Highly efficient and reusable hydrogel-supported nano-palladium catalyst: Evaluation for Suzuki–Miyaura reaction in water

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ABSTRACT

Ligand-free, palladium-supported, poly(*N*-isopropylacrylamide-*co*-potassium methacrylate) [poly(NIPA-*co*-PMA)] hydrogel nanocomposite with different comonomer ratios were synthesized. The developed hydrogel–palladium composites were characterized by SEM, TEM, UV–vis DRS and XRD. The catalytic performance of these hydrogel–palladium nanocomposites was examined for Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids in an aqueous medium. The hydrogel with comonomer ratio of 8.8:1.6 mmol of NIPA:PMA exhibited optimum catalytic activity, which can be effectively reused 5–6 times without loss of catalytic activity.

1. Introduction

During the last two decades, palladium catalyzed C–C bond forming reactions have gained wide acceptance by synthetic chemists [1–9]. Among them, the Suzuki–Miyaura (SM) [10–12] reaction has become the most popular for accessing biaryls. The organoboranes are used in the SM reactions that are air/moisture stable with relatively low toxicity and easy to be removed as boron-containing by-products [13]. This reaction is used in the synthesis of natural products and widely practiced in the sythesis of pharmaceuticals, herbicides, and natural products as biaryl motif [14]. Natural products possessing such a structural motif are known to display antitumor, antiviral and estrogenic activities, and also present angiotensin II antagonistic or tubulin binding properties [15–24].

Most of the catalysts used in SM reaction are based on palladium phosphine complexes [25–26] or homogeneous nickel [27], which are difficult to recover and therefore economically and environmentally undesirable. Moreover, phosphine ligands are toxic, expensive and suffer from the contamination of the ligand residue in the products. In recent years there has been an increasing interest in heterogeneous catalysts, which are easy to recover and reusable in the aqueous medium for several cycles [28]. Catalytic activity of palladium (Pd) nanoparticles is found as one of the significant frontiers of research that can avoid the formation of phosphines as byproducts in the reaction. In this context, functional resins are considered to be intelligent supports for the immobilization of palladium nanoparticles. Further, reasonable chemical and thermal stability as well as fine tunability of nanostructure and physico-chemical properties make them attractive and environmentally friendly catalysts. Macro-reticular (permanent porosity) and gel (nano-porous in swollen state) type of macromolecular resins are extensively explored for effective immobilization of palladium nanoparticles [29]. Uozumi et al. studied the Suzuki–Miyaura coupling of aryl halides and aryl boronic acids under heterogeneous aqueous conditions by use of a PS-PEG resin-supported palladium-phosphine complex. Selective monoarylation of dibromoarenes was also performed using this catalyst in water [30–32]. Cross-linked polystyrene resins and silica gels have been reported to be useful catalysts for Suzuki–Miyaura reactions but they suffered from low mass transfer and selectivity [33–34]. Template synthesis of homogeneously dispersed and size

controlled metal nanoparticles is possible by using cross-linked hydrogels [35]. The matrices of these functional hydrogels with ion exchange ability are considered to have "nano-reactors" designable for a variety of purposes. The appropriate selection of suitable co-monomers shall influence the physico-chemical features of the nano-reactors that can be tailor-made suitably [36].

Most of the reported literature is based on Pd anchored polymer supports with ligands. Recently, a polymer-supported palladium(II) salen-type complexes has been reported [37] for the coupling of aryl bromides with phenylboronic acid in a mini-continuous flow reactor system. This system requires elevated temperatures and demonstrates small-scale reactions. Palladium-dodecanethiolate nanoparticles [38] and amphiphilic polymer-supported N-heterocyclic carbene palladium complex [39] were reported to catalyze SM reaction. However, they suffer from long reaction times and handling. These polymer-supported Pd ligand complexes enable the SM reaction with aryl chlorides (lower reactivity) as well as aryl bromides and iodides, but the ability of recycling was not found in the case of the aryl chlorides. The ligand-free palladium acetate Pd(OAc)$_2$ was used as catalyst for aryl chlorides at higher temperatures of >150 °C [40–44]. Using water, the green solvent, is an integral part of a chemical manufacturing process. Therefore, it is of great importance to develop a reusable and ligand-free catalytic system for SM reaction in the aqueous medium.

