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Halloysite nanoclay decorated with 2-amino pyrimidine functionalized poly glycidyl methacrylate: An efficient support for the immobilization of Pd nanoparticles

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ABSTRACT

Taking advantage of the synergistic effects between polymer (P) and halloysite clay (Hal) as well as the capability of heteroatom-containing polymers for anchoring nanoparticles and suppressing their leaching, a novel support composed of Hal and 2-amino pyrimidine (Py) functionalized poly glycidyl methacrylate (P) was prepared through initial functionalization of Hal followed by polymerization with glycidyl methacrylate and functionalization with 2-amino pyrimidine. The support (Hal-P-Py) was then used for the immobilization of Pd nanoparticles to afford a heterogeneous catalyst (Pd@Hal-P-Py) with high catalytic activity for Sonogashira coupling reaction under mild and eco-friendly reaction condition. Preparing various control catalysts, i.e. Pd@Hal-P, Pd@Hal, Pd@P and Pd@P-Py, and comparing their catalytic activities with that of the catalyst, the contribution of polymer and 2-amino pyrimidine to the catalysis was confirmed. Noteworthy, the catalyst was recyclable and could be recovered and used up to six times with insignificant loss of the catalytic activity and Pd leaching. Moreover, hot filtration experiment confirmed the heterogeneous nature of the catalysis.

1. Introduction

Recently, development of heterogeneous catalysts through immobilization of catalytic species on the halloysite nanotubes, Hal, has received increasing interest and several research groups focused on disclosing different Hal-based catalysts for catalyzing diverse range of chemical transformations [1–5]. It is worth noting that the unique tubular morphology of Hal [4,6,7], as well as its bio-compatibility, availability, high thermal and mechanical resistance, chemical composition (general formula of $Al_2Si_2O_5(OH)_4{\cdot}nH_2O$ with Al-OH octahedral sheet groups on the interior surface and Si-O-Si groups on the exterior surface) and charged nature [8–12] render Hal a distinguished support for catalytic purposes. To provide better dispersion of catalytic species on the surface of Hal and/or furnish bifunctional catalysts, Hal can be hybridized with other materials or surface functionalized on one or both inner and outer surfaces [1,13,14].

Functionalized polymers, including glycidyl methacrylate polymers [15] have been extensively used as catalyst support for development of heterogeneous catalysts [16,17]. It is known that polymers as support can effectively improve the dispersion of the catalytic species. Moreover, the functionalities on the polymer backbone can interact with the catalytic species through ionic, hydrophobic interactions as well as covalent, non-covalent or hydrogen bridges and suppress their leaching and consequently enhance the recovery of the catalyst [18–21]. Recently, some hybrid systems of Hal-polymer have been disclosed and employed for the catalytic purposes. One of the first examples was reported by Riela and Lazzara, in which Hal was decorated with thermo-responsive poly(*N*-isopropylacrylamide) and then the hybrid system was applied for immobilization of Pd nanoparticles [1]. This research group also reported Pd immobilized on hybrid system based on thiol functionalized Hal and highly cross-linked imidazolium salts [22]. Moreover, Pd nanoparticles immobilized on ternary hybrid system composed of Hal, polyacrylamide and cyclodextrin has also been reported [23]. The results confirmed that incorporation of polymer not only could suppress leaching of nanoparticles, but also could improve the catalytic activity of the final catalyst through synergistic effects between Hal and polymer.

One of the most important class of Pd-catalyzed chemical transformations is C–C coupling reaction. These reactions, such as Heck, Sonogashira and Suzuki reactions have been widely applied for the synthesis of natural products as well as diverse range of synthetic compounds and organic building blocks [24]. Classically, these reac-

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tions have been catalyzed using homogeneous Pd-based catalysts along with copper co-catalysts and phosphorous ligands [25]. Taking the environmental considerations and economic issues into account, development of co-catalyst and ligand free protocols in the presence of heterogeneous catalysts gained tremendous attentions in the last decade. In this line, various heterogeneous Pd catalysts have been prepared through immobilization of Pd on various supports such as clays, silica, metal-organic frameworks etc. [26–30].

In the following of our study on Hal-based heterogeneous catalysts [31–34] and encouraged by the catalytic results of Hal-polymer hybrid systems [23], herein, we wish to report a novel Hal-polymer hybrid system, Hal- poly glycidyl methacrylate, that was further functionalized with 2-amino pyrimidine and applied for the immobilization of Pd nanoparticles to afford a novel catalyst, Pd@Hal-P-Py, with the utility for Sonogashira coupling reaction. In the following, the effects of incorporation of polymer and 2-amino pyrimidine on the catalytic activity are investigated. Moreover, the recyclability of the catalyst as well as Pd leaching are studied.

