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Immobilized Pd complexes over HMMS as catalysts for Heck cross-coupling and selective hydrogenation reactions†

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High-performance Pd(0) on the surface of hollow magnetic mesoporous spheres (HMMS), with Fe_3O_4 nanoparticles embedded in the mesoporous shell was prepared. The catalyst was characterized by TEM, XRD, VSM and ICP. It showed high activity for selective hydrogenation of alkynes to alkenes and the Heck coupling reaction. The catalyst could be recovered in a facile manner from the reaction mixture and recycled six times without loss in activity.

Introduction

Selective hydrogenation of alkynes to alkenes without further reduction to alkanes is of significant importance in modern chemical transformations. For effective polymerization, the trace alkynes should be removed from the alkenes feed because alkynes deactivate the polymerization catalyst and lower the degree of polymerization.[1] Selective hydrogenation using Pd catalysts is one of the most effective methods to reduce alkynes content to a low ppm level in the alkenes.[2] Accordingly, a highly selective catalyst, which can readily convert alkynes to alkenes but does not convert alkenes to alkanes, was prepared.

On the other hand, much recent work has been directed toward the Heck reaction because it is the most powerful and widely used method to couple alkenes with organic moieties bearing suitable leaving groups, such as halide, triflate or diazonium.[3] The resulting products have found extensive applications as intermediates in the preparation of materials,[4] natural products[5] and bioactive compounds.[6] The palladium-catalyzed application of Heck reaction has drawn considerable attention. However, the separation and reuse of homogeneous Pd catalyst remains a scientific challenge.

In the last few years, numerous methods have been developed to immobilize palladium on a large variety of solid supports, such as microporous polymers,[7] mesoporous silica,[8] amorphous silica[9] and carbon nanofibers,[10] making it easy and simple to separate the catalyst from the mixture. Here we prepared a catalyst that Pd was immobilized on monodispersed hollow magnetic spheres (HMMS). Monodispersed hollow magnetic spheres (HMMS) with well-defined structures have attracted considerable interest in the past few decades, owing to their unique properties such as well defined morphology, uniform size, low density, large surface, good compatibilities, and wide range of important applications.[11] Compared to conventional mesoporous materials such as MCM-41 and SBA-15, the HMMS may be more suitable for drug delivery because of large internal volumes that could provide high drug loading and homogeneous spherical morphologies.[12] As is well-known, magnetic materials have been widely applied in catalytic system because they could be easily handled and recovered.[13] Nevertheless, a key problem is to functionalize the magnetic nanoparticles surface such that it allows for the immobilization of the catalytically active metal on its surface whilst preventing their agglomeration. In particular, much attention has been focused on amine functionalization, since amines are well known to stabilize nanoparticles against aggregation without disturbing their desirable properties and are also recognized to increase their catalytic activity.[14] For example, amine-functionalized magnetic nanoparticles have been employed in a range of organic transformations, showing excellent catalytic activities in oxidation,[15] hydrogenation[16] and C–C coupling reactions.[17] We reported an effective catalyst system composed of Pd on the surface of hollow magnetic mesoporous spheres in ethanol for hydrogenation and Suzuki coupling reactions using K_2CO_3 as a base. The catalyst was successfully applied to hydrogenation and Suzuki coupling reaction with high activity. Encouraged by these results, we have recently applied the catalyst system to selective hydrogenation and the Heck coupling reaction.

Herein, we report an amine-functionalized magnetite nanoparticle-supported stable Pd catalyst for application in selective hydrogenation and the Heck coupling reaction.

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Experimental

Styrene (St) and acrylic acid (AA) were purchased from Sinopharm Chemical Reagent Company and distilled under reduced pressure before use to remove the inhibitor. Tetraethoxysilane (TEOS, 98%), *n*-octadecyltrimethoxysilane (C18TMS, Aldrich), were used as received without further purification.

Synthesis of the hydrophobic magnetite nanoparticles (Fe_3O_4 NPs)

The Fe_3O_4 NPs were prepared using a published method with a slight modification.[18] First, 4.8 g of $FeCl_3{\cdot}6H_2O$, 2.0 g $FeCl_2{\cdot}4H_2O$ were added to 40 mL of deionized water under vigorous stirring. Second, the mixture solution was purged with nitrogen gas for 30 min under nitrogen atmosphere. Third, the mixture solution was heated to 90 °C. Finally, 10 mL of ammonium hydroxide (28 wt%) was added rapidly to the solution, and it immediately turned black. The reaction was kept at 90 °C for 2.5 h. The black precipitate was obtained with the help of a magnet and dried at 323 K overnight.

