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Palladium Coordination Biopolymer: A Versatile Access to Highly Porous Dispersed Catalyst for Suzuki Reaction

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This work describes a simple procedure to obtain hybrid materials based on palladium alginate acting as heterogeneous catalysts for the Suzuki carbon−carbon coupling reactions. When reacted with Na_2PdCl_4, the carboxylate groups of alginate matrix act as chelating agent for Pd cations, which in turn behave as gelling agent of the support. During further steps of preparation, Pd cations spontaneously reduce to metallic species, and metal nanoparticles are obtained, homogeneously and highly dispersed in the biopolymer matrix. CO_2 supercritical drying leads to porous materials with surface area between 500 and 700 m^2/g. Pure Pd samples show several unsatisfactory properties; mixed Pd, Ca exchanged samples have been therefore considered. These latter materials show high activity for the Suzuki carbon−carbon coupling reactions and the stability of the catalyst allows several reuses with only a slight loss of activity. The intimate contact between host and metal prevents any leaching of active species.

Introduction

Although palladium-based catalysis has been studied to a large extent in the past few years, the main current issues are still the need of specific ligands and the instability of the palladium complexes. Whereas some phosphine ligands, like biphenyl[1] or xanthyl[2] derivatives, form palladium complexes exhibiting very high catalytic activity for cross-coupling carbon−carbon bond forming reactions, unsolved problems are the availability of these ligands and the tendency of the complexes to decompose under the reaction conditions, eventually leading to deactivation of the catalytic system.

One alternative to palladium homogeneous catalysis is to use supported palladium catalysts. The situation in this field is, however, yet less satisfactory than for soluble complexes because the catalytic activity of these solids is remarkably lower than that achieved with soluble palladium phosphine ligands while deactivation still remains to be solved. It is known that the increase in nanoparticle size and the agglomeration of metallic catalysts are involved in the deactivation process. For this reason, many papers have focused on the control of dispersion and growth of catalyst species in host support.[3] Indeed, El-Sayed describes the synthesis and the catalytic activity of palladium nanoparticles prepared in the presence of different stabilizers such as poly(amido-amino) dendrimers, block copolymer polystyrene-b-poly(sodium acrylate) and poly(*N*-vinyl-2-pyrrolidone).[4] However, the synthesis of efficient Pd nanoparticles necessitates a judicious choice of stabilizers type, metal precursor, base, and solvent as well as the reactants used in the reaction system. For instance, although dendrimers provide an effective protective action of Pd particles, strong encapsulation of the latter within the dendrimers results in a loss of catalytic activity. In addition, the common way to prepare metallic nanoparticles is the use of reducing agents as $NaBH_4$ or hydrazine. Unfortunately, this strategy has many drawbacks, such as their relative cost, difficulty in handling, and environmental concerns. Regarding their versatility, the interaction of the reducing agent with the support and the difficulty in controlling the reduction kinetics constitute serious limitations.

Different palladium/polysaccharide heterogeneous catalysts are described in the literature such as Pd/chitosan,[5] Pd/starch,[6] and Pd/arabinogalactan.[7] Unfortunately, these systems present various limitations, e.g., (i) the low surface area of the supports, which decreases the adsorption of the reactants,

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the dispersion of metallic sites, and their accessibility; (ii) The interaction "palladium−support" is unknown and remains under investigation; (iii) palladium immobilization induces a dramatic decrease in catalytic activity as compared to the homogeneous version. The poor stability of these catalysts and the metal leaching constitute major drawbacks, both for selectivity and recycling of the catalyst.[8] Thus, the design of new, simple, and efficient pairs "support/metal" is rather relevant. For catalytic applications, a parameter playing a pivotal role is the texture of the support. Porosity (both meso and macro) can facilitate adsorption of the reactants and desorption of the products, making the catalytic process faster than the nonporous materials. In this context, many works are devoted to the preparation of porous materials and although a new generation of catalysts with highly catalytic performance[6,9] was recently described, it remains a stimulating challenge.