2. Experimental section

2.1. Materials

The chemicals used for the preparation of Pd@Hal-P-Py and studying its catalytic activity included Hal, 3- (tri-methoxysilyl) propyl methacrylate, glycidyl methacrylate, 2-amino pyrimidine, potassium peroxide sulfate (KPS), $Pd(OAc)_2$, toluene, sodium hydroxide, $NaBH_4$, distilled water, acetonitrile, chloroform and MeOH, all was purchased from Sigma-Aldrich and used as received.

2.2. Instruments and characterization techniques

Verification of formation of the catalyst was achieved using various techniques, including TGA, TEM, BET, XRD, FTIR and ICP-AES. Tecnai microscope (200 kV) was applied for recording TEM images. To record the images, the catalyst was dispersed in water and the analysis was performed after evaporation of the solvent. The BET analysis of the pristine Hal and the catalyst was accomplished by using BELSORP Mini II instrument. To perform this analysis, the samples were pre-heated at 100 °C for 3 h. XRD patterns of pristine Hal and that of the catalyst were recorded by applying a Siemens, D5000. Cu Kα radiation from a sealed tube. FTIR spectra of fresh and recycled catalyst, pristine Hal and polymer decorated Hal were obtained by using PERKIN-ELMER- Spectrum 65 instrument. Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere over the range of 50–800 °C by using METTLER TOLEDO thermogravimetric analysis apparatus with heating rate of $10\,°C\,min^{-1}$. The content of Pd in the catalyst and amount of Pd leaching upon catalyst recycling were estimated by using ICP analyzer (Varian, Vista-pro).

2.3. Synthesis of the catalyst

2.3.1. Functionalization of Hal with 3-(trimethoxysilyl)propyl methacrylate: synthesis of Hal-A

Hal was first surface functionalized with 3- (tri-methoxysilyl) propyl methacrylate. To this purpose, Hal (5 g) and 3- (tri-methoxysilyl) propyl methacrylate (4.5 mL) were added into toluene (60 mL) and the mixture was ultrasounded for 20 min. Then, the resulting well-dispersed suspension was refluxed at 125 °C for 24 h. After that, the obtained precipitate was washed with toluene for three times and dried at 80 °C overnight.

2.3.2. Decoration of Hal surface with polyglycidyl methacrylate: synthesis of Hal-P

Hal-A (3 g) was suspended in distilled water under ultrasonic irradiation for half an hour. Then, glycidyl methacrylate monomer (3 g) and KPS (1.8 mg) as polymerization initiator were added to the aforementioned suspension. Subsequently, the reaction mixture was stirred under N_2 atmosphere at 60 °C for 12 h. Upon completion of polymerization, the solid was filtered, washed several times with distilled water to remove oligomers and un-reacted monomers and dried at 80 °C overnight. For further purification, the product was purified by Soxhlet with chloroform for 72 h. Finally, Hal-P was achieved after dying at 70 °C for 12 h.

2.3.3. Synthesis of Hal-P-Py

2-amino pyridine (4.01 g) and NaOH (2 M, 2 mL) were added to the suspension of Hal-P (6 g) in acetonitrile (2 mL). Then, the resulting mixture was refluxed at 24 h. At the end of the reaction, Hal-P-Py was filtered, washed with acetonitrile and dried at 80 °C overnight.

2.3.4. Immobilization of Pd nanoparticles on Hal-P-Py: Pd@Hal-P-Py

To incorporate Pd nanoparticles on Hal-P-Py, Hal-P-Py (6 g) was added in toluene (20 mL) containing Pd (0.18 g). The resulting mixture was then stirred for 24 h. To reduce Pd (II) to Pd (0), a solution of $NaBH_4$ in a mixture of toluene and methanol (10 mL, 0.2 N) was applied. In detail, the reducing agent was added to the Pd(II)@Hal-P-Py in a dropwise manner and then the mixture was stirred for 24 h. Finally, the solid was filtered, washed with toluene and dried at 70 °C. Schematic representation of the procedure for the synthesis of the catalyst is illustrated in Fig. 1. For the synthesis of the control catalysts, Pd@Hal-P, Pd@Hal, Pd@P and Pd@P-Py, the same procedure was applied, except the used support was Hal-P, Hal, P and P-Py respectively.

2.4. Catalytic test: typical procedure for Sonogashira reaction

A mixture of acetylene (1.2 mmol), halobenzene (1. mmol), catalyst (1.5 mol%) and K_2CO_3 (2.0 mmol in 5.0 mL water) in aqueous media (2:1 mixture of water: EtOH) was heated at 75 °C for appropriate reaction time. The reaction was monitored by TLC and upon completion of the reaction, the catalyst was easily filtered, washed with EtOH several times and dried in oven at 90 °C overnight. On the other hand, the organic layer in filtrate was extracted with diethyl ether (15 mL). The desired product was purified by column chromatography over silica gel (Scheme 1).

