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Dramatic Effect of the Gelling Cation on the Catalytic Performances of Alginate-Supported Palladium Nanoparticles for the Suzuki–Miyaura Reaction

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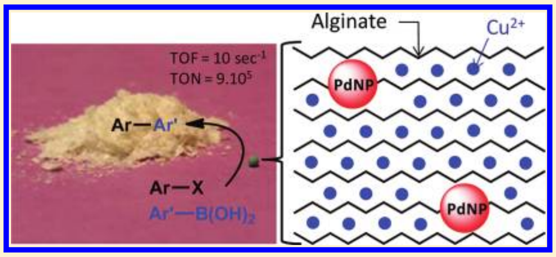
Ⓢ *Supporting Information*



ABSTRACT: This work describes the preparation and characterization of a library of alginate-supported palladium nanoparticles together with their catalytic capabilities to promote the Suzuki–Miyaura reaction. Using the chelating properties of the carboxylate functions of the alginate matrix a series of Ca, Ba, Mn, Zn, Ni, Ce, Cu, and Co alginate gels were first prepared and then reacted with Pd^{2+} salts. Partial exchange of metal cations followed by Pd reduction into palladium nanoparticles and supercritical CO_2 drying generated a panel of bimetallic alginate aerogels. Physical characterizations of these materials showed a significant influence of both the gelling metal nature and the Pd loading on surface areas and nanoparticles size. A comparative study of the catalytic performances of these heterogeneous catalytic systems is then reported for the Suzuki–Miyaura reaction. This study highlighted the superior performances of palladium nanoparticles supported on copper-alginate aerogels. This heterogeneous catalyst showed high catalytic activities as illustrated by a TOF value of 10 s^{-1} and a TON value close to 10^6. The robustness of the catalyst allowed several reuses with no significant loss of activity or metal leaching.

KEYWORDS: *heterogeneous catalysis, polysaccharides, cross-coupling, palladium, boronic acids*

■ INTRODUCTION

The Suzuki–Miyaura coupling reaction has gained wide acceptance in the synthetic community as one of the most powerful tools in C–C bond formation. Many laboratories have developed highly active homogeneous catalyst systems that process challenging combinations of aryl halides and boronic acids[1] and display very high TON and TOF values.[2] Because sustainable development involves the utilization of recyclable catalysts, the search for greener palladium-based catalysts to replace existing homogeneous ones is an important goal. In this regard, supported palladium nanoparticles (PdNPs) have attracted much attention as a major advance in this field.[3] Numerous supports including carbon structures,[4] polymers,[5] dendrimers,[6] micelles,[7] aluminum hydroxide,[8] polyoxometales,[9] gold nanocores,[10] resins,[11] biomolecules,[12] and various inorganic materials[13] have been successfully employed. As most of the mass of these systems is constituted by the support, the development of heterogeneous catalysts using renewable, biodegradable, and inexpensive supports is one important issue.

Recent work in our groups proved that polysaccharides are promising biopolymer supports for heterogeneous catalysis.[14] Polysaccharides have indeed unlimited availability as renewable agro-resources, are biodegradable, and present interesting rheological properties that may be successfully exploited as support for catalysts. Among those polysaccharides, alginate is a particularly interesting anionic biopolymer to create high performance heterogeneous Pd-based catalysts. Alginate, commonly isolated from brown algae, is a linear unbranched polysaccharide composed of (1–4)-linked *β*-D-mannuronate (M) and *α*-L-guluronate (G) monomers that are organized in blocks along the polymeric chains. A particular advantageous characteristic of alginate solutions is their capacity to form hydrogels when exposed to metal cations.[15] The rheology of calcium cross-linked alginate gels has been extensively studied, and their structures have been described by the so-called egg-box model in which each calcium atom is coordinated to the carboxylates and hydroxyl groups of four G monomers from two adjacent chains of alginate.[16] The metal loading capacity of alginate is therefore quite high; it has been estimated at around 5.6 mmol·g^{-1}. Recent investigations conducted by our group[17] proved that simple incubation of such alginate/Ca^{2+} gels in solutions containing Pd^{2+} salts allows partial metal exchange through the gel structure, thus generating a heterogeneous bimetallic alginate/Ca^{2+}/Pd^{2+} gel. The supported Pd^{2+} can then easily be reduced by simple treatment with EtOH to generate PdNPs (Figure 1). Since this alginate/Ca^{2+}/PdNPs heteroge-