Hollow magnetic mesoporous silica spherical magnetite nanoparticles were synthesized *via* the versatile solvothermal reaction reported by Rong.[12]

Preparation of polystyrene latex with attached Fe_3O_4 nanoparticles

Briefly, carboxylic polystyrene (PS) latex was prepared by soap-free emulsion polymerization of St with acrylic acid (AA). 1.5 g Fe_3O_4 nanoparticles and 2.5 g negatively charged PS latex were dispersed in 84 mL and 60 mL hydrochloric acid solution (pH = 2.3), respectively. Then the latter suspension was added dropwise into the former under vigorous stirring at room temperature. After 6 h, the heteroaggregates, *i.e.* Fe_3O_4 nanoparticles attached on the surface of PS latex particles, were separated from the solution by an external magnet and washed several times with water until the pH value of the solution was close to 7.

Preparation of hollow magnetic mesoporous silica spheres (HMMS)

First, 2.0 g heteroaggregate of the PS latex and Fe_3O_4 nanoparticles were dispersed in a solution composed of 75 mL of ethanol, 5 mL of H_2O, and 3.8 mL of $NH_3{\cdot}H_2O$ (28 wt%). After stirring for 10 min, 0.4 mL TEOS and C_{18}TMS mixture with a molar ratio of 4.7 : 1 was added dropwise under vigorous stirring. Then, the reaction proceeded for 8 h at room temperature under stirring. The resultant particles were separated by centrifugation, purified by three cycles of magnetic separation/washing in ethanol, and dried at room temperature for 12 h, finally, the as-prepared products were dried at 313 K overnight and calcined in air at 823 K for 7 h.

Synthesis of aminopropyl-modified silica coated HMMS (HMMS-NH_2)

The 1.0 g of HMMS was prepared by adding 0.5 mL of aminopropyl trimethoxysilane to 200 mL of dry toluene. The resulting solution was refluxed for 24 h and then washed with toluene and acetone. The obtained solid material was dried in vacuum at 50 °C for 24 h.

Loading of Pd on aminopropyl-modified silica coated HMMS (HMMS-NH_2-Pd)

500 mg of HMMS-NH_2 samples were first dispersed in a 50 mL ethanol solution under ultrasonication for 0.5 h. The formed orange suspension was ultrasonically mixed with 3.0 mmol of a $PdCl_2$ solution for 1 h, and then an excess 0.01 M $NaBH_4$ solution was slowly dropped into the above mixture with vigorous stirring. After 2 h of reduction, the products were obtained with the help of a magnet, washed thoroughly with deionized water and then dried in a vacuum at room temperature overnight. The content of Pd in the HMMS-NH_2-Pd, as determined by inductive coupled plasma emission spectrometer (ICP) analysis was 5.18 wt%.

Typical procedure for selective hydrogenation reaction

In a typical experiment, 1 mmol of the reagent was dissolved in 5 mL ethanol with 10 mg of catalyst under an atmosphere of hydrogen (rubber balloon) at room temperature. The reaction process was monitored by thin layer chromatography (TLC). After the reaction, the catalyst was separated by a small magnet, and the conversion was estimated by GC (P.E. AutoSystem XL) or GC-MS (Agilent 6890N/5973N). The separated catalyst was washed several times with ethanol and dried at room temperature for use the next time.

Typical procedure for the Heck coupling reaction

For Heck coupling reactions, 0.5 mmol of the aryl halides, 0.6 mmol of styrene or *n*-butyl acrylate, and 0.6 mmol of K_2CO_3 were taken into 5 mL of *N*-methyl-2-pyrrolidone (NMP). The amount of catalyst used in each reaction was 20 mg, and the reaction mixture was refluxed at 130 °C. The reaction process was monitored by thin layer chromatography (TLC). After completion of the reaction, the mixture was cooled to room temperature, separated by magnetic decantation, the resultant residual mixture diluted with 20 mL H_2O, followed by extraction twice (2×15 mL) with ethyl acetate. The organic fraction was dried over $MgSO_4$, the solvents evaporated under vacuum and the residue redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GC or GC-MS analysis. Yields were calculated against the consumption of the aryl halides. After the first cycle of the reaction, the catalyst was recovered with the help of a magnet, successively rinsed with NMP, distilled water (to remove excess of base) and ethanol, and dried at room temperature ready for the next cycle.