3. Result and discussion

3.1. Catalyst characterization

In Fig. 2 the morphology of Pd@Hal-P-Py and Hal are illustrated. According to the literature [35], pristine Hal exhibited tubular morphology. The comparison of two TEM images showed that the morphology of the catalyst is distinguished from that of pristine Hal. In the TEM images of Pd@Hal-P-Py, apart from dark short tubes, polymeric sheet can be observed. Moreover, the dark small spots are indicative of Pd nanoparticles. Noteworthy, the average Pd particle size was estimated to be 5 nm.

The formation of Pd@Hal-P and Pd@Hal-P-Py was investigated by recording FTIR spectra of both materials and comparing them with that of Hal, Fig. 3. According to the literature [33], the pristine Hal characteristic bands included the bands at $3697\,cm^{-1}$ and $3623\,cm^{-1}$ (inner surface -OH and inner -OH groups), $540\,cm^{-1}$ (Al-O-Si vibration), $1035\,cm^{-1}$ (Si–O stretching) as well as the bands at 2928, 1698, $1635\,cm^{-1}$. The FTIR spectra of both Pd@Hal-P and Pd@Hal-P-Py showed the characteristic bands of Hal, implying that the Hal structure did not collapse upon polymerization process and Pd immobilization. The precise comparison of these two spectra with that of pristine Hal revealed that in Pd@Hal-P and Pd@Hal-P-Py spectra, an additional band at $1463\,cm^{-1}$ is emerged that can be attributed to the $-C{=}C$ functional groups of the polymeric backbone. Moreover, the observed band at $1726\,cm^{-1}$ can be assigned to the esteric ($-C{=}O$) functionalities

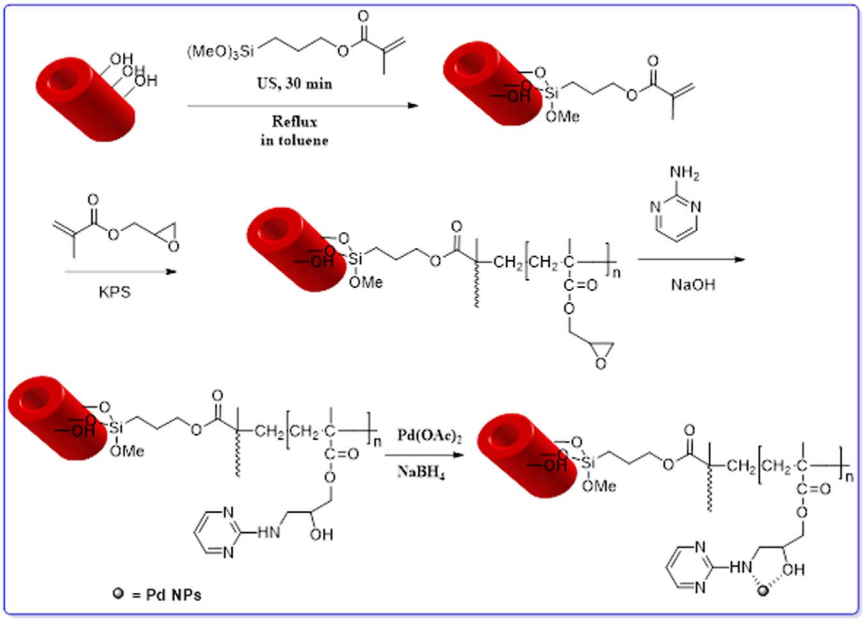
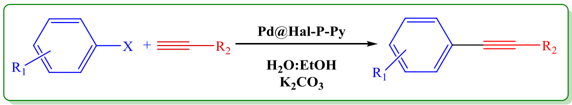


Fig. 1. Schematic representation of the procedure for the synthesis of the catalyst.



Scheme 1. Sonogashira reaction.

in the polymer. The quantitative studies also showed that the content of –C≡C in the FTIR spectrum of Pd@Hal-P-Py is higher than that of Pd@Hal-P, confirming the conjugation of 2-amino pyrimidine moiety.

In the following, nitrogen adsorption–desorption isotherm of Pd@Hal-P-Py was recorded, Fig. 4a, and compared with that of pristine Hal (Fig. 4b). The results established that the type of two isotherms were

a

b

Fig. 2. a: TEM images of the catalyst and b: the TEM image of the pristine Hal.

