

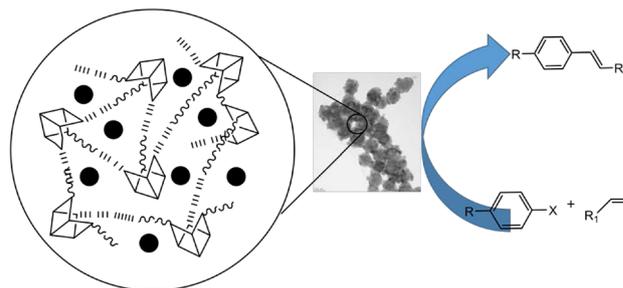
# POSS-Based Covalent Networks: Supporting and Stabilizing Pd for Heck Reaction in Aqueous Media

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**Abstract** Palladium nanoparticles supported on Incompletely Condensed Polyhedral Oligomeric Silsesquioxane (IC-POSS) based poly (Acrylamide-co-Hydroxy ethyl methacrylate) as a novel nanohybrid catalyst were synthesized and characterized. This catalyst was found to be an efficient and reusable heterogeneous catalyst for the Heck reaction using water as the solvent in the absence of a phosphine ligand and phase transfer catalyst.

## Graphical Abstract



**Keywords** Polyhedral Oligomeric Silsesquioxane · Hybrid copolymer · Heck reaction · And radical polymerization

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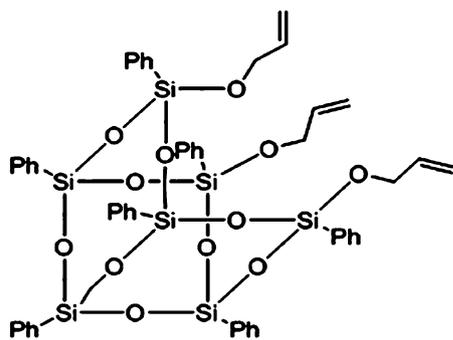
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## 1 Introduction

Coupling of olefins with vinyl or aryl halides is commonly called Heck reaction. It is one of the most important methods for C–C bond formation in organic chemistry in the synthesis of various pharmaceutical intermediates facilitated by palladium (Pd) nanoparticles [1, 2]. Traditionally Heck reaction is carried out in organic solvents with homogenous Pd complexes as the catalyst [3]. Heck reaction carried out in homogeneous media has several limitations and drawbacks such as product contamination by catalyst [4], laborious purification, low catalytic activity [5] and difficult to recover and reuse the catalyst [6, 7]. Aggregation of Pd nanoparticles (NPs) greatly reduces catalytic activity and selectivity of Pd. As a result, various insoluble solid supports such as porous silica [8, 9], Alumina [10], ionic liquids [11], and polymers [12, 13] have been used to immobilize palladium NPs to reduce their aggregation.

For polymeric supports, catalytic activity in organic media is strongly dependent on hydrophilicity of the nanoparticle-polymer composite [14]. Therefore, synthesis of new organic-inorganic hybrid Pd catalysts with balanced hydrophobicity and hydrophilicity is desirable. These limitations inspired us to synthesize novel heterogeneous Pd complexes immobilized on a host as a catalyst for C–C bond formation. From green chemistry point of view, replacement of danger, flammable and toxic organic solvents by water as the green and benign solvent highly recommended in recent organic reactions [15].

Recently, three-dimensional (3D) silica networks mesoporous silica [16, 17] such as SBA-1, SBA-16 and KIT-5 has received attention as a support for Pd NPs [18–20]. Polyhedral oligomeric silsesquioxanes (POSS) ( $R_8Si_8O_{12}$ ,  $R=H$  or an organic group) is an organic-inorganic hybrid nanoscale building block with unique properties such as rigidity, and high symmetry with thermally-robust cage structure [21]. Furthermore, POSS compounds can be easily incorporated into polymers as nanofillers by blending, grafting, and/or copolymerization to control the degree of hydrophobicity and thermal properties. POSS compounds are divided into completely condensed silsesquioxanes (CC-POSS) and incompletely condensed silsesquioxanes (IC-POSS). There has been less interest in IC-POSS with one or two open corners because it is mainly used as an intermediate for the preparation of CC-POSS by the corner capping reactions [22, 23]. For copolymerization with other monomers, the active silanol or sodium silanolate IC-POSS derivatives need to be converted to vinyl or allyl groups [21]. Guozheng Liang and coworkers [24] synthesized an IC-POSS containing three reactive allyl groups (TAP-POSS, Fig. 1) in moderate yields for developing thermally stable and dielectric bismaleimid resins. Recently, we have prepared a new series of hybrid nanocomposites based on poly (vinyl pyrrolidone) (PVP) containing TAP-POSS in order to increase the thermal properties of PVP as well as the hydrophobicity of PVP [25].