Our research activity in the field of polysaccharide-based porous materials[10] prompted us to investigate the ability of alginate to serve as green support material for palladium heterogeneization. Alginate is a natural block polymer of the mannuronic and guluronic acids, extracted from the cell walls of several brown algae. Because of their biodegradability, biocompatibility, and ready availability, alginates are attracting growing interest as environmentally friendly substitutes for classical inorganic supports. The structure of the ionotropic alginate gels has been described by the so-called "egg-box model" (Figure 1), in which each divalent cation is coordinated to the carboxyl and hydroxyl groups of four guluronate monomers from two adjacent chains of the polymer.[11] This structure confers a high rigidity to the parallel aggregates of polymer chains. The presence of one carboxylate group per pyranosic ring confers to the alginate a cation exchange capacity of 5.6 mmol g^{-1}. For this characteristic, alginate has been employed as adsorbent of heavy metals.[12]

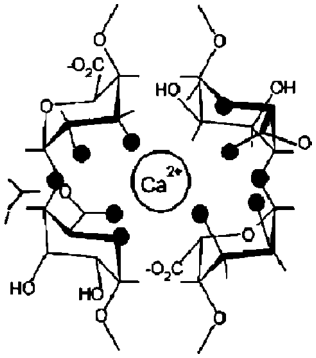

Figure 1. Schematic representation of the chelation of divalent cations between two chains of uronic acid polymer.[11c]

In this work, we report the synthesis, characterization, and catalytic activity of palladium alginate aerogel materials for the Suzuki coupling reaction. When reacted with palladium complex, the carboxylate groups of alginate matrix act as chelating agent for metallic species. At the same time, the palladium, which is the catalytic center, behaves as gelling agent of the support. To the best of our knowledge, the use of palladium as the gelling cation has never been reported.

Experimental Section

Sodium alginate (Sigma medium viscosity from brown algae, viscosity 3500 cps for a 2 wt% aqueous solution at 20 °C, mannuronic/guluronic ratio 1.82 by spectroscopic evaluation[13]) was used as the polymer component. Na_2PdCl_4 and $CaCl_2$ were purchased from Aldrich.

Characterization of Materials. Transmission electron microscopy (TEM) was performed with JEOL 1200 EXII TEM, operated at 120 kV. Nitrogen adsorption/desorption isotherms were recorded in a Micromeritics ASAP 2010 apparatus at 77 K after outgassing the sample at 323 K under vacuum until a stable 3×10^{-5} Torr pressure was obtained without pumping. Sample outgassing was performed at 323 K for all the catalysts to prevent any thermal decomposition of organic polymer or any undesirable evolution of metallic species. The organic polymers suffer from lower thermal stability compared with inorganic matrixes (silica for instance). According to our previous research activity for hydrophilic alginate gel beads,[10b] the optimal activation temperature for nitrogen sorption measurements was found to be 323 K. There are no differences in the amount of water with a higher outgassing temperature, which has to remain lower than 353 K. Surface area and mesopore volume were evaluated by the BET method. The local composition on gel cross sections was analyzed by an energy-dispersive X-ray (EDX) microprobe on a Quanta 200 F from FEI. DRIFT spectra were performed on Bruker vector 22.

Synthesis of Catalyst (Pd/Alginate 17.6). A 1% (w/w) solution of sodium alginate is added drop by drop, at room temperature, to a stirred Na_2PdCl_4 solution (0.068 M) using a syringe with a 0.8 mm diameter needle. The gel beads are left in the gelling solution for 2 h and then filtered and washed with distilled water. Hydrogel beads are then dehydrated in a series of successive ethanol−water baths of increasing alcohol concentration (10, 30, 50, 70, 90, and 100%) for 15 min each. Reduction of palladium occurs during the step of dehydratation with ethanol. The alcogel beads are then dried under supercritical CO_2 conditions (slightly beyond 73 bar and 31 °C) in a Polaron 3100 apparatus, so yielding aerogel beads.