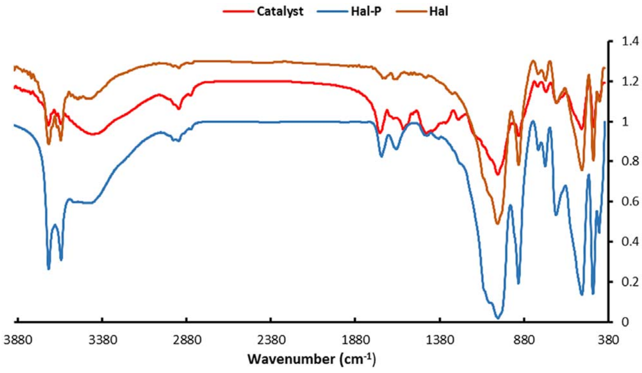


Fig. 3. FTIR spectra of the catalyst, pristine Hal and Hal-P.

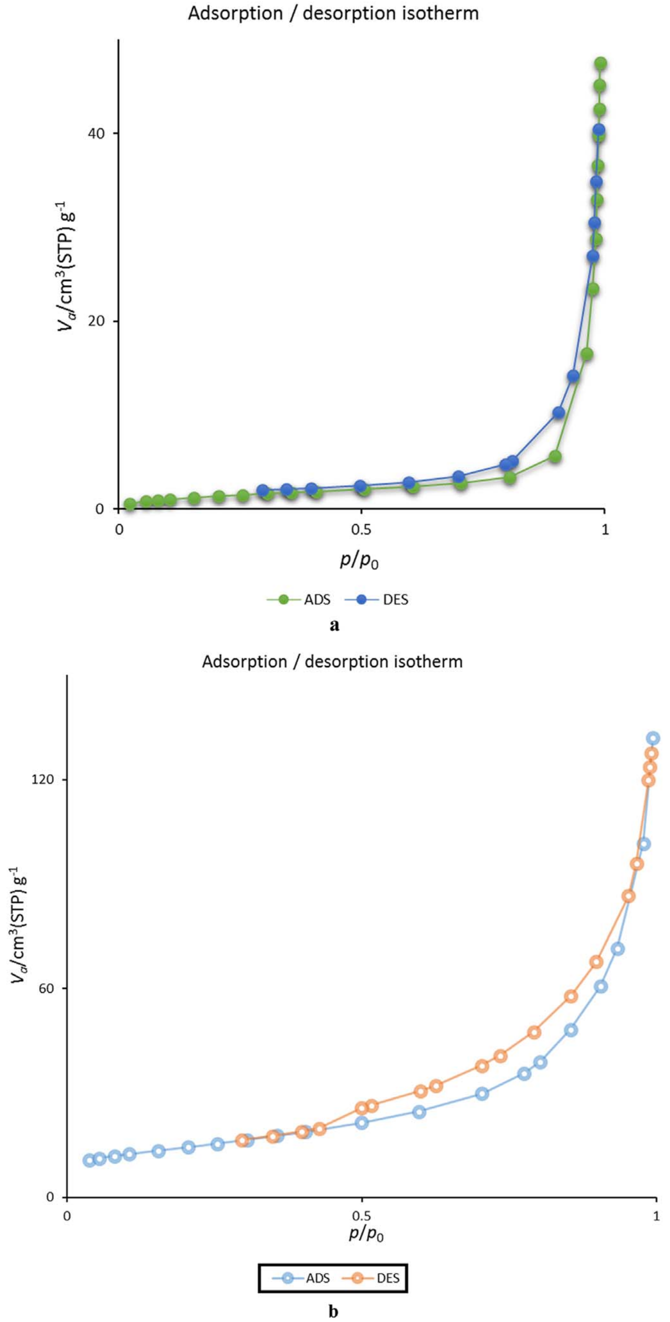


Fig. 4. a: N_2 adsorption-desorption isotherm of the catalyst and **b**: the N_2 adsorption-desorption isotherm of Hal.

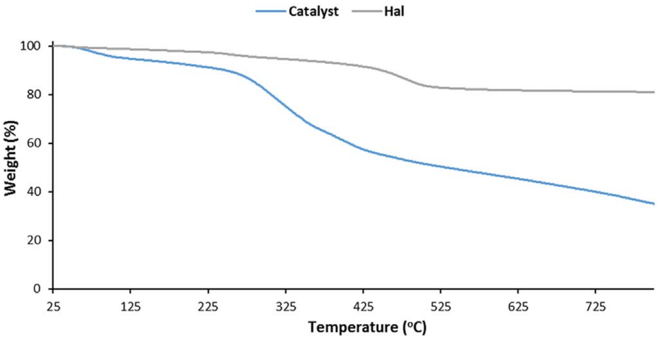


Fig. 5. Thermograms of the catalyst and pristine Hal.

similar, type II isotherms with H3 hysteresis loops. The comparison of the specific surface area of Pd@Hal-P-Py and that of pristine Hal, however, demonstrated that the specific surface area of the catalyst (5.2 $m^2\ g^{-1}$) was significantly lower than that of pristine Hal (51 $m^2\ g^{-1}$), indicating that large portion of exterior surface of Hal is covered by the polymer.