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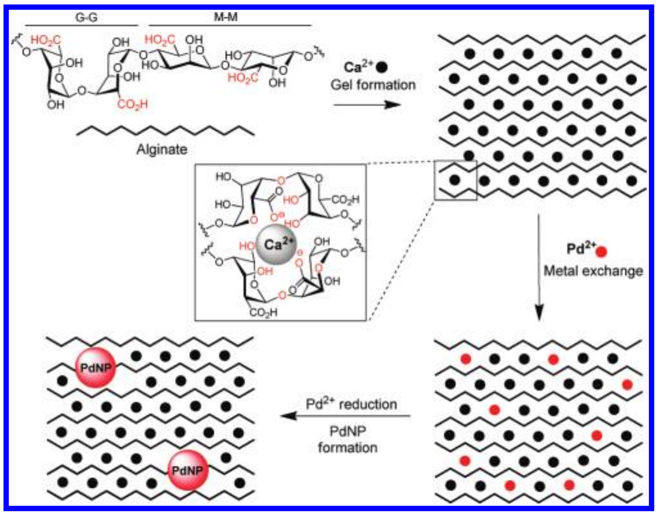


Figure 1. Chemical structure of alginate and schematic presentation of alginate/Ca^{2+}/PdNP preparation.

neous catalyst was found to display interesting features for the Suzuki–Miyaura reaction,[17] we were interested in extending our procedure to the preparation of PdNPs supported on numerous alginate/M^{n+} gels to look at their catalytic activities.

In this contribution we show how our procedure is general and might be applied to many gelling metals M^{n+} allowing the straightforward preparation of a panel of alginate/M^{n+}/PdNPs gels. The resulting bimetallic hybrid catalysts are of prime interest since they combine the textural properties of alginate, the high catalytic activity of palladium nanoparticles and the presence of a second metal species that might influence the catalytic performances. After systematic evaluation of the catalytic properties of these heterogeneous catalysts for the Suzuki reaction, a dramatic influence of the gelling metal M^{n+} was highlighted.

■ EXPERIMENTAL SECTION

Chemicals and Instruments. Chemicals were purchased from Aldrich. Organic solvents (Aldrich) were used without further purification. Purifications of reaction products were carried out by flash chromatography using Merck silica gel (40–63 μm). Melting points (Mp) were obtained on a BÜCHI Melting Point B-540. Infrared spectra (IR) were obtained on a Perkin-Elmer system 2000 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were collected by preparing a KBr pellet containing the title compound. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were measured on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual solvents peaks, and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), and so forth. Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were obtained using an ESI/TOF Mariner Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

Alginate (viscosity 3500 cps for a 2 wt % aqueous solution at 20 °C, mannuronic/guluronic ratio 1.82 by spectroscopic evaluation) was purchased from Aldrich.

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.

Surface areas 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.

General Procedure for the Alginate/M^{n+}/PdNP Preparation. The procedure involves three main steps: (i) the formation of alginate/M^{n+} gels, (ii) partial exchange of M^{n+} by Pd^{2+}, and (iii) reduction of Pd^{2+} to generate PdNP (Figure 2).

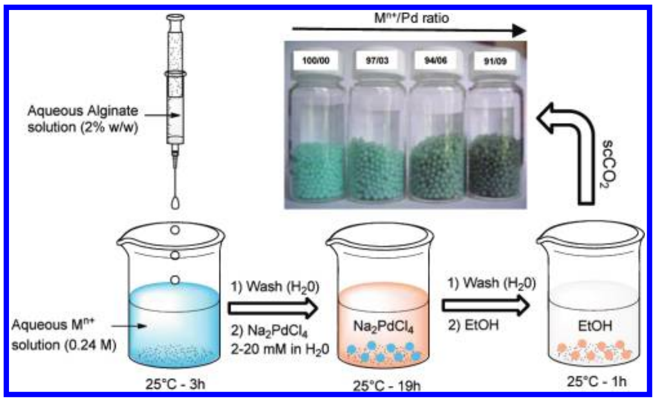


Figure 2. Experimental procedure used to make alginate/M^{n+}/PdNP. Picture of alginate/Cu^{2+}/PdNP beads.

