Journal of
Materials Chemistry A

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c4ta04200j

An easily prepared palladium-hydrogel nanocomposite catalyst for C–C coupling reactions†

Mitasree Maity and Uday Maitra*

Received 14th August 2014
Accepted 14th September 2014

DOI: 10.1039/c4ta04200j

www.rsc.org/MaterialsA

Supported metallic nanoparticles are important composite materials owing to their enormous potential for applications in various fields. In this work, palladium nanoparticles were prepared *in situ* in a calcium-cholate (Ca-Ch) hydrogel by reduction with sodium cyanoborohydride. The hydrogel matrix appeared to assist the controlled growth as well as stabilization of palladium nanoparticles. The palladium nanoparticle/Ca-Ch hydrogel hybrid was characterized by scanning and transmission electron microscopy, atomic force microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy. Furthermore, the PdNP/Ca-Ch hybrid xerogel was shown to act as an active catalyst for the Suzuki reaction under aqueous aerobic conditions. The PdNP/Ca-Ch xerogel retains its catalytic activities on storage for several months.

Introduction

The design and synthesis of novel hybrid materials with superior properties and application potential has been an active area of research in recent years.[1] Among various hybrid materials those derived through supramolecular hydrogel/organogel routes are easy to design and fabricate. Supramolecular hydrogels can be used to control the spatial organization of nanoparticle assemblies to prepare gel-nanocomposite hybrid materials where gels are used as templates for nanomaterials.[2] The rigid matrices of hydrogels can assist the controlled growth and stabilize nanomaterials. These nanoparticle-gel hybrid materials have a wide range of applications as biosensors, chiral catalysts, nonlinear optics, and in materials science.[3,1b]

A previous report from Shinkai *et al.* described the preparation of silica nanostructures using a cholesterol-based gel as a scaffold.[4] Since then, small molecule-derived gels have been used as templates to direct the growth of nano-sized particles, tubes, helices, ribbons, hollow fibers, *etc.*, derived from metals, metal oxides and other materials.[5] From our laboratory, gel-nanocomposite hybrid materials were reported in which calcium-cholate (Ca-Ch) nanofibres of the hydrogel were used for the synthesis of metal and metal sulphide nanoparticles.[6] Metal nanoparticles are increasingly being used in catalysis owing to several advantages such as narrow size distribution, large surface area and higher efficiency.[7]

Palladium metal has been extensively used for hydrogenation and/or reduction of double bonds and the catalytic formation of C–C bonds with homogeneous catalytic systems based on Pd(II) or Pd(0).[8] Moreover, Pd nanoparticles are being investigated for applications in hydrogen storage, sensing and surface-enhanced Raman spectroscopy (SERS).[9] Palladium nanoparticles have been prepared on various organic/inorganic supports such as zeolites,[10,11] polymers,[12,13] mesoporous silica,[14,15] inorganic oxides,[16,17] graphene,[18–21] carbon nanotubes[22] and activated carbon[23,24] so that they can be used as heterogeneous catalysts. These systems have advantages of easy recovery and reuse of the catalyst. We now report a facile, *in situ* synthesis of uniform sized palladium nanoparticles in a rigid Ca-Ch hydrogel matrix and the use of this hybrid material for C–C bond formation in aqueous media.

Results and discussion

1) Preparation of the palladium nanoparticle-incorporated calcium-cholate hybrid gel (PdNP/Ca-Ch gel)

The synthesis of PdNPs incorporated in calcium-cholate gel was performed according to a recently reported procedure using Ca-Ch as the rigid soft template[6] and potassium tetrachloropalladate(II) as the palladium source. Even though the chemical reduction of Pd(II) salts remains as the mainly used method for the synthesis of Pd(0) nanoparticles,[8] a carefully controlled reaction condition is frequently needed. The availability of an inexpensive and facile method for the preparation of palladium nanoparticles is important due to the unique applications of these nanoparticles. A translucent Ca-Ch gel was prepared by mixing equal volumes of preheated (60 °C)

Department of Organic Chemistry, Indian Institute of Science, Bangalore, 560012, Karnataka, India. E-mail: maitra@orgchem.iisc.ernet.in; Fax: +91-80-2360-0529

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ta04200j

solutions of sodium cholate (60 mM) and $Ca(NO_3)_2$ (120 mM). We found that this gel can be doped with 0.4-4 mM of K_2PdCl_4.

For the preparation of the Pd-doped Ca-Ch gel, aqueous K_2PdCl_4 mixed with sodium cholate and $Ca(NO_3)_2$ were heated separately at 60 °C for 5 min and then mixed rapidly and sonicated for 1 min (ESI†). A translucent yellowish gel was formed (Fig. 1a).

Palladium nanoparticles were prepared *in situ* by adding aqueous sodium cyanoborohydride on the top of the gel. After 10 min a brown color appeared at the interface (Fig. 1b), and after 10 h the entire gel turned deep brown (Fig. 1c), signifying the conversion of Pd(II) to Pd(0).

2) Xerogel preparation/catalyst preparation

The wet gel was freeze dried (Fig. 1d) and was used directly for catalysis. The SEM image of the xerogel showed fibrous networks (Fig. 2) and ICP analysis revealed that the actual Pd content was 0.4 wt% (ESI†). For subsequent discussion, the Ca-Ch xerogel and the Pd(0)-containing the Ca-Ch xerogel will be referred to as **XG** and **XG-Pd**, respectively.