To further characterize Pd@Hal-P-Py, ICP analysis was exploited. In this line, the sample for ICP analysis was prepared by digesting the polymeric moiety in the concentrated acidic solution. The result indicated low Pd loading of the catalyst (0.5 wt%).

Next, the thermogram of the catalyst was obtained and compared with that of pristine Hal, Fig. 5. The comparison of these two thermograms revealed that Pd@Hal-P-Py exhibited more mass losses steps and its thermal stability was lower than that of pristine Hal. In detail, thermogram of the catalyst not only showed the mass losses at 150 °C and 550 °C that are due to the loss of the structural water and dehydroxylation of the Hal matrix respectively [36,37], but also exhibited an additional mass loss step at 310 °C that can be attributed to the degradation of polymer and organosilane. Comparing two thermograms, the content of the organic moiety was calculated to be ~30 wt%.

To elucidate whether Hal structure would be preserved upon introduction of polymer and Pd immobilization, the XRD pattern of pristine Hal was compared with that of Pd@Hal-P and Pd@Hal-P-Py, Fig. 6. As depicted in both XRD patterns of Pd@Hal-P and Pd@Hal-P-Py, the characteristic bands of pristine Hal ($2\theta = 14.3°, 22.0°, 26.6°, 28.6°, 37.1°, 40.4°, 57.5°$ and $64.7°$ (JCPDS No. 29–1487)) [38,39] can be observed, implying that the structure of Hal in both samples was preserved. It can also be found out that in both XRD patterns, the position of the characteristic bands are similar and no displacement and shift is observable, indicating that the interlayer distance remained intact. This observation can confirm that the polymer and Pd nanoparticles were located on the exterior surface of Hal nanotubes. Notably, in the comparison of the XRD patterns of the catalyst and that of pristine Hal showed that the intensities of the characteristic bands of Hal in the XRD pattern of the catalyst decreased significantly.

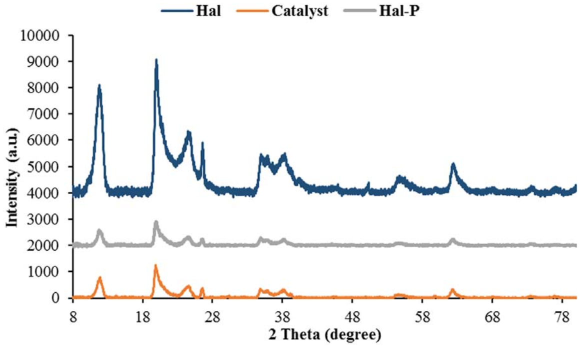


Fig. 6. XRD patterns of pristine Hal, Hal-P and the catalyst.

Table 1
Optimization of reaction conditions in the Sonogashira coupling reaction of iodobenzene with phenylacetylene[a].

Entry	Pd loading wt%	Pd average particle size (nm)	Catalyst loading (mol%)	Condition (solvent/temperature °C)	Time (h:min)	Base	Yield[b] (%)
1	0.5	5	1.5	H_2O:EtOH (2:1)/75	1:15	K_2CO_3	90
2	0.5	5	1.5	H_2O:EtOH (4:1)/75	1:25	K_2CO_3	80
3	0.5	5	1.5	H_2O:EtOH (1:2)/75	1:10	K_2CO_3	85
4	0.5	5	1.5	H_2O:EtOH (1:4)/75	1:10	K_2CO_3	84
5	0.5	5	1.5	H_2O	1:30	K_2CO_3	80
6	0.5	5	1.5	EtOH	1:10	K_2CO_3	86
7	0.5	5	1.5	Toluene	1:40	K_2CO_3	75
8	0.5	5	1.5	CH_3CN	1:30	K_2CO_3	80
9	0.5	5	1.5	H_2O:EtOH (2:1)/100	1:10	K_2CO_3	83
10	0.5	5	1.5	H_2O:EtOH (2:1)/25	1:45	K_2CO_3	71
11	0.5	5	1.5	H_2O:EtOH (2:1)/50	1:30	K_2CO_3	78
12	0.5	5	0.5	H_2O:EtOH (1:4)/75	2	K_2CO_3	75
13	0.5	5	1	H_2O:EtOH (1:4)/75	1:35	K_2CO_3	80
14	0.5	5	2	H_2O:EtOH (1:4)/75	1:15	K_2CO_3	90
15	0.5	5	1.5	H_2O:EtOH (2:1)/75	1:34	KOH	82
16	0.5	5	1.5	H_2O:EtOH (2:1)/75	1:30	NaOH	86
17	0.5	5	1.5	H_2O:EtOH (2:1)/75	1:15	Cs_2CO_3	90
18	0.2	4.5	1.5	H_2O:EtOH (2:1)/75	2	K_2CO_3	79
19	0.3	4.8	1.5	H_2O:EtOH (2:1)/75	1:40	K_2CO_3	82
20	0.7	6.5	1.5	H_2O:EtOH (2:1)/75	1:15	K_2CO_3	88
21	0.2	4.5	2	H_2O:EtOH (2:1)/75	1:40	K_2CO_3	81
22	0.3	4.8	2	H_2O:EtOH (2:1)/75	1:30	K_2CO_3	88
23	0.7	5.8	1	H_2O:EtOH (2:1)/75	1:15	K_2CO_3	86