Characterization

XRD measurement was performed on a Rigaku D/max-2400 diffractometer using Cu-K_α radiation as the X-ray source in the 2θ range of 10–70°. The size and morphology of the magnetic nanoparticles were observed by a Tecnai G^2 F30 transmission electron microscopy and samples were obtained by placing a drop of a colloidal solution onto a copper grid and evaporated in air at room temperature. Magnetic measurement of HMMS,

$HMMS-NH_2$ and $HMMS-NH_2-Pd$ was investigated with a quantum design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from −15 to 15 kOe.

Results and discussions

Catalyst preparation and characterization

The preparation of the $HMMS-NH_2-Pd$ catalyst follows the steps described in Scheme 1. Firstly, HMMS were prepared. Secondly, the functionalization of the silica coated HMMS with 3-(2-aminoethylamino) propyltrimethoxysilane. Thirdly, palladium chloride was supported on the surface of HMMS, and the palladium chloride reduced to palladium particles with sodium borohydride.

The typical TEM image of HMMS, $HMMS-NH_2-Pd$ is showed in Fig. 1. The average diameter of the HMMS was about 300 nm in Fig. 1a. The resultant $HMMS-NH_2-Pd$ composites had good dispersibility and spherical morphology. In the TEM image of $HMMS-NH_2-Pd$ (Fig. 1b), the catalyst did not significantly change, and the palladium nanoparticles deposited on the surface of the magnetic properties of the hollow magnetic silica sphere in Fig. 1c. It also can be observed from the picture that the wall thickness was about 20 nm.

The elemental composition of the $HMM-NH_2-Pd$ samples was determined by EDX analysis. The result shown in Fig. 2 reveals that the as-prepared products contain Fe, Si, Pd, Cu, C and O. Among these elements, Cu, C and O are generally influenced by the copper network support films and their degree of oxidation, Si, O, Fe and Pd signals result from the HMMS and Pd particles which form the products (Fig. 2).

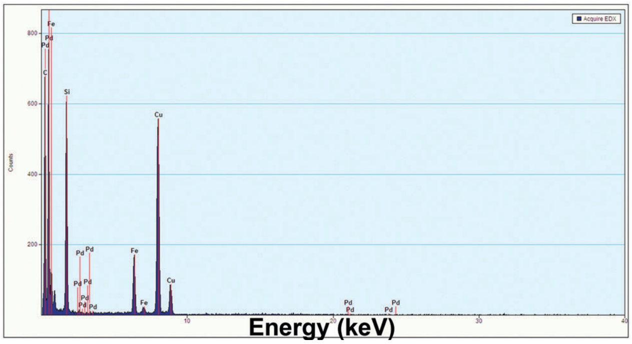


Fig. 2 EDX spectrum of $HMMS-NH_2-Pd$.

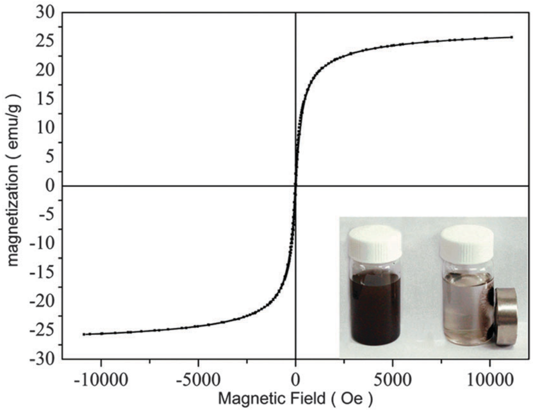
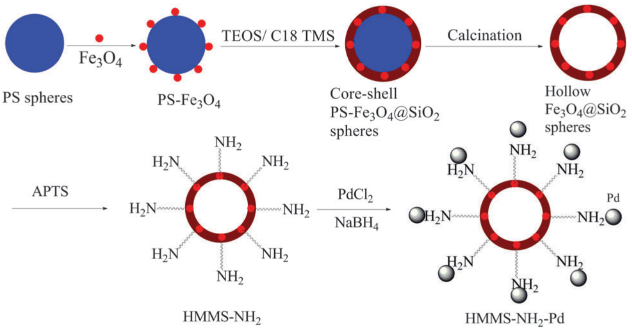


Fig. 3 Room temperature magnetization curves of $HMMS-NH_2-Pd$.