A 2% (w/w) solution of alginate is added drop by drop, at room temperature, to a $M^{n+}Cl^{n-}$ aqueous solution (0.24 M) with stirring, using a syringe with a 0.8 mm diameter needle. Gel microspheres are cured in the M^{n+} solution for 3 h, separated from the solution, and washed with distilled water. The spheres are then immersed for 19 h in a Na_2PdCl_4 aqueous solution containing the exact amount of Pd to ensure the exchange of 3, 6, or 9% of M^{n+} ions in the alginate gel. The beads are 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 dehydration step 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, thus yielding aerogel beads. The catalyst is used as obtained from supercritical drying without any further reduction step.

General Procedure for the Alginate/Cu^{2+}/PdNP-Catalyzed Suzuki Reaction. No precautions were taken to exclude oxygen. One bead of alginate/Cu^{2+}/PdNP (0.2 mg, 18 nmol, 0.01% mol), boronic acid (0.18 mmol, 1 equiv), K_2CO_3 (0.54 mmol, 3 equiv) and aryl bromide (0.18 mmol, 1 equiv.) in 2 mL of EtOH was heated at 70 °C for 14 h in a closed vial. The mixture was separated from the catalyst, and solvent was removed in vacuo to afford after purification on silica gel pure biaryl products.

■ RESULTS AND DISCUSSION

Catalysts Preparation and Characterization. A library of 24 alginate supported M^{n+}/PdNP hybrid catalysts was prepared according to the above-described procedure by using eight different gelling metals and three M^{n+}/Pd ratios (97/03, 94/06, and 91/09). Acidic alginate gels (free of gelling metal) and alginate/M^{n+} gels (free of Pd) were also prepared for comparison. Thus, a total of 36 alginate aerogels were prepared and characterized. First, the metals content of the different materials was determined by ICP (plasma with inductive coupling). The obtained analytical data (Figure 3A and Supporting Information) indicated that the M^{n+}/Pd^{2+} exchange is quantitative in a solution containing the exact number of Pd ions needed for a desired Pd loading and is independent of the nature of the gelling cation.

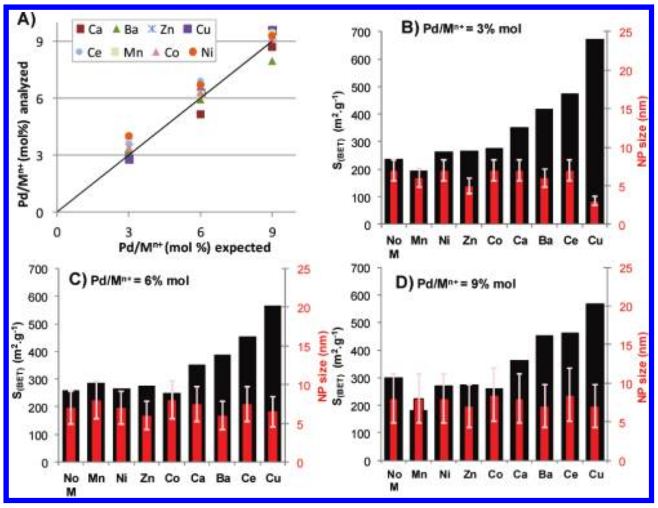


Figure 3. (A) Correlation between expected and obtained Pd/M^{n+} ratios. (B−D) Surface areas and NP size distribution of alginate/M^{n+}/PdNP containing 3, 6, and 9% of Pd compared with M^{n+}.

The surface areas and the size of PdNPs of each alginate aerogel were then determined. Globally, all microspheres dried in supercritical CO_2 provide a porous material with large surface areas (over 200 $m^2 \cdot g^{-1}$, Figure 3B−D) that are entirely accessible due to an open pore structure of the network (pore size > 10 nm according to SEM analysis). A strong influence of the gelling metal nature on the surface areas of alginate/M^{n+}/PdNP aerogels has been observed. Although Mn^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+} did not induce significant change, the use Ca^{2+}, Ba^{2+}, Ce^{3+}, and Cu^{2+} increased the surface areas when compared with the solids obtained without gelling metal M^{n+}. This effect is more particularly observed in the case of Cu^{2+} which doubles the surface area of the aerogel beads.