In the present work, we describe the synthesis and characterization of Pd@Poly(N-isopropyl acrylamide-co-potassium methacrylate) [Pd@Poly(NIPA-co-PMA)] hydrogel supports. The catalytic performance of these supports in the SM cross-coupling reaction of aryl halides with aryl boronic acids in aqueous medium and the recycling efficiency are reported.

2. Experimental

2.1. Materials

Methacrylic acid, palladium chloride, N-isopropylacrylamide (NIPA), ammonium persulfate (APS), N,N[I]-methylenebisacrylamide (MBA), N,N,N',N''-tetramethylethylenediamine (TEMED) and hydrazine hydrate were purchased from Aldrich chemicals (Milwaukee, WI, USA). Potassium hydroxide was purchased from S.D. Fine Chemicals (Mumbai, India).

2.2. Preparation of potassium methacrylate (PMA)

Potassium hydroxide (1 mol) solution was prepared in methanol and titrated against methacrylic acid (1 mol) taken in a 500-mL conical flask in methanol. The precipitated white solid (PMA) was filtered and dried in vacuum [45].

2.3. Preparation of hydrogels

Poly(NIPA-co-PMA) was synthesized by simultaneous free-radical cross-linking polymerization.

Polymerizations were carried out employing NIPA 8.8 mmol with varied PMA concentration from 0.4 to 2.0 mmol in the presence of 1 mL of MBA (1 wt.%). The above solution was purged with nitrogen gas for about 5 min to remove dissolved oxygen. Then, the polymerizations were initiated by adding 1 mL of APS (1 wt.%) and TEMED (1 wt.%). Subsequently solution turned into highly viscous liquid and finally formed solid gel within a few minutes at 25 °C. However, the reaction was left for 24 h to complete the reaction. The gels obtained were removed from a petri dish and cut into discs (3 mm high, 12 mm diameter). The hydrogel discs were thoroughly washed with distilled water for 3 days to leach out the un-reacted compounds.

2.4. Preparation of poly(NIPA-co-PMA)-Pd composites

To prepare these composite, 150 mg of dry gel was taken in 100 mL water and allowed to complete swelling for 24 h. After that, these swollen gel discs were utilized for complexation with palladium chloride (15 mg in 150 mL water) and the subsequent reduction reaction was performed with hydrazine hydrate.

2.5. Characterization

X-ray diffraction (XRD) of hydrogel and composites were done on a Rigaku Dmax-γA X-ray diffractometer (Rigaku, Tokyo, Japan) using Cu Kα radiation (λ = 1.54178 Å). Transmission electron microscope (TEM) images were obtained using a Technai-12 model instrument (FEI Company, Czech Republic) at an acceleration voltage of 100 kV. Scanning electron microscope (SEM) studies were performed on a Hitachi S 520 SEM (Hitachi, Tokyo, Japan) under high vacuum, 0.1 Torr, and high voltage of 1.2 kV, by mounting the gold-coated samples on aluminum stubs with double-sided adhesive tape. Diffuse reflectance UV–vis spectra for samples as KBr pellets were recorded on a GBC Cintra 10e UV–vis DRS spectrometer (Cintra, Australia) in the range of 200–800 nm with a scan speed of 200 nm/min.

2.6. Suzuki–Miyaura cross-coupling reaction

A mixture of aryl halide (1 mmol), aryl boronic acid (1.5 mmol), Pd catalyst (1% w/w Pd@GEL5 9.84 μmol Pd), Na$_2$CO$_3$ (3 equiv.), and H$_2$O (8 mL) was added to a 50 mL R.B. Flask fitted with a reflux condenser under nitrogen atmosphere. The reaction mixture was stirred at reflux temperature until the complete consumption of the starting material as judged by thin layer chromatography (TLC).

The reaction was carried out as above. After cooling to room temperature and addition of CH$_2$Cl$_2$ (10 mL), the reaction was vacuum filtered through a Buchner funnel. The organic layer was washed with water, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The pure compound was obtained by column chromatography. The recovered catalyst was washed with CH$_2$Cl$_2$ twice, dried under vacuum at room temperature and reused for further reactions.

