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Magnetic porous chitosan-based palladium catalyst: A green, highly efficient and reusable catalyst for Mizoroki-Heck reaction in aqueous media

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A novel, biodegradable and environmentally benign magnetic porous chitosan-thienyl imine palladium(II) complex, MPCS-TI/Pd, was prepared and characterized by FT-IR, SEM, TEM, EDX, XRD, BET, VSM and TG-DTA analysis. This complex, with high surface areas and low catalyst loading, was found to be a highly active and robust heterogeneous catalyst for the Mizoroki-Heck reactions of aryl bromides and chlorides with various terminal olefins in aqueous media in good to excellent yields. The catalyst was easily separated by an external magnet and the recovered catalyst was reused in seven cycles without significant loss of catalytic activity.

Introduction

Palladium-catalyzed carbon-carbon bond-forming reactions have played a crucial role in synthetic organic chemistry. The palladium-catalyzed coupling of aryl halides and terminal alkenes (the Mizoroki-Heck reaction) is regarded as the most successful method for the preparation of various substituted olefins, dienes, and precursors of conjugated polymers.[1,2]

The Mizoroki-Heck reaction has shown to have a widespread application in the synthesis of natural products,[3,4] agrochemicals,[5] and pharmaceuticals.[6] Many catalytic systems have been developed for this reaction using different palladium catalysts together with phosphane and phosphorous ligands.[7,8] However, phosphane ligands are sensitive to air oxidation, as well as being toxic, expensive, and unstable at high temperatures. Efforts have been made to eliminate phosphorous from this reaction.[9, 10] Moreover, many catalysts used in the Heck reactions are homogeneous, which are impossible to be recovered and the residual palladium left in the product, confines the reaction; therefore, in recent years, the development of heterogeneous catalytic systems has increased. The advantages of heterogeneous catalysts which make them valuable for the environment are having more surface areas and simpler isolation of the reaction products and recyclability of the catalyst.[11,12] The heterogeneous catalysts have been immobilized onto various supporters, such as zeolites,[13] silica,[14] ionic liquids,[15] multi-walled carbon nanotubes[16-18] and polymers such as polystyrene,[19-21] polyethylene glycol,[22] polyvinyl chloride-polyethylene,[23] and polysaccharides.[24]

Chitosan is a safe, inexpensive, natural, and biodegradable polysaccharide which is derived from animal resources such as the shells of several crustaceans, shrimp shell, fish shell and some fungi. This biopolymer has been employed for various applications in agriculture,[25] food,[26] biosensors,[27] biomedical,[28] adsorption of heavy metals,[29-32] drug delivery,[33] as well as stable support for Pd-catalyzed cross-coupling reactions.[34,35] Chitosan is derived from deacetylation of chitin and is usually obtained in a powdered or flaked form, but these forms have relatively low specific surface area.[36] Highly porous chitosan microspheres (PCMS)-supported palladium catalyst with a high specific surface area of the porous structure has been reported to show high catalytic activity, stability, and recyclability for homocoupling and cross-coupling reactions of aryl halides.[37]

During the last two decades, magnetically recoverable nanoparticles have attracted a great attention as heterogeneous catalysts due to their inherent properties,[38,39] such as simple handling, simple renewability and recovery with magnetic separation, thermal stability, biocompatibility, large surface area, and high catalytic activity in various organic reactions.[40,41]

In the present work, we wish to report a new reusable and efficient heterogeneous magnetic porous catalyst from chitosan-supported imine palladium complex for the Heck reaction of

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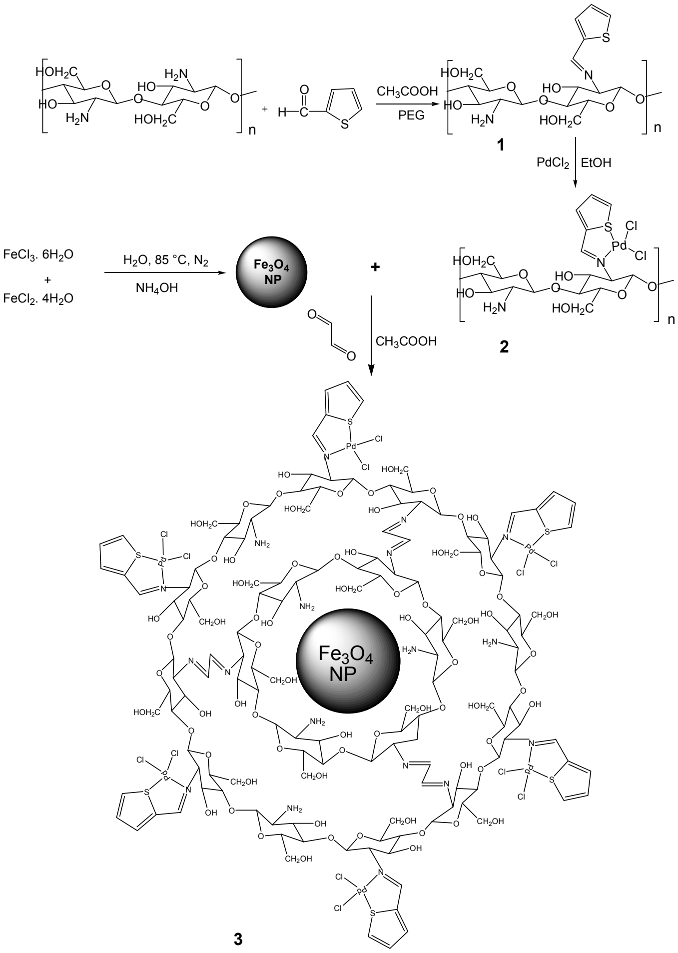

Scheme 1. Preparation of MPCS-TI/Pd catalyst.

aryl bromides and chlorides with various olefins in aqueous media.