3) Characterization of the PdNP/Ca-Ch hybrid gel (XG-Pd)

A) Scanning electron microscopy (SEM). Gels are known to be formed from one dimensional aggregates with various morphologies such as fibers, tape, twisted ribbons, globules, *etc.*, which cross-link into 3-dimensional networks. SEM images of the Ca-Ch (**XG**) and PdNP/Ca-Ch (**XG-Pd**) xerogels showed that both had very similar three dimensional fibrous network structures. The images also suggested that while the **XG** fibers were smooth, the **XG-Pd** fibers appeared rough, possibly caused by the Pd nanoparticles (Fig. 2, additional SEM images in SI).

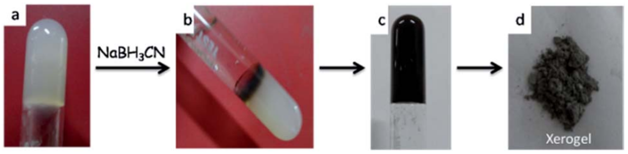


Fig. 1 (a–c) Preparation of PdNPs embedded in Ca-Ch hydrogel fibers and (d) PdNP/Ca-Ch xerogel (**XG-Pd**).

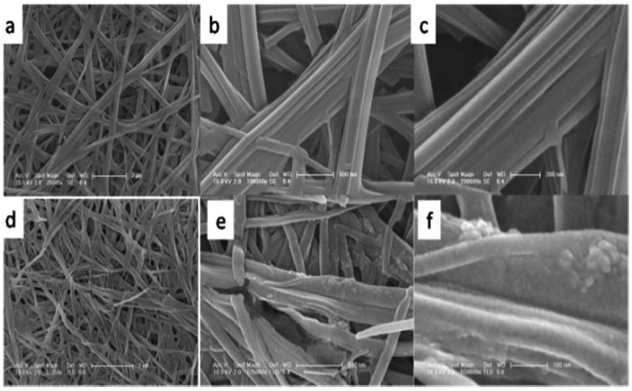


Fig. 2 SEM images of **XG** (a-c) and **XG-Pd** xerogels (d-f); scale bars a, d 2 μm; b, e 500 nm; c 200 nm and f 100 nm.

B) Powder X-ray diffraction. The formation of palladium nanoparticles was confirmed from the wide angle powder XRD pattern of the **XG-Pd** hybrid. The XRD data suggested that the Ca-Ch xerogel was amorphous as no characteristic peaks were observed, while **XG-Pd** showed (Fig. 3) a characteristic diffraction peak at a 2θ value of 39.3° which has been attributed to the (111) lattice plane of Pd nanoparticles.[25] This result indicated that the palladium nanoparticles were formed in the face-centered cubic (fcc) structure. The Pd (111) facets are in general regarded as the active surface in catalysis.[26] The palladium nanoparticles were stable in the xerogel for several (>6) months in a closed container at room temperature.

C) Transmission electron microscopy (TEM) of XG-Pd. To get insight into the morphology of XG-Pd at a higher resolution, TEM images were recorded, which showed the formation of uniform sized spherical palladium nanoparticles on calcium-cholate nanofibers (Fig. 4, additional TEM images on SI). The average particle size was 8.3 nm (Fig. 5a). HRTEM images showed a lattice spacing of 0.228 nm which is consistent with the (111) plane of palladium nanoparticles (XPS data in SI).[27a]

The selected area electron diffraction (SAED) pattern (Fig. 4f) exhibited five diffused rings, which were assigned to the (111), (200), (220), (222) and (311) reflection of face-centered cubic Pd

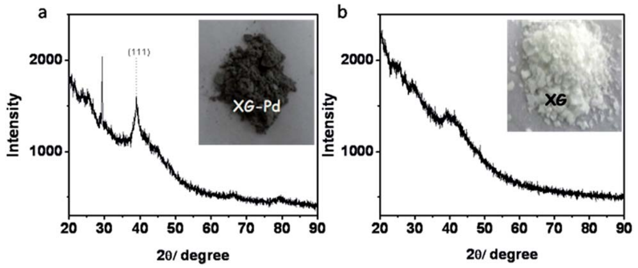


Fig. 3 pXRD of a) **XG-Pd** and b) **XG** (inset photograph of **XG-Pd** and **XG**).

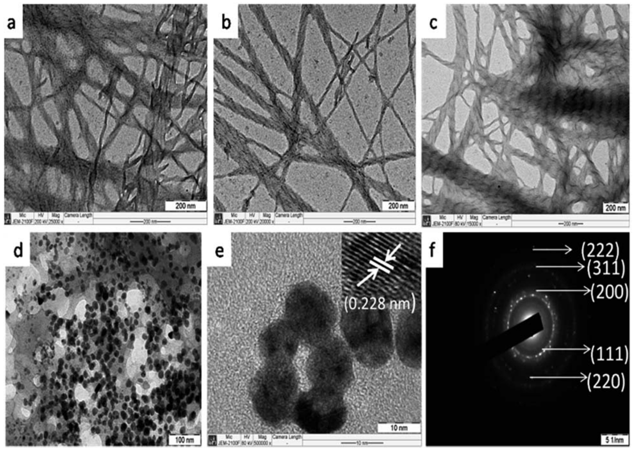


Fig. 4 TEM images of **XG-Pd** fibers (a-c), HRTEM images of PdNPs (d-e), SAED pattern (f); scale bars a-c 200 nm; d 100 nm and e 10 nm.