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Table 1. Composition of (Ca, Pd)/Alginate Materials

sample	wt % Pd	wt % Ca
Ca,Pd/alginate (1.3%)	1.3	7.2
Ca,Pd/alginate (2.5%)	2.5	6.3
Ca,Pd/alginate (3.8%)	3.8	6
Ca,Pd/alginate (5%)	5	5.8
Pd/alginate (17.6%)	17.6	0

Synthesis of Catalyst Ca, Pd/Alginate. The 1% (w/w) solution of sodium alginate is added drop by drop, at room temperature, to a $CaCl_2$ solution (0.24 M) under stirring, using a syringe with a 0.8 mm diameter needle. Gel microspheres are cured in the Ca^{2+} solution for 3 h, separated from the cationic solution and washed with distilled water. The spheres are then immersed for 19 h in a solution at different concentrations of Pd (2, 4.1, 6.8, 13.6, 20.4 mM) depending of the % Pd loading required in the solid. The beads are washed with distilled water. Aerogel beads are obtained as described above. Reduction of palladium occurs during the step of dehydratation with ethanol. The catalyst is used as obtained from supercritical drying without any further reduction step. The cation content of the different materials was determined by ICP (plasma with inductive coupling). Labels and metal loading of the materials are reported in Table 1.

General Procedure for the Suzuki Coupling of Halobenzene and Phenylboronic Acid. A solution with halobenzene (3.6 mmol), phenylboronic acid (5.4 mmol), and K_2CO_3 (10.8 mmol) and 5 mL of DMF is prepared in a 10 mL round-bottom flask. The mixture is then stirred and heated in an oil bath at 70 °C. When this temperature is reached, the catalyst (0.4 mol% Pd) is added. The reaction is monitored by GC analysis (Varian 3900, running with a HP-5 column and FID) using nitrobenzene as internal standard.

Three-Phase Test. According to Baleizao et al.[14] a sample of 4-bromobenzamide covalently bound to silica is obtained by reacting in toluene at reflux temperature a suspension of commercial 3-aminopropyl-functionalized silica (Aldrich) and 4-bromobenzoyl chloride in the presence of a few drops of pyridine. The silica functionalized solid is stable under the reaction conditions in the absence of palladium catalyst. Blank controls show that 4-bromobenzoic acid can be recovered from the solid in 60% efficiency by refluxing a suspension of the silica containing attached 4-bromobenzamide in 0.5 M aqueous solution of NaOH for 3 days. The corresponding organic compounds or its derivative could be isolated after blank controls. The resulting silica bound 4-bromobenzamide is reacted with phenylboronic acid and bromobenzene under analogous conditions as those indicated in the previous section. At the end of the reaction, the solids (catalyst, inorganic salts, and functionalized silica) are collected, washed, and submitted to digestion at reflux temperature with an aqueous 0.5 M solution of NaOH for 3 days. After this time, the solution is acidified and the products extracted with CH_2Cl_2. The combined liquid solutions are concentrated under reduced pressure and analyzed by GC. Formation of benzoic acid and 4-carboxybiphenyl is determined by GC-MS.

Results and Discussion

The first solid was prepared using only Pd^{2+} as gelling agent for alginate. Dropping the alginate solution into the Na_2PdCl_4 solution yields yellow-brown hydrogel bead microspheres. During the exchange of water by ethanol, the microspheres turn black because of Pd reduction. After supercritical drying, dark-gray beads are obtained. The aerogel is a macroporous solid with a rather low surface area (52 m^2/g). The loading of palladium was estimated to be 17.6% by elemental analysis (Table 1). With this procedure, it is not possible to control the loading of Pd, which corresponds thus to the complexation of all the available carboxylic groups with the ratio COO^-: Pd of 2. Higher Pd^{2+} concentrations do not incorporate more Pd in the alginate spheres, and lower Pd^{2+} concentrations can not provoke the gelling of alginate. Transmission electronic microscopy (TEM) reveals palladium nanoparticles size of 10−11 nm. Total conversion in the Suzuki carbon−carbon coupling reaction with bromobenzene (Scheme 1), with this solid, is obtained in the first run. Unfortunately, when recycling the catalyst, a conversion of only 30% is reached and crumbling of the material is observed. This is probably due to the reduction and clustering of palladium, inducing a decrease in the number of reticulation sites and thus causing the weakening of the gel, resulting in a low-surface-area material with poor mechanical stability. Moreover, the size of palladium nanoparticles is not really optimized for catalysis and the low surface area limits the accessibility of reactants and the dispersion of palladium particles; these are the main drawbacks of this catalyst.