Results and discussion

Characterization of MPCS-TI/Pd

The porous chitosan-thienyl imine support (PCS-TI, **1)** was easily prepared by treating chitosan with an appropriate amount of 2- thiophenecarbaldehyde and polyethylene glycol (PEG) in dilute acetic acid for 24 h at room temperature (Scheme 1). Then the reaction mixture was dripped into a 1N NaOH aq. solution through a needle, washed with hot water until neutral, followed by extraction of the PEG component (Scheme 1). Similarly, the bead chitosan-supported ligand (BCS-TI) was prepared by the same protocol in the absence of PEG. Also, the normal chitosan-supported ligand (NCS-TI) was produced by mixing chitosan and 2-thiophenecarbaldehyde in EtOH. Fig. 1, shows the difference in size and appearance among NCS-TI, BCS-TI, and PCS-TI supports with the same weight of the samples. The PCS-TI ligand was characterized by elemental analysis. The sulfur and nitrogen contents of this polymer were 1.65 and 5.32 mmol/g, respectively, indicating that the degree of substitution was 0.31. The FT-IR spectra in Fig. 2 indicate the differences between unmodified chitosan, modified chitosan-supported (chelate ligand), and its palladium complexes; the successful functionalization to an imine is indicated by several observations. Comparison of the FT-IR spectra of modified chitosan support (**1**, Fig. 2b) to unmodified chitosan (Fig. 2a) reveals a new band at 720 cm^{-1} which is characteristic =CH OOP band for thiophene. At 1637 cm^{-1}, a noticeably strong band is observed which is caused by C=N stretching vibration of the imine group. FT-IR spectrum of the TI-functionalized chitosan-supported PdCl$_2$ complex (**2**, PCS-TI/Pd), Fig. 2c, shows its C=N vibrational band at 1630 cm^{-1}, a lower frequency than that observed for the free ligand (**1**), supporting the assumption that the ligand coordinates to the metal ion through the nitrogen atoms of the ligand. Finally, the cross-linked magnetic porous chitosan-thienyl imine Pd complex, MPCS-TI/Pd (**3**) was prepared by treatment of PCS-TI/Pd with the suspension of Fe$_3$O$_4$ in glyoxal and aq. acetic acid solution at room temperature. The vibration band at 569 cm^{-1} is the typical IR absorbance induced by structure Fe-O vibration of the Fe$_3$O$_4$ MNPs (Fig. 2d). Also, in addition to the C=N vibrational band of the PCS-TI/Pd complex **2** at 1630 cm^{-1}, another band at 1636 cm^{-1} is observed which is attributed to the C=N of the imine groups between remained amino groups of the complex **2** and glyoxal cross-linker agent.

Fig. 1. The picture of NCS-TI(a), BCS-TI (b), PCS-TI (c).

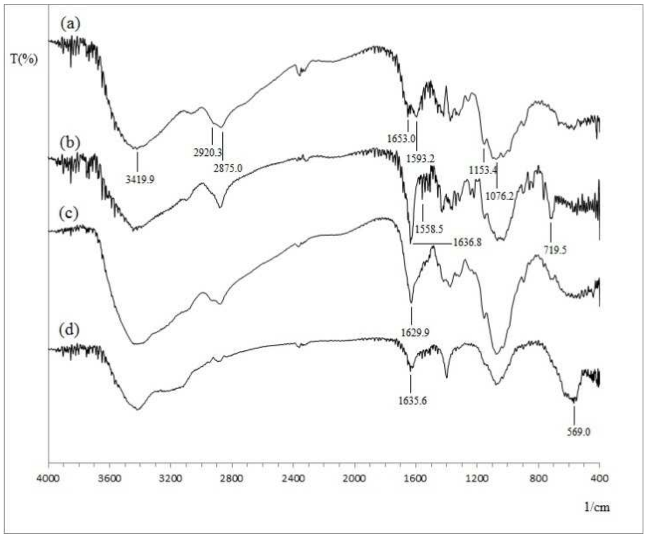

Fig. 2. FT-IR spectra of chitosan (a), PCS-TI (b), PCS-TI/Pd (c), and MPCS-TI/Pd complexes (d).

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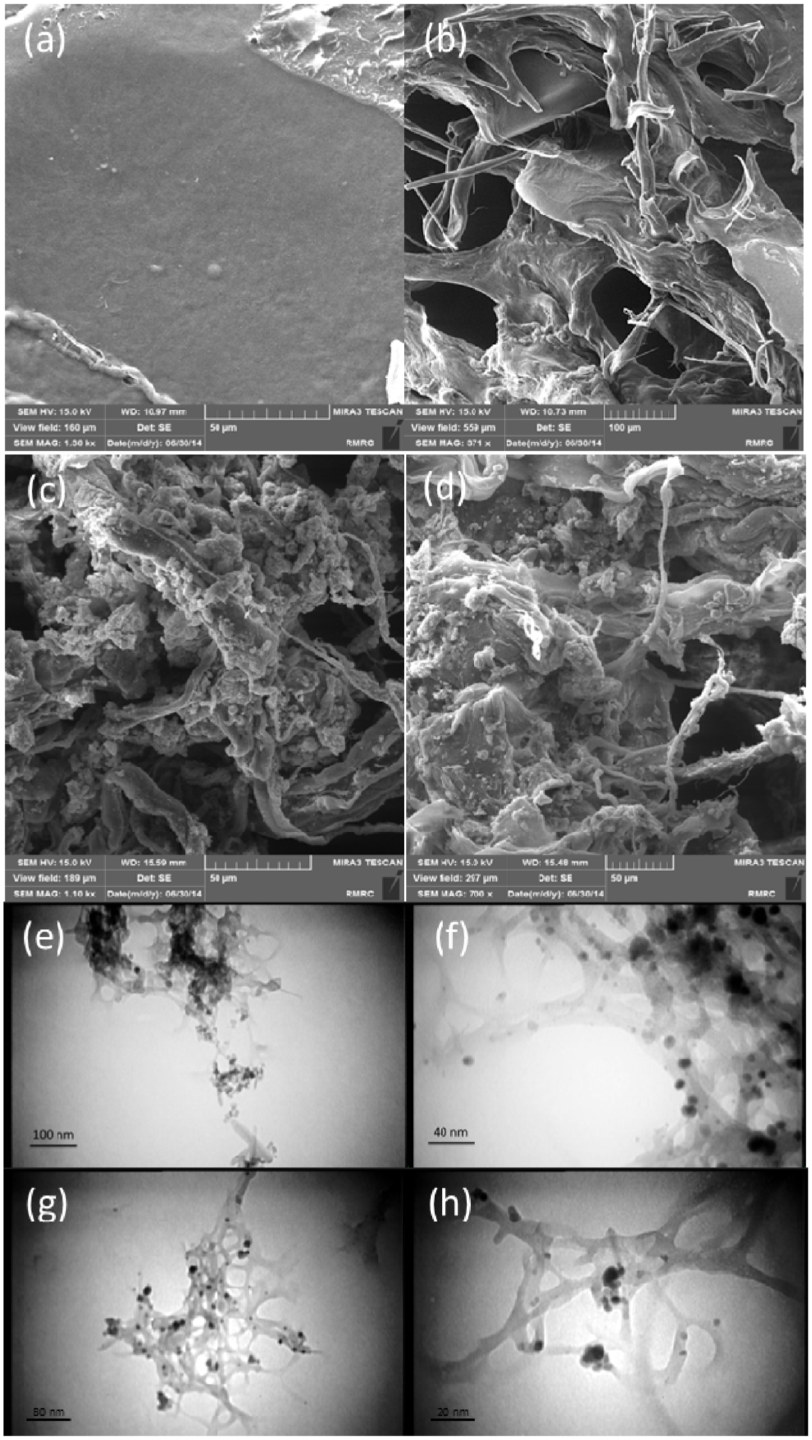