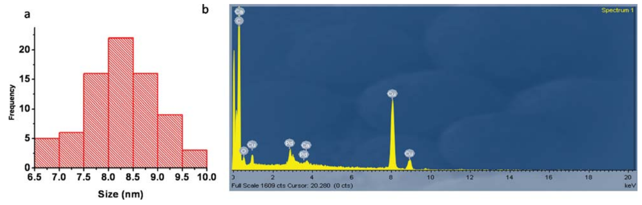


Fig. 5 a) Histogram of palladium nanoparticles and (b) EDX spectra.

nanoparticles, and confirmed the crystalline nature.[27b] The EDX spectrum of **XG-Pd** (Fig. 5b) showed the presence of metallic Pd signals in addition to carbon and oxygen (functional entities).

D) Atomic force microscopy (AFM) images. For further confirmation of gel nanostructure AFM images were recorded (Fig. 6). These were similar to SEM and TEM images showing an entangled 3-D fibrous network where Pd nanoparticle growth was on the fibers.

4) C–C coupling reaction with the palladium nanocomposite xerogel

After thorough characterization of **XG-Pd** we decided to explore the use of the nanocomposite for catalyzing organic reactions. Carbon–carbon coupling reactions with palladium are usually carried out in inert atmospheres in organic solvents in the presence of expensive phosphine ligands. We explored reactions in water under phosphine free conditions.[28] To assess the catalytic activities of Pd nanoparticles in the Ca-Ch xerogel, Suzuki and Sonogashira coupling reactions were done. The amount of Pd in **XG-Pd** was estimated to be 0.4 wt% by the ICP-MS measurement (for details see SI). Therefore, 10 mg **XG-Pd** contained *ca.* 0.37 μmol of palladium. Initially, the reactions were carried out with *ca.* 0.5 mmol of iodobenzene as the limiting reactant.

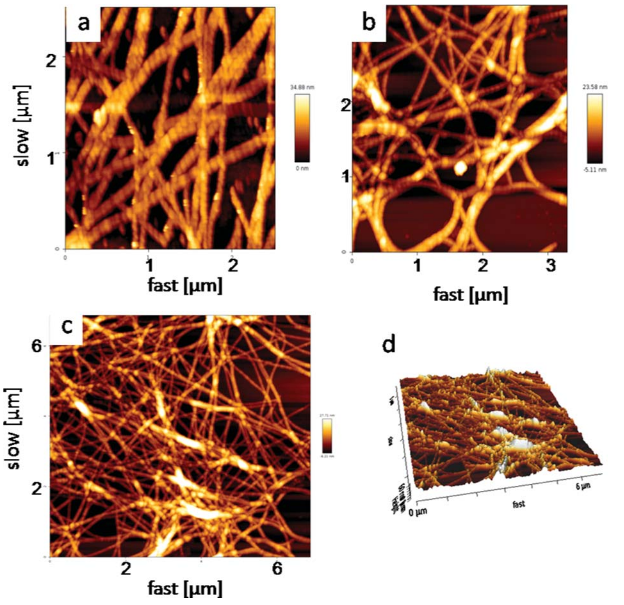


Fig. 6 AFM images (a) XG, (b, c) XG-Pd and (d) 3D view of XG-Pd, formed on mica sheets from the wet hybrid gel.

A) Suzuki reaction. The Suzuki coupling reaction between iodobenzene and phenylboronic acid was carried out with 10 mg of **XG-Pd** and K_2CO_3 as the base at 90 °C in water. The optimal reaction temperature was established by monitoring the coupling reaction of iodobenzene **1** with phenylboronic acid **2** as a function of temperature, from room temperature to 90 °C (Table 1).

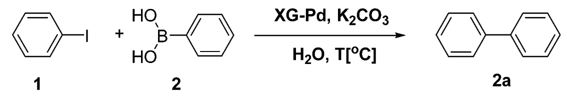
At room temperature only 12% and at 60 °C, about 68% isolated yields were measured, even with a reaction time of 24 h. At 90 °C, 99% yield was achieved in 4 h (TOF = 331 h^{-1}).

For further exploration, 90 °C was chosen as the optimum temperature. As a control, the reaction with the Ca-Ch xerogel without the Pd catalyst showed no detectable product. It is noteworthy that no inert atmosphere was required for this reaction. Also, the reaction with 10% Pd/C under the same reaction conditions (0.07 mol%) with a longer reaction time (10 h) gave 79% yield, while the reaction with K_2PdCl_4 gave 79% yield after 24 h. These results showed a higher catalytic activity of **XG-Pd** compared to the other catalysts.