All reactions were monitored by thin layer chromatography (TLC) using silica-coated plates and visualizing under UV light. Light petroleum of the distillation range 60–80 °C was used. Yields refer to chromatographically and spectroscopically (¹H NMR, ¹³C NMR) homogeneous material. Air sensitive reagents were transferred by syringe or with a double-ended needle. Evaporation of solvents was performed at reduced pressure, using a Buchi rotary evaporator. ¹H NMR spectra were recorded on Varian FT-200 MHz (Gemini) and Bruker UXNMR FT-300 MHz (Avance) spectrometers in CDCl$_3$. Chemical shift values were reported in parts per million (δ) relative to tetramethylsilane (δ 0.0) as an internal standard. Mass spectra were recorded under electron impact at 70 eV on LC-MSD (Agilent technologies). Column chromatography was performed on silica gel (60–120 mesh) supplied by Acme Chemical Co., India. Thin-layer chromatography was performed on Merck 60 F-254 silica gel plates.

2.6.1. Spectral data for selected compounds

Compound **3b** IR (KBr): ν 2924, 2848, 1693, 1599, 1213, 831, 760 cm^{-1}. ¹H NMR (200 MHz, CDCl$_3$): δ 9.97 (s, 1H), 7.85 (t, 2H, J = 8.5 Hz), 7.65–7.68 (m, 2H), 7.53–7.60 (m, 2H), 7.31–7.40 (m, 3H). ¹³C NMR (75 MHz, CDCl$_3$): 191.9, 147.2, 139.8, 135.1, 130.4, 129.0, 128.6, 127.5, 127.4. Mass: m/z 205 [M+Na]$^+$.
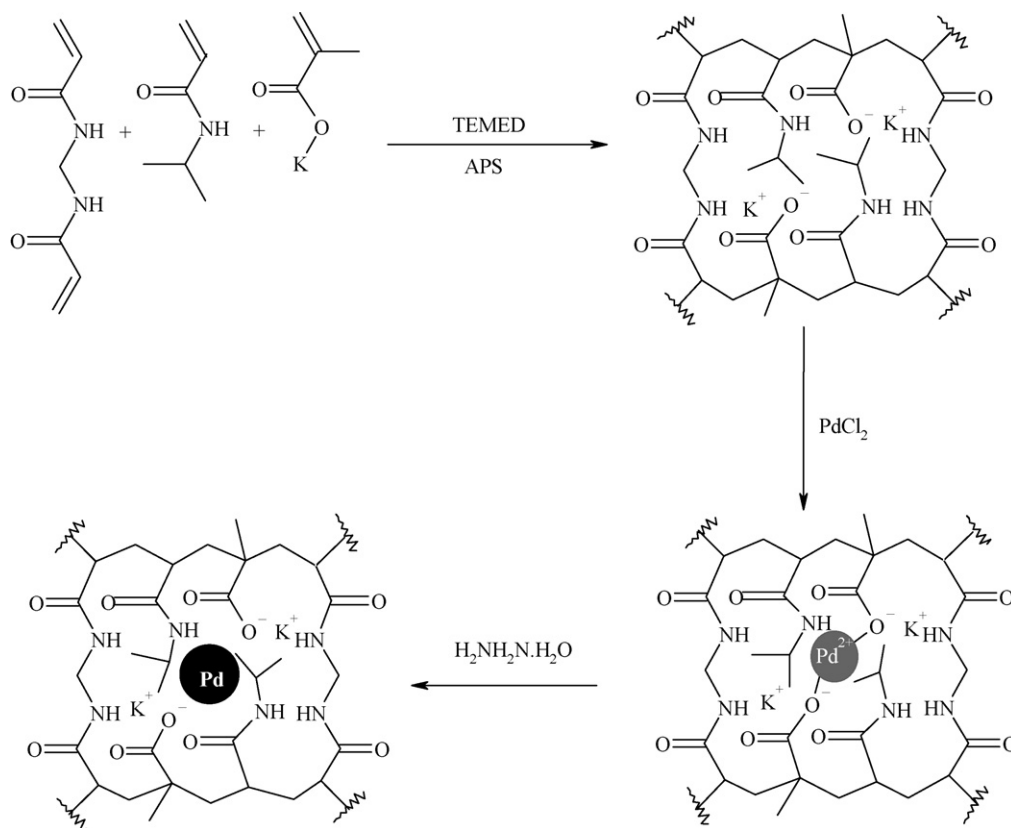
Fig. 1. Schematic representation of synthesis mechanism of Pd@Poly(NIPA-*co*-PMA) hydrogel catalyst.

Compound **3i** IR (KBr): ν 2892, 1603, 1477, 1224, 1039, 759, 696 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.47–7.41 (m, 2H), 7.40–7.19 (m, 3H), 7.08–6.92 (m, 2H), 6.88–6.79 (m, 1H), 5.92 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): 148.0, 147.1, 140.9, 135.3, 131.9, 128.7, 126.6, 120.2, 108.5, 107.6, 100.9. Mass: *m/z* 205 [M+Na]$^+$.