**Fig. 1** The structure of TAP-POSS

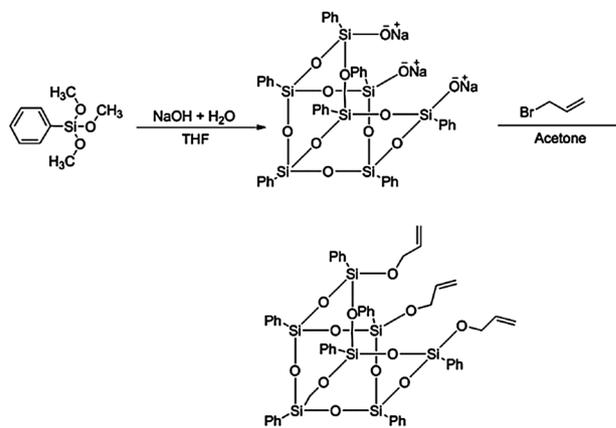
There are very few reports in the literature on catalytic applications of POSS. For example, we have recently synthesized Schiff base derivative of POSS and immobilized copper metal on POSS for efficient click reaction [26]. In one report, molybdenum metal ions were immobilized on POSS for epoxidation reaction [27–29]. In another work, organorhodium-functionalized POSS were synthesized and used as a bifunctional heterogeneous catalyst for asymmetric transfer hydrogenation of aromatic ketones [30]. POSS has been also used for stabilization of palladium NPs in direct hydrogenation of 1,4 diphenylbutadiyne [31]. However in all these cases, POSS was used as a direct support for immobilization of metal ions. In continuation of our study on the POSS chemistry [25, 26], herein we now report a simple, new and inexpensive protocol for the preparation of TAP-POSS (5% wt) based acrylamide/hydroxyethyl methacrylate copolymeric material as a support for Pd nanoparticles. The provided catalyst is heterogeneous and reusable. To the best of our knowledge, the use of POSS-based polymer composites as a metal support in catalytic reactions has not been investigated.

In the next step, we hereby explain the development of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@ PdNPs (5% TAP-POSS) nanocomposite as an effective and stable heterogeneous catalyst for Heck coupling reaction in aqueous media under ligand-free condition. The structure of the nanohybrid catalyst was characterized by FT-IR, XRD, SEM, EDX, Si and Pd mapping and TEM.

## 2 Experimental Procedure

### 2.1 Materials

Allyl bromide was purchased from Sigma-Aldrich, phenyltrimethoxysilane [ $C_6H_5Si(OCH_3)_3$ ; 98%] was supplied



**Scheme 1** Steps for the synthesis of TAP-POSS

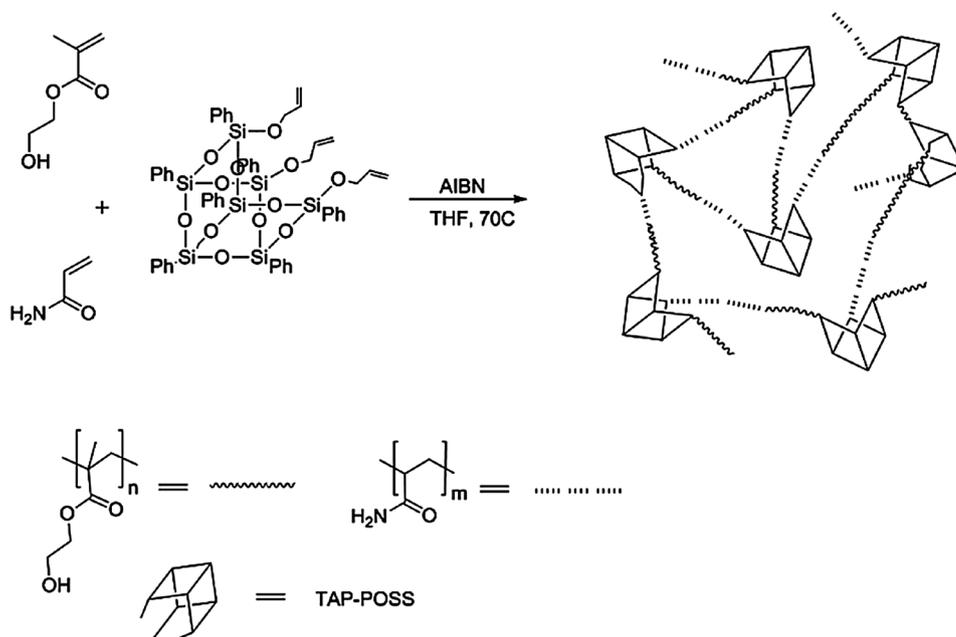
from Acros, hydroxyethyl methacrylate (HEMA) and Acrylamide (AAm) were purchased from Sigma-Aldrich. azobis (isobutyronitrile) (AIBN) from Sigma-Aldrich was recrystallized from methanol before use. Sodium hydroxide (NaOH) and solvents tetrahydrofuran (THF), acetone, acetonitrile and *n*-hexane were purchased from Merck. THF was purified by distillation over Na/benzophenone under nitrogen atmosphere immediately before use.