Fig. 3. SEM images of the NCS-TI ligand (a), PCS-TI(b), PCS-TI/Pd (c), MPCS-TI/Pd (d), and TEM images of MPCS-TI/Pd before reaction (e, f), after eight cycles of reaction (g, h).

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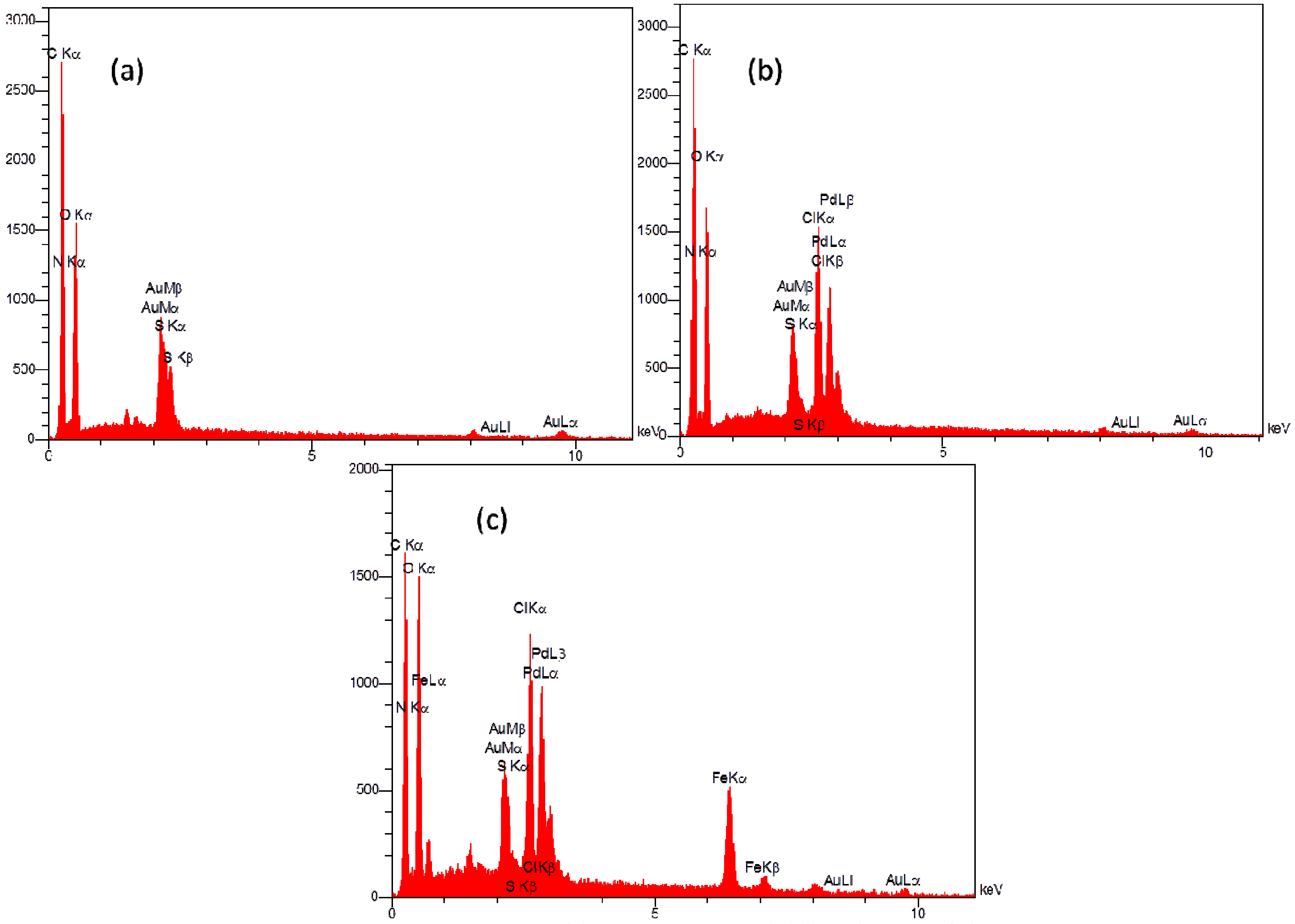

Fig. 4. EDX spectra of the PCS-TI (a), PCS-TI/Pd (b), and MPCS-TI/Pd (c).