3. Results and discussion

3.1. Preparation of Pd@Poly(NIPA-co-PMA) hydrogel catalyst

We aimed at the preparation of a hydrogel catalyst (Fig. 1) that can anchor the optimum number of Pd nanoparticles, providing complete access to them in water (reaction medium) with a balance attained between the water uptake capacity and gel integrity. The influence of cross-link density of the template using *N,N′*-methylenebisacrylamide (MBA) as a cross-linker and copolymer compositions (NIPA:PMA) on loading capacity and the size of Pd particles were investigated. The plain hydrogel with 0.064 mmol of MBA was chosen based on its higher swelling capacity in water in comparison to the others. The presence of polar moieties (PMA) extends hydrophilicity to the GEL (poly(NIPA-*co*-PMA)) samples in addition to the ion binding property. Six hydrogel formulations with an increased PMA content (0–2 mmol) in the gel were prepared [0.0 (GEL1), 0.4 (GEL2), 0.8 (GEL3), 1.2 (GEL4), 1.6 (GEL5) and 2.0 (GEL6)]. All the three-dimensional functional hydrogel networks can effectively anchor Pd nanoparticles (Pd@Poly(NIPA-*co*-PMA)) [Pd@GEL1–6] by the *in situ* method. Initially, Pd ions were adsorbed from its salt solution into the preformed polymer network by utilizing the ion exchange ability of the methacrylate groups and the co-ordination capability of nitrogen atom in the NIPA of the hydrogel. On complex formation with metal species, they expel water and turn brownish from transparent. Then, the metal ion loaded

networks are treated with the reducing agent, which turn black and regain the original water uptake capacity (Fig. 2a–c). Contribution to the swelling property in water is found to be directly proportional to the PMA content of the gels (Table 1), which indicates negligible participation of NIPA in binding the Pd ions. However, Pd@GEL6 could not maintain the integrity of the gel on swelling and creates problems while handling. A decrease in the swelling ratio for the composites in comparison to the plain gels is due to the additional cross-linking caused by the anchored Pd nanoparticles. It is therefore proved that the Pd particles are immobilized by chemical binding in the hydrogel networks that can reswell on drying and therefore suitable as a recyclable catalyst.
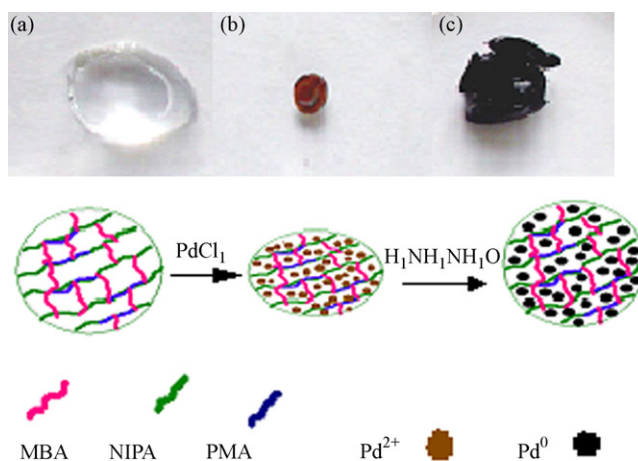

Fig. 2. Swelling images of GEL5: (a) swollen, (b) after complexation and (c) after reduction.

Table 1
Palladium content and swelling ratios of the hydrogel catalyst

S. no.	Gel type	Swelling ratio in water (g/g)			Palladium weight (%) (AAS)
		Before complexation	After complexation	After reduction	
1	GEL1	14.6	14.24	14.18	b.d.
2	GEL2	83.58	10.8	30.71	0.2
3	GEL3	110.07	8.89	47.07	0.58
4	GEL4	120.36	8.31	49.19	0.73
5	GEL5	132.03	10.97	59.23	1.06
6	GEL6	140.03	23.46	95.94	1.26

3.2. Characterization of Pd@Poly(NIPA-co-PMA) catalyst

The metal uptake capacity was found to be directly proportional to the potassium methacrylate content of the gel as indicated by the AAS results listed in Table 1. The TEM images (Fig. 3) show the increase in the number of Pd particles present in the gels with respect to the PMA content. The results are in good agreement with the AAS findings. The narrow size distribution of the Pd particles is noticed in all the gels with an average size of 5 nm. In the aqueous medium, the water uptake capacity of the gels was directly proportional to its PMA content with a maximum for Pd@GEL6. However, Pd@GEL6 could not maintain the gel integrity in the swollen state. An agglomeration of the particles was also noticed. Therefore, Pd@GEL5 (1.6 mmol of PMA) was considered as the best choice for catalytic application in SM reaction because of the optimum-swelling ratio in water, gel integrity, higher metal content and homogeneous distribution of palladium nanoparticles without agglomeration.