## 2.2 Synthesis of Poly (AAm-co-HEMA)@TAP-POSS

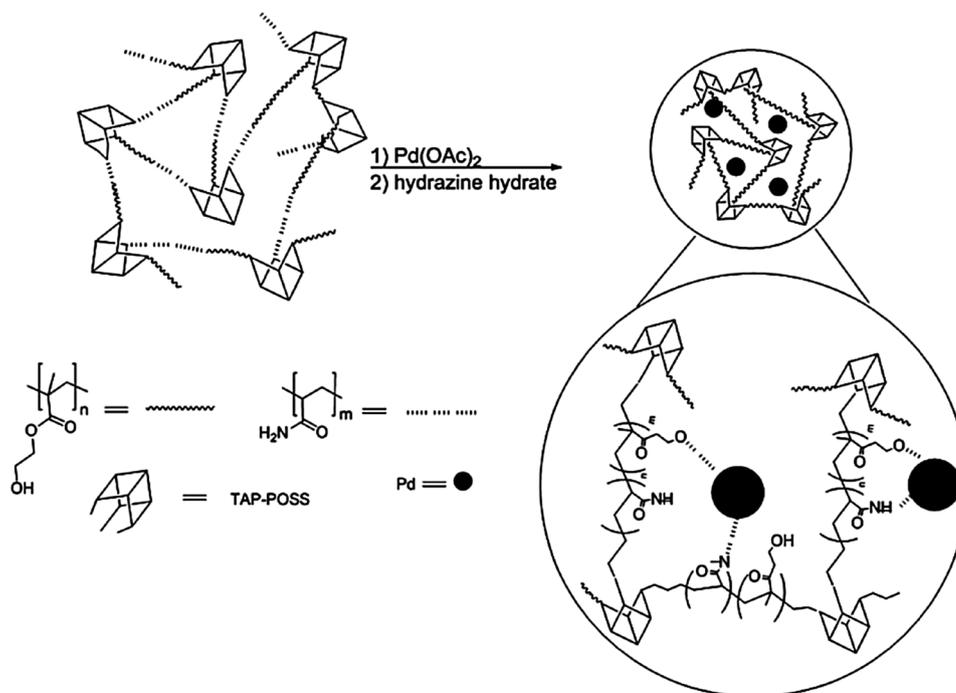
TAP-POSS was prepared via sol-gel chemistry with two-step procedure according to our previously described procedure as shown in Scheme 1, [25].

The following procedure was used for synthesis of the nanocomposites as shown in Scheme 2. 0.5 g AAm (0.007 mol), 0.5 g HEMA (0.004 mol) and 5% wt of

**Scheme 2** Reaction scheme for the synthesis of poly (AAm-co-HEMA)@TAP-POSS by radical polymerization



**Scheme 3** Preparation of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs



TAP-POSS (relative to % wt of monomers) were added to a 50 mL three-neck round bottom flask containing 10 mL dried THF fitted with condenser and  $N_2$  inlet. Next, temperature of the mixture was increased slowly to  $70^\circ\text{C}$ , followed by the addition of 1% wt AIBN relative to the monomers. The reaction mixture became milky after 30 min and a sticky white solid after 3 h. After the reaction, the product was washed with THF and *n*-hexane  $3\times$  each and dried in vacuum at  $50^\circ\text{C}$  for 48 h to obtain a white powder.

### 2.3 Synthesis of Poly (AAm-co-HEMA) @ TAP-POSS<sub>5</sub>@ Pd-NPs

Palladium NPs supported on Poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub> was prepared by impregnation using  $\text{Pd}(\text{OAc})_2$  as the Pd source. The required amount of  $\text{Pd}(\text{OAc})_2$  for 2 wt% Pd loading was added to the polymer with 20 mL of methanol. The mixture was rigorously stirred to ensure homogeneous distribution of  $\text{Pd}(\text{OAc})_2$  in the polymer. After stirring, methanol was removed under vacuum using a rotary evaporator. After impregnation, the Pd(II) in poly(AAm-co-HEMA)@TAP-POSS<sub>5</sub>@ Pd(OAc)<sub>2</sub> was

reduced with hydrazine hydrate as shown in Scheme 3 to generate Pd(0) NPs.