[a] Reaction condition: aryl halide (1.0 mmol), terminal alkyne (1.2 mmol), base (2 mmol), solvent (5 mL).
[b] Isolated yield.

Considering the fact that the content of Pd in the catalyst is relatively low and the characteristic bands of Pd are of low intensity [40], in the XRD pattern of the catalyst that the intensities of the bands are significantly decreased, the characteristic bands of Pd nanoparticles were not observable.

3.2. Catalytic activity

In the following, the catalytic activity of the catalyst was studied. To this purpose, a Pd-catalyzed reaction, Sonogashira C-C coupling reaction, was selected and the catalytic activity of Pd@Hal-P-Py for promoting a typical Sonogashira reaction (reaction of iodobenzene and phenyl acetylene) in the presence of K_2CO_3 as base, catalytic amount of the catalyst (1.5 mol%) at 75 °C in aqueous media (mixture of water and EtOH) was studied. The result showed that in this condition, the desired product was furnished in high yield (90%). Notably, increase of the amount of the catalyst did not affect the yield of the reaction, Table 1. Moreover, examining various solvents including water, acetonitrile and toluene, confirmed that the mixture of water and EtOH was the solvent of the choice, Table 1. Having optimum reaction condition in hand, the effect of Pd loading was also studied. In this line, several control samples with Pd loadings of 0.2, 0.3 and 0.5 wt% were synthesized (the loading of Pd was verified by using ICP) and their catalytic activities for promoting the model reaction under optimum reaction condition was studied, Table 1. The results indicated that very low loading of Pd led to the longer reaction times and lower yields of the desired product, while use of higher Pd loading did not have a positive effect on the catalytic activity of the catalyst and the catalyst with 0.7 wt% Pd showed slightly lower catalytic activity compared to that of the catalyst with 0.5 wt% Pd loading. On the other hand, the results of use of higher quantities of the catalysts with lower Pd loading (0.2 and 0.3 wt%) confirmed that although higher amount of those catalysts improved the catalytic activities, the observed catalytic activities were lower than that of the catalyst with 0.5 wt% Pd loading. Moreover, the result showed that use of lower content of the catalyst with high Pd loading (0.7 wt%) resulted in lower yield of the desired product. These results proved that loading of Pd is not the only determining factor on the catalytic activity. As Pd particle size can be considered as a crucial parameter on the catalytic activity and affect the catalytic activity, the Pd particle sizes of the samples were estimated and compared, Table 1. The results, Table 1, indicated that in the case of the catalyst with 0.7 wt% Pd loading, the Pd particle size was bigger than other samples. This observation showed that both Pd content and Pd average particle size can affect the catalytic activity. In detail, low amount of Pd resulted in lower catalytic activity, while high amount of Pd loading resulted in bigger Pd particles and consequently lower catalytic activity. According to the result, the optimum loading of Pd was found to be 0.5 wt%.