The reaction scope was also investigated using a broader range of funtionalized aryl halides and phenylboronic acid (Table 2). While many aryl iodides gave good yields, the yield was moderate with aryl iodides with electron-donating groups, such as -OMe and -Me (Table 2, Entries 1 and 2). This outcome is consistent with literature data.[29]

A number of heterocyclic iodides were also successfully coupled to phenylboronic acid with good yields (Table 2, Entries 8-11). In addition, the reaction of pyrene-1-boronic acid with iodobenzene worked well (Table 2, Entry 13). As expected, the reactivity decreased from iodo to bromoarenes and moderate yields (*ca.* 48-90%) were obtained (Table 3). The reaction of chlorobenzene with phenylboronic acid under the standard reaction conditions gave only 9% product. No further improvement was observed for the chloro arene by changing the base and using additives (ESI†).

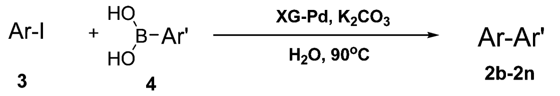
Table 1 Suzuki reaction of iodobenzene **1** and phenylboronic acid **2** with different catalysts as a function of temperature[a]

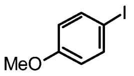
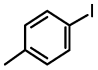
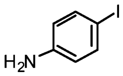
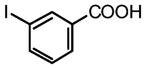
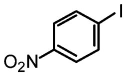
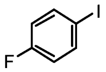
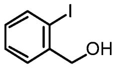
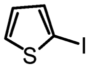
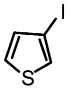
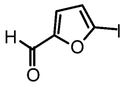
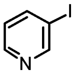
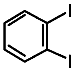
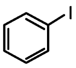


Entry	Catalyst	T [°C]	Time	% Yield[b]	TOF[g]/h
1	XG	90	4 h	Traces[c]	0
2	10% Pd/C	90	10 h	79[d]	103.8
3	K_2PdCl_4	90	4 h	79[e]	246.1
4	XG-Pd	25	24 h	12	—
5	XG-Pd	60	24 h	68	—
6	XG-Pd	90	4 h	99	331
7	XG-Pd	90	4 h	93[f]	615.3

[a] Reaction conditions: Iodobenzene (0.49 mmol), phenylboronic acid (0.74 mmol), K_2CO_3 (0.98 mmol), H_2O (1.0 mL), and XG-Pd (10 mg, 0.077 mol % Pd). [b] Isolated yield. [c] With XG (10 mg). [d] With 0.37 mg 10% Pd/C (0.07 mol% Pd). [e] With K_2PdCl_4 (0.13 mg, 0.08 mol% of Pd). [f] With XG-Pd (5 mg, 0.038 mol % of Pd). [g] Based on the total metal loading (TOF = the number of moles of the product per mole of catalyst per hour).

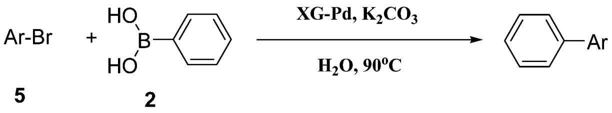
Table 2 Suzuki reaction of various iodo derivatives **3** and aryl boronic acid **4** with **XG-Pd** at 90 °C in water (all the reactions were carried out with phenylboronic acid, except entry 13 in which pyrene-1-boronic acid was used)[a]

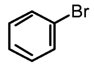
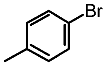
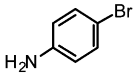
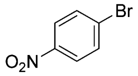
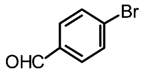
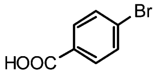
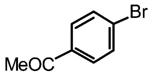
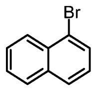


Entry	3	Time	Product	% Yield[b]	TOF[e]/h
1		12 h	2b	60[c]	32.6
2		10 h	2c	59[c]	37.8
3		12 h	2d	78	85.5
4		24 h	2e	43	24.4
5		24 h	2f	88[c]	24.2
6		5 h	2g	93[c]	124
7		18 h	2h	97	71.3
8		11 h	2i	98	117.9
9		12 h	2j	99	109.2
10		8 h	2k	94	156.1
11		12 h	2l	78	85.2
12		9 h	2m	67[d]	50.4
13		12 h	2n	71[c]	39.2

[a] Reaction conditions: Aryl iodide (0.49 mmol), phenylboronic acid (0.74 mmol), K_2CO_3 (0.98 mmol), H_2O (1.0 mL), and XG-Pd (10 mg, 0.077 mol % Pd, 0.37 μmol). [b] Isolated yield. [c] With XG-Pd (20 mg, 0.15 mol % of Pd). [d] 1,2-diiodobenzene (0.25 mmol), phenylboronic acid (0.74 mmol) and product 1,2-diphenylbenzene. [e] Based on the total metal loading.

Table 3 Suzuki reaction of various aryl bromides 5 and phenylboronic acid 2 with **XG-Pd** at 90 °C in water[a]



Entry	5	Time	Product	% Yield[b]	TOF[c]/h
1		12 h	2a	90	49.6
2		12 h	2c	48	26.5
3		24 h	2d	78	21.5
4		12 h	2f	57	31.4
5		24 h	2o	87	23.9
6		24 h	2p	83	22.9
7		18 h	2q	86	31.6
8		24 h	2r	66	18.1

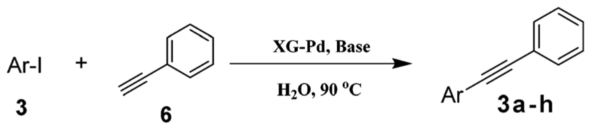
[a] Reaction conditions: Aryl bromide (0.49 mmol), phenylboronic acid (0.74 mmol), K_2CO_3 (0.98 mmol), H_2O (1.0 mL), and XG-Pd (20 mg, 0.15 mol% of Pd). [b] Isolated yield. [c] Based on the total metal loading.