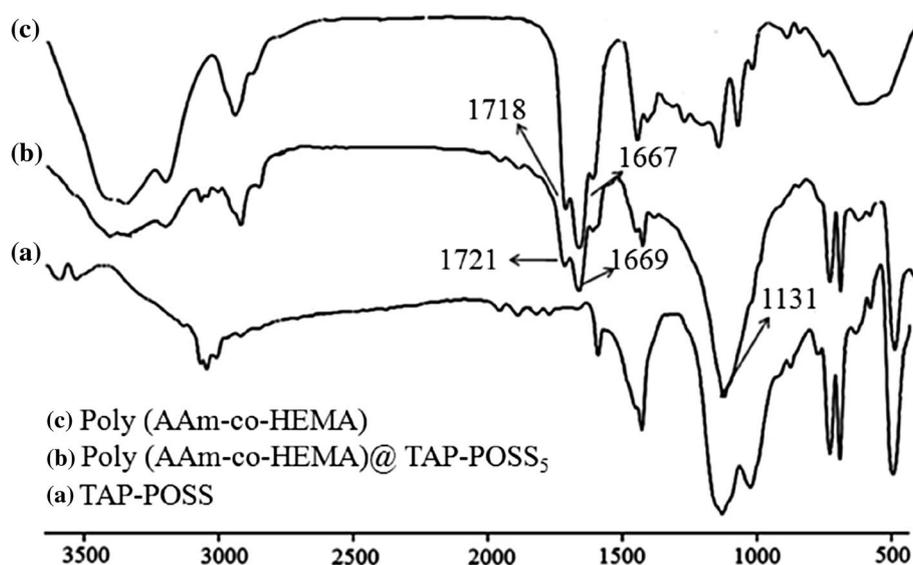
### 2.4 Procedure for the Heck Reaction

The aryl halide (1.0 mmol), olefin (1.1 mmol) and  $\text{K}_2\text{CO}_3$  (2.0 mmol) were added to a suspension of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@ Pd-NPs in 2 mL of water. The mixture was heated to  $100^\circ\text{C}$  with stirring for a specified period of time. After the reaction, the mixture was cooled to ambient temperature and the product was extracted with diethyl ether ( $2\times 10$  mL). The aqueous solution was separated from the organic layer and the diethyl ether solution was evaporated over  $\text{CaCl}_2$ . Next, the product was washed with hexane ( $3\times 5$  mL) and dried under reduced pressure. The purity of the reaction product was checked by GC and NMR and the reaction yield was calculated based on the aryl halide.

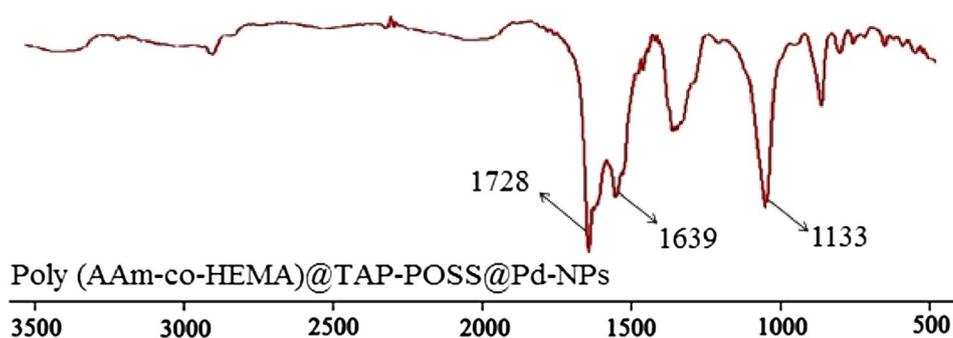
### 2.5 Instrumentation

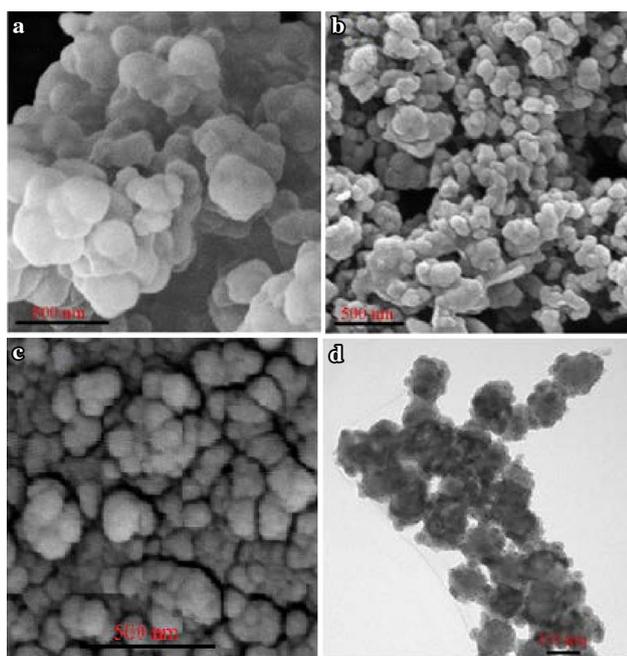
Fourier transform infrared (FT-IR) spectrum of the synthesized compounds was collected with a Tensor-27