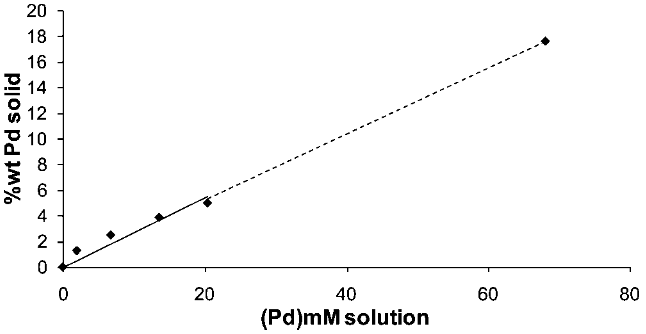
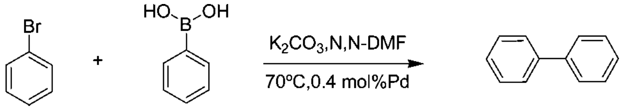


Figure 2. Relation between the wt % Pd solid with respect to the Pd concentration in the solution.

The preparation of highly porous support and the control of the interaction "support-metal" constitute the key point in designing highly active catalyst, as recently reported by Clark et al.[6] With this aim, a new strategy was defined, consisting in use of Ca^{2+} as gelling cation for alginate polymer[11a] followed by exchange of calcium by palladium at different loadings. Eventually, CO_2 super critical drying allows the preparation of Ca- Pd alginate aerogels. Figure 2 shows that the cation exchange allows the control of the palladium loading, as the latter (determined by ICP) is proportional to the palladium concentration in the solution. The last point corresponds to Pd/alginate (17.6%) obtained by the previous procedure.

The textural properties of the resulting materials were investigated by adsorption−desorption of nitrogen. The

Scheme 1. Scheme of the Suzuki Cross-Coupling Reaction between Bromobenzene and Phenylboronic Acid



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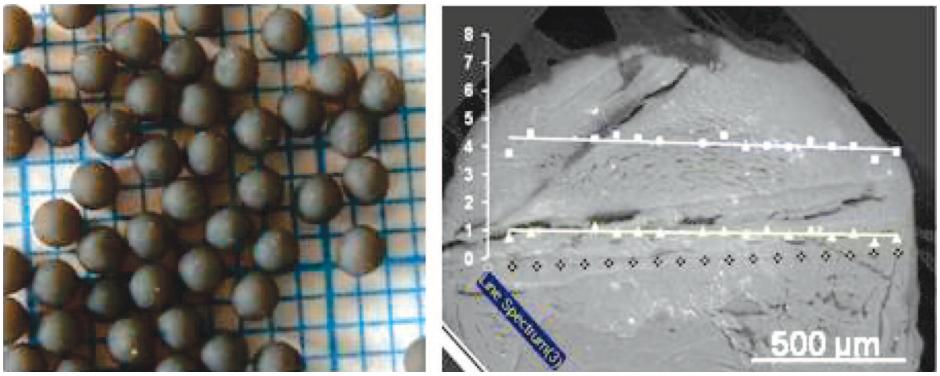

Figure 3. Optical and SEM pictures of the catalyst Ca,Pd/alginate (2.5%). The graphics superimposed represent the at % of Ca (square) and Pd (triangle) along the spheres diameter determined by EDX analysis of a cross-section.

materials are highly porous with surface areas ranging from 390 to 700 $m^2\ g^{-1}$ and mesoporous volumes ranging from 1.8 to 4.8 $cm^3\ g^{-1}$. Comparison with the solid obtained without calcium (Pd/alginate 17.6) shows that the presence of calcium increases significantly the textural properties of the materials because of the strong interactions between alginate polymer and calcium cations.

The beads are spherical in shape and similar in size as shown in Figure 3, which refers to Ca-alginate with 2.5% palladium loading. The size is estimated to 1.6 ± 0.1 mm (average size measured with 20 beads). The radial distribution of calcium and palladium cations in the material beads was determined by energy-dispersive X-ray (EDX) microprobe analysis of a microsphere cross-section. Results indicate that both palladium and calcium loading is rather constant from the core of the sphere to the surface. This confirms the homogeneity and the dispersion of particles in the polysaccharide fibrils indicating the absence of any core−shell structure. The exchange of Ca by Pd is illustrated by the decrease in the amount of Ca when the loading of Pd increased in the materials (Table 1).