This catalyst was also characterized by ICP, SEM, TEM, EDX, XRD, XPS, VSM, and TGA. The palladium content of the catalyst (**3**), as determined by ICP was obtained to be 2.8% (0.263 mmol/g). The morphological structures of the NCS-TI and PCS-TI were examined by SEM, which show the change on the surface of the porous polymer, as compared with the uniform normal polymer (Fig. 3a and 3b). TEM images of the fresh catalyst (MPCS-TI/Pd, **3**) at two different magnifications were recorded (Fig. 3e and 3f); these images clearly show that Pd nanoparticles were formed and well-defined spherical particles dispersed in the polymer matrix with a size in the range of 6-8 nm (see ESI). The TEM images of the catalyst after eight times of use (Fig. 3g and 3h) exhibits slight aggregation of palladium(II) NPs with average size of 6-12 nm. The EDX spectra of PCS-TI/Pd and MPCS-TI/Pd (Fig. 4b-c) were carried out to examine the existence of palladium and iron; Fig. 4b reveals the presence of palladium on the surface of chitosan matrix with energy bands of 2.6 and 2.8 KeV (L lines). The presence of both Fe_3O_4 MNPs cores (6.43 and 7.2 KeV) and palladium of chitosan matrix were also confirmed by EDX analysis (Fig. 4c). The XRD patterns of PCS-TI, PCS-TI/Pd, and the cross-linked magnetic MPCS-TI/Pd are shown in Fig. 5a. As presented in Fig. 5a (i), the diffraction pattern of chitosan-thienyl imine support shows a characteristic peak at $2\theta = 20.60°$. The XRD pattern of PCS-TI/Pd shows three peaks at $2\theta = 40.13°, 46.24°, 68.27°$ which are attributed to (1 1 1), (2 0 0) and (2 2 0) facets of elemental palladium (Fig. 5a (ii)). The XRD measurement of the magnetic MPCS-TI/Pd catalyst (Fig. 5a (iii)) exhibits diffraction peak at $2\theta = 29.17°, 35.67°, 43.02°, 53.51°, 57.57°, 62.92°, 71.23°$, and $74.09°$; these values are in good agreement with the standard XRD pattern of Fe_3O_4 (JCPDS file No. 19-0629). Further evidence for the attachment of thiophenecarbaldehyde and metal on to the polymeric support is confirmed by X-ray photoelectron spectroscopy (XPS) of the complex. The peaks at 285.0, 399.78, 530.14, 162.36, and 711.86 eV are attributed to C, N, O, S, and , Fe atoms, respectively (Fig. 5b); The Pd^{II} $3d_{5/2}$ and $3d_{3/2}$ binding energies of the fresh MPCS-TI/Pd catalyst were determined to be 337.58 and 342.98 eV, respectively (Fig. 5c top); also, the binding energies of 334.57 ($3d_{5/2}$) and 340.82 ($3d_{3/2}$) eV are attributed to Pd^0. The results showed the presence of 86.2% of Pd^{II} and 13.8% of Pd^0 in the fresh (original) MPCS-TI/Pd catalyst, and 93.12% of Pd^0 and 6.9% of Pd^{II} after reaction (Fig. 5c bottom).

The magnetic properties of Fe_3O_4 MNPs and the catalyst **3** were investigated by VSM measurement (Fig. 6). Fig. 6a exhibits typical magnetization curves of the pristine Fe_3O_4 MNPs and the catalyst **3** as a function of the applied magnetic field at 300 K. The two hysteresis loops of supermagnetic

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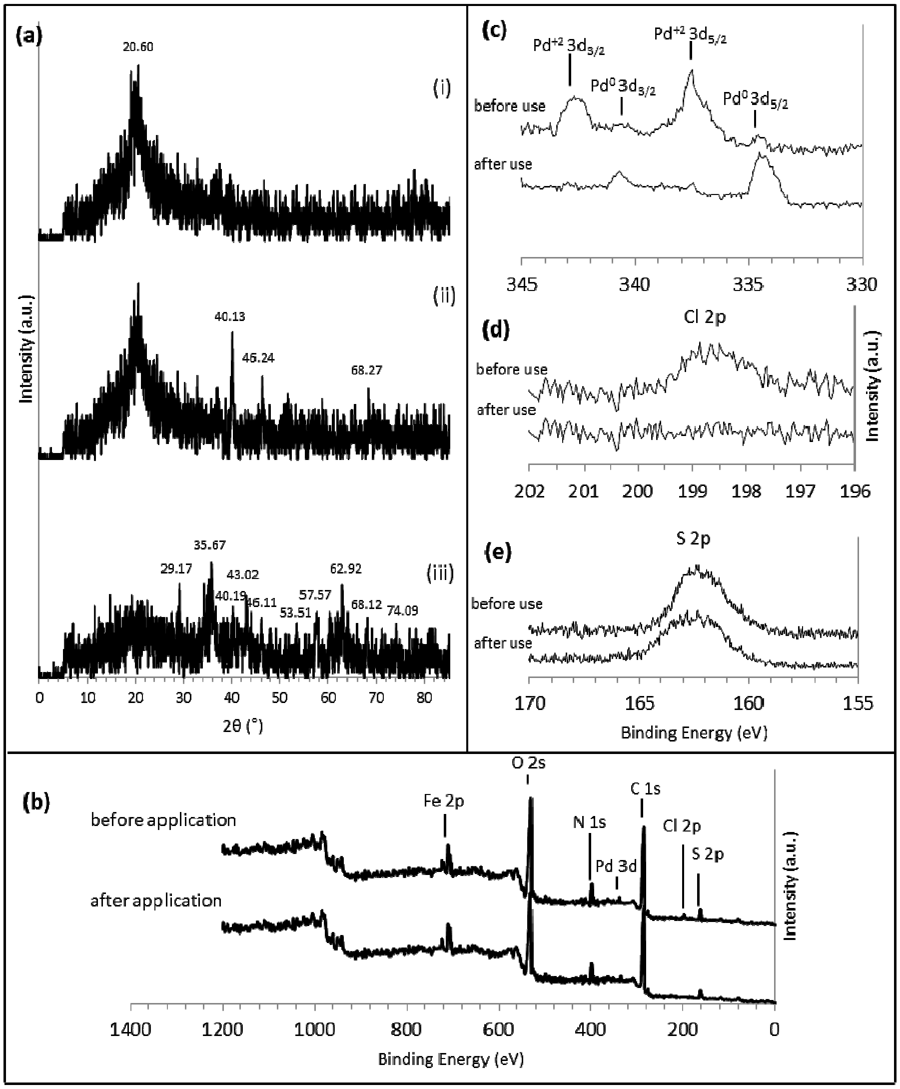

Fig. 5. (a) Powder XRD patterns of the PCS-TI (i), PCS-TI/Pd (ii), and MPCS-TI/Pd (iii). (b) XPS spectrum of the MPCS-TI/Pd, (c) XPS of the Pd 3d, (d) Cl 2p, (e) S 2p, and up, before reaction, down, after reaction.