The magnetic properties of the $HMMS-NH_2-Pd$ catalyst were characterized using a vibrating sample magnetometer (VSM). The magnetization curve of $HMMS-NH_2-Pd$ exhibited no remanence effect (superparamagnetic property) with saturation magnetization of about 27.6 emu g^{-1} (Fig. 3). The figure also showed that the catalyst can be efficiently separated from the solution by an external magnetic field.

The XRD pattern of the samples HMMS, $HMMS-NH_2$ and $HMMS-NH_2-Pd$ are shown in Fig. 4, respectively. The reflection peaks of iron oxide nanocrystals obviously indicate the existence of magnetic components in the as-obtained products. Fig. 4c shows that apart from the original peaks, the appearance of the new peaks at $2\theta = 40.1$ and 46.5 was attributed to the Pd species. The results from XRD implied that the Pd nanoparticles had been successfully immobilized on the surface of magnetic nanoparticles.



Scheme 1 Preparation of the catalysts.

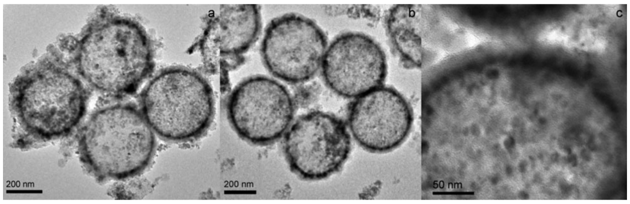


Fig. 1 TEM images of (a) HMMS and (b, c) $HMMS-NH_2-Pd$.

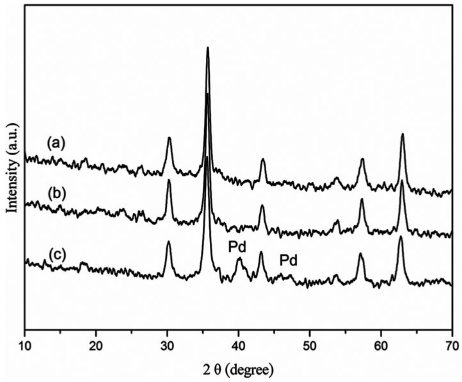


Fig. 4 XRD patterns of (a) HMMS, (b) $HMMS-NH_2$ and (c) $HMMS-NH_2-Pd$.

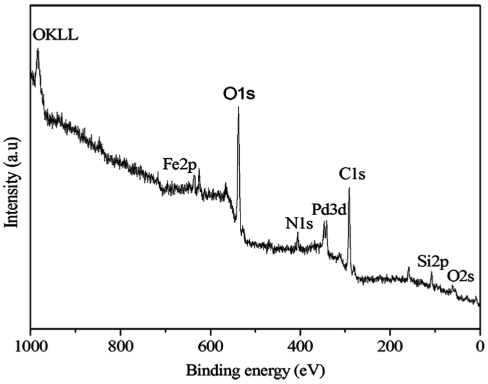


Fig. 5 XPS spectrum of the HMMS-NH_2-Pd showing Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies.

Fig. 5 presented XPS elemental survey scans of the surface of the HMMS-NH_2-Pd catalyst. Peaks corresponding to oxygen, carbon, nitrogen, palladium and iron are clearly observed. To ascertain the oxidation state of the Pd, X-ray photoelectron spectroscopy (XPS) studies were carried out. In Fig. 6, the Pd binding energy of HMMS-NH_2-Pd exhibits two strong peaks centered at 340.9 and 335.5 eV, which were assigned to Pd $3d_{3/2}$ and Pd $3d_{5/2}$, respectively.