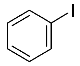
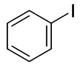
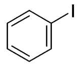
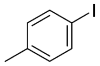
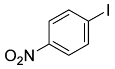
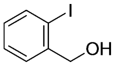
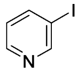
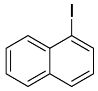
B) Sonogashira reaction. We have also attempted the Sonogashira reaction using **XG-Pd** as the catalyst. The reactions were carried out with iodo arenes and phenylacetylene using **XG-Pd** with pyrrolidine as the base in water at 90 °C without any copper salt (Table 4). But the recyclability of the catalyst was not possible as the catalyst degraded under the reaction conditions. The reaction in general afforded only moderate yields with most substrates, and was not explored further.

C) Catalyst reuse in Suzuki reaction. Since the as-prepared catalyst contains Pd nanoparticles embedded in the xerogel of calcium cholate, and the reaction is carried out in the presence of K_2CO_3, it is likely that under the reaction conditions $CaCO_3$ would form, and the xerogel network may get (partially) destroyed. It was also observed later that phenylboronic acid destroyed the gel morphology completely (ESI†). However, we reasoned that this process might not lead to the destruction (agglomeration) of the Pd nanoparticles and that they will retain the catalytic activity.

(i) "One-pot" reuse of the XG-Pd catalyst. The recyclability of the catalyst was examined for the Suzuki reaction between iodobenzene and phenylboronic acid under standard conditions with 0.11 mol% palladium. After the reaction was completed, the product was extracted out with diethyl ether and the aqueous phase containing the catalyst was used for the next cycle. Fresh iodobenzene (0.49 mmol) and phenylboronic acid (0.74 mmol) were added to the aqueous layer and the

Table 4 Sonogashira reaction of various aryl iodides **3** and phenylacetylene **6** with **XG-Pd** at 90 °C in water[a]



Entry	3	Base	Time	3	% Yield[b]	TOF[c]/h
1		K_2CO_3	24 h	3a	—	—
2		Pyrrolidine	2 h	3a	98	654
3		Piperidine	1 h	3a	94	1254
4		Pyrrolidine	12 h	3b	51	56.2
5		Pyrrolidine	9 h	3c	20	28.2
6		Pyrrolidine	9 h	3d	98	144
7		Pyrrolidine	5 h	3e	44	116
8		Pyrrolidine	20 h	3f	43	27.8

[a] Reaction conditions: Aryl iodide (0.49 mmol), phenylacetylene (0.60 mmol, 1.2 eq), base (2.45 mmol, 5 eq), H_2O (600 µL), and XG-Pd (10 mg, 0.077 mol% of Pd). [b] Isolated yield. [c] Based on the total metal loading.

subsequent cycle was executed (Fig. 7). The same procedure was repeated for additional cycles.

The one pot reuse of the catalyst has an advantage as it avoids the tricky separation of a small amount of the catalyst. The consumption of iodobenzene in the reaction mixture after each cycle was monitored by TLC. The results are shown in Table 5. The catalytic activity decreased slightly after each cycle. In the 4th cycle, the reaction was not complete after 24h and the yield was also decreased to 63%.

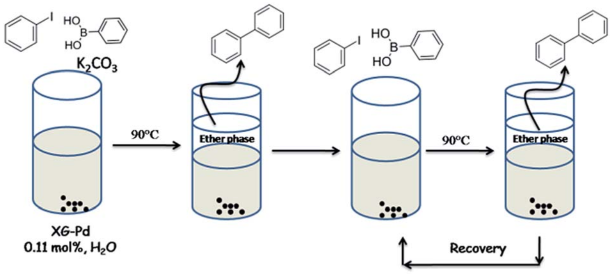


Fig. 7 "One pot" catalyst reuse.

Table 5 "One-pot" recyclability test of **XG-Pd** in the Suzuki cross-coupling reaction of iodobenzene and phenylboronic acid[a]

No	Cycle	Time	% Yield[b]
1	1	4 h	99
2	2	5.5 h	91
3	3	7.5 h	88
4	4	24 h	63

[a] Reaction conditions: Iodobenzene (0.49 mmol), phenylboronic acid (0.74 mmol), K_2CO_3 (0.98 mmol) and H_2O (1.0 mL) at 90 °C, XG-Pd (0.11 mol% Pd). [b] Isolated yield.

(ii) Reuse of the recovered XG-Pd catalyst. In order to understand the data in Table 5, the isolation of the catalyst was attempted after a Suzuki coupling between iodobenzene and phenylboronic acid. After the completion of the first cycle, the reaction mixture was cooled to room temperature, the product was extracted with diethyl ether and the catalyst was recovered by centrifuging the reaction mixture. Filtration and vacuum drying of the catalyst gave a recovery of about 20%. The recovered catalyst was used in the 2nd run under the same reaction conditions as the first (88% yield). Run 3 took a slightly longer time for completion (Table 6). A control experiment showed that phenylboronic acid and K_2CO_3 destroy the xerogel structure, so the amount of recovered xerogel catalyst was reduced. Although the use of large amounts of K_2CO_3 destroyed the gel structure, good catalytic activity remained up to the 3rd cycle. Interestingly, the ICP measurement revealed that the quantity of palladium in the recovered catalyst remained almost unchanged. There was no leaching of palladium in the solution after separation of the product and the catalyst. The palladium content in the (biphenyl) product was less than 2 ppb (ESI†).