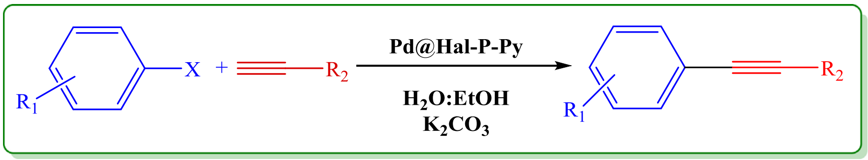
Next, it was studied whether hybridization of Hal with polymer can improve the catalytic activity of the final catalyst. In this line, two control catalysts, Pd@Hal and Pd@P-Py were synthesized and their catalytic activities for the model Sonogashira reaction were compared with that of the catalyst, Table 2. The results indicated that both control catalysts exhibited moderate catalytic activities that were inferior to that of the catalyst, confirming that hybridization of Hal and P-Py could improve the catalytic activity. This observation can indicate the synergism between polymer and clay. Next, it was investigated whether incorporation of 2-amino pyrimidine (Py) can affect the catalytic activity. In this line, two other control catalysts, Pd@Hal-P and Pd@P, were synthesized. The comparison of the catalytic activity of Pd@Hal-P for the model reaction was compared with that of the catalyst, Table 2. The result proved the superior catalytic activity of the latter. Moreover, the comparison of the catalytic activities of Pd@P and Pd@P-Py showed that Pd@P-Py exhibited higher catalytic activity. These results indicated that the presence of Py can slightly improve the catalytic activity of the final catalyst. According to the literature [41], as introduction of Py in the backbone of the catalyst can increase the

Table 2
Comparison of the catalytic activities of the control catalysts with that of the catalyst.

Entry	Catalyst	Reaction time (h:min)	Yield (%)[b]
1	Pd@Hal	2	70
2	Pd@P	2	60
3	Pd@P-Py	1:30	64
4	Pd@Hal-P	1.:15	82
5	Pd@Hal-P-Py	1:15	90

[b] Isolated Yield.

Table 3
Pd@Hal-P-Py catalyzed Sonogashira reaction of various halides with terminal alkynes[a] [41].



Entry	R^1	R^2	X	Time (h:min)	Yield (%)
1	H	Ph	I	1:15	90
2	*p*-Me	Ph	I	2:25	85
3	*p*-OMe	Ph	I	2:25	85
4	*p*-COMe	Ph	I	2:10	82
5	*p*-NO_2	Ph	I	2:15	81
6	1-naphtalene	Ph	I	2:20	80
7	H	CH_2OH	I	1:50	85
8	*p*-OMe	CH_2OH	I	1:50	82
9	*p*-Me	CH_2OH	I	2:30	95
10	*p*-COMe	CH_2OH	I	2:00	75
11	*p*-NO_2	CH_2OH	I	2:15	85
12	1-naphtalene	CH_2OH	I	2:20	80
13	H	Ph	Br	3:15	70
14	H	Ph	Cl	3:25	60

[a] Reaction condition: aryl halide (1.0 mmol), terminal alkyne (1.2 mmol), Pd@Hal-P-Py (1.5 mol%), K_2CO_3 (2.0 mmol) in water:EtOH (5.0 mL) at 75 °C.

number of heteroatoms, especially nitrogen atoms, it can increase of the electrostatic interaction of Pd nanoparticles and the support and consequently anchor Pd nanoparticles more effectively [15]. To verify this assumption, the Pd loadings of Pd@Hal-P and Pd@Hal-P-Py were calculated via ICP analysis. The results showed that the Pd loading in the catalyst (0.5 wt%) was slightly higher than that of the Pd@Hal-P (0.46 wt%).

Confirming high catalytic activity of the catalyst for the model Sonogashira reaction, the generality of this protocol was examined for other aryl halides and terminal alkynes, Table 3. As tabulated, various substrates with diverse range of electronic and steric features could undergo the reaction to furnish the desired products in relatively short reaction time and high yields. As shown, the reaction of aromatic alkynes was more efficient than aliphatic ones. Moreover, use of aryl iodide led to the higher yields compared to aryl chloride and bromides. This is due to the lower activities of aryl chloride and bromides. Noteworthy, among various aryl iodide, the ones with electron withdrawing groups and lower steric hindrance resulted in the higher yields.

In the following the merit of this protocol was studied by comparison of the catalytic activity of Pd@Hal-P-Py with some of the previously reported catalytic protocols, Table 4. As illustrated, the yield of the desired product using Pd@Hal-P-Py is higher or comparative to the tabulated catalysts. Moreover, using this catalyst, the reaction could proceed in aqueous media in the presence of cost-effective base at relatively low reaction temperature to afford the product in short reaction time. Notably, compared to the homogeneous catalysts, Pd@Hal-P-Py is recyclable.

3.3. Catalyst recyclability

The final part of this study was devoted to the investigation of the recyclability of the catalyst and studying the efficiency of Hal-P-Py support for suppressing Pd leaching. As described in the Experimental section, the recovered catalyst was washed, dried and used for the next consecutive reaction run. The results of the recycling tests, Fig. 7, showed that upon the second reaction run, the catalyst preserved its catalytic activity, while further recycling up to sixth run led to slight decrease of the catalytic activity. Upon the seventh recycling, a significant loss of the catalytic activity was observed.