Transmission electronic microscopy provides useful information concerning the dispersion of the metallic nanoparticles in the polysaccharide matrix, as homogeneous and highly dispersed palladium particles were obtained (Figure 4). The size and the dispersion depend on the amount of palladium. With 1.3% Pd, homogeneity of the dispersion of Pd was not optimum and the size of particles was close to the size of particles obtained with 3.8% (not shown in the figure). To achieve the best dispersion, the optimum quantity of palladium is found to be 2.5%, after which a significant formation of palladium cluster and aggregation of nanoparticles occurs.

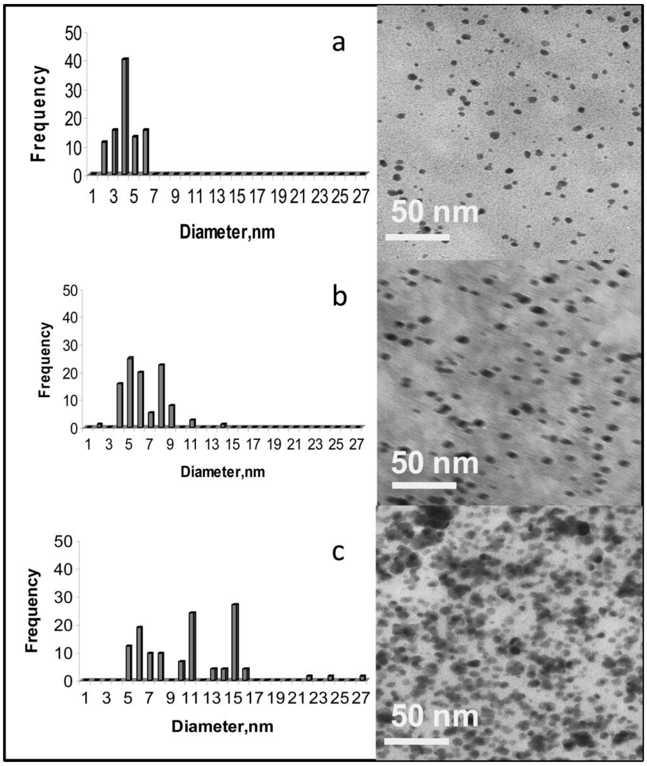

Figure 4. Particle size distributions (from populations of >100 particles) and TEM images of catalysts (a) Pd,Ca/alginate(2.5), (b) Pd,Ca/alginate(3.8), and (c) Pd/alginate(17.6).

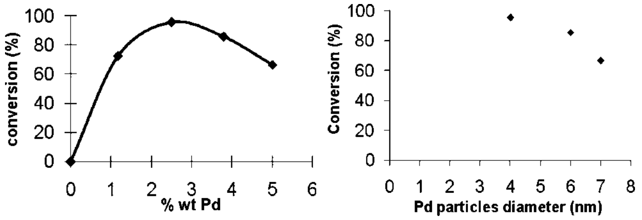

Figure 5. (a) Relation between bromobenzene conversion with Pd loading of the catalyst and (b) with the palladium particles size. [Suzuki reaction with bromobenzene (1.2 equiv of. phenylboronic acid, 0.4% mol Pd/substrate, 3 equiv. of K_2CO_3, *N,N*-DMF, 70 °C, 5 h)].

The catalytic activity of these porous materials at different Pd loading were then assessed for Suzuki carbon−carbon cross-coupling reaction between bromobenzene and phenylboronic acid in the conditions commonly chosen for homogeneous catalysts.[1b,15] Figure 5a illustrates the conversion of bromobenzene at 70 °C reached for materials with various amount of palladium. All tested materials reveal good activity and selectivity toward biphenyl synthesis. The optimum of catalytic activity is achieved for solid loaded with 2.5 wt % Pd (conversion = 95.4% and selectivity = 100%).

