amount of Pd was bound very weakly. Much better results were obtained for polymers modified with diamines, and consequently the GMA-CHDA polymer was selected as the support for further experiments.

When preparing the catalysts, the swelling properties of the solvents were carefully considered, and finally DMF was chosen because it strongly interacted with the polymer, while at the same time was a good solvent for $PdCl_2$. During the preparation of the P1 catalyst, the GMA-CHDA resin was first treated with a DMF solution of hydrazine, and then $PdCl_2$ dissolved in DMF was added. In the synthesis of the P2 catalyst, the reactants were added in the reverse order, *i.e.* freshly prepared Pd(0) nanoparticles were introduced to GMA-CHDA. The third procedure was based on direct impregnation of $PdCl_2$ onto the polymer, followed by the reduction of Pd(II) with hydrazine.



Where:
R = H, H for GMA-EDA resin,
R = $-(CH_2)_4-$ for GMA-CHDA resin

Scheme 2 Modifications of GMA-resin.

It may be concluded from the IR spectra (in the region 1500–1750 cm^{-1}) of the polymer-supported Pd catalysts that, most probably, Pd interacts with the oxygens of ester functional groups. The most significant changes in the IR spectra are visible in the region between 1500 and 1750 cm^{-1}, including in particular a decrease in the intensity of the band at 1730 cm^{-1}, a ν_{CO} band very characteristic of the polymer, and the appearance of a new intensive ν_{CO} band at 1656 cm^{-1}. Such changes were observed for all the polymer-supported Pd catalysts (P1, P2 and P3).

The Pd contents of all the three catalysts under study were similar: 3.5% for the P1–P3 catalysts. It is, however, worth noting that the method of preparation has an important effect on catalyst composition, as can be illustrated by the Cl/Pd atomic ratio determined by EDS spectroscopy, which amounted to 0.62, 0.52 and 1.11 for P1, P2 and P3, respectively. During the impregnation procedure, most of the chlorine remains in the catalyst (P3).

SEM studies of the GMA-CHDA resin before and after impregnation with $PdCl_2$ did not show any visible structural changes. The resin beads have different shapes, regular spherical or irregular. The presence of Pd caused only small changes, demonstrated by the polymer particle size decrease, but without shape changes (Fig. 1).

The Pd nanoparticle size determined by XRD was 4.8 nm for P1, 5 nm for P2 and 15 nm for P3. Similar results were also obtained from TEM measurements. The measured histograms, as well as their parameters, are given in Fig. 2 and

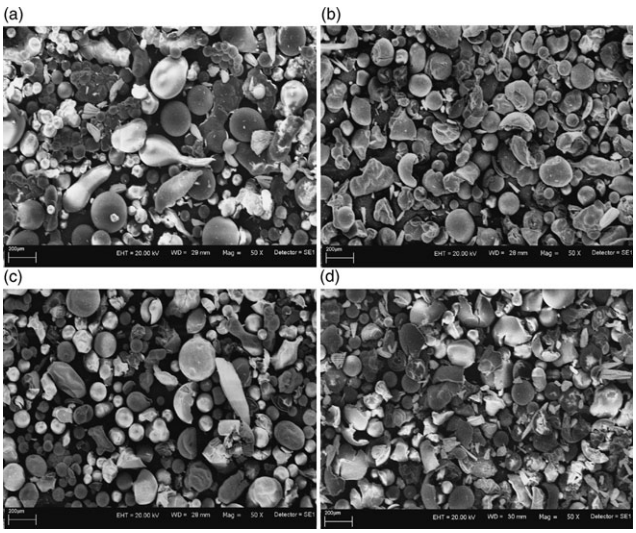


Fig. 1 SEM images of (a) GMA-CHDA polymer, (b) P1 catalyst, (c) P2 catalyst and (d) P3 catalyst.