D) Catalytic activity of the mother liquor. In order to prove the heterogeneous nature of the catalyst and the absence of Pd leaching, the following reaction conditions were examined. First, the standard reaction was left stirring at 90 °C for 2 h (48% yield, checked by column purification of the product) and then the hot reaction mixture was filtered. A reaction was carried out in this filtrate after adding fresh iodobenzene (0.49 mmol), phenylboronic acid (0.74 mmol) and K_2CO_3 (0.98 mmol) followed by stirring at 90 °C for 5 h. The product yield was only 6%. In another test, after full conversion (4 h, 99% yield), the filtrate was used as the medium as described previously, to give only 7% yield even after 24 h. ICP-MS analysis of the filtrate showed that

Table 6 Suzuki reaction of iodobenzene and phenylboronic acid using recovered **XG-Pd** (**XG-Pd 1**) as the catalyst[a]

Run	Amount of catalyst	Time	% Yield[b]
1st	50 mg	4 h	99
2nd	10 mg	4 h	88
3rd	6 mg	5.3 h	84

[a] Reaction conditions: Iodobenzene (0.49 mmol), phenylboronic acid (0.74 mmol), K_2CO_3 (0.98 mmol) and H_2O (1.0 mL) at 90 °C. [b] Isolated yield.

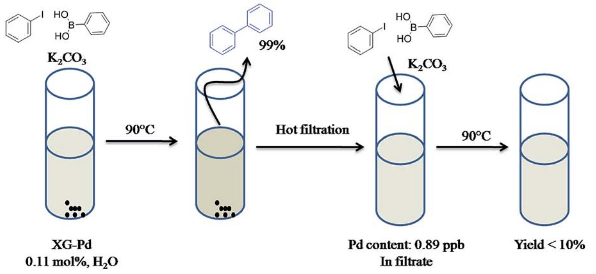


Fig. 8 Catalytic activity of the mother liquor.

the amount of palladium was only <1 ppb. This indicated that leaching of palladium metal in the reaction mixture was negligible and the nature of the reaction was heterogeneous (Fig. 8).

E) Characterization of the recovered xerogel catalyst after the 1st cycle reaction. The loss of mass of XG-Pd after the first cycle was as much as 80%, yet its high catalytic activity prompted us to examine the catalyst recovered after the first cycle. SEM analysis revealed that the morphology of XG-Pd after the reaction was very different (Fig. 9). We confirmed that the morphology of the xerogel did not change by heating only in water, but it changed under the reaction conditions (ESI†).

A flat ribbon like morphology of XG-Pd was absent, and small cubic particles were observed. TEM images (Fig. 10) showed that the size of palladium nanoparticles increased from 8 nm to 30–60 nm of average size, while some smaller nanoparticles (8–10 nm) remained (Fig. 10e). The ICP measurement of recovered XG-Pd showed that percentage of Pd increased in the recovered material to 1.82 wt% (fresh XG-Pd 0.4 wt %). Although the support degraded under the reaction conditions, the amount of palladium before and after the reaction was almost unchanged. This implied that the Ca-Ch support degraded under the reaction conditions and PdNPs were supported on the remaining Ca-Ch xerogel or on the cubic $CaCO_3$ (ESI†).

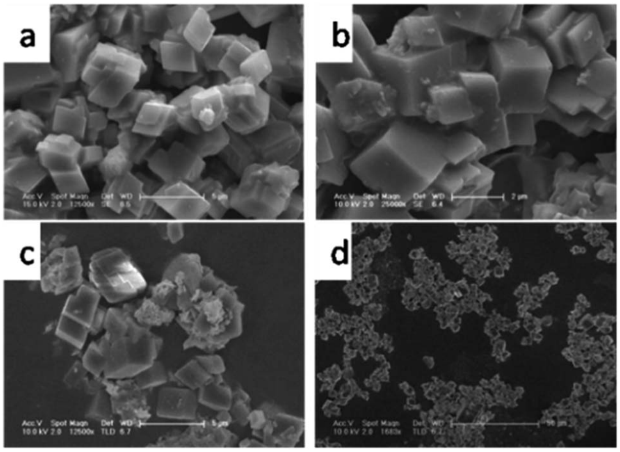


Fig. 9 SEM images of "recovered **XG-Pd**" after cycle1 (a–d); scale bars a, c 5 μm; b 2 μm; and d 50 μm.