Fe_3O_4NPs and MPCS- Fe_3O_4 (66.96 emu/g); this reduced magnetic strength is due to the chitosan shells covered on magnetic particles.

From the N_2 adsorption/desorption isotherm of MPCS-TI/Pd catalyst **3**, the BET surface area of the particles is 205.6 m^2g^{-1} as calculated by linear part of the BET plot, and the total pore volume at $P/P^0 = 0.98$ is 0.4741 cm^3g^{-1}. The BET isotherm is of type IV and H3 hysteresis loop (IUPAC classification) is the characteristic of mesoporous adsorbents.[42] The pore distribution of this catalyst is in the mesoporous regime, with mean pore diameter of 1.64 nm (see ESI. Fig. S25, S26).

Thermal stability is necessary for the catalytic activity and recyclability of a catalyst, because C-C coupling reactions are carried out under high temperature conditions. TGA and DTA with heating in a range varying from room temperature to 850 °C showed weight losses peaks around 75-180, 180-310, and 310-440 °C which could be attributed to the evaporation of the residual water, chitosan-chain of low molecular weight decomposistion, and chitosan-thienyl imine over Fe_3O_4 NPs decomposition (see ESI, Fig. S27).

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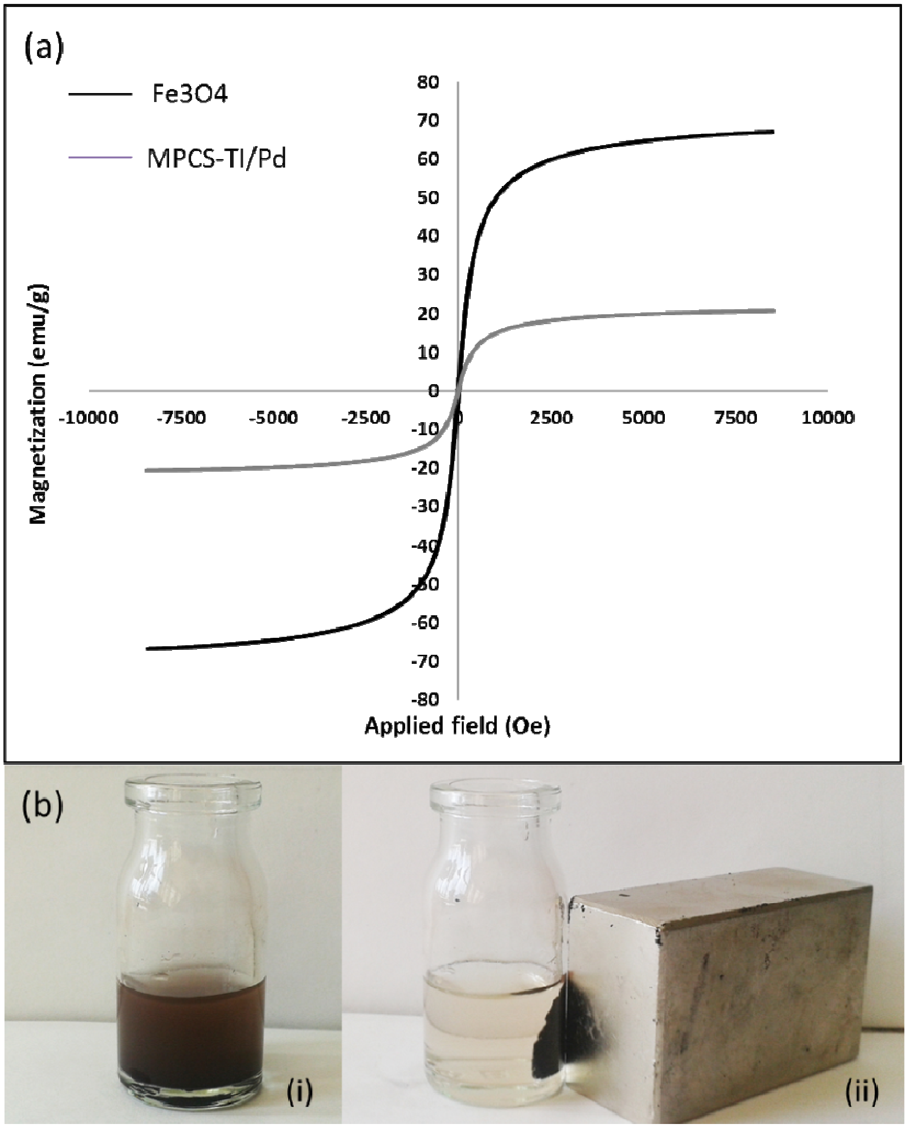

Fig. 6. (a) Magnetization (M) as a function of field (H) for Fe_3O_4 nanoparticles (black curve) and **3** (gray curve). (b) The MPCS-TI/Pd in a typical reaction mixture in the absence (i) and the presence of a magnetic field (ii).

Catalytic performance of MPCS-TI/Pd catalyst for the Heck reaction

To explore the catalytic activity of various Pd catalysts, the Mizoroki-Heck reaction of 4-bromoanisole with styrene, as model substrates, was investigated under various reaction conditions. The results are summarized in Table 1. As can be seen, the NCS-TI/Pd catalyst has considerably lower catalytic activity than the corresponding bead and porous catalysts (Table 1, entries 1-3). Similar results were obtained for their magnetic counterparts (Table 1, entries 4-6). Among the Pd catalysts investigated, the porous catalysts PCS-TI/Pd and MPCS-TI/Pd (Table 1, entries 3 and 6) showed better catalytic performances because of high surface area in their structures.