Pd@GEL5 was characterized using UV–vis DRS, XRD, SEM, TGA and AAS. The formation of the composite catalyst was confirmed by XRD (Fig. 4) showing a diffraction pattern with broad peaks at 5–20° corresponding to the polymer and Pd at 40.1° (1 1 1) and 46.6° [46–48]. The broad nature of the peaks suggests the presence of very fine particles, which are around 4.6 nm according to Scherrer's equation in agreement with the findings from TEM. The UV–vis DRS spectrum of the catalyst shows a clear absorption at 420 nm (Fig. 5) originating from d–d transition [49]. The absence of this band in the range of 200–800 nm on reduction with hydrazine hydrate confirms the formation of Pd^0. SEM pictures (Fig. 6) show the morphological difference in the porous nature of the plain hydrogel and the catalyst in which the pores are filled with Pd nanoparticles known as nano-reactors that enable access to the reaction medium. The overall thermal stability of the Pd@Poly(NIPA-co-PMA) was also checked with a standard TGA under N_2 atmosphere. An increase in the thermal stability of the hydrogel catalysts was displayed by the shift in degradation temperature from 375 °C of the pure gel to
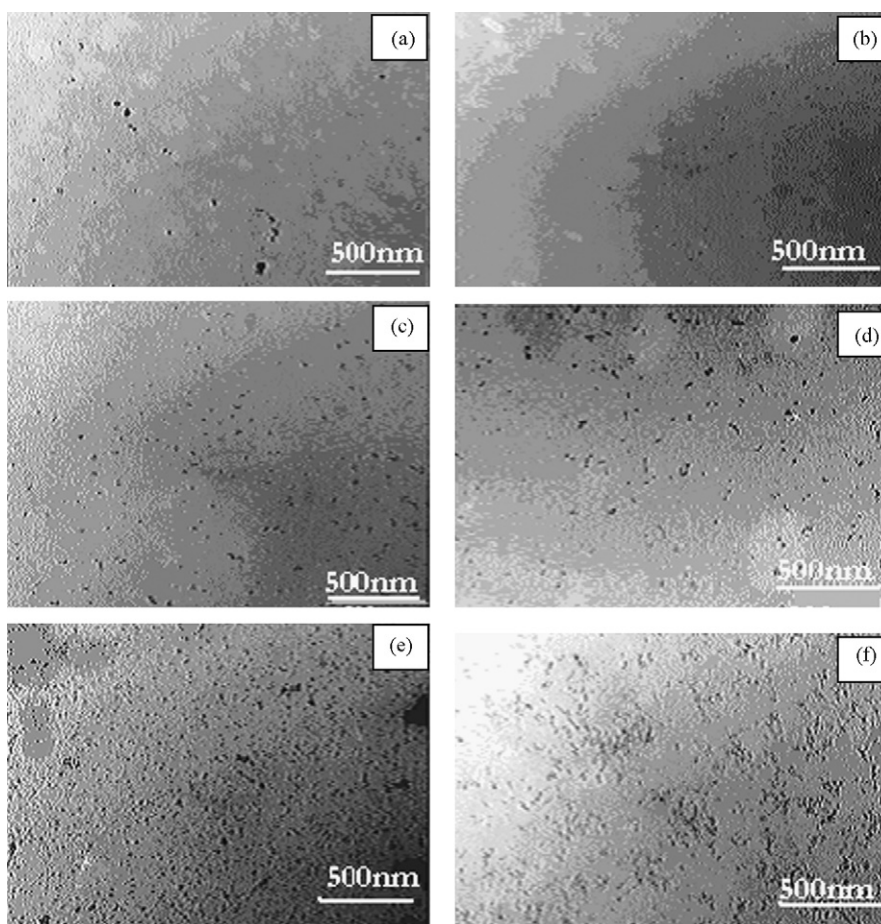