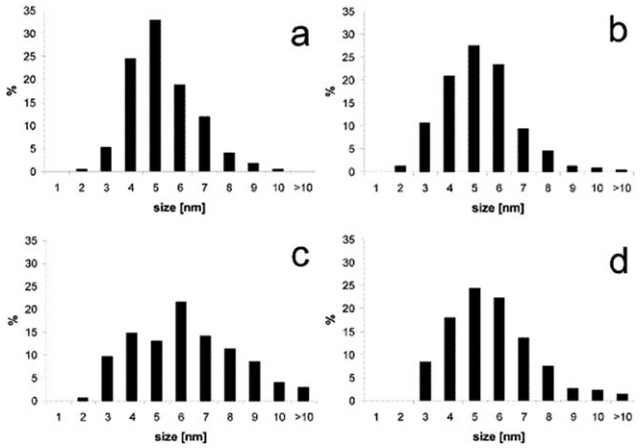
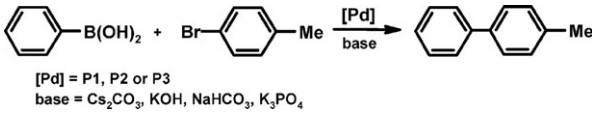


Fig. 2 Pd particle size distribution: (a) P2, (b) P1, (c) P3 and (d) P1 after Suzuki–Miyaura reaction.

Table 2, respectively. Representative TEM images for samples P1, P3 and P1 after the Suzuki reaction are presented in Fig. 3(a)–(c). The TEM results obtained for P2 are summarized in Fig. 4. It appears that the distribution of Pd on the support is rather non-uniform (Fig. 4a). In addition to small, individual particles a few nm in size, there are large aggregates of particles. In a high-resolution image (Fig. 4b), it can be seen that Pd nanoparticles of *ca.* 4 nm are crystalline and exhibit 0.24 nm lattice fringes corresponding to Pd(1 1 1). The SAED (Selected Area Electron Diffraction) pattern obtained from the aggregate in Fig. 4a contains broad rings that could be assigned to Pd (Fig. 4c).

It is known from the literature that hydrogen adsorbed onto supported Pd catalysts is only partly de-gassed at 120 °C.[31] Depending on the kind of Pd catalyst, about 60–80% of the total adsorbed hydrogen remains on the surface of Pd particles. The total removal of hydrogen from the surface of supported Pd catalysts is achieved during de-gassing at temperatures as high as 300–400 °C.[33] In the experimental conditions we used, it was impossible to apply such high temperatures, and consequently, after final de-gassing of the P1 and P3 catalysts at 120 °C, the majority of the adsorbed hydrogen (from the reduction procedure) remained at the Pd surface. For that reason, hydrogen chemisorption was not used to estimate the dispersion of Pd in the P1 and P3 catalysts. However, it was possible to determine the total uptake of hydrogen at room temperature (adsorption/absorption) on pre-treated catalyst samples, and next to determine the amount of hydrogen absorbed in the Pd bulk (β-hydride). This was possible because Pd β-hydride decomposes easily after short de-gassing at room temperature[34]. The results presented in Table 3 clearly show that only Pd in the P1 catalyst was able to form β-hydride, and therefore also to adsorb hydrogen at the surface. In contrast, Pd nanoparticles in the P3 catalyst exhibited no activity in Pd β-hydride formation, indicating that the surface of the Pd particles was totally blocked. This is in agreement with very low catalytic activity of the P3 catalyst (Table 2).



Scheme 3 Suzuki–Miyaura reaction pattern.

Catalytic activity of Pd nanoparticles supported on GMA-CHDA (P1, P2, P3) and Pd/PVP in Suzuki–Miyaura cross-coupling

Catalytic tests on the Suzuki–Miyaura coupling reaction were performed in ethylene glycol, which was selected as the best solvent in preliminary screening experiments (Scheme 3). It is very interesting to note a remarkable difference in the reaction yields obtained with the P1, P2 and P3 catalysts. The highest yield, 90% of biaryl, was obtained in a reaction catalyzed by P1, 42% was produced by P2, whereas P3 was practically inactive. A soluble Pd colloid, Pd/PVP, yielded 79% of 4-methylbiphenyl under the same conditions, slightly less than P1. The low activity of P2 can be explained by the presence of large aggregates of nanoparticles, probably catalytically-inactive. According to TEM results, the P1 and P3 catalysts have similar structures. However, the lack of activity of P3 can be caused by blocking of the active centres by polymers or other molecules, as was shown by chemisorption tests (Table 3).

