Pd colloid grafted mesoporous silica and its extraordinarily high catalytic activity for Mizoroki–Heck reactions

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ABSTRACT

A Pd colloid grafted heterogeneous catalyst, with as low as 0.1 mol% Pd loading in mesoporous silica, was presented. In this composite, the palladium was evenly reduced by Si–H group to form metal colloids existing as isolated islands both on the inner and outer surfaces. The evenly dispersed catalyst species showed high catalytic activity with extremely low amounts of Pd catalysts for Mizoroki–Heck reactions. The large and open pore network, ultrahigh specific surface area and highly dispersed catalyst species made it one of the most active heterogeneous catalysts. The palladium colloid showed very high stability against leaching from the support and can be recycled for repeated use.

1. Introduction

The application of metal nano-particles in catalysis has been an important frontier of researches in recent years, as they have a characteristic high surface-to-volume ratio and consequently more active sites, which make them promising catalysts in chemical synthesis [1,2]. However, the direct application of noble metal nano-particles in catalysis is often difficult due to their ultra-small size and high tendency toward aggregation. Generally, these metal nano-particles are often supported on solid matrix and employed as heterogeneous catalysts [3–8]. The selectivity and activity of these systems are often found to be strongly dependent on surface structure, particle morphology, and size of the supports, and also on the presence of promoters and poisons. Thus, recent protocols in developing new metal catalysts mostly concern the high dispersion of metal species on the high surface area porous support, such as silica, alumina, titania, and zirconia, as well as the increased stability of the active species [9–15]. Although extensive efforts have been made and significant progress has been achieved, the development of more simple methodology for preparing highly dispersed metal catalysts with high catalytic activities still remains a great challenge.

The palladium catalyzed Mizoroki–Heck reaction is among the most important and widely used reactions for the formation of carbon–carbon bonds, which allows the arylation or vinylation of various alkenes through their reaction with aryl, vinyl, benzyl or allyl halides, acetates, or triflates in the presence of suitable base in a single step under mild conditions [16–19]. It constitutes extremely useful tools in organic synthesis, and its applications have significantly broadened when new variants of the reaction with heteroatom nucleophiles are developed [20]. Academic and industrial interest in this reaction has increased in recent years and much progress has been made in preparation of new supported palladium catalyst to catalyze these kind of reactions. Among them, the majority of the novel heterogenized catalysts are based on ordered mesoporous silica supports [14–16,20–23], primarily not only because of their excellent stability (chemical and thermal), good accessibility and the fact that organic groups can be robustly anchored to the surface to provide catalytic centers but also their well defined, nanosized and size-tunable porosity and large surface area. Metallic palladium has been incorporated into various ordered mesoporous silica such as MCM-41 [14,21], HMS [22], SAB-15 [15] and ETS-10 [23]. These heterogeneous systems have been effectively used as catalysts in hydrogenation and in Mizoroki–Heck coupling reactions.

In our previous studies [15a], we reported an *in situ* reduction method for the controlled deposition of metals onto the inner surface of mesoporous silica materials. It was shown that the immobilized Si–H group on the pore channel surface was able to *in situ* reduce metal ions resulting in the formation of a uniform thin metal

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colloid layer on the pore channels [15a]. Recent studies indicated that even if this kind of colloid layer was also present on the outer surface of the matrix, the catalyst species still showed very high stability against leaching from the support in the reaction [15b]. In both of the previous work, the metal loading levels and used amounts in catalytic reaction, though already very low as compared with the literature, was still as high as 5 wt% (for both Pd and Rh) and 0.02 mol%, respectively.

Considering the special metal colloid coating structure, we believed it would be necessary to further lower the loading amount of metal colloids in the mesoporous matrix and investigate its catalytic performance with used amount of the catalyst minimized. Therefore, in the present work, we report the synthesis and catalytic properties of palladium colloids grafted mesoporous silica materials with extremely low loading amount of 0.1 mol% Pd in mesoporous matrix and also very low amount of 0.002 mol% Pd in Mizoroki–Heck reactions. The metal colloids were evenly dispersed on both the outer and inner surfaces of the mesoporous silica materials. The catalytic experimental results show that the synthesized composite catalysis materials still have high catalytic activity and high TOF value in Mizoroki–Heck reactions compared with the previous reports [14,15a].