**Fig. 2** FT-IR spectra of TAP-POSS, poly (AAm-co-HEMA), and poly (AAm-co-HEMA)@TAP-POSS



**Fig. 3** FT-IR spectrum of poly (AAm-co-HEMA) @TAP-POSS<sub>5</sub>@ Pd-NPs

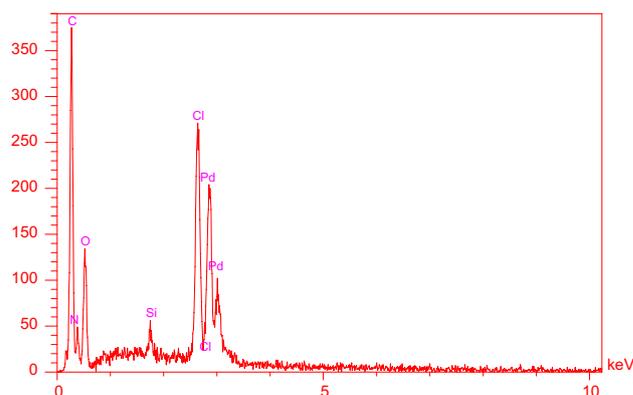
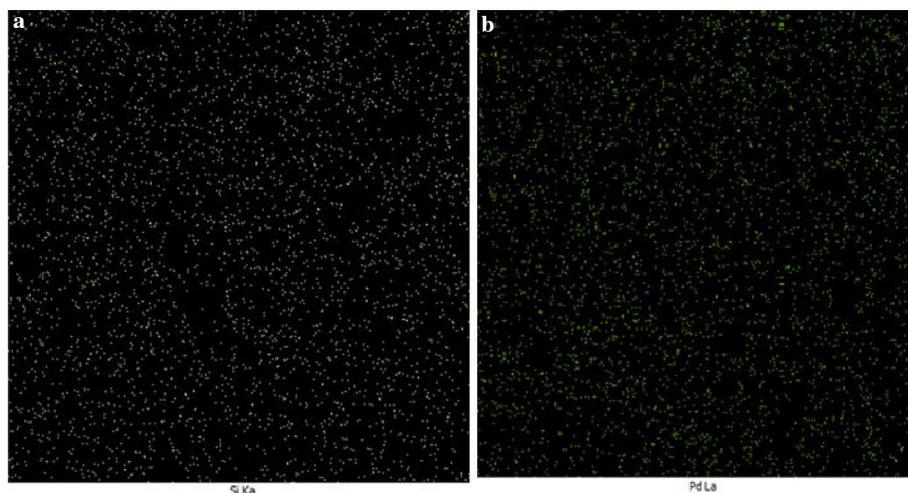




**Fig. 4** SEM images of poly (AAm-co-HEMA) (a) and poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub> (b); SEM (c) and TEM (d) images of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs

Bruker FT-IR spectrometer on a KBr disk over the range of 500–3500  $\text{cm}^{-1}$ . The diffraction spectrum of samples was collected with a Siemens D-500 diffractometer using a Cu  $\text{K}\alpha$  radiation source ( $\lambda = 1.54059 \text{ \AA}$ ) at 30 keV in the scan range ( $2\theta$ ) from  $5^\circ$  to  $70^\circ$ . The samples were imaged with a TescanMIRA3 field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 30 kV and with a Tecnai G2 F20 transmission electron microscope (TEM) at an accelerating voltage of 200 kV.

**Fig. 6** a Si mapping and b Pd mapping of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs



**Fig. 5** EDX spectrum of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs

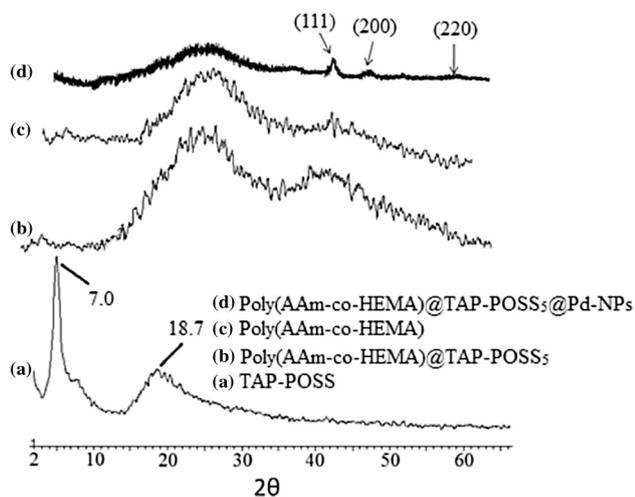
### 3 Results and Discussion

#### 3.1 Characterization of Poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd Nanocomposite

FT-IR spectra of TAP-POSS, poly (AAm-co-HEMA) and poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub> are shown in Fig. 2. Characteristic absorption bands in the FT-IR spectrum of poly (AAm-co-HEMA) at 3353, 2947, and 1718 and 1667  $\text{cm}^{-1}$  were attributed to the stretching mode of O–H, N–H, C–H and C=O groups of HEMA and acrylamide, respectively. After chemical modification by TAP-POSS, The two new bands with peak positions at 1130 and 3073  $\text{cm}^{-1}$  [32] associated with the Si–O–Si and C–H stretching, respectively, and the shift to higher wavenumbers for carbonyl absorptions at 1721 and 1669  $\text{cm}^{-1}$  in the spectrum of poly (AAm-co-HEMA)@TAP-POSS

confirmed the incorporation of TAP-POSS in the composite [33].