The catalytic activity of the P1 catalyst was also checked in other solvents, as well as in the presence of different bases. The highest yields (100 and 99%) were obtained in mixtures of DMF and water (1 : 1), and 2-propanol and water (1 : 1), and it is clear that the presence of water increased the reaction yield compared to DMF (0%) and 2-propanol alone (32%). In contrast, the addition of water to ethylene glycol or MeOH

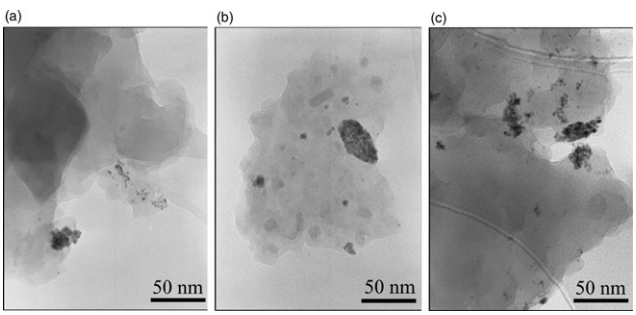


Fig. 3 Representative TEM images of (a) P1, (b) P3 and (c) P1 after Suzuki–Miyaura reaction.

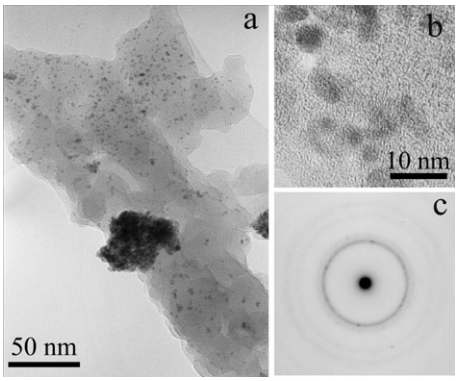


Fig. 4 TEM results for the P2 sample: (a) general view, (b) high resolution image and (c) SAED pattern.

Table 3 Adsorption of hydrogen by P1 and P3 catalysts

Catalyst	Total uptake of hydrogen/ μmol H_2 g cat.$^{-1}$	Hydrogen absorbed in Pd bulk/μmol H_2/g cat.$^{-1}$
P1	28.0	19.1
P3	0.0	0.0

leads to a decrease in yield from 90 to 66% and from 87 to 53%, respectively. High yields were also obtained in ethylene glycol and in 2-propanol–water mixtures at lower temperature (60 °C).

The data in Table 4 do not make it possible to formulate a simple correlation between the catalytic results and the swelling properties of the solvent. However, the best solvents for Suzuki coupling do not cause volume increase in the GMA-CHDA resin.

P1 also catalyzes the Suzuki coupling of 2-bromotoluene with phenylboronic acid with a yield of 88%. Some decrease of reaction yield was observed when the amount of Pd was lower than 0.37 mol% (Fig. 5). It was also checked that after separation of the organic products, the glycol solution was not catalytically active; used as a catalyst, it produced only 1% of 2-methylbiphenyl. This provides evidence that only Pd nanoparticles immobilized on the GMA-CHDA polymer are responsible for the catalytic activity of the system. Additional evidence of P1 catalyst stability was obtained from ICP analysis of the Pd content in the solution after the Suzuki reaction, which confirmed the lack of leaching into the solution (Pd content was below the detection limit).