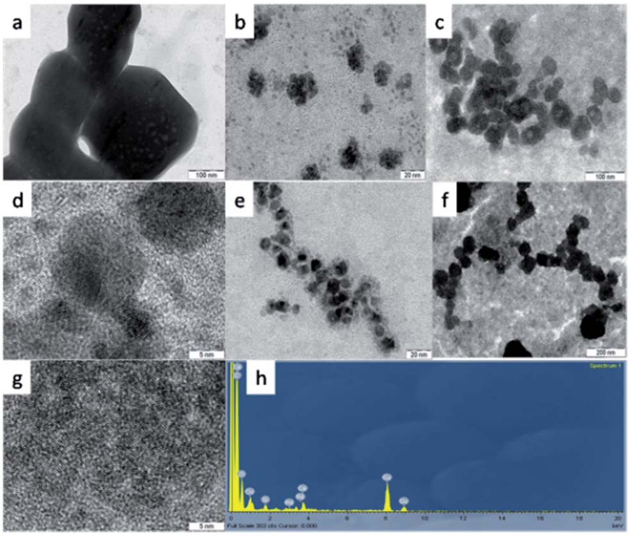


Fig. 10 TEM images (a–f), HR-TEM images of **XG-Pd** 1 (g): crystalline PdNPs with a resolvable atomic lattice and EDX spectra (h); scale bars a, c 100 nm; b, e 20 nm; d, g 5 nm; f 200 nm.

The decrease in the catalytic activity of **XG-Pd** observed in the Suzuki coupling reaction after each catalytic cycle can therefore be caused by the degradation of the Ca-Ch support and increase in the size of the supported palladium nanoparticles during catalysis which made them catalytically less active.

Conclusions

In conclusion, we have demonstrated that a known Ca-Ch gel can be readily adapted to provide new functionalized hybrid gels. The self-assembly of doped calcium cholate gel was used for palladium nanoparticle preparation. The preparation and stabilization of catalytically active PdNPs in a hydrogel support have several advantages, as expensive ligands and organic solvents can be avoided. The xerogel with PdNPs showed good catalytic activity for the Suzuki reaction and could be reused up to 4 catalytic cycles. This xerogel catalyst was stable and active for several months. While the Suzuki reaction conditions employed (hot aq. K_2CO_3) led to the degradation of the xerogel structure, it is expected that the use of neutral conditions would retain the structure and make the hybrid material more useful. This method for preparation of hybrid materials could in principle be adapted to other systems. Such gel networks may be further modified by loading with other nanoparticles and used for their unique applications. Studies along these lines are in progress in our laboratory and these results will be reported elsewhere.

Acknowledgements

We are grateful to the Indo-French Center for the Promotion of Advanced Research, New Delhi for the support of this work through grant no 4805-1. UM also thanks the DST for the award of a J. C. Bose Fellowship. MM thanks the CSIR for a research fellowship.

Notes and references

1 (*a*) A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith, *Angew. Chem., Int. Ed.*, 2008, **47**, 8002; (*b*) D. Das, T. Kar and P. K. Das, *Soft Matter*, 2012, **8**, 2348; (*c*) C. Sanchez, P. Belleville, M. Popall and L. Nicole, *Chem. Soc. Rev.*, 2011, **40**, 696; (*d*) C. Sanchez, K. J. Shea and S. Kitagawa, *Chem. Soc. Rev.*, 2011, **40**, 471; (*e*) H. Liu, K. Wang, L. Zhang, X. Qian, Y. Li and Y. Li, *Dalton Trans.*, 2014, **43**, 432.

2 (*a*) C. S. Love, V. Chechik, D. K. Smith, K. Wilson, I. Ashworth and C. Brennan, *Chem. Commun.*, 2005, 1971; (*b*) S. Bhattacharya, A. Srivastava and A. Pal, *Angew. Chem., Int. Ed.*, 2006, **45**, 2934; (*c*) S. Bhat and U. Maitra, *Chem. Mater.*, 2006, **18**, 4224; (*d*) S. Ray, A. K. Das and A. Banerjee, *Chem. Commun.*, 2006, 2816.

3 (*a*) A. N. Shipway, E. Katz and I. Willner, *ChemPhysChem*, 2000, **1**, 18; (*b*) M. Bahram, F. Hoseinzadeh, K. Farhadi, M. Saadat, P. Najafi-Moghaddama and A. Afkhami, *Colloids Surf., A*, 2014, **441**, 517; (*c*) A. R. Hajipour, Z. Shirdashtzade and G. Azizi, *J. Chem. Sci.*, 2014, **126**, 85; (*d*) Z. Wu, Y. Wu, T. Pei, H. Wang and B. Geng, *Nanoscale*, 2014, **6**, 2738; (*e*) A. L. Gomes, R. Lang, E. Armelin, C. Alemán and J. S. D. C. Campos, *J. Mater. Chem. C*, 2014, **2**, 2502; (*f*) M. C. Orilall and U. Wiesner, *Chem. Soc. Rev.*, 2011, **40**, 520.

4 Y. Ono, K. Nakashima, M. Sano, Y. Kanekiyo, K. Inone, J. Hojo and S. Shinkai, *Chem. Commun.*, 1998, 1477.

5 (*a*) J. H. Jung, Y. Ono, K. Hanabusa and S. Shinkai, *J. Am. Chem. Soc.*, 2000, **122**, 5008; (*b*) J. H. Jung, Y. Ono and S. Shinkai, *Langmuir*, 2000, **16**, 1643; (*c*) G. Roy, J. F. Miravet, B. Escuder, C. Sanchez and M. Llusar, *J. Mater. Chem.*, 2006, **16**, 1817; (*d*) G. Gundiah, S. Mukhopadhyay, U. G. Tumkurkar, A. Govindaraj, U. Maitra and C. N. R. Rao, *J. Mater. Chem.*, 2003, **13**, 2118.

