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Combination of polymer and halloysite chemistry for development of a novel catalytic hybrid system

Samahe Sadjadi, et al. ***[full author details at the end of the article]***

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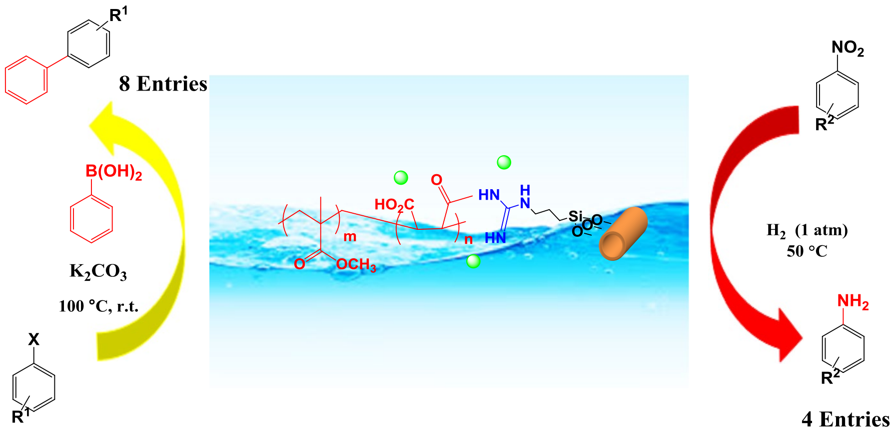
Abstract

A covalent hybrid of halloysite-poly(methyl methacrylate-*co*-maleic anhydride) was prepared and applied for the immobilization of Pd nanoparticles. The hybrid system, Pd@Hal-Gua-Poly, was then characterized via TEM, TGA, ICP, BET, FTIR and XRD and successfully used as a heterogeneous catalyst for promoting two main Pd-catalyzed reactions, i.e. hydrogenation of nitro-arenes and Suzuki coupling reaction under mild and eco-friendly conditions. The study of recyclability of the catalyst confirmed high recyclability and low Pd leaching of Pd@Hal-Gua-Poly. Moreover, the hot-filtration test showed the heterogeneous nature of the catalysts. Notably, the comparison of the activity of the catalyst with that of Pd@Hal and Pd@Poly confirmed the superior catalytic activity of the former, indicating that the hybridization of Hal and Poly could lead to the improvement of the catalytic activity.

Graphical abstract



Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11164-019-03835-y) contains supplementary material, which is available to authorized users.

Keywords Halloysite · Heterogeneous catalyst · Hybrid · Polymer · Hydrogenation · Suzuki reaction

Introduction

Halloysite nanoclay (Hal) is a natural tubular alumosilicate [1] with formula of ($Al_2Si_2O_5(OH)_4{\cdot}nH_2O$) that was first described by Berthier in 1826. However, since 1940 it has regained growing attention, and its utility for various scientific domains, including catalysis [2–4], composites, cleaning, drug delivery, adsorbents, polymer fillers, packaging, flame retardants and protection has been increased [5–8]. Apart from the chemical and physical properties of Hal, such as morphological stability, differently charged inner and outer surface, mechanical and chemical stability, low-cytotoxicity and biocompatibility, its low cost and availability on a large scale render it a promising alternative for other tubular nanomaterials such as carbon nanotubes [9–15]. A useful strategy for the modification of Hal properties is surface functionalization. The inner, outer or even both surfaces of Hal can be chemically tuned in a way that adjusts the surface properties for the targeted use [10].

Pd is one of the most used metals for catalytic purposes. A broad range of chemical transformation ranging from hydrogenation to Heck and Sonogashira C–C coupling reactions can be catalyzed by homogeneous or heterogeneous Pd-based catalysts [16–20]. Although homogeneous catalysis benefits from some advantages such as high catalytic activity and selectivity, the tedious recovery and recycling of the catalyst render it unattractive from the economic and environmental points of view. Hence, in recent years increasing attempts have focused on development of heterogeneous Pd catalysts [21–27]. Moreover, considering the growing environmental concerns, disclose of protocols that can proceed under mild and environmentally benign condition is of great importance [28–40].

In the following, our research on the utility of Hal for catalysis [5, 41–43], recently, we have disclosed the preparation and application of a Hal-polymer hybrid system for catalytic purposes [44]. The promising results and the observed synergism between Hal and polymer encouraged us to design and prepare a novel Hal-polymer hybrid based on the covalent conjugation of guanidine-functionalized Hal with poly(methyl methacrylate-*co*-maleic anhydride). The resulting hybrid, Hal-Gua-Poly, was applied for the immobilization of Pd nanoparticles to afford Pd@Hal-Gua-Poly. The catalytic activity of the latter was then studied for two class of Pd-catalyzed reactions, hydrogenation of nitroarenes and Suzuki coupling reaction. Moreover, the recyclability and Pd leaching of the Pd@Hal-Gua-Poly were investigated. Finally, using two control catalysts, Pd@Hal and Pd@Poly, the contribution of both hybrid components to the catalysis was confirmed.

Experimental

Materials and instruments

The chemicals used for the preparation of Pd@Hal-Gua-Poly and study of its catalytic activity included Hal, (3-chloropropyl) trimethoxysilan, $Pd(Cl)_2$, $NaBH_4$, distilled water, EtOH, MeOH, triethylamine, toluene and DMSO, which were all purchased from Sigma-Aldrich and used as received. Poly(methyl methacrylate-*co*-maleic anhydride) with trade name KARABOND® COPM12 was provided from Karangin Co.

The organic compounds used for performing the Suzuki–Miyaura coupling reaction and hydrogenation reaction included aryl halides, nitroarenes, aryl boronic acid, K_2CO_3, Cs_2CO_3, KOH, NaOH, EtOH, MeOH, CH_3CH, toluene, DMSO and deionized water. All were provided by Sigma-Aldrich and used without further purification. The progress of the cross-coupling reactions was monitored by TLC on commercial aluminum-backed plates of silica gel 60 F254 and visualized using ultraviolet light [45]. All the organic products were known and their identification was performed by comparing their melting points and FTIR spectra with those of the authentic samples. For a selected sample, the ^{1}HNMR spectra was also recorded, Figure S1.