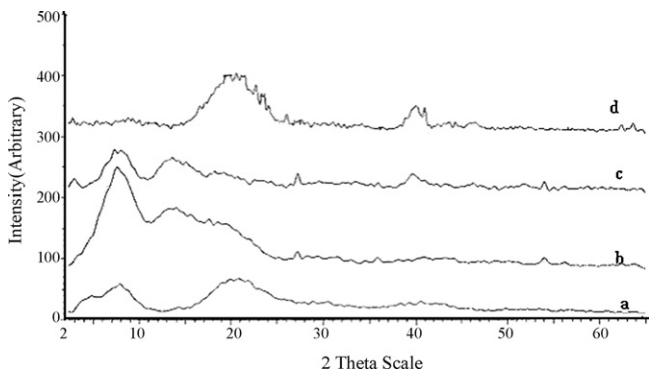**Fig. 3.** TEM micrograph of (a) Pd@GEL1, (b) Pd@GEL2, (c) Pd@GEL3, (d) Pd@GEL4, (e) Pd@GEL5 and (f) Pd@GEL6.

Fig. 4. X-ray diffraction pattern of (a) GEL5, (b) Pd(II)GEL5, (c) Pd@GEL5 and (d) recycled catalyst.

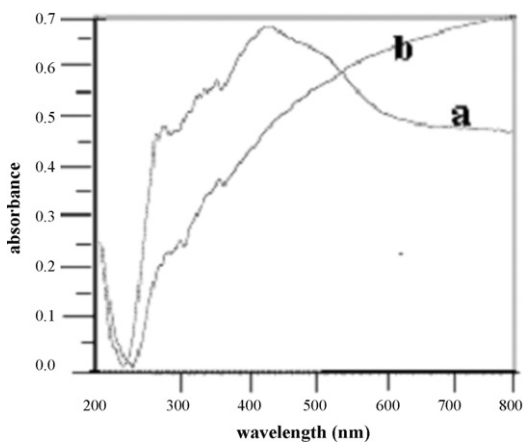**Fig. 7.** Thermograms of (a) GEL5 and (b) Pd@GEL5.

Fig. 5. UV–vis spectra of (a) Pd(II)GEL5 and (b) Pd@GEL5.

420 °C (Fig. 7). The char yield of nanocomposite at 700 °C was 1.5%, which coincides with the metal uptake values found in AAS.

3.3. Catalytic Suzuki–Miyaura coupling of haloarenes

We initially studied the reaction of bromobenzene **1b** with *p*-formylphenylboronic acid **2b** as a model system in the presence of 100 mg Pd@GEL5 and 3 equiv. of Na$_2$CO$_3$. The reaction proceeded in 1.5 h at 90 °C in water to produce the corresponding biaryl product **3b** in 96% yield (Fig.2). The structure of the product was confirmed by spectral data. Encouraged by this result, to demonstrate the utility of the reaction, a diversity of aryl- and heteroarylboronic acids reacted with halobenzenes using the Pd@GEL5 catalyst to
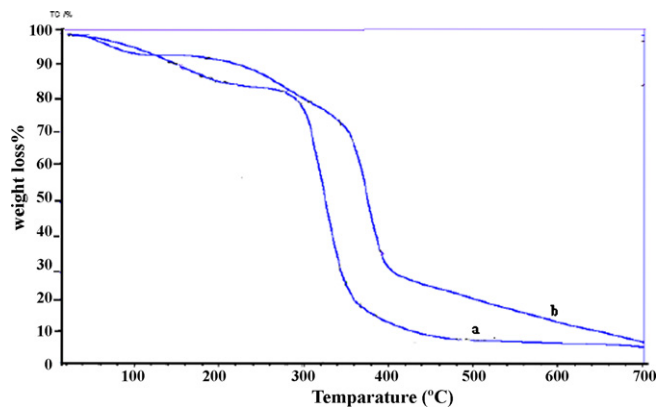
furnish the desired coupled products in excellent yields and the results are shown in Table 2. No obvious difference in the catalytic activity was observed when aryl iodides or bromides were used in the reactions. It was reported that when poly(amidoamine) (PAMAM)-encapsulated Pd^0 nanoparticles were used as catalysts, aryl bromides reacted only at elevated temperature (153 °C in DMF)[50]. However, in the present protocol using Pd@GEL5 catalyst aryl bromides reacted efficiently at 90 °C to produce the corresponding biaryl products in good to excellent yields. Similarly, 4-bromoacetophenone successfully reacted with 4-fluoroboronic acid (entry k) giving 90% yield of biaryl product. In our case 10 μmol-supported catalyst was sufficient to push the reaction forward towards the product formation, whereas 20 μmol of catalyst was used by Oliver et al. [51] for the same reaction.