The correlation between bromobenzene conversion and the size of nanoparticles confirms the dependency of catalytic

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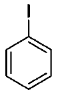
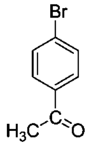
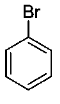
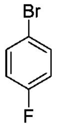
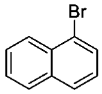
Table 2. Conversion of the Different Substrates in the Suzuki Reaction with Phenylboronic Acid (1.2 eq.) and Ca,Pd/Alginate (2.5%), (0.4% mol Pd/substrate, 3 equiv. of K_2CO_3, *N*,*N*-DMF, 70°C, 5 h)

entry	substrate	Conversion (%)	Selectivity (%)
1		70	100
2		97.2	100
3		95.4	100
4		92.3	100
5		94.2	100

activity with the size of metallic catalyst (Figure 5b). Thus, the higher catalytic activity is obtained for catalyst with 2.5−3.5 nm particles. The increase of size of nanoparticles dramatically decreases the catalytic activity.

The reaction was extended to others substrates with the best catalyst, Ca,Pd/alginate (2.5%). The conversion reached with bromo- or iodo-aryls with Ca,Pd/alginate (2.5%) are reported in Table 2. The results obtained for the bromo-substituted substrates are similar and quantitative conversions are achieved. Interestingly, no homocoupling reaction occurs, so showing the high selectivity of this catalyst. Surprisingly, despite the known higher reactivity of aryl iodide compared to aryl bromide and aryl chloride, in our case, lower conversion is obtained with aryl iodide (entry 1). Nevertheless, this behavior is not unique. It has been reported in the literature that palladium nanoparticles supported on clays also exhibited an unexpected "reverse" catalytic behavior and lower activity than expected for supposedly more reactive aryl halides, including iodobenzene.[16] This finding illustrates the role of the support nature in the catalytic activity.[17]

Compared to the analogous homogeneous reaction systems, the heterogeneous version can be affected by the polarity of the support and the polarity and shape of the reactants.[17] However, these two hypotheses can be ruled out in our case because with para fluoro- and para aceto-bromobenzene, quantitative conversion are reached (entries 3 and 4). The size of the reactant has no influence because 95% of conversion is reached with a sterically hindered naphthalene bromide (entry 5).

When competitive bromo and iodobenzene Suzuki reaction is performed, the normal tendency is observed: 30.5% conversion for bromobenzene and 43.3% for iodobenzene are obtained. Taking into account that the only difference between the two reactants used is the generation of I_2 in the case of the iodobenzene, it was supposed that the latter can act as inhibitor during the catalytic process. In fact, when Suzuki reaction with bromobenzene is performed in presence of a small quantity of I_2, only 31.1% of conversion is reached. The color of the sample (Ca,Pd/alginate) spheres changes from dark brown (typical of zerovalent palladium) before reaction to clear yellow after the reaction. To get insight about the deactivation process, we monitored the state of the catalysts by TEM analyses (Figure 6). Concerning bromobenzene as reactant, a similar nanoparticle distribution was observed before and after catalysis. In contrast, use of iodobenzene as reactant or addition of I_2 in the solution of bromobenzene results in the decrease of the number of particles observable by TEM. This suggests that in presence of iodide, the surface of the particles is oxidized, which can eventually result in its solubilization and loss of catalytic activity.

The recycling of the catalyst was tested for the Suzuki reaction of bromobenzene. After each run, the catalyst was washed with ethanol and dried by supercritical CO_2 in order to desorb any remaining products. The catalyst could be used three times. TEM confirms that after three runs, the distribution of palladium particles remains the same and no metallic aggregation is observed (Figure 7a). This evidence the higher stability of the catalysts under study and the strong interactions between the alginate matrix and the palladium nanoparticles. The decrease in PhBr conversion from 95 to 70% can be explained by the poisoning of pores of the catalyst, limiting the accessibility of other reactants (figure 7b).

To observe the heterogeneous nature of the catalysis taking place in our system and to disprove any possibility of homogeneous catalysis due to the leaching of the palladium into the solution, we performed two different checks of leaching (hot filtration test and three-phase tests). Hot filtration test consists in stopping the reaction at half-conversion and filtering of the catalyst without cooling the solution so as to avoid redeposition of the palladium particles in the support. As shown in Figure 8, after the filtration process, no supplementary conversion was observed, showing the absence of any active species in the solution.