Catalyst testing for selective hydrogenation reactions

The efficacies of the HMMS-NH_2-Pd catalyst for selective hydrogenation were evaluated in a H_2-filled flask. The products were analyzed *via* gas chromatography. Remarkably, the HMMS-NH_2-Pd catalyst achieved almost complete conversion (>99%) within 30 min in the absence of any additives, with a high selectivity of over 94% toward styrene (Table 1, entry 1). For phenylacetylenes with substituents such as $-CH_3$, $-OCH_3$ and –F, complete conversions were observed and the products in 70–98% yields were also achieved within 16–60 min (Table 1 entries 3–8). The phenylacetylenes bearing strong electron-withdrawing groups needs a relatively longer time to obtain a moderate yield.

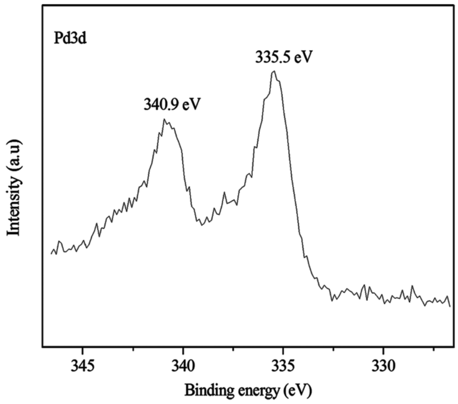
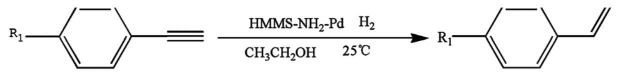


Fig. 6 XPS spectrum of the reused HMMS-NH_2-Pd showing Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies.

Table 1 Selective hydrogenation of phenylacetylene derivatives with HMMS-NH_2-Pd[a]



Entry	R_1	Time (min)	Conversion[b] (%)	Selectivity (%)
1	H	30	>99	94.7
2	H	40	>99	10.6
3	CH_3	40	93	100
4	CH_3	50	97.5	100
5	OCH_3	40	69.4	97.3
6	OCH_3	60	94	98
7	F	10	74.7	91.1
8	F	16	95	98

[a] Reaction conditions: phenylacetylene 0.5 mmol, catalyst 10 mg, ethanol 5 mL, H_2 balloon (about 1 atm). [b] Determined by GC or GC-MS.

Since the good results from selective hydrogenation of phenylacetylene derivatives encouraged us, we wanted to further test the catalyst for selective hydrogenation properties of heterocyclic alkynes. The reactions were carried out in ethanol at room temperature and under 1 atm pressure. The conversion and selectivity of 2-ethynyl pyridine and 2-ethynyl thiophene are shown in Fig. 7 and 8. The HMMS-NH_2-Pd catalyst was highly active for the selective hydrogenation under such mild conditions, since the amine groups are known to enhance the catalytic activity of Pd.

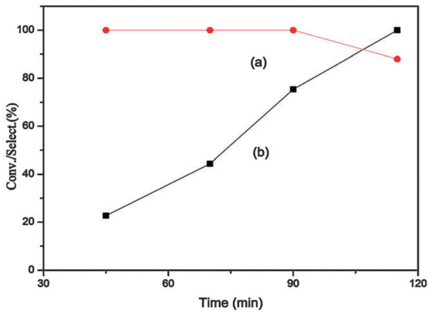


Fig. 7 Selective hydrogenation of 2-acetylene pyridine (a) selectivity and (b) conversion.

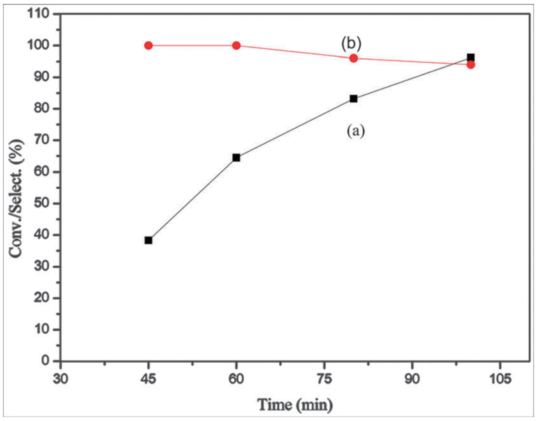
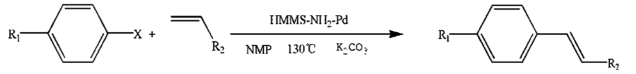


Fig. 8 Selective hydrogenation of 2-ethynyl-thiophene (a) conversion and (b) selectivity.