Under similar conditions, bromo(iodo)benzenes reacted with heteroarylboronic acids such as 3-thienylboronic acid, 3-furylboronic acid and 2-pyridylboronic acid (Table 2, entries g, h and l–q) to give cross-coupled products in good yields in 3 h. Since heterobiaryl derivatives have synthetic importance, these results show the significance of this catalyst. In literature [37], it was observed that 2-bromopyridine did not react with phenylboronic acid using palladium catalysts to provide the corresponding heterobiaryl derivative, but in the present protocol this product formation was achieved by reacting either bromo or iodobenzene with 2-pyridylboronic acid (entries g and h). It was observed that the cross-coupling reaction of aryl halides went smoothly also with *meta*-substituted boronic acids. The generality of the reaction was demonstrated by the reaction of aryl halides with boronic acids incorporating a variety of functional groups. As illustrated in Table 2, the strategy is widely applicable to the preparation of diversely functionalized biaryl products. Regardless of their electronic characters, aryl boronic acids coupled smoothly with
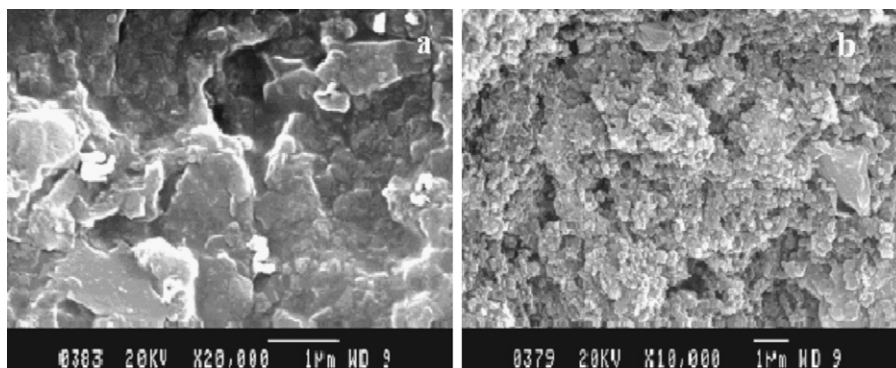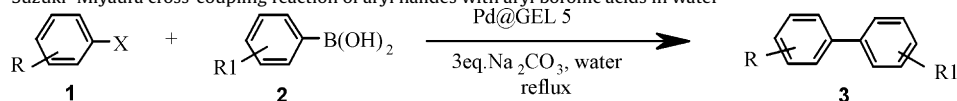

Fig. 6. SEM micrograph of (a) GEL5 and (b) Pd@GEL5.

Table 2
Suzuki–Miyaura cross-coupling reaction of aryl halides with aryl boronic acids in water

Entry	ArX	ArB(OH)₂	time (h)	yield (%)[a]
a	⟨I⟩	OHC–⟨⟩–B(OH)₂	1.5	98
b	⟨Br⟩	OHC–⟨⟩–B(OH)₂	1.5	96
c	⟨I⟩	Cl–⟨⟩–B(OH)₂	2.0	98
d	⟨Br⟩	Cl–⟨⟩–B(OH)₂	2.0	94
e	⟨I⟩	F–⟨⟩–B(OH)₂	2.5	94
f	⟨Br⟩	F–⟨⟩–B(OH)₂	2.5	90
g	⟨I⟩	pyridin-2-yl–B(OH)₂	3.0	98
h	⟨Br⟩	pyridin-2-yl–B(OH)₂	3.0	95
i	⟨I⟩	benzodioxole–B(OH)₂	3.0	92
j	⟨Br⟩	benzodioxole–B(OH)₂	3.5	90
k	CH₃CO–⟨⟩–Br	F–⟨⟩–B(OH)₂	3.0	90
l	⟨I⟩	furan-2-yl–B(OH)₂	3.0	94
m	⟨Br⟩	furan-2-yl–B(OH)₂	3.0	92
n	⟨I⟩	thiophen-2-yl–B(OH)₂	3.0	88
o	⟨Br⟩	thiophen-2-yl–B(OH)₂	3.0	86
p	⟨I⟩	MeO–pyridin-2-yl–B(OH)₂	3.0	92
q	⟨Br⟩	MeO–pyridin-2-yl–B(OH)₂	3.0	90
r	⟨I⟩	OHC–⟨⟩–B(OH)₂	1.5	94
s	⟨Br⟩	OHC–⟨⟩–B(OH)₂	2.0	90