The three-phase test proposed by Davies et al.[18] consists in anchoring one of the reagents onto a solid in addition to using the solid catalyst. In this way, if the process is completely heterogeneous, no transformation should be observed for the anchored reagent, whereas if during the course of the reaction some active palladium species is present in the solution, the anchored reagent will be converted to some degree. Accordingly, *p*-bromobenzoylamide was immobilized onto 3-aminopropyl-functionalized silica gel. This grafted material was added to the reaction medium along with bromobenzene and phenylboronic acid in the presence of the catalyst Ca,Pd/alginate (2.5) using the conditions reported in experimental section. Analysis of the filtrate at the end of the reaction showed 98.5% conversion of

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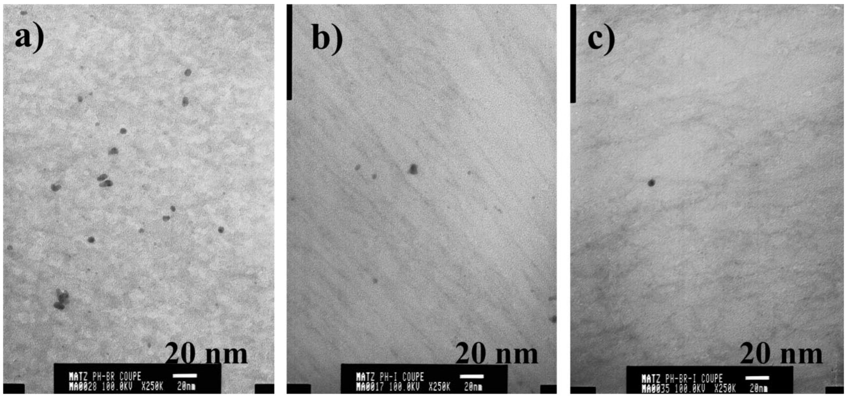

Figure 6. TEM images of the catalyst Ca,Pd/alginate (2.5%) after reaction with (a) PhBr, (b) PhI, (c) PhBr in the presence of I_2.

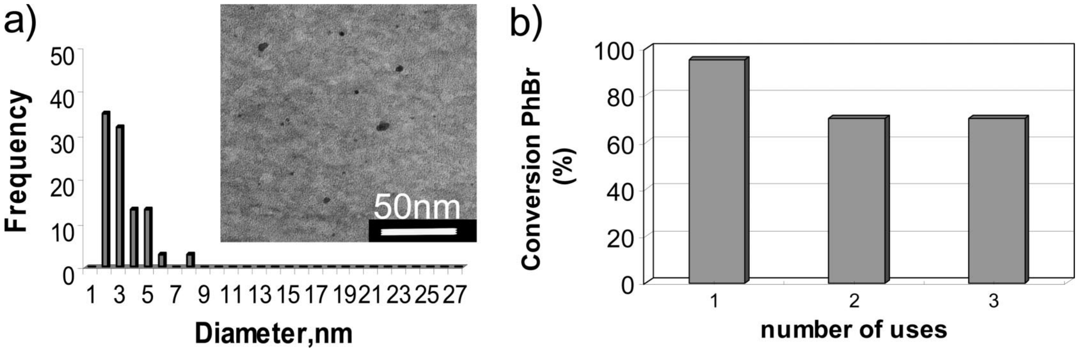

Figure 7. (a) Particle size distributions (from populations of >100 particles) and TEM images of catalysts Pd,Ca/alginate (2.5%) after reaction and (b) representation of the percentage of PhBr conversion at different uses of the catalyst.