Although the catalytic activity of the former was higher than the latter in the first run (96% vs 91%), the magnetic porous catalyst was more reusable, as seen in their run 2. The effects of the type of solvent, base, temperature, as well as

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catalyst loadings were investigated using MPCS-TI/Pd as the catalyst. It was revealed that single solvents such as DMF, DMSO, and H_2O, and even the solventless condition gave lower yields (Table 1, entries 8-10 and 12). The best reaction solvent was found to be DMF/H_2O (v/v = 1:2) (Table 1, entry 6). It was also found that Et_3N gives a better result than *N,N*-diisopropylethylamine (DIPEA), K_2CO_3, and NaOAc (Table 1, entries 6, 13-15). When the reaction was carried out at different temperatures, it was found that increasing the temperature from 100 to 110 °C increases the yield, while raising the temperature even further up to 120 °C and 130 °C gives little improvements (Table 1, entries 6, 17 and 18). It was confirmed that TBAB was necessary for the reaction; the results listed in Table 1 showed that a much poorer yield was obtained in the absence of this additive (Table 1, entry 7). When 0.5 equiv. of TBAB was used, the best result was achieved (Table 1, entry 6). Then, different catalyst loadings between 0.05 and 0.2 mol% were studied for the reaction (Table 1, entries 6, 19 and 20. Among those, 0.1 mol% of the catalyst was found to be the best. Therefore, it was decided to use DMF/H_2O in volume ratio of 1:2 as the solvent, Et_3N as the base, 0.1 mol% catalyst at 110 °C as the optimal condition in further studies.

Due to the fact that MPCS-TI/Pd is an efficient and reusable catalyst for the Mizoroki-Heck reaction of 4-bromoanisole with styrene under optimized conditions, the catalyst was then applied to other cross-coupling reactions of aromatic bromides and chlorides carrying either electron-withdrawing or electron-releasing constituents in aromatic rings with various vinylic substrates (styrenes, acrylates, acrylic acid, acrylonitrile, and acrylamide) (Table 2). The *trans*-products were selectively obtained in all cases. The results show that the above catalytic system is remarkably active and tolerates a range of functional groups. Table 2 shows that the reaction of aryl bromides with terminal olefins all proceeded very smoothly within 4 to 6 hours to give the desired products in 83-96% isolated yields (Table 2, entries 1-19). There was no significant difference in the yield of product between electron-deficient and electron-rich bromides (Table 2, entries 1-6, 9-15). On the basis of the above results, to extend the scope and generality of this protocol, the coupling of aryl chlorides was also studied. Compared with the corresponding bromo analogues, the reactions of chloro derivatives gave moderate to good yields and required longer times (Table 2, entries 20-27).

Stability and recyclability of MPCS-TI/Pd catalyst

Another point of great concern for heterogeneous catalysts is the possibility of transition metal leaching when used in a polar medium, especially for those prepared by adsorption of transition metal on solid matrices, such as polymer, silica, charcoal, and aluminum oxide.[43] Matrix surface modification by the introduction of special ligands has been extensively studied to minimize the transition metal leaching and to enhance chelation of transition metals with the introduced surface ligands.

The reusability of our magnetic catalyst was also examined by carrying out repeated runs on the same batch of 0.1 mol% MPCS-TI/Pd catalyst used in the Mizoroki-Heck reaction of 4-bromoanisole (1 mmol) and styrene (1.3 mmol) under the reaction conditions. After each cycle, the reaction mixture was cooled down to room temperature and H_2O (10 mL) was added, the catalyst was magnetically separated, washed with water and Et_2O, and dried in vacuum at 50 °C for 2 h before being used for the next round of the reaction. The catalyst shows unchanged catalytic activities up to seven reaction cycles (Fig. 7); no catalyst deterioration was observed, confirming the high stability of the heterogeneous catalyst under the reaction conditions.

To determine whether the catalyst is truly functioning in a heterogeneous manner, a hot filtration test was performed in the Heck reaction of 4-bromoanisole and styrene under the reaction conditions. During the catalytic reaction, the solid catalyst was removed from the reaction mixture by using an external magnet after 1 h and the determined conversion was 27%. The residual solution was, then, allowed to react for a further 4 h and the obtained conversion was the same (27%). Also, the amount of the Pd species dissolved into solution caused by leaching of the catalyst was determined using ICP after evaporation of the solution to dryness. The ICP result showed that 0.07% of the total amount of the original Pd species is lost into solution during the course of the reaction. These results suggested that minimal leaching of palladium takes place during the reaction and the catalyst is purely heterogeneous in nature.

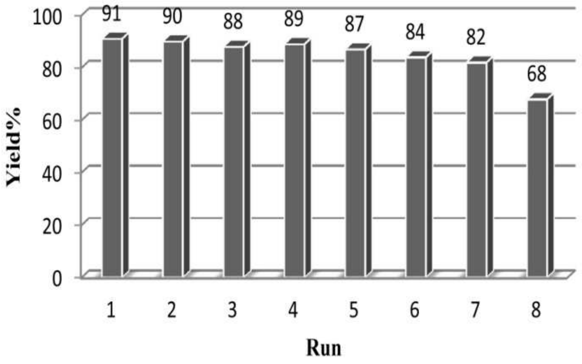

Fig. 7. Recycling activity of the MPCS-TI/Pd catalyst.

Conclusions

In summary, we have prepared and characterized a novel stable low leaching magnetic porous chitosan-thienyl imine palladium complex catalyst. This green, heterogeneous and biodegradable catalyst proved to be a highly active, selective, and recyclable catalyst for the Mizoroki-Heck reaction of aromatic bromides and chlorides with various terminal olefins in aqueous media. The advantages of this procedure is simple operation, low catalyst loading (0.1 mol%), easy separation of the catalyst, excellent yields of the products, and environmental friendliness.