2. Experiment

The mesoporous silica SBA-15 was synthesized according to the literature by using tri-block poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), $EO_{20}PO_{70}EO_{20}$, as a template in acidic conditions [14]. The mesoporous silica SBA-15 was directly used as support without any pretreatment.

2.1. Preparation of Pd/SBA catalyst

SBA-15 (1.5 g) was dispersed in dry $CHCl_3$ (50 mL) and $(CH_3O)_3SiH$ (10 mL) was added dropwise under stirring. The mixture was filtered after being heated at 80 °C under N_2 atmosphere for 24 h. The solid obtained after repeated washing with $CHCl_3$ was named H/SBA.

H/SBA (1.5 g) was dispersed in dry THF (20 mL); 0.05 M palladium acetate THF solution (30 mL) was added slowly afterwards. After stirring for 4 h, the solid was filtered, washed with THF and dried in vacuum at room temperature.

2.2. Catalytic studies

The 20 mmol aryl halide, 30 mmol vinyl substrate, 22 mmol triethylamine, 10 mmol dodecane (as internal standard for GC analysis) and 20 mL NMP were introduced into a three-necked flask. Catalyst (Pd/SBA) was added through a funnel and the reaction mixture was heated to reaction temperature (mol% catalyst used, reaction time and temperature are shown in Table 1).

2.3. Characterization of Pd–SBA

Transmission electron microscopy (TEM) observations and energy dispersive spectrum (EDS) detections were performed on a field emission JEM-3000F (JEOL) electron microscope operated at 300 kV and equipped with a Gatan-666 electron energy loss spectrometer and energy dispersive X-ray spectrometer. X-ray photoelectron spectra (XPS) were recorded on a Physical Electronics XPS-5700 spectrometer with Al Kα X-ray line (1486.6 eV). X-ray diffraction (XRD) data were collected on Bruk D8 Focus diffractometer with a graphite-monochromatized Cu Kα radiation ($\lambda = 0.15405$ nm). FT-IR spectra were obtained on Nicolet 7000-C with 4 cm^{-1} resolution. Powder samples were dispersed in KBr pellets for IR analysis. N_2 adsorption and desorption isotherms were measured at 77 K on a Micromeritics ASAP2020 system. The specific surface area and the pore size distribution were calculated by using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Content of Pd in the solution was determined by inductively coupled plasma (ICP) atomic emission spectroscopy (Seiko SPS1700HVR).

3. Results and discussion

3.1. Structure and textural characterization

The transmission electron microscopy (TEM) investigation presents a direct evidence for the mesoporous structure and distribution of Pd in Pd/SBA. Fig. 1a and b shows the TEM images of a Pd/SBA sample with the electron beam parallel and perpendicular to the pore channel, respectively. The mesoporous channels were well ordered with a characteristic hexagonal structure. Although Pd^{2+} ions were reduced both on the outer and inner surface of the matrix, the structure and morphology of matrix were kept intact and the Pd colloidal could be scarcely perceived even in a high magnification image. No metal bulk aggregates or nano-particles could be found on the mesoporous particle surface or in pore channels, even after the catalytic reaction (Fig. 1c), and the pore channels are still open. The only noticeable difference was the scattering contrast between walls and pores, compared with the original SBA-15. The distribution of the metal colloids was, therefore, uniform not only on the inner but also on the outer surface. The existence of Pd colloids can be further proved by energy dispersive spectroscopy analysis of X-ray (EDAX), which revealed the Pd content of about 0.1 mol% on average.

X-ray photoelectron spectrum (XPS) analysis was used here to identify the status of palladium in Pd/SBA. As shown in Fig. 2, two peaks centered at a binding energy of 340 and 335 eV, matched well with Pd^0 3d$_{3/2}$ and Pd^0 3d$_{5/2}$, respectively. For Pd^{2+}, these two peaks are expected at 342.2 and 336.8 eV, which were not observed in the XPS survey spectrum. Accordingly, almost all of the Pd species in Pd/SBA had been reduced *in situ* to Pd^0 by Si–H groups on the surface of parent materials.

Table 1
Catalytic properties of the prepared Pd/SBA for Mizoroki–Heck reactions[a].