Extensive TEM analysis of each alginate bead indicated that the size and dispersion of PdNPs depends both on the nature of M^{n+} and on the Pd/M^{n+} ratio. The optimum Pd/M^{n+} ratio was found to be 97/03 which allows the formation of monodispersed PdNPs; higher ratios generated a larger range of sizes and some formation of nanoparticles aggregation. At this Pd/M^{n+} ratio particle size was close to 7 ± 2 nm whatever the gelling metal M^{n+}, except Cu^{2+} for which a particular narrow size distribution was obtained. Physical characterizations of this solid showed palladium nanoparticles of 3 ± 1 nm size (Figure 4) dispersed in a high surface area of 671 $m^2 \cdot g^{-1}$ (Figure 3B). Scanning electron microscopy (SEM) showed an open network of fibrils and a high dispersion of palladium within the network: the same range of metal concentration was found from the external surface to the core of the microspheres (EDX analysis), and no metal agglomeration was observed.

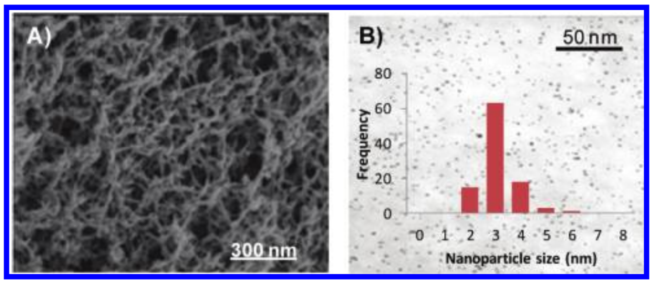


Figure 4. (A) SEM image of alginate/Cu^{2+}/PdNP (97/03). (B) NP size distribution and TEM image of alginate/Cu^{2+}/PdNP (97/03).

Catalytic Properties of the Alginate Materials. The 36 hybrid catalysts were first screened for their ability to catalyze the Suzuki coupling reaction of reactants **1a** and **2a** in a panel of reaction conditions. The fluorescence properties of the coupling product **3a** allowed a rapid screening of the influence of several reaction parameters, including solvents and bases, on the activity and recyclability of the catalyst library. A total of 1296 reactions (catalysts tested in six solvents and six bases) were run and screened in microtiter plates. Each tested catalyst was recovered after the reaction and tested again in three additional catalytic cycles to look at its recyclability. Representative results obtained in DMF in the presence of K_2CO_3 are indicated in Figure 5.

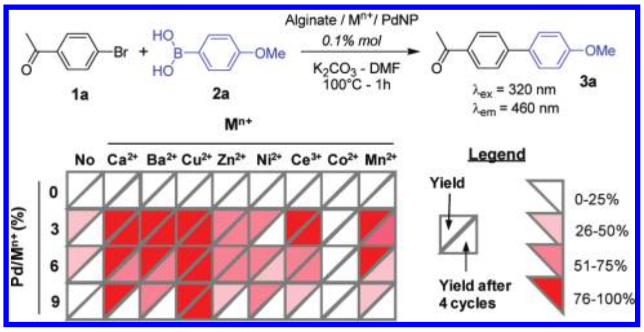


Figure 5. Screening results. Experiments were carried out at 2 mM substrates, 6 mM K_2CO_3, and 0.1% mol of Pd in DMF at 50 °C for 1 h.

The screening results first indicated that the percentage of Pd compared with the gelling metal M^{n+} strongly influences the recyclability of the heterogeneous catalysts: in many cases percentages higher than 3% resulted in loss of catalytic efficiencies even after the first cycle. Deactivation may be due to palladium nanoparticles aggregation and/or textural instability depending on the solvent. In this respect, the alginate/Cu^{2+}/PdNP catalysts were the most recyclable since they displayed intact catalytic efficiency (99% yield of **3a**) after the fourth cycle. This result suggests a better stability of copper cross-linked alginate gels over those obtained with other gelling metals.

The gelling metal also has a strong effect on the catalytic properties of the alginate aerogels, in terms of both activity and recyclability. With the exception of Co^{2+}, all other gelling metals induced a positive effect on the catalytic efficiencies of the alginate supported catalysts. Kinetic experiments conducted with 0.01% mol of Pd showed a particular benefit in using Cu^{2+} as gelling metal (Figure 6).