The FT-IR spectrum of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs is shown in Fig. 3. The band with peak



**Fig. 7** XRD spectra of TAP-POSS (a), poly (AAm-co-HEMA) (c), poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub> (b), and poly AAm-co-HEMA@TAP-POSS<sub>5</sub>@Pd-NPs (d)

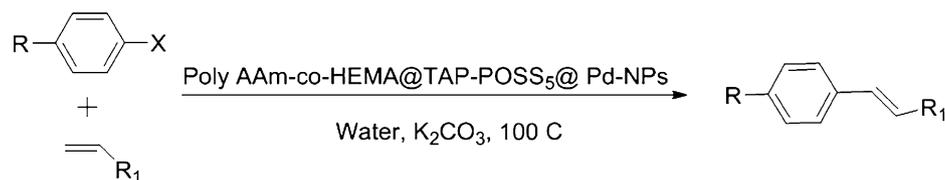
**Table 1** Effect of reaction conditions on product yield of the Heck reaction

Entry	Base	Temperature (°C)	Yield (%) <sup>a</sup>
1	Et <sub>3</sub> N	100	13
2	Bu <sub>3</sub> N	100	9
3	K <sub>2</sub> CO <sub>3</sub>	100	96
4	NaOAc	100	35
5	KOH	100	41
6	Na <sub>2</sub> CO <sub>3</sub>	100	59
7	K <sub>2</sub> CO <sub>3</sub>	rt	5
8	K <sub>2</sub> CO <sub>3</sub>	60	54
9	K <sub>2</sub> CO <sub>3</sub>	80	87

Reaction conditions: 1.0 mmol aryl halide, 1.2 mmol olefin, 2 mmol base

<sup>a</sup>Isolated yield

**Scheme 4** Heck coupling reaction between aryl halides and olefins in the presence of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs nano-catalyst



R= H, OMe, COMe  
X= Br, I  
R<sub>1</sub>= Ph, COOEt, COOBu<sup>t</sup>

position at 1669 cm<sup>-1</sup> corresponding to carbonyl absorption in acrylamide was shifted to a lower wave number at 1639 cm<sup>-1</sup> in the spectrum of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs which was attributed to the interaction of Pd NPs with the acrylamide functional group [34]. The presence of this peak supported uniform dispersion of the Pd-NPs in the organic–inorganic composite matrix which is in a good agreement with Pd-mapping analyses.

SEM images of poly (AAm-co-HEMA) and poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub> in Fig. 4a, b, respectively, show spherical particles with a uniform size distribution. Based on the SEM images, poly (AAm-co-HEMA) has a higher degree of aggregation and higher particle size than poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub> which was attributed to the higher hydrophilicity of poly (AAm-co-HEMA) and its regulation by incorporation of TAP-POSS in the copolymer. The size of POSS NPs in the range 1–3 nm was not discernable in the SEM images [35]. Figure 4c shows the SEM micrograph of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs. Figure 4c indicated that with the incorporation of Pd nano particles in the structure of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>, degree of aggregation increased because of successful complexation of Pd nano particles with the polymer matrix. The TEM image of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs in Fig. 4d shows that the particle size of Pd-NPs was in the range of 10–20 nm.

The elemental composition of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs was determined by the EDX analysis. Figure 5 illustrated the EDX spectrum of the catalyst. As it can be seen, peaks related to C, N, Si and Pd were observed with the concentrations of 41.6, 20 and 7.2% respectively.

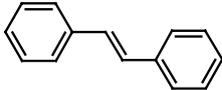
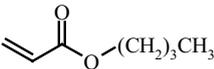
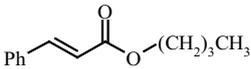
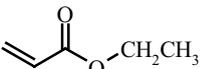
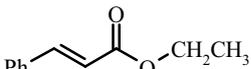
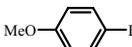
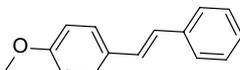
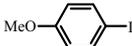
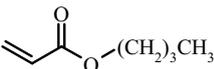
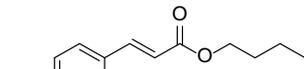
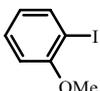
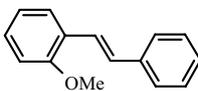
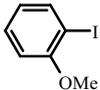
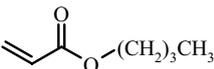
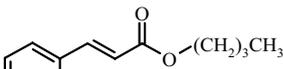
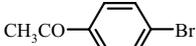
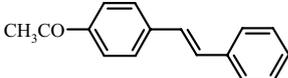
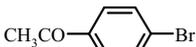
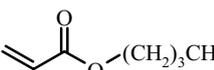
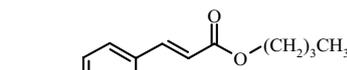
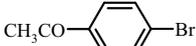
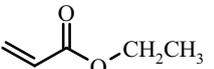
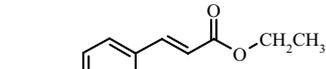
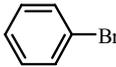
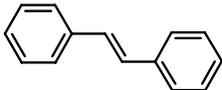
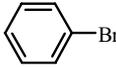
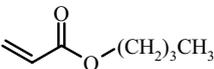
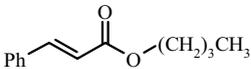
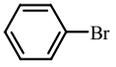
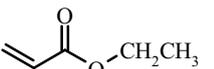
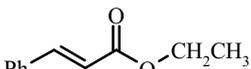
In addition, Fig. 6a, b depicted EDX Si and Pd mapping of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs which confirmed the homogeneously distribution of POSS nano-fillers and Pd nano particles throughout the mother polymer matrices.