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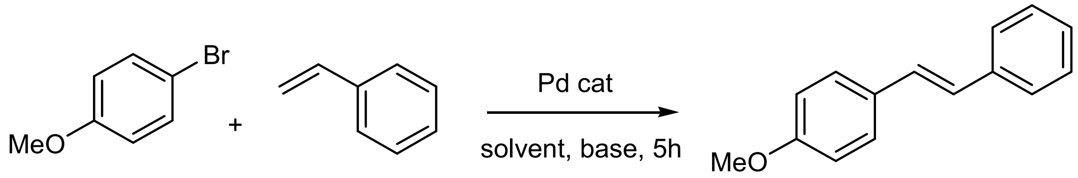
Table 1. Effect of various Pd catalysts, solvents, bases, and temperatures for the Mizoroki-Heck reaction.[a]



Entry	Catalyst (mol% of Pd)	Solvent	Base	Temp (°C)	Yield (%)[b,c]
1	NCS-TI/Pd (0.1)	DMF/H_2O (v/v = 1:2)	Et_3N	110	54(53)
2	BCS-TI/Pd (0.1)	DMF/H_2O (v/v = 1:2)	Et_3N	110	87(78)
3	PCS-TI/Pd (0.1)	DMF/H_2O (v/v = 1:2)	Et_3N	110	96(81)
4	MNCS-TI/Pd (0.1)	DMF/H_2O (v/v = 1:2)	Et_3N	110	62(59)
5	MBCS-TI/Pd (0.1)	DMF/H_2O (v/v = 1:2)	Et_3N	110	75(73)
6	MPCS-TI/Pd (0.1)	DMF/H_2O (v/v = 1:2)	Et_3N	110	91(90)
7	MPCS-TI/Pd(0.1)	DMF/H_2O (v/v = 1:2)	Et_3N	110	15[d]
8	MPCS-TI/Pd(0.1)	DMF	Et_3N	110	86
9	MPCS-TI/Pd(0.1)	DMSO	Et_3N	110	75
10	MPCS-TI/Pd(0.1)	H_2O	Et_3N	100	72
11	MPCS-TI/Pd(0.1)	DMF/H_2O (v/v = 1:1)	Et_3N	110	89
12	MPCS-TI/Pd(0.1)	–	Et_3N	120	53
13	MPCS-TI/Pd(0.1)	DMF/H_2O (v/v = 1:2)	DIPEA	110	83
14	MPCS-TI/Pd(0.1)	DMF/H_2O (v/v = 1:2)	K_2CO_3	110	73
15	MPCS-TI/Pd(0.1)	DMF/H_2O (v/v = 1:2)	NaOAc	110	77
16	MPCS-TI/Pd(0.1)	DMF/H_2O (v/v = 1:2)	Et_3N	100	85
17	MPCS-TI/Pd(0.1)	DMF/H_2O (v/v = 1:2)	Et_3N	120	91
18	MPCS-TI/Pd(0.1)	DMF/H_2O (v/v = 1:2)	Et_3N	130	90
19	MPCS-TI/Pd(0.05)	DMF/H_2O (v/v = 1:2)	Et_3N	110	82
20	MPCS-TI/Pd(0.2)	DMF/H_2O (v/v = 1:2)	Et_3N	110	91

[a] Reaction conditions: 4-bromoanisole (1 mmol), styrene (1.3 mmol), base (2 mmol), TBAB (0.5 mmol), in solvent (3 mL) for 5 h.
[b] Isolated yields.
[c] In paranthesis yields obtained in run 2.
[d] No TBAB was added.

Furthermore, the catalyst can be recovered and reused up to seven times with no significant loss of activity.

Experimental

General

As received chitosan (CS) powder with average MW = 100000-300000 and the deacetylation degree of 70-85% (from Acros company) was used without further purification. All chemicals were commercial reagent grades and purchased from Merck and Aldrich. Polyethylene glycol (PEG, MW = 10000) was purchased from Aldrich. Thermogravimetric-diffraction thermal analysis (TG-DTA) was carried out using a thermal gravimetric analysis instrument (NETZSCH TG 209 F1 Iris) with a heating rate of 10 ºC min^{-1}. XRD patterns were recorded by an EQUINOX 3000, X-ray diffractometer using Cu Kα radiation ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded using a Bruker AQS-300 Avance spectrometer. Transmission electron microscope, TEM (Zeiss-EM10C-80 KV) was used to obtain TEM images. The scanning electron microscopy (SEM) images were obtained using a scanning electron microscope MIRA3\\TESCAN-LMU. The magnetic

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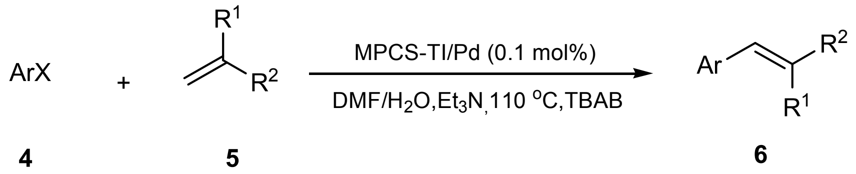
Table 2. Mizoroki-Heck reaction of aryl bromides and chlorides with various olefins.[a]



Entry	ArX	R^1	R^2	Product	Time (h)	Yield (%)[b]
1	PhBr	Ph	H	**6a**	4	93[44]
2	4-$MeCOC_6H_4Br$	Ph	H	**6b**	4	93[44]
3	4-NCC_6H_4Br	Ph	H	**6c**	4	90[44]
4	4-$OHCC_6H_4Br$	Ph	H	**6d**	5	89[45]
5	4-$O_2NC_6H_4Br$	Ph	H	**6e**	4	93[46]
6	4-$MeOC_6H_4Br$	Ph	H	**6f**	5	91[46]
7	2-MeC_6H_4Br	Ph	H	**6g**	6	86[45]
8	1-Bromonaphthalene	Ph	H	**6h**	6	85[45]
9	PhBr	4-ClC_6H_4	H	**6i**	5	88[47]
10	PhBr	4-$MeOC_6H_4$	H	**6j**	5	87[45]
11	PhBr	COOH	H	**6k**	4	96[23]
12	4-$MeOC_6H_4Br$	COOH	H	**6l**	5	91[23]
13	PhBr	CO_2Bu^n	H	**6m**	4	92[24]
14	4-MeC_6H_4Br	CO_2Me	H	**6n**	5	94[22]
15	4-$O_2NC_6H_4Br$	CO_2Me	H	**6o**	3	95[46]
16	PhBr	CO_2Me	CH_3	**6p**	5	83[48]
17	1-Bromonaphthalene	CO_2Et	H	**6q**	6	92[48]
18	PhBr	CN	H	**6r**	6	87[45]
19	PhBr	$CONH_2$	H	**6s**	4	94[45]
20	PhCl	Ph	H	**6a**	8	79[44]
21	4-$MeCOC_6H_4Cl$	Ph	H	**6b**	7	77[44]
22	4-NCC_6H_4Cl	Ph	H	**6c**	7	73[44]
23	4-$OHCC_6H_4Cl$	Ph	H	**6d**	8	71[45]
24	PhCl	4-ClC_6H_4	H	**6i**	8	69[47]
25	PhCl	COOH	H	**6k**	7	81[23]
26	PhCl	CO_2Me	CH_3	**6p**	9	75[48]
27	PhCl	$CONH_2$	H	**6s**	7	81[45]