The high value of alginate/Cu^{2+}/PdNP (97/03) in regard to its efficiency and practicability was further confirmed by a series of experiments conducted at the millimole scale on the target reaction. Only 10 ppm of Pd (10 beads, 2 mg) in EtOH at 70 °C was required for complete conversion of 5.6 g of reactants **1a** and **2a** to the biaryl product **3a** in only 3 h (Table 1, entry 7).

Control experiments conducted with 100 ppm of the alginate/Cu^{2+}/PdNP (97/03) catalyst are in agreement with a heterogeneous catalysis mode. First, the recyclability of the catalyst has been confirmed on six cycles of reaction (Figure 7A). Quantitative ICP analysis of the product from each cycle

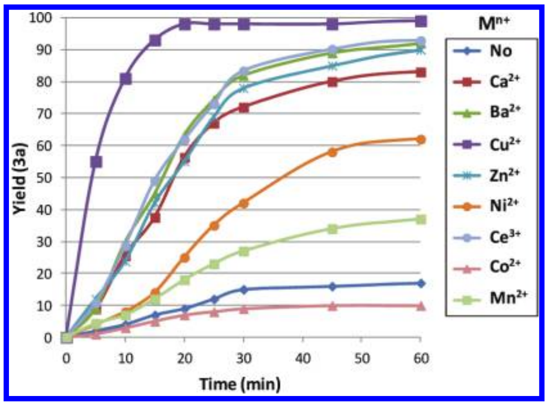


Figure 6. Influence of M^{n+} on the formation of **3a** from **1a** and **2a**. Experiments were carried out at 2 mM substrate, 6 mM K_2CO_3, and 0.01% mol of Pd using alginate/M^{n+}/PdNP (97/03) in DMF at 100 °C for 1 h.

Table 1. Comparison of the Catalytic Efficiencies[a] (TOF values) for the Alginate/M^{n+}/PdNP (97/03) Catalysts Highlighted by Screening

entry	M^{n+}	catalyst (% mol)	time (h)	yield of 3a[b]	TOF (h^{-1})	TON
1	No	0.01	2	39%	1950	3900
2	Mn^{2+}	0.01	2	73%	3650	7300
3	Ca^{2+}	0.01	1	75%	7500	7500
4	Ba^{2+}	0.01	0.75	90%	12000	9000
5	Ce^{3+}	0.01	0.75	91%	12130	9100
6	Cu^{2+}	0.01	0.33	99%	30000	
7	Cu^{2+}	0.001	3	99%	33000	
8	Cu^{2+}	0.0001	26	91%	**35000**	**910000**

[a]Reactions were carried out at 0.1 M for substrates **1a** and **2a**, 0.3 M K_2CO_3 in EtOH at 70 °C. [b]Isolated yields.

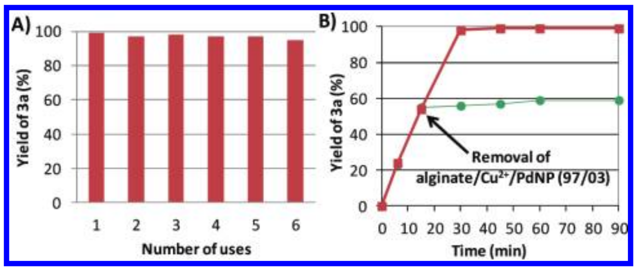
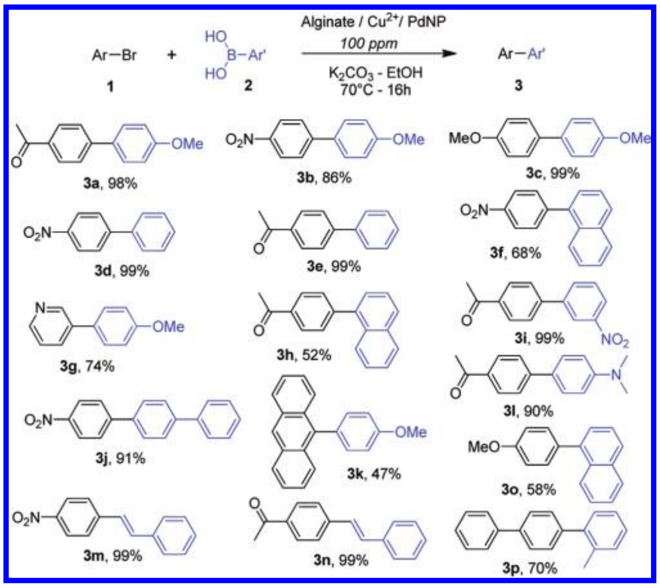