The structure of Pd@Hal-Gua-Poly was confirmed by applying TEM, XRD, BET, TGA, FTIR, ICP-AES analyses. TEM images of Pd@Hal-Gua-Poly was recorded by using Philips CM30300Kv field emission transmission electron microscope. X-ray diffraction patterns were obtained by using a Siemens, D5000. CuKα radiation from a sealed tube. To record N_2-adsorption–desorption isotherm and study the textural properties of the catalyst, BELSORP Mini II instrument was employed. To perform the analysis, all the samples were pre-heated at 423 K for 3 h. To perform thermogravimetric analyses (TGA), a METTLER TOLEDO thermogravimetric analysis apparatus with a heating rate of 10 °C min^{-1} from 50 to 800 °C under N_2 atmosphere was used. To record the FTIR spectra of all samples, we used a PERKIN-ELMER- Spectrum 65 instrument. The ultrasonic apparatus applied for the synthesis of Pd@Hal-Gua-Poly was Bandelin HD 3200 with output power of 150 W and tip TT13.

Preparation of the catalyst

Cl functionalization of Hal: synthesis of Hal-Cl (1)

In order to introduce Cl functionality on the outer surface of Hal, Hal (2 g) was dispersed in 60 mL dry toluene and subsequently (3-chloropropyl) trimethoxysilan (3 mL) was added in a drop-wise manner. Subsequently, the resulting mixture was homogenized by using ultrasonic irradiation of power 100 W for 0.5 h. The dispersed suspension was then refluxed under inert (N_2) atmosphere for 24 h at 140 °C. Upon completion of the reaction, the precipitate was separated via simple filtering. To remove the unreacted reagents, the product was washed with methanol several times and then dried at 140 °C overnight.

Incorporation of guanidine: synthesis of Hal-Gua (2)

Guanidine hydrochloride (1.35 g) was added to a suspension of Hal-Cl (2 g) in dry toluene (50 mL) in the presence of catalytic amount of trietylamine (2 mL). The resulting mixture was then refluxed at 110 °C for 24 h. Upon completion of the reaction, the precipitate was filtered off, washed with dry toluene repeatedly and then dried at 100 °C overnight. To confirm the conjugation of Gua on the Hal surface, ninhydrin test was performed. The change in the color of Hal-Gua upon introduction of ninhydrin proved the presence of amine functionalities on the Hal.

Decoration of imine functionalized Hal with polymer: synthesis of Hal-Gua-Poly (3)

The poly(methyl methacrylate-*co*-maleic anhydride) (1.25 g) was suspended in DMSO and sonicated under ultrasonic irradiation of power 180 W for 15 min. To the resulting suspension, the well dispersed mixture of Hal-Gua (2 g) in EtOH was added. Then, the reaction temperature was increased to 140 °C and the mixture was stirred for 24 h. Upon completion of the reaction, the precipitate was filtered, washed with distilled water repeatedly and dried for 12 h at 70 °C.

Immobilization of Pd nanoparticles on Hal-Gua-Poly: Pd@Hal-Gua-Poly (4)

To incorporate Pd NPs on Hal-Gua-Poly, Hal-Gua-Poly (2 g) was suspended in dry toluene (15 mL) containing $Pd(Cl)_2$ (2 wt%) and then stirred at ambient temperature for 8 h. To reduce Pd(II) to Pd(0), a solution of $NaBH_4$ in a mixture of toluene and ethanol (10 mL, 0.2 N) was prepared and slowly introduced into the above mentioned suspension. The resulting mixture was then stirred for 2 h. Finally, the precipitate was filtered, washed with ethanol and dried in oven at 70 °C overnight. The procedure for the synthesis of the catalyst is described in Fig. 1.

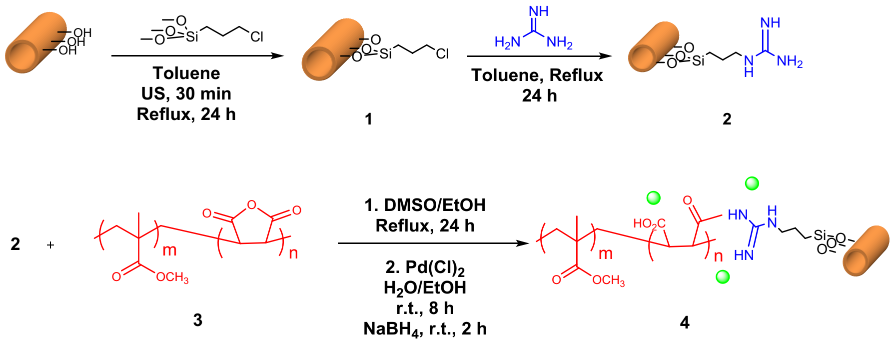


Fig. 1 Schematic procedure for the synthesis of Pd@Hal-Gua-Poly

To prepare Pd@Hal and Pd@Poly, the similar procedure was used except, Hal and polymer were applied as supports, respectively.

Typical procedure for the Suzuki reaction

Aryl halide (1.0 mmol), aryl boronic acid (1.2 mmol), K_2CO_3 (2.0 mmol) and Pd@Hal-Gua-Poly (1.0 mol%) were put into a mixture of water/EtOH (5 mL) and placed in an oil bath (100 °C). Then, the flask containing reaction mixture was stirred under air atmosphere for appropriate time. Upon completion of the reaction (traced by TLC, ratio of *n*-hexane/ethyl acetate, 7:3), the mixture was cooled to room temperature and the catalyst was separated by simple filtration, washed with EtOH several times and dried in oven at 60 °C for 6 h. On the other hand, the solvent of filtrate was removed under reduced pressure and the product was extracted with hexane (10 mL). The resulting coupling product was purified by column chromatography over silica gel to give the corresponding biaryl.

Hydrogenation of nitrobenzene to form an aniline

Pd@Hal-Gua-Poly as a catalyst (1.0 mol%) and nitrobenzene (1.0 mmol) were put into a 5 mL deionized water. Then, the reactor was purged with 1.0 atm. H_2 and the reaction mixture was stirred vigorously (700 rpm) at room temperature for appropriate reaction time. Upon completion of the reaction (monitored by TLC, ratio of *n*-hexane/ethyl acetate, 7:3), the reactor was slowly depressurized and then, Pd@Hal-Gua-Poly was separated by simple filtration, washed with water several times and dried in oven at 60 °C for 6 h. The product was obtained by evaporating the solvent and washing with EtOH.

Result and discussion

Catalyst characterization

The recorded TEM images of Pd@Hal-Gua-Poly are depicted in Fig. 2. In all images, the Hal tube can be recognized as the main morphology. It also can be detected that the outer surface of Hal is covered with polymer. This result was further confirmed by other analyses (vide infra). The fine darker spots on the Hal tubes in the TEM images of the catalyst can be assigned to the Pd nanoparticles. The images showed that Pd nanoparticles are almost fine and well-dispersed with average particle size of 5 nm.

To investigate the change of the surface morphology of Hal upon incorporation of Poly and Pd, the SEM images of Hal, Hal-Gua-Poly, and Pd@Hal-Gua-Poly were recorded and compared, Fig. 3. As depicted in Fig. 3, in all SEM images, the tubes of Hal can be detected, implying that upon functionalization with Poly and immobilization of Pd the tubular morphology of Hal is preserved. However, it can be

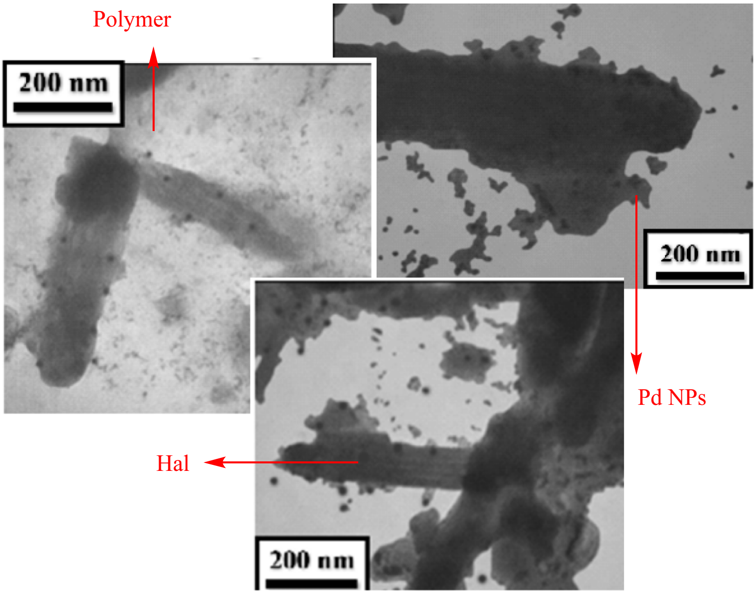


Fig. 2 The TEM images of Pd@Hal-Gua-Poly catalyst

seen that in the case of the catalyst and Hal-Gua-Poly, the morphologies are more compact.

TGA thermograms of pristine Hal, Hal-Si, Hal-Gua and Pd@Hal-Gua-Poly are illustrated in Fig. 4. The thermogram of Hal and Hal-Si are very similar, except, the latter exhibited three weight losses stages, at ~ 150 °C (loss of water in the structure of Hal), at 330 °C (loss of silane) and ~ 590 °C (dehydroxylation of the Hal matrix), while the former showed only two weight losses stages (the ones related to the loss of water and Hal dehydroxylation) [46, 47]. The thermogram of Hal-Gua is very similar to that of Hal-Si. Comparison of this thermogram with that of Hal-Si revealed that the content of Gua was about 4.2 wt%. The thermogram of Pd@Hal-Gua-Poly is distinguished from the others and exhibited lower thermal stability and an additional weight loss stage at 560 °C that can be assigned to the degradation of Poly. Comparing this thermogram with that of Hal-Gua revealed that the content of Poly 17.3 wt%.

To further characterize Pd@Hal-Gua-Poly, Pd content of the catalyst was measured using ICP analysis. The result revealed the low content of Pd in Pd@Hal-Gua-Poly (0.5 wt%).

In Fig. 5 the XRD patterns of Pd@Hal-Gua-Poly and Hal-Gua-Poly are presented and compared with that of pristine Hal. As illustrated, the XRD pattern of Hal-Gua-Poly exhibited the characteristic bands of pristine Hal ($2\theta = 12.5°$, 20.6°, 27.6°, 35.6°, 50.7°, 55.5° and 63.7° (JCPDS No. 29-1487) [48]. Notably, the comparison of the XRD patterns of pristine Hal and Hal-Gua-Poly confirmed that the characteristic bands of Hal in Hal-Gua-Poly were of lower intensities. However, no shift and displacement was observed, indicating that the modification was occurred

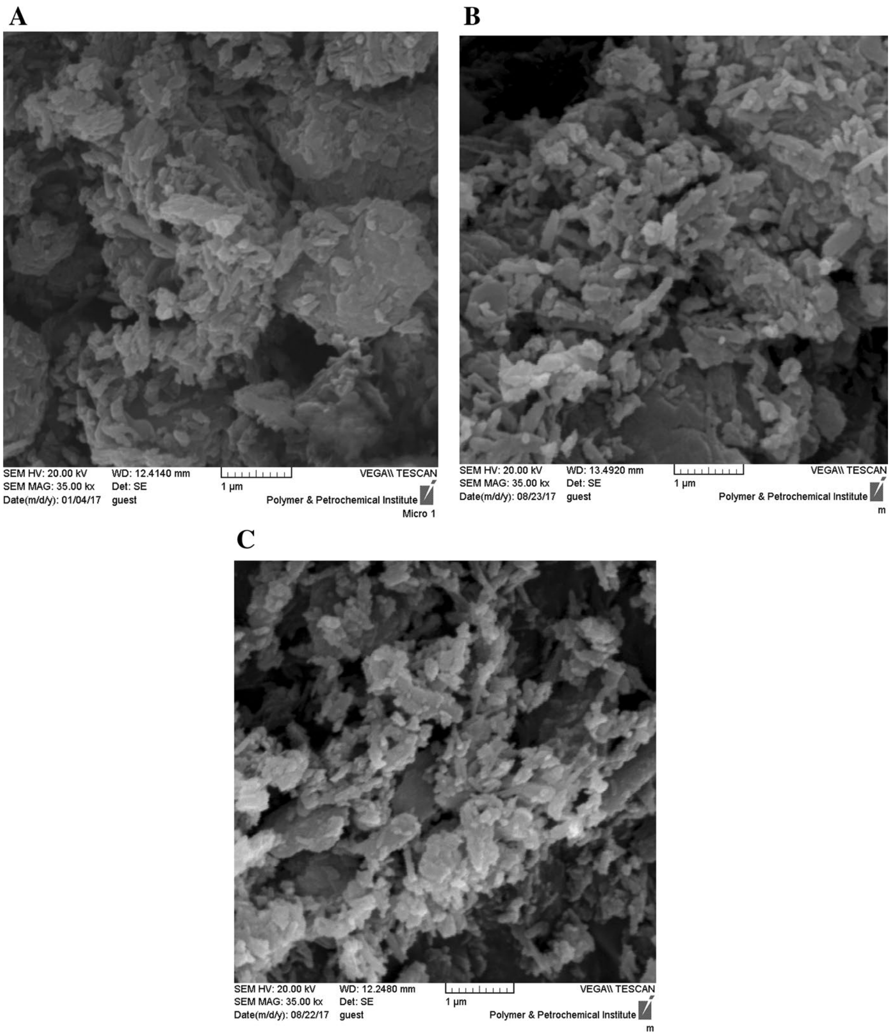


Fig. 3 SEM images of **a** Hal, **b** Hal-Gua-Poly, and **c** Pd@Hal-Gua-Poly

on the outer surface of Hal. The XRD pattern of Pd@Hal-Gua-Poly is very similar to that of Hal-Gua-Poly and exhibited the characteristic bands of Hal with lower intensities as well as the characteristic bands of Pd nanoparticles (labeled as O) can be detected.

The structure of Pd@Hal-Gua-Poly was also verified by FTIR spectroscopy. In detail, the FTIR spectra of the catalyst was recorded and compared with that of Hal-Gua-Poly, Hal-Gua and pristine Hal Fig. 6. According to the literature, the characteristic bands of Hal are as follows: the bands at 3693 and 3624 cm^{-1} (vibration of –OH on interior surface of Hal) 1022 cm^{-1} (Si–O stretching), and 540 cm^{-1} (Al–O–Si vibration) [49]. These bands can be detected in the FTIR

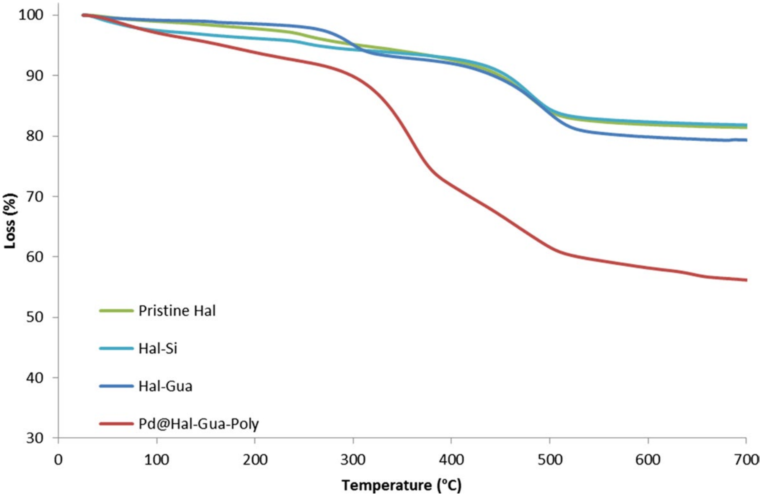


Fig. 4 The TG analyses of pristine Hal, Hal-Si, Hal-Gua and Pd@Hal-Gua-Poly catalyst

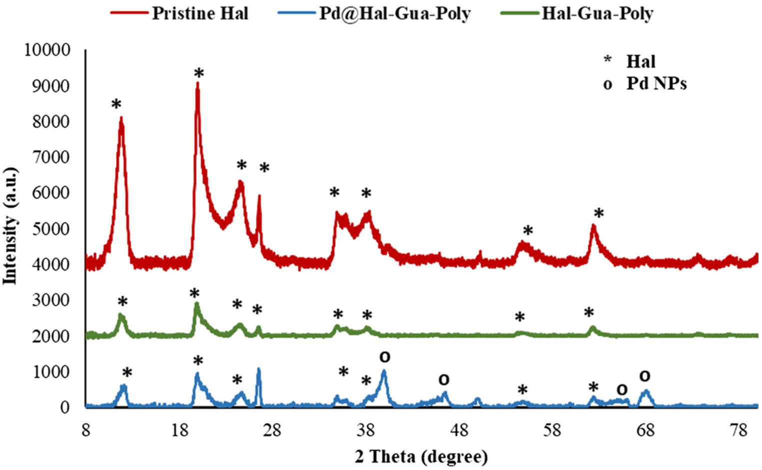


Fig. 5 The XRD patterns of pristine Hal, Hal-Gua-Poly and Pd@Hal-Gua-Poly catalyst

spectra of Hal-Gua-Poly, Hal-Gua and Pd@Hal-Gua-Poly, indicating that upon introduction of Gua, Poly and Pd nanoparticles, the structure of Hal is preserved. In the FTIR spectra of Hal-Gua-Poly and Pd@Hal-Gua-Poly, an additional band at 1733 cm^{-1} can be observed that can be attributed to the –C=O functionality in the backbone of the polymer and confirm conjugation of polymer with Hal.

In the following, BET analysis was exploited to estimate the specific surface area of Pd@Hal-Gua-Poly and pristine Hal. The result showed upon introduction of polymer, this value decreased significantly (from 51 to 10 $m^2\ g^{-1}$), implying

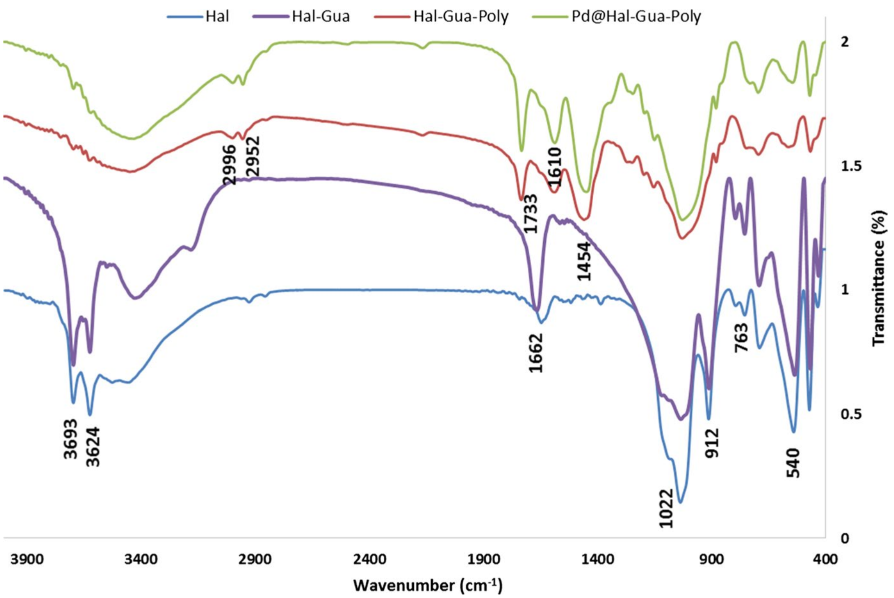


Fig. 6 The FTIR spectra of Pd@Hal-Gua-Poly, Hal-Gua-Poly, Hal-Gua and pristine Hal

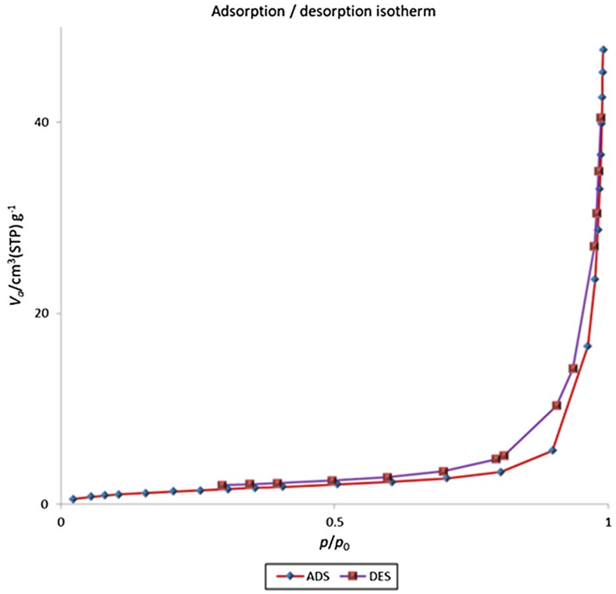


Fig. 7 N_2 adsorption–desorption isotherm of the catalyst

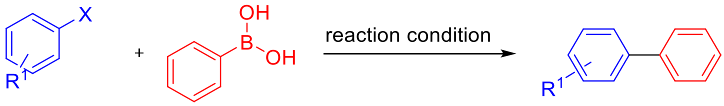
the placement of Poly on the outer surface of Hal. Notably, the nitrogen adsorption–desorption isotherm of Pd@Hal-Gua-Poly (Fig. 7) was of type II [50].

Catalytic activity

Following characterization of the hybrid system, its catalytic activity for two main Pd-catalyzed reactions, Suzuki coupling reaction and hydrogenation of the nitro group to amine functionality, has been investigated. The initial experiments were carried out for two model hydrogenation and coupling reactions, the coupling reaction of iodobenzene with boronic acid and hydrogenation of nitro benzene respectively. Using the two model reactions and altering the reaction variables, the optimum reaction condition for each reaction was found, Tables 1 and 2 in SI. Gratifyingly, the catalyst could promote the hydrogenation reaction under mild and eco-friendly condition, i.e. use of water as solvent at 50 °C, to afford the desired product in short reaction time. The catalyst also showed high catalytic activity for Suzuki coupling reaction and led to the formation of coupling product in high yield in the presence of K_2CO_3 as base and the mixture of water/ethanol as solvent at 100 °C.

Encouraged by high catalytic activity of Pd@Hal-Gua-Poly for catalyzing both hydrogenation and coupling reactions, the generality of the developed protocols was studied by applying several substrates with different electronic and steric properties, Tables 1 and 2. In the case of Suzuki coupling reaction, the results indicated that Pd@Hal-Gua-Poly not only could promote the reaction of aryl iodide that is an active substrate, but also it can successfully catalyze the reaction of less active substrates, i.e. aryl chloride and aryl bromide. Moreover, steric substrate, 1-naphtalene,

Table 1 Pd@Hal-Gua-Poly catalyzed Suzuki–Miyaura reaction of various halides with terminal alkynes

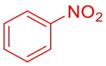
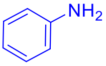
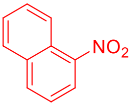
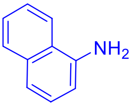
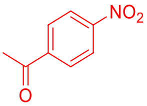
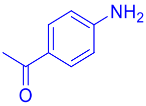
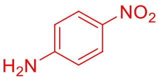
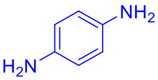


Entry	X	R^1	Time (min)	Yield[a] (%)	TON	TOF (h^{-1})
1	I	H	120	90	9000	4500
2	I	*p*-Me	170	83	8300	2964
3	I	*p*-OMe	100	92	9200	5750
4	I	*p*-COMe	130	93	9300	4400
5	I	*p*-NO_2	110	90	9000	4600
6	I	1-Naphtalene	180	75	7500	2500
7	Br	H	195	85	8500	2600
8	Cl	H	210	90	9000	2500

Reaction condition: aryl halide (1.0 mmol), boronic acid (1.2 mmol), Pd@Hal-Gua-Poly (1 mol%), K_2CO_3 (2.0 mmol) in water:EtOH (5 mL) at 100 °C

[a] Isolated yield

Table 2 Pd@Hal-Gua-Poly catalyzed hydrogenation reaction of nitroarene

Entry	Reagent	Product	Time (min)	Yield[a] (%)	TON	TOF (h^{-1})
1			80	95	9500	7307
2			180	90	9000	6000
3			120	80	8000	4000
4			100	92	9200	7666

Reaction condition: nitroarene (1 mmol), Pd@Hal-Gua-Poly (1 mol%) in water (5 mL) at 50 °C under 1 atm. H_2 gas

[a]Isolated yield

could also tolerate the Suzuki coupling reaction to afford the corresponding product in relatively high yield.

In the case of hydrogenation reaction, the investigation of the scope of the reaction showed that Pd@Hal-Gua-Poly could successfully promote the reaction of sterically demanding substrate, nitro-naphtalene and 4-nitroacetophenone that has carbonyl functionality as a competing group for hydrogenation in its structure to afford only 4-aminoacetophenone as a sole product. This result indicated the high selectivity of the catalyst toward nitro functionality.

Next, it was shown whether hybridization of Hal with poly(methyl methacrylate-*co*-maleic anhydride) could result in synergism and improve the catalytic activity of the final catalyst compared to that of individual components. In this line, two control catalysts, including Pd@Hal, Pd@Poly were synthesized and their catalytic activities for hydrogenation of nitrobenzene under optimum reaction condition was investigated and compared, Table 3. As tabulated, the catalytic activities

Table 3 Comparison of the catalytic activity of the present catalyst with the other prepared catalysts for the hydrogenation reaction

Entry	Catalyst	Yield[a] (%)	Time (min)	Loading of Pd NPs (wt%)
1	Pd@Hal-Gua-Poly	95	80	1.13
2	Pd@Hal	65	80	0.68
3	Pd@Poly	70	80	1.02

Reaction condition: nitrobenzene (1 mmol), catalyst (1 mol%) in water (5 mL) at 50 °C under 1 atm. H_2 gas

[a]Isolated yield

of the studied catalysts decreased in the following order: Pd@Hal-Gua-Poly > Pd@Poly > Pd@Hal. This result indicated that Hal-Poly was a better catalyst support than individual Hal and Poly. To shed light to the origin of the different observed catalytic activities of the control catalysts, the Pd loading of each sample was calculated and compared, Table 3. As shown, the loading of Pd in these samples increased in the following order: Pd@Hal-Gua-Poly > Pd@Poly > Pd@Hal. This trend is similar to the trend of an increase of the catalytic activity and indicates the key role of Pd loading in the catalytic activity. In other words, Hal-Gua-Poly had better capacity to anchor Pd nanoparticles that are the main catalytic species and consequently showed the highest catalytic activity.

In the last part of the study of the catalytic activity, the catalytic activity of Pd@Hal-Gua-Poly was compared with some of other catalysts, reported in the literature, Table 4. As tabulated, various protocols with use of various catalysts, solvents and reducing agents have been reported. Comparing the yield of the catalysts, it can be concluded that the catalytic activity of the catalyst is comparable to that of Pd-based catalysts. Moreover, the mild reaction condition, i.e. aqueous media, use of environmentally benign reducing agent (hydrogen gas) with low pressure, relatively facile and cost-effective synthetic procedure and recyclability of the catalyst render the present protocol a potential methodology for hydrogenation reaction.

Catalyst recyclability

Motivated by high catalytic activity of Pd@Hal-Gua-Poly, the recyclability and Pd leaching of the catalyst were also investigated. The recyclability of the catalyst was simply studied by reusing the recovered catalyst for the next run of the model hydrogenation and Suzuki reactions (see experimental section). Repeating the reuse of the catalyst for seven consecutive reaction runs (Fig. 8), it was found that upon each run, the catalytic activity decreased slightly (except the second run of recycling for the Suzuki reaction that the catalyst preserved its catalytic activity) and after seven reaction runs only 20% loss of the catalytic activities were observed. Regarding the Pd leaching that is important from economic and environmental points of view, the ICP analysis demonstrated that this value for the first four runs of the recycling was negligible. However, upon further recycling, this value gradually increased and reached its highest value (0.4 wt% Pd loading) upon seventh recycling.

Next, the catalyst stability upon recycling was studied by recording the FTIR spectrum of the recycled Pd@Hal-Gua-Poly and comparing it with that of the fresh one, Fig. 9. As depicted, the two spectra are quite similar and showed the characteristic bands of Pd@Hal-Gua-Poly. However, the intensities of the characteristic bands in the FTIR spectrum of the recycled catalyst are lower than those of the fresh one.

To investigate the effect of recycling on the catalyst morphology, the recycled catalyst after seven reaction runs has been subjected to the TEM and SEM analyses, Fig. 10. As depicted in Fig. 10, the TEM and SEM images of the recycled catalyst are similar to those of the fresh catalyst. In the TEM image of the recycled catalyst, the Hal tubes decorated with Poly, as well as the dark spots that

Table 4 The comparison of the catalytic activities of various reported catalysts with Pd@Hal-Gua-Poly for the hydrogenation of nitrobenzene

Entry	Catalyst**	Temperature (°C)	Solvent and pressure	Reducing agent	Time (h:min)	Yield (%)	References
20	Pd@Hal-Gua-Poly, 1 mol%	50	H_2O	H_2/1 atm		95	This work
4	Pd@Hal/di-urea[a] (1.5 wt%)	50	H_2O	H_2/1 bar	1:00	100	[51]
1	Pd-$CH_3NH_2BH_3$ (6 mol%)	r.t.	H_2O/MeOH	$CH_3NH_2BH_3$	0:10	99	[52]
6	Pd/PPh_3@FDU-12[b] (8.33×10^{-4} mmol Pd)	40	EtOH/10 bar	H_2/10 bar	1:00	99	[53]
3	APSNP[c] (1 mol%)	r.t.	EtOH	H_2/40 atm	2:00	100	[54]
2	PdNP(0.5%)/Al_2O_3 (0.3 g)	r.t.	THF	H_2/1 atm	3:00	100	[55]
5	Pd0-AmP-MCF[d] (0.5 mol%)	r.t	EtOAc	H_2/1 bar	0.75	90	[56]
9	PdNP@PPh_2-PEGPIILP[e] (0.05 mol%	r.t.	H_2O	$NaBH_4$	2:00	99	[57]
11	PdCu/graphene (2 mol% Pd)	50	H_2O/EtOH	$NaBH_4$	1:30	98	[58]
15	Pd NPs/RGO (6 mg)	50	H_2O/EtOH	$NaBH_4$	1:30	98	[59]
12	PdCu/C (2 mol% Pd)	50	H_2O/EtOH	$NaBH_4$	1:30	85	[58]
7	Cu–Acac@Am–Si–Fe_3O_4[f](20 mg per 1 mmol substrate)	r.t.	H_2O	$NaBH_4$	0:12	97	[60]
8	Cu·Am-Sil@SiO_2[g] (20 mg per 1 mmol substrate)	r.t.	H_2O	$NaBH_4$	0:11	94	[61]
10	Cu NPs (10 mol%)	50	THF/H_2O	$NaBH_4$	2:00	98	[62]
14	Cu/graphene	50	H_2O/EtOH	$NaBH_4$	1:30	65	[58]

[a] Pd immobilized on functionalized halloysite clay

[b] Pd NPs (1.1 nm) with triphenylphosphine (PPh3) cross-linked in the nanopore of FDU-12

[c] Activated palladium sucrose nanoparticles

[d] Pd nanoparticles supported on aminopropyl-functionalized siliceous mesocellular foam

[e] Palladium nanoparticles stabilized by lightly cross-linked phosphine-decorated polymer immobilized ionic liquids (PIIL) and their PEGylated counterparts (PEGPIIL)

[f] Copper(II) acetylacetonate compleximmobilized over amine functionalized silica@magnetite nanoparticles

[g] Copper (II) impregnatedorganic-inorganic nano-hybrid

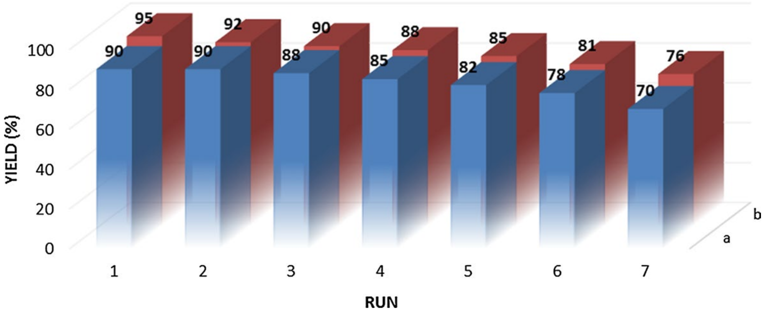


Fig. 8 Recyclability of the Pd@Hal-Gua-Poly catalyst in Suzuki coupling reaction (a) and hydrogenation reaction (b)

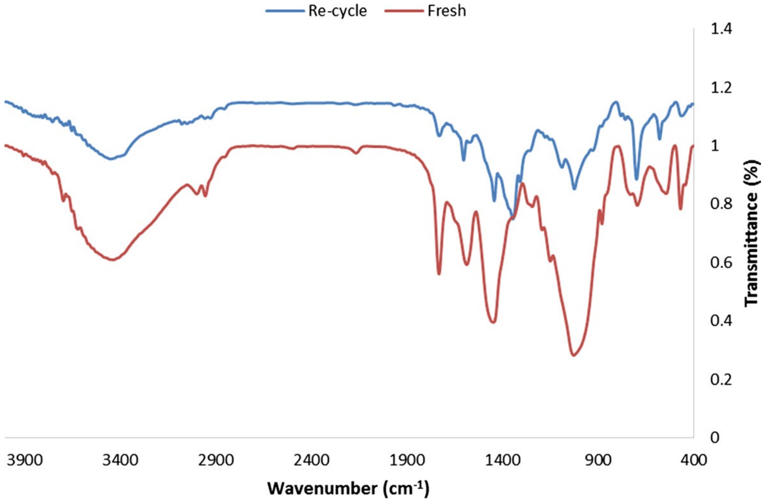


Fig. 9 The FTIR spectra of fresh Pd@Hal-Gua-Poly and after seven runs

are indicative of Pd nanoparticles can be detected. In SEM image of the catalyst also the Hal tubes can be seen.

The EDX analysis of the recycled catalyst, Fig. 11, also confirmed the presence of Pd nanoparticles. Moreover, the presence of Si, Al and O can be attributed to the structure of Hal. The C and N and O elements can also be indicative of the functionality (Poly and Gua) on the surface of Hal.

Finally, the nature of the catalysis was studied by hot-filtration test. The results of this experiment proved that in the course of the both reactions, Pd nanoparticles did not leach from the surface of the support to the reaction mixture and re-deposited on the support at the end of the reaction. This confirmed the heterogeneous nature of the catalysis.

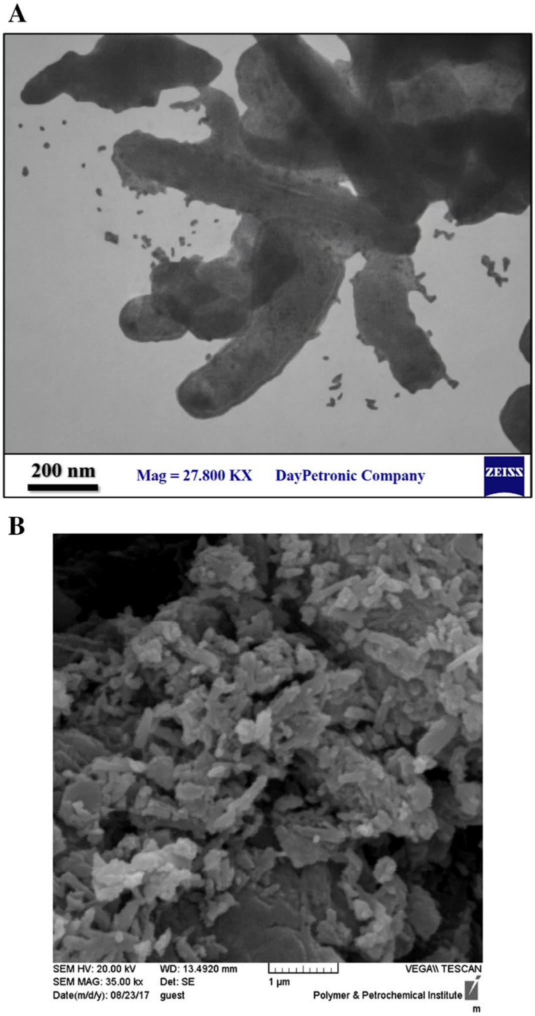


Fig. 10 **a** TEM and **b** SEM images of the recycled catalyst after seven reaction runs

Conclusion

Guanidine functionalized Hal was reacted with poly(methyl methacrylate-*co*-maleic anhydride) to form a covalent hybrid system, Hal-Poly. The latter was then applied for the immobilization of Pd nanoparticles and formation of Pd@Hal-Gua-Poly that was an efficient catalyst for promoting two class of Pd-catalyzed reactions, hydrogenation of nitroarenes and Suzuki coupling reaction, under mild and environmentally benign condition. The comparison of the catalytic activity of the catalyst with two control samples, i.e. Pd@Hal and Pd@Poly confirmed the synergism between Hal and Poly. Noteworthy, the catalyst was highly recyclable (up to seven reaction runs) and showed low loss of the catalytic activity and Pd leaching upon recycling. Considering the relatively simple protocol for the synthesis of the catalyst, its high

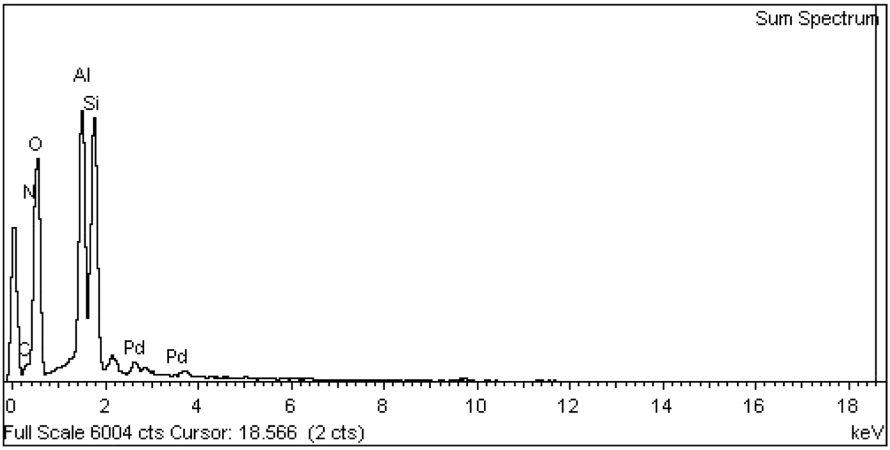


Fig. 11 EDX analysis of the recycled catalyst

catalytic activity for two model reactions as well as high recyclability, Pd@Hal-Gua-Poly can be considered as a potential heterogeneous catalyst for promoting various Pd-catalyst chemical transformations, such as C–C coupling, C=C hydrogenation, A^3 and KA^2 reactions that are utile reactions for the synthesis of more complex compounds with utility for drug and chemical industries. Moreover, it can be assumed that Hal-Gua-Poly can be applied for the immobilization of other catalytic species such as silver and copper species to furnish the catalysts that can be applied for diverse range of organic reactions.

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Affiliations

Samahe Sadjadi[1] · Masoumeh Malmir[2] · Nargess Pourmohammad[2] · Shervin Ahmadi[3] · Majid M. Heravi[2]

✉ Samahe Sadjadi
samahesadjadi@yahoo.com; s.sadjadi@ippi.ac.ir

✉ Shervin Ahmadi
Sh.Ahmadi@ippi.ac.ir

✉ Majid M. Heravi
mmh1331@yahoo.com; m.heravi@alzahra.ac.ir

[1] Gas Conversion Department, Faculty of Petrochemicals, Iran Polymer and Petrochemicals Institute, PO Box 14975-112, Tehran, Iran

[2] Department of Chemistry, School of Science, Alzahra University, PO Box 1993891176, Vanak, Tehran, Iran

[3] Department of Polymer Processing, Iran Polymer and Petrochemical Institute, Tehran, Iran