Catalyst testing for the Heck reaction

After having proven the good activity of catalyst for selective hydrogenation of acetylene compounds, we further tested the activity of the catalyst for heck reaction. Table 2 shows the results of the Heck reaction of aryl halides with styrene or *n*-butyl acrylate. Excellent catalytic activity was established for activated iodobenzene derivatives (Table 2, entries 1–10). The HMMS-NH_2-Pd catalyst showed a lower catalytic activity in the bromobenzene and chlorobenzene systems, as normally observed in the Heck reactions, using the identical conditions to the study of iodobenzene. Additionally, there was a great effect on increasing the reaction time from 8 h to 25 h. As expected, for electron poor aryl bromides and chlorides (Table 2, entries 13, 14, 18, 19, 22 and 24) the reaction time is short, and conversely for electron rich bromobenzene and chlorobenzene (Table 2, entries 12, 15, 17, 20) the reaction time was relatively long.

Table 2 Heck reaction in the presence of HMMS-NH_2-Pd[a]



Entry	R_1	X	R_2	*T* (h)	Yield[b] (%)
1	H	I	Ph	8	>99
2	CH_3	I	Ph	8	>99
3	OCH_3	I	Ph	8	>99
4	OH	I	Ph	8	98
5	$COCH_3$	I	Ph	6	>99
6	H	I	$CO_2{}^nBu$	8	98
7	CH_3	I	$CO_2{}^nBu$	8	98
8	OCH_3	I	$CO_2{}^nBu$	8	97
9	OH	I	$CO_2{}^nBu$	8	97
10	$COCH_3$	I	$CO_2{}^nBu$	6	>99
11	H	Br	Ph	20	96
12	CH_3	Br	Ph	20	96
13	$COCH_3$	Br	Ph	8	>99
14	NO_2	Br	Ph	8	>99
15	NH_2	Br	Ph	25	86
16	H	Br	$CO_2{}^nBu$	20	96
17	CH_3	Br	$CO_2{}^nBu$	20	94
18	$COCH_3$	Br	$CO_2{}^nBu$	8	>99
19	NO_2	Br	$CO_2{}^nBu$	8	>99
20	NH_2	Br	$CO_2{}^nBu$	25	84
21	H	Cl	Ph	26	92
22	NO_2	Cl	Ph	18	96
23	H	Cl	$CO_2{}^nBu$	26	90
24	NO_2	Cl	$CO_2{}^nBu$	18	95

[a] The reaction was carried out with 0.5 mmol of aryl halides, 0.75 mmol of styrene (or *n*-butyl acrylate), 0.75 mmol of K_2CO_3, 4 mol% Pd with respect to the aryl halides and 5 mL of NMP under an N_2 atmosphere. [b] Determined by GC or GC-MS.

Table 3 Recycling of the HMMS-NH_2-Pd catalyst in a Heck reaction[a]

Entry	Yield (%)	Entry	Yield (%)
1	>99	4	95
2	99	5	93
3	98	6	93

[a] Reaction conditions: 4-bromoacetophenone (0.5 mmol), styrene (0.75 mmol), recycled Pd catalyst, K_2CO_3 (1.0 mmol), NMP (5 mL) under an N_2 atmosphere.

Recycling the HHMS-NH_2-Pd catalyst was investigated, along with the reaction of the 4-bromoacetophenone with styrene. After each reaction, the catalyst could be easily separated magnetically from the reaction mixture, washed three times with ethanol and finally dried for the next run. As shown in Table 3, the catalyst was recycled six times within 10 h under each cycle and without a significant loss of activity. The results further confirmed the high recyclability of HMMS-NH_2-Pd.

Conclusions

We have established a simple method for preparing a novel recoverable catalyst that immobilized Pd on a hollow magnetic mesoporous silica sphere under mild conditions. This novel palladium catalyst can be conveniently prepared by the general method, it exhibits higher activity and selectivity for Heck coupling reaction and selective hydrogenation of arylacetylenes and could be reused six times without significant loss in catalytic activity and selectivity.

Acknowledgements

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