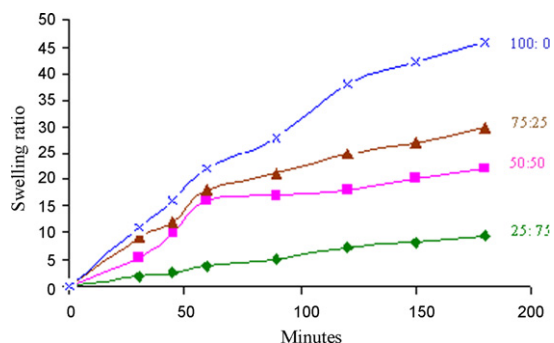[a] Isolated yield after column chromatography.

Fig. 8. Swelling studies of Pd@GEL5 in water:dioxane.

bromo- or iodo-benzene to produce the desired products. In all the cases, the reactions were complete within 1.5–3 h affording the corresponding biaryl and heteroaryl products in good to excellent yields. After examining the set of solvents like H_2O, dioxane, toluene, MeCN, and water as solvent was found to be excellent in these reactions.

3.4. Catalytic efficiency of Pd@GEL5

The regular polymer-based heterogeneous catalysts are insoluble in the organic medium and therefore only the surface metal atoms are accessible to the reactants. However, in the present study the hydrogel swells in the reaction medium leading to nanoporosity. Thus the total number of Pd atoms present in it are accessible to the reactants (Table 2). The Pd@GEL5 catalyst offers an interesting environment for the synthesis of coupling reactions. The original thermoresponsive property of the NIPA network at 32 °C (reversible transition of expulsion of water and reswelling) results in no agglomeration of the Pd particles. PMA serves not only as a source of ion-exchange but also extends hydrophilicity to the gel. A complete access to the metal nanoparticles anchored on the polymer support is a prerequisite for better catalytic performance. In other words, the swelling ratio of the gel with good gel integrity becomes an important parameter for the catalyst. The time taken for completion of the reaction using Pd@GEL5 catalyst was 2 h at 90 °C in a co-solvent mixture of dioxane:water (75:25), a common solvent for model SM reactions shown in Fig. 2. A reduction in the time of reaction was noticed with an increase in the water content of the co-solvent ratio, which happens to be just 1 h 30 min in the pure water medium with 96–98% yields. Thus, it is confirmed that the performance of the catalyst in water medium depends mainly on the swelling capacity of the hydrogel (Fig. 8). It is important to note that the catalyst was separated from the reaction mixture by simple filtration, washed with ethyl acetate and water, dried and reused in the next cycle. It is noteworthy that the recovered Pd@GEL5 catalyst possesses enough catalytic activity for the next coupling reaction. Therefore, the catalyst was repeatedly used five times in the reaction of iodobenzene and *p*-formylboronic acid (Table 2, entry a) under similar conditions. Although the catalytic activity was gradually diminished, the yield was still 86% even in the sixth reuse. The salient features of this protocol are mild, environmentally benign, phosphine-free reaction conditions using water as solvent, simple operation, and high-product yields with reduced reaction times.

4. Conclusions

The synthesis of Pd@GEL5 catalyst with homogeneously anchored Pd nanoparticles generated *in situ* on the hydrogel networks using the chemical reduction method has been described.

The methacrylate groups were employed as a protocol to make a bridge between Pd nanoparticles and the gel. A large number of Pd nanoparticles with 5 nm in diameter are found strongly attached to Pd@GEL5 in comparison to the others. The efficiency of these gel catalysts was demonstrated for the Suzuki–Miyaura reaction of aryl halides with arylboronic acids. The advantages using Pd@GEL5 were: use of water as a solvent, recoverability and reusability of the catalyst (six runs) and high yields (98%) of products in less reaction time (1 h 30 min to 3 h) taken for the completion of the reaction. The study has revealed that the hydrophilicity of the catalyst and its swelling in the water medium played a decisive role in determining the catalytic performance. The advantages of the present protocol are mild, efficient, environmentally benign and ligand-free reaction conditions using water as solvent, operational simplicity, and high-product yields.

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