The XRD diffraction pattern of TAP-POSS, poly (AAm-co-HEMA), poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub> and poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs are

shown in Fig. 7. The disappearance of crystalline peaks at  $2\theta=7.0^\circ$  and  $18.7^\circ$  in the XRD spectrum of poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub> and poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@ Pd-NPs confirmed uniform dispersion of TAP-POSS in the organic-inorganic composites [36].

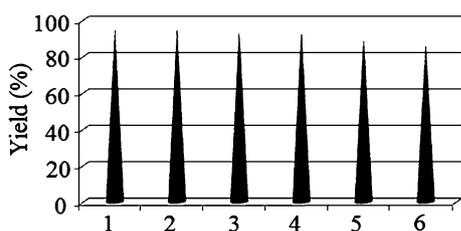
There was shift to smaller angles in the position of the amorphous peak of poly (AAm-co-HEMA) with the incorporation of TAP-POSS, as observed previously [37]. Further, the presence of crystalline peaks centered at  $2\theta=40.3^\circ$ ,  $47.2^\circ$  and  $68.9^\circ$  corresponding to (111), (200)

**Table 2** Product yield for Heck reaction between aryl halides and olefins

Entry	Ar-X	Olefins	Products	Yield (%) <sup>a</sup>
1		Ph-CH=CH <sub>2</sub>		96
2				96
3				96
4		Ph-CH=CH <sub>2</sub>		93
5				94
6		Ph-CH=CH <sub>2</sub>		76
7				79
8		Ph-CH=CH <sub>2</sub>		96
9				96
10				95
11		Ph-CH=CH <sub>2</sub>		39
12				36
13				40

Reaction conditions: 1.0 mmol aryl halide, 1.2 mmol olefins, 2 mmol K<sub>2</sub>CO<sub>3</sub>, 100 °C, 5 h

<sup>a</sup>Isolated yield



**Fig. 8** Effect of recycling of poly (AAM-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs nano-catalyst on the product yield of Heck reaction

and (220) planes of Pd(0), respectively, indicated that the Pd NPs had face-centered cubic structure in poly (AAM-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs.

### 3.2 Catalytic Activity of Poly AAM-co-HEMA @ TAP-POSS<sub>5</sub>@ Pd-NPs

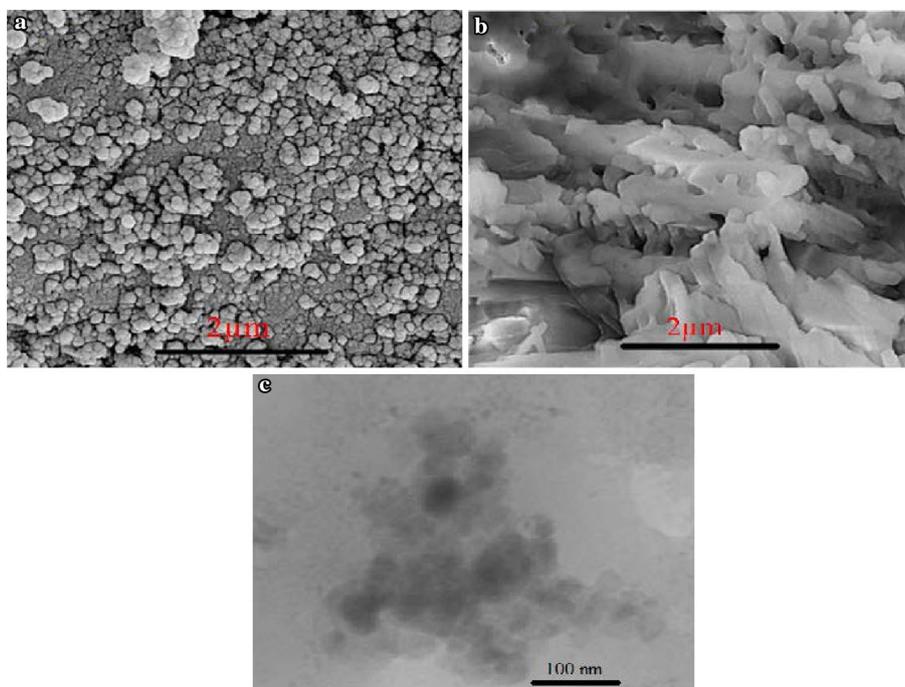
The Heck reaction between 4-acetylbromobenzene and styrene was selected as a model reaction to evaluate the catalytic activity of the poly (AAM-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs in aqueous media because this reaction provides a reasonable yield of Heck product, thereby allowing the observation of small changes in the activity of the catalyst. All reactions were performed under ambient condition and 0.5 mol% Pd. The effect of reaction conditions on Heck reaction yield is shown in Table 1. The yield of the desired Heck product was low with the use of organic bases Et<sub>3</sub>N and Bu<sub>3</sub>N (entries 1, 2) whereas the product yield was significantly higher with the use of inorganic bases K<sub>2</sub>CO<sub>3</sub>,