6 A. Chakrabarty and U. Maitra, *J. Mater. Chem.*, 2012, **22**, 18268.

7 A. Balanta, C. Godard and C. Claver, *Chem. Soc. Rev.*, 2011, **40**, 4973.

8 (*a*) C. C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot and V. Snieckus, *Angew. Chem., Int. Ed.*, 2012, **51**, 5062; (*b*) K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem., Int. Ed*, 2005, **44**, 4442.

9 (*a*) M. E. Abdelsalam, S. Mahajan, P. N. Bartlett, J. J. Baumberg and A. E. Russel, *J. Am. Chem. Soc.*, 2007, **129**, 7399; (*b*) S. Choi, H. Jeong, K.-H. Choi, J. Y. Song and J. Kim, *ACS Appl. Mater. Interfaces*, 2014, **6**, 3002; (*c*) Y. E. Cheon and M. P. Suh, *Angew. Chem., Int. Ed*, 2009, **48**, 2899; (*d*) B. Xie, M. Zheng, F. Liu, X. Peng, G. Wang and M. Han, *J. Nanopart Res.*, 2013, **15**, 1746.

10 L. Djakovitch and K. Koehler, *J. Am. Chem. Soc.*, 2001, **123**, 5990.

11 X. Liu, W. Liu, J. Li, Y. Zhang, L. Lang, L. Ma and B. Zhang, *Ind. Eng. Chem. Res.*, 2010, **49**, 8826.

12 J. Li, A. W.-H. Mau and C. R. Strauss, *Chem. Commun.*, 1997, 1275.

13 (*a*) H. Erdoğan, Ö. Metin and S. Özkar, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10519; (*b*) A. K. Shil, N. R. Guha, D. Sharma and P. Das, *RSC Adv.*, 2013, **3**, 13671; (*c*) Y. Yang, S. Ogasawara, G. Li and S. Kato, *J. Mater. Chem. A*, 2013, **1**, 3700.

14 L. Djakovitch, V. Dufaud and R. Zaidi, *Adv. Synth. Catal.*, 2006, **348**, 715.

15 S. E. Hankari, A. E. Kadib, A. Finiels, A. Bouhaouss, J. J. E. Moreau, C. M. Crudden, D. Brunel and P. Hesemann, *Chem.–Eur. J.*, 2011, **17**, 8984.

16 P. D. Stevens, J. Fan, H. M. R. Gardimalla, M. Yen and Y. Gao, *Org. Lett.*, 2005, **7**, 2085.

17 E. Formo, M. S. Yavuz, E. P. Lee, L. Lane and Y. Xia, *J. Mater. Chem.*, 2009, **19**, 3878.

18 G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth and R. Mülhaupt, *J. Am. Chem. Soc.*, 2009, **131**, 8262.

19 S. Moussa, A. R. Siamaki, B. F. Gupton and M. S. EI-Shall, *ACS Catal.*, 2012, **2**, 145.

20 J. Hu, Y. Wang, M. Han, Y. Zhou, X. Jiang and P. Sun, *Catal. Sci. Technol.*, 2012, **2**, 2332.

21 Y. Nishina, J. Miyata, R. Kawai and K. Gotoh, *RSC Adv.*, 2012, **2**, 9380.

22 (*a*) A. R. Siamaki, Y. Lin, K. Woodberry, J. W. Connell and B. F. Gupton, *J. Mater. Chem. A*, 2013, **1**, 12909; (*b*) B. Cornelio, G. A. Rance, M. Laronze-Cochard, A. Fontana, J. Sapi and A. N. Khlobystov, *J. Mater. Chem. A*, 2013, **1**, 8737.

23 X. Sun and Y. Li, *Angew. Chem., Int. Ed*, 2004, **43**, 597.

24 K. Köhler, R. G. Heidenreich, S. S. Soomro and S. S. Pröckl, *Adv. Synth. Catal.*, 2008, **350**, 2930.

25 D. Zhou, L. Ding, H. Cui, H. An, J. Zhai and Q. Li, *J. Power Sources*, 2013, **222**, 510.

26 (*a*) T. M. Gentle and E. L. Muetterties, *J. Phys. Chem.*, 1983, **87**, 2469; (*b*) T. G. Rucker, M. A. Logan, T. M. Gentle, E. L. Muetterties and G. A. Somorjai, *J. Phys. Chem.*, 1986, **90**, 2703.

27 (*a*) D. Berger, G. A. Trăistaru, B. S. Vasile, I. Jitaru and C. Matei, *Univ. "Politeh." Bucharest, Sci. Bull., Ser. B*, 2010, **72**, 113; (*b*) S. Navaladian, B. Viswanathan, T. K. Varadarajan and R. P. Viswanath, *Nanoscale Res Lett.*, 2009, **4**, 181.

28 R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, F. Petrucci, A. Prastaro, S. Niembro, A. Shafir and A. Vallribera, *Green Chem.*, 2010, **12**, 150.

29 B. Inés, R. SanMartin, M. J. Moure and E. Domínguez, *Adv. Synth. Catal.*, 2009, **351**, 2124.