To study the reason behind the loss of catalytic activity at seventh reaction run and elucidate whether recycling could triggered Pd leaching, the catalyst recycled for seven runs was subjected to the ICP analysis. The result indicated that the Pd leaching for the catalyst recycled for seven runs was considerable.

To further characterize the recycled catalyst, the TEM image of the recycled catalyst after seven reaction run was recorded, Fig. 8. Comparing the TEM images of the fresh and recycled catalysts, it can be concluded that recycling did not cause significant aggregation of Pd nanoparticles.

Table 4
Comparison of catalytic activity of the present catalyst with the other reported catalysts in the Sonogashira coupling reaction between iodobenzene and phenylacetylene.

Entry	Catalyst	Reaction conditions	Yield (%)	Time (h:min)	[Ref]
1	Pd@Hal-P-Py	H_2O: EtOH (2:1)/75 °C	90	1.15	This work
2	$Pd(OAc)_2$	MeCN/DABCO/air	100	18	[42]
3	$NiCl_2 \cdot 6H_2O$	n-Bu_4-NBr/NaOH/EG/120 °C	86	2	[43]
4	Pd-LHMS-3	Hexamine/H_2O/Reflux	85	10	[44]
5	Pd/MgLa	DMF/Et_3N/80 °C	90	10	[45]
6	NHC-palladium complex	DMSO/K_3PO_4/100 °C	81	1	[46]
7	Fe_3O_4@SiO_2/Schiff base/Pd(II)	DMF/K_2CO_3/90 °C	93	1	[47]
8	I-Pd	CH_3CN/Et_3N/Reflux	80	24	[48]
9	Nano Pd@Fe_3O_4	DMF/piperidine/110 °C	83	24	[49]
10	polymeric N-heterocyclic carbene–Pd complex-grafted silica	DMF/K_2CO_3/120 °C	93	1:25	[50]

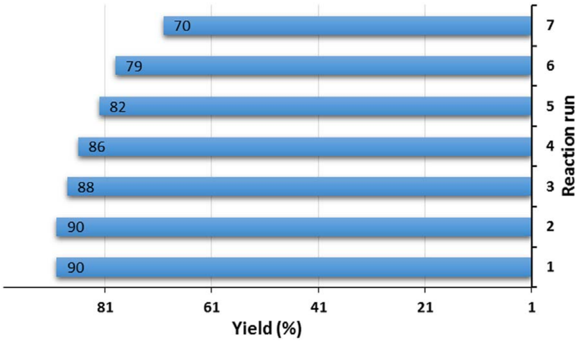


Fig. 7. The results of recyclability of the catalyst.

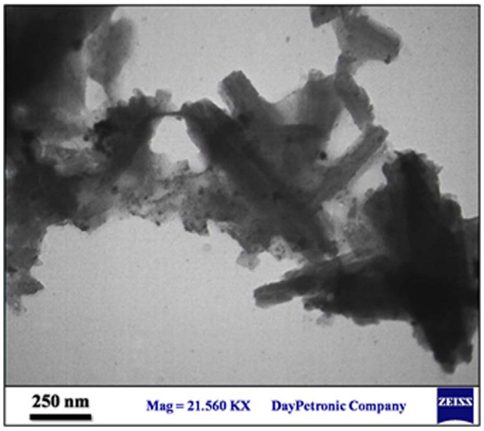


Fig. 8. TEM image of the recycled catalyst.

Finally, to investigate the nature of the catalysis, the hot filtration test was performed. The results confirmed that the catalysis was heterogeneous and Pd leaching and re-disposition on the Hal-P-Py support did not occur in the course of the reaction.

4. Conclusion

A novel heterogeneous catalyst (Pd@Hal-P-Py) was designed and prepared through functionalization of Hal with 3- (tri-methoxysilyl) propyl methacrylate followed by polymerization with glycidyl methacrylate, functionalization with 2-amino pyrimidine and Pd immobilization. The study of the catalytic activity of Pd@Hal-P-Py for promoting Sonogashira reaction confirmed high catalytic activity of the catalyst under mild reaction condition. Moreover, the catalyst showed high recyclability up to six recycling runs with slight loss of the catalytic activity and Pd leaching. The study of the role of polymer and 2-amino pyrimidine in the catalysis was carried out by preparing control catalysts, i.e. Pd@Hal-P, Pd@Hal, Pd@P and Pd@P-Py, and comparing their catalytic activities with that of the catalyst. The results indicated the synergistic effect between polymer and Hal. Moreover, it was found that incorporation of 2-amino pyrimidine led to better catalytic activity and lower Pd leaching that can be due to the electrostatic interaction of multi-nitrogen atoms in the backbone of P-Py with Pd nanoparticles. Notably, the hot filtration test indicated the heterogeneous nature of the catalysis.

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