Figure 7. (A) Recyclability of the alginate/Cu^{2+}/PdNP (97/03) catalyst. (B) Control experiment. Kinetics were carried out without removal (red squares) and with removal of the catalyst after 15 min (green ciricles) as indicated by the arrow. Reactions and kinetics were conducted using 0.1 M of substrates **1a** and **2a** and 0.3 M K_2CO_3 in EtOH at 70 °C for 90 min. The catalyst was used at 100 ppm of Pd.

revealed undetectable leaching of palladium and copper. TEM micrographs recorded before and after the reactions showed no evidence of palladium precipitates or nanoparticle aggregation. Second, removal of the catalyst during the reaction stopped the evolution of the coupling reaction (Figure 7B).

To look at the scope of the alginate/Cu^{2+}/PdNP (97/03) catalysis, a series of reactions were conducted with 100 ppm of the catalyst. As shown in Scheme 1, good yields were obtained even with hindered and basic nitrogen-containing starting reactants.

Scheme 1. Suzuki Coupling of Aryl Bromides with Aryl Boronic Acids[a]



[a]Reactions were carried out at 0.1 M for substrates **1** and **2** and 0.3 M K_2CO_3.

The high catalytic properties of the alginate/Cu^{2+}/PdNP catalyst, illustrated by high TOF and TON values (Table 1, entry 8), may be first explained by the atypical physical properties of the material due to Cu^{2+} alginate chelation. The small size of Pd nanoparticles (3 ± 1 nm), their high dispersion within the polysaccharide network, and the high surface area of the material (671 $m^2 \cdot g^{-1}$) may explain the superior activity of this catalyst over those obtained with other gelling metals. However, one cannot exclude a synergic Cu−Pd effect on the catalysis as previously observed for mixed Pd−Cu nanocluster colloids.[18]

Boronic acids are well-known to undergo boronate formation when heated with sugar backbones.[19] We therefore wondered whether such a phenomenon might happen between the boronic reactant and the polysaccharide support and whether it can impact the catalytic reaction. For that purpose we reacted the blue-colored azulene-2-boronic acid[20] with the alginate/Cu^{2+}/PdNP catalyst and found that only 5% of the diols present in the alginate backbone are available for boronate formation. During the reaction the alginate microspheres turn deep blue; no discoloration was observed after several washing with DMF. Upon addition of aryl bromide **1a**, this alginate-supported azulene-2-boronate undergoes complete and rapid conversion to the corresponding Suzuki product **3q** (Figure 8).

Figure 8. Reaction of azulene-2-boronic acid with alginate/Cu^{2+}/PdNP (97/03) catalyst. The structure of the boronate−alginate adduct is hypothetical.

Although this control experiment does not provide unambiguous mechanistic rationale, it proves that boronic substrates may react with the sugar backbone of the catalyst but this phenomenon is, at least, not prejudicial to the catalysis.

■ CONCLUSION

In conclusion, we report an easily recoverable hybrid catalyst which combines the catalytic power of palladium nanoparticles with the architecture of a metal/alginate network that displays high catalytic efficiency for the Suzuki reaction. One of the main advantages of the reported heterogeneous catalysts is the simplicity and inexpensiveness of their preparation. The procedure is easily scaled-up to multigram catalyst preparation with a cost depending almost exclusively on the price of the metal. Besides the fact that the procedure is trivial to run, an added bonus is that it is easy to manage the M^{n+}/Pd ratio simply by changing the concentration of the Pd^{2+} solution used in the incubation step. Recent investigation in our laboratories indicated that the described procedure is easily extended to the preparation of alginate-supported gold and platinum nanoparticles, emphasizing the great potential of this technique.

■ ASSOCIATED CONTENT

Supporting Information

Analytical data for products **3**. Synthesis and fluorescence properties of compound **3a**. S_{BET} and composition of all alginate/M^{n+}/PdNP materials. Reaction with azulene-2-boronic acid. Influence of solvents and bases on the catalytic properties of alginate/Cu^{2+}/PdNP (97/03) catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

PdNP, palladium nanoparticles; TOF, turnover frequency; TON, turnover number

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