Na<sub>2</sub>CO<sub>3</sub>, KOH and NaOAc (entries 3–6). Among inorganic bases, K<sub>2</sub>CO<sub>3</sub> had the highest yield with 96% (entry 3) at a reaction temperature of 80 °C. The product yield was a function of reaction temperature and decreased significantly with decreasing temperature (entries 3, 7–9). Thus, the optimum reaction condition for the Heck reaction in aqueous media was 0.5 mol% Pd, K<sub>2</sub>CO<sub>3</sub> as the base, and 100 °C (Table 1).

The Heck reaction was carried out with various substituted aryl halides and olefins under the optimized reactions in the presence of poly (AAM-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs nano-catalyst in aqueous media (Scheme 4) and the product yield is listed in Table 2. In general, the product yield was good to excellent. The product yield for aryl iodide with electron-withdrawing substituents was higher than those with electron donating substituents. Further due to steric hindrance, iodobenzene bearing a methoxy group at the *Ortho* position had lower yield than that with a methoxy group at the *Para* or *Meta* position (Table 2, entries 4–7).

arylbromide with an electron-withdrawing group was successfully coupled to olefins in good yield (entries 8–10). However, the Heck coupling reaction between bromobenzene and olefins did not proceed under the same reaction conditions (entries 11–13). Recyclability of poly (AAM-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs nano-catalyst was evaluated in a separate set of experiments for the Heck reaction between 4-acetylbromobenzene and styrene. After each reaction at 100 °C for 5 h, the catalyst was recovered by filtration, washed three times with distilled water and ethyl

**Fig. 9** a, b SEM images of fresh and reused nano-catalyst; c TEM image of reused poly (AAM-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPs nano-catalyst



ether, dried at 50 °C for 30 min, and used in the next reaction. There was no significant change in the product yield after six catalysts recycling, as shown in Fig. 8 with almost complete conversion of the reactants to the desired Heck product.

It worth to noted that the SEM, TEM and XRD analyses of fresh and recycled catalyst (after six runs) are similar. But with the comparison of the SEM images for the fresh (Fig. 9a) and recycled poly (AAm-co-HEMA)@TAP-POSS5@Pd-NPs nano-catalyst (Fig. 9b), it can be concluded that the recovered catalyst show signs of morphological changes after repeated of the Heck reaction for more than ten times. Also comparison of the TEM images of the fresh (Fig. 4d) and reused catalyst signifies that some changes in particles size have occurred in the reused catalyst (Fig. 9c). Thus, changes in morphology and size of particles may be primarily responsible for the reduction in poly (AAm-co-HEMA)@TAP-POSS5@Pd-NPs catalytic activity upon its repeated use (after ten runs).

#### 4 Conclusion

Palladium NPs were dispersed in an organic–inorganic composite based on IC-POSS and poly (AAm-co-HEMA) as a novel catalytic system for heterogeneous Heck reaction between aryl halides and olefins in aqueous media. FT-IR, XRD, SEM, and TEM results demonstrated that the Pd(0) NPs were homogeneously dispersed in IC-POSS/polymer composite. Size of the Pd NPs in the composite ranged 10–20 nm. The product yield in the presence of nano-catalyst for the reaction of aryl halides and olefins ranged from 36 to 96% with aryl halides having electron-withdrawing substituents having higher reactivity than those with electron donating groups. Further, there was no significant loss of activity of the nano-catalyst after recycling six times. By using the nano-catalyst more than six times, the product yield decreased. This fact can be attributed to changes in the morphology of reused catalyst. The poly (AAm-co-HEMA)@TAP-POSS<sub>5</sub>@Pd-NPsnanocatalyst system provides a green alternative for the Heck reaction between aryl halides and olefins for the formation of C–C bonds in organic reactions.

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