Fig. 6 summarizes the results of a recycling experiment performed with the P1 catalyst in ethylene glycol. It can be concluded that the second reaction is slower than the first one, but still quite satisfactory results can be obtained after a prolonged reaction time. Similarly, in the third reaction, 86% of 4-methylbiphenyl was obtained after 24 h. To obtain a higher yield of the product in a recycling experiment, it is better not to filter off the catalyst.

Table 4 Effect of solvent and base in a Suzuki–Miyaura coupling reaction catalyzed by P1[a]

Solvent	Base	Yield (%)
Ethylene glycol	Cs_2CO_3	90
Ethylene glycol	K_3PO_4	93
Ethylene glycol	KOH	86
Ethylene glycol[b]	KOH	89
Ethylene glycol	$NaHCO_3$	90
Ethylene glycol–H_2O (1 : 1 v/v)	Cs_2CO_3	66
MeOH	Cs_2CO_3	87
MeOH	$NaHCO_3$	67
MeOH–H_2O (3.5 : 1.5 v/v)	Cs_2CO_3	86
MeOH–H_2O (1.5 : 3.5 v/v)	Cs_2CO_3	53
Dioxane	Cs_2CO_3	1
Toluene	Cs_2CO_3	1
DMF	Cs_2CO_3	0
DMF–H_2O (1 : 1 v/v)	Cs_2CO_3	100
2-Propanol	Cs_2CO_3	5
2-Propanol	KOH	32
2-Propanol–H_2O (4.5 : 0.5 v/v)	KOH	87
2-Propanol–H_2O (3.5 : 1.5 v/v)	KOH	88
2-Propanol–H_2O (1 : 1 v/v)	KOH	99
2-Propanol–H_2O (1 : 1 v/v)[b]	KOH	98

[a] Reaction conditions: [Pd] = 1% mol, [4-bromotoluene] = 0.172 g, [$BPh(OH)_2$] = 0.184 g, 80 °C, 3 h. [b] Reaction at 60 °C.

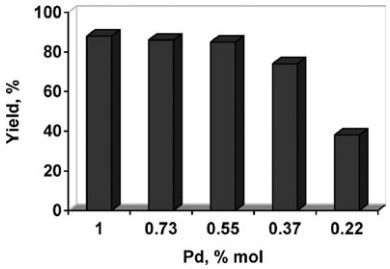


Fig. 5 The yield of 2-methylbiphenyl obtained with different amounts of catalyst P1 in ethylene glycol at 80 °C with Cs_2CO_3 base over 3 h.

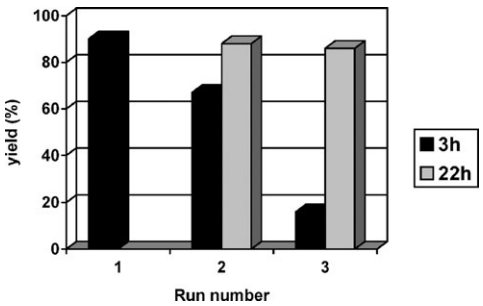


Fig. 6 The yield of 4-methylbiphenyl obtained in recycling experiments with catalyst P1 in ethylene glycol at 80 °C with Cs_2CO_3 base.

Conclusions

A new Pd catalyst obtained by the encapsulation of Pd(0) nanoparticles in a GMA-CHDA polymer acts as a heterogeneous catalyst in Suzuki–Miyaura cross-coupling reactions in different organic solvents. The lack of leaching was confirmed through analysis of the Pd content, as well as by the observation that the post-reaction solution, when used as a catalyst, is practically inactive. In contrast to the PolyHipe catalyst,[17] ours is highly active in the absence of phosphine or other additives.

Catalyst recycling is quite good, but it is complicated by the presence of side products (mainly boron compounds) in the reaction mixture that can block the active centres of the catalyst.

It was found that water has a very interesting effect on the course of the Suzuki–Miyaura reaction. In most cases, the addition of water led to an increase in biphenyl yield; however, recycling of the catalyst from the reaction mixture led to a total loss of activity. Similarly, washing the catalyst with water caused its deactivation.

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