Vinyl	Aryl halide substrate	Reaction condition	Conversion %[b] (selectivity %)[c]	Pd in solution (ppm)	TOF (mol/mol h)
Styrene	C_6H_5I	140 °C; 2 h	100 (100)	0.010	2.5×10^4
	C_6H_5Br	140 °C; 2 h	57 (94)	0.036	1.3×10^4
	4-Br-$C_6H_4OCH_3$	120 °C; 2 h	60 (91)	0.017	1.4×10^4
Methyl acrylate	C_6H_5I	140 °C; 2 h	100 (100)	0.078	2.5×10^4
	C_6H_5Br	140 °C; 2 h	54 (94)	0.036	1.3×10^4
	4-Br-$C_6H_4OCH_3$	120 °C; 2 h	62 (98)	<0.01	1.5×10^4

[a] All reactions were carried out in air with 0.002 mol% Pd as catalyst in form of Pd/SBA.
[b] Conversion of reactant was determined by GC–MS.
[c] Selectivity = mole of coupling product/mole of reactant converted.

Fig. 3 depicts the small-angle XRD pattern of SBA-15 and palladium colloid grafted mesoporous silica composite (Pd/SBA). In agreement with the above TEM observations, both samples show well-resolved reflections corresponding to hexagonal mesoporous structure. The location of diffraction peaks had no great change after metal ions was reduced on the surface of the matrix. Three peaks at a 2θ value of about $0.95°$, $1.58°$ and $1.82°$ can be indexed as the (1 0 0), (1 1 0) and (2 0 0) reflections. These diffraction features can be ascribed to the basal series arising from $p6mm$ hexagonal symmetry. The only difference between them is the peak intensity due to the guest loading in Pd/SBA. In general, palladium metal
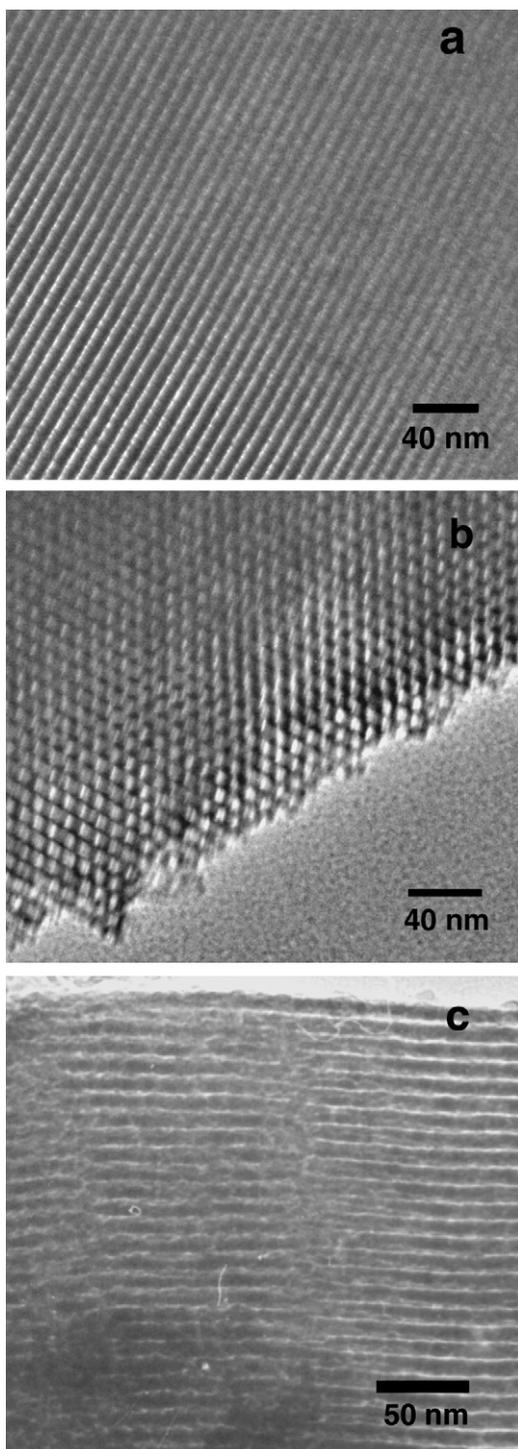