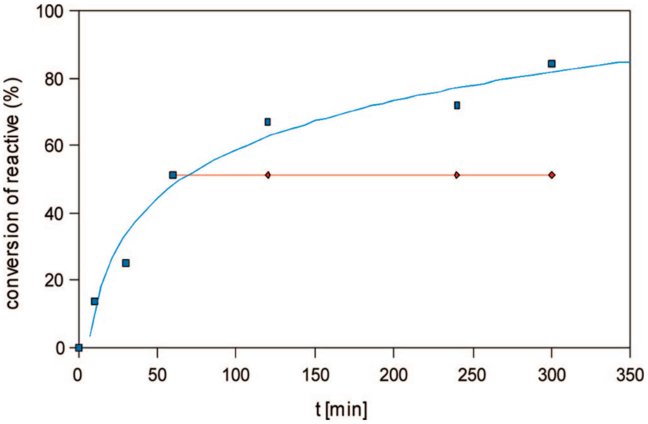

Figure 8. Time conversion plot for the Suzuki reaction of PhBr (1 equiv.), phenylboronic acid (1.2 equiv.), K_2CO_3 (3 equiv.) in *N*,*N*-DMF (5 mL) at 70 °C catalyzed by Ca,Pd/alginate (2.5) (50 mg). One of the reactions (□) was carried out in the presence of catalyst, whereas for the other (◇), the solid was filtered while the suspension was still hot and the clear solution was allowed to continue the reaction.

bromobenzene. The supported compound was brought into solution by hydrolyzing in 2 M KOH, then neutralized with HCl, and isolated as carboxylic acids. After the extraction and evaporation of the solvent under vacuum, the product was analyzed by mass spectroscopy, and no reaction product was detected. This finding highlights the heterogeneous nature of the catalyst. To get more insight on the type of the interactions between Pd nanoparticles and alginate, some IR spectra were recorded. The IR spectrum provides useful information about the chemical environment of carboxylic groups. The free carboxylic acid shows an asymmetrical C=O stretching band at 1745 cm^{-1}. Complexed carboxylate groups exhibit two bands: a strong asymmetrical stretching band (around 1618 cm^{-1}) and a weaker symmetrical stretching band (around 1420 cm^{-1}). The shift wavenumbers corresponding to the asymmetric (ν_{asym}) and the symmetric (ν_{sym}) stretches of the carboxylate group ($\Delta\nu COO^-$) can be correlated with the nature of the cation complexed.[19] In the case of Ca-alginate, $\Delta\nu COO^- = 177$ cm^{-1} and in the case of Pd/Ca-alginate, $\Delta\nu COO^- = 192$ cm^{-1} which prove the exchange of some Ca cations by Pd cations. The values are lower than the value of Na/alginate ($\Delta\nu COO^- = 230$ cm^{-1}), indicating that carboxylic group coordinates the cations in bidentate chelating mode. During the reduction of palladium by ethanol, the protonation of part of the carboxylate groups occurs (evidenced by the apparition of the shoulder at 1745 cm^{-1}). The carboxylic acid is a neutral ligand expected to stabilize palladium nanoparticles. In addition, their stabilization by adjacent hydroxyl groups cannot be completely ruled out. During the catalysis, the base transforms the (COOH) to carboxylate ligand (COO^-), which act as a strong chelating ligand for Pd(II), preventing the leaching of the palladium. Before the recycling, the material was washed with EtOH and dried with supercritical CO_2. At this stage, the neutral ligand (COOH) was generated again. So, the tuneable acidity of the support provides a driving force against palladium leaching. To assess the reaction of K_2CO_3 on the alginate support, we stirred the catalyst under the reaction conditions for several hours and subsequently analyzed it by infrared spectroscopy. The absence of any differences in $\Delta\nu COO^-$

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confirms that all the cations coordinated to carboxylic groups are divalent, rejecting any possible exchange of calcium or palladium by potassium cations.

Conclusions

In this work, the first example of heterogeneous catalysts based on palladium chelated in the framework of alginate biopolymer is reported. The templating effect of the polysaccharide polymer and the electrostatic interactions between the support and the metal allow the preparation of hybrid materials with high stability, allowing the size of metallic particles to be tuned. Palladium nanoparticles are formed during the dehydratation process by immersion of hydrogel beads in ethanol solvent. This strategy appears very simple, fulfills some of the principles of green chemistry, and can be applied to other transition metal complexes.

The textural properties of the material are improved by CO_2 super critical drying method. These catalysts exhibit high activity for the Suzuki carbon−carbon coupling reaction. The catalytic activity depends on the size of the particles and the nature of halobenzene. The intimate contact between alginate and palladium confers them the possibility of the recycling of the catalysts without metallic agregation. The heterogeneous nature of the reaction was evidenced by the hot filtration tests and the three-phase catalysis.

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