[a] Reaction conditions: aryl halide (1 mmol), olefin (1.3 mmol), Et_3N (2 mmol), catalyst (0.1 mol %), TBAB (0.5 mmol), in DMF/H_2O (v/v =1:2, 3 mL), at 110 °C.
[b] Isolated yields.
[c] References provided for the known compounds.

measurement of samples were carried out in a vibrating sample magnetometer (VSM) (4 inch, Daghigh Meghnatis Kashan Co., Kashan, Iran) at room temperature. FT-IR spectra were obtained using a Shimadzu model FT-IR8400 instrument. The Pd content of the complex was determined using inductively coupled plasma (ICP, Varian vista-mpx), and surface morphology of the catalyst was analyzed using Energy-dispersive-X-ray (MIRA3, TESCAN-LMU) equipped with EDX facility. The X-Ray photoelectron spectroscopy (XPS) data were recorded with 8025-BesTec twin anode XR3E2 X-ray source system. Micro analytical data was collected by a Perkin-Elmer, USA, 2400C elemental analyzer. The N_2-sorption was carried out in a Belsorp-mini-BEL Japan, Inc. at 298 K (see ESI).

Preparations

Fe_3O_4

The synthesis of Fe_3O_4 was achieved using the procedure described by Luo and co-workers.[49] In a typical preparation procedure, ferric chloride hexahydrate $FeCl_3.6H_2O$ (5.5 g, 20.35 mmol) and ferrous chloride tetrahydrate $FeCl_2.4H_2O$ (2.0 g, 20.1 mmol) were dissolved in deionized water (125 mL) under nitrogen atmosphere with mechanical stirrer at 85 °C. The pH value of the solution was adjusted to 9-11 using aqueous NH_3 (25 %). After continuous stirring for 4 h, the magnetite precipitates were washed with distilled water until the pH value descended to 7.0. The black precipitate (Fe_3O_4) was collected with a permanent magnet at the bottom of the reaction flask (Scheme 1).

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Porous chitosan-thienyl imine support, PCS-TI (1)

In a 200 mL round-bottom flask equipped with a magnetic stirring bar, chitosan (1 g) was allowed to dissolve slowly in aqueous acetic acid solution (0.87 M, 100 mL), for 1 h at room temperature; then PEG (1 g) was added to the above flask and stirred for 10 min, followed by addition of 2-thiophenecarbaldehyde (2.24 g, 20 mmol) and the mixture was stirred for 24 h under N_2 atmosphere. The reaction mixture was dripped into a 1 N NaOH aqueous solution (250 mL) through a needle of 0.9 mm diameter. The gelatin like CS-TI was collected and washed with hot distilled water until neutral (pH ~ 7), followed by extraction of the PEG component with about 2 liters of hot water (Scheme 1). Similarly, the bead chitosan-supported ligand (BCS-TI) was prepared by the same protocol in the absence of PEG. Also, the normal chitosan-supported ligand (NCS-TI) was produced by mixing chitosan and 2-thiophenecarbaldehyde in EtOH (10 mL).

Porous chitosan-thienyl imine Pd complex, PCS-TI/Pd (2)

In a 50 mL round-bottom flask, $PdCl_2$ (0.088 g, 0.5 mmol) was added to PCS-TI (**1**) in EtOH (30 mL). The mixture was heated at reflux for 24 h. The product formed was filtered off, washed with EtOH and finally dried in vacuum for 24 h at 50 °C (Scheme 1). Similarly, the bead and normal chitosan-thienyl Pd complexes (BCS-TI/Pd and NCS-TI/Pd) were prepared by the same protocol.

Cross-linked magnetic porous chitosan-thienyl imine Pd complex MPCS-TI/Pd (3)

In order to minimize dissolution of chitosan in polar solutions, and reinforce the chemical and physical stability of PCS-TI/Pd catalyst, the catalyst was cross-linked with a bifunctional reagent such as glyoxal, which could react with the amino functional group to form the Schiff's base (imine) (Scheme 1). PCS-TI/Pd (**2**) was added to aqueous acetic acid solution (0.17 M, 30 mL); a suspension of Fe_3O_4 (0.5 g) in glyoxal (3 mL) and EtOH (5 mL) was then added dropwise to the above mixture. More glyoxal (1.5 mL) was added and the reaction mixture was mechanically stirred for 1 h at room temperature. The product formed was collected, washed with water, ethanol, and then dried in vacuum at 50 °C for 24 h (Scheme 1). Similarly, magnetic bead and normal catalysts (MBCS-TI/Pd and MNCS-TI/Pd) were prepared by the same protocol.

General procedure for Mizoroki-Heck coupling reaction

A mixture of aryl halide (1.0 mmol), alkene (1.3 mmol), triethylamine (2 mmol), TBAB (0.5 mmol) H_2O/DMF (v/v = 2:1, 3 mL), and the catalyst (0.001 mmol, 0.1 mol% Pd) was stirred at 110 °C for an appropriate time under aerial condition. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature, poured into H_2O (10 mL), and the catalyst was separated by magnetic decantation. In the case of acrylic acid, aqueous solution of Na_2CO_3 (10 mL, 3% w/v) was added; after separation of the catalyst, 1 N aq. HCl (5 mL) was added, and the product was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with brine (2 × 10 mL), dried ($MgSO_4$), and concentrated in vacuum. The crude product was further purified by preparative TLC (silica gel) using *n*-hexane–EtOAc (9:1) to afford the desired product.

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We have prepared a highly active and recyclable heterogeneous catalyst for the Heck reaction in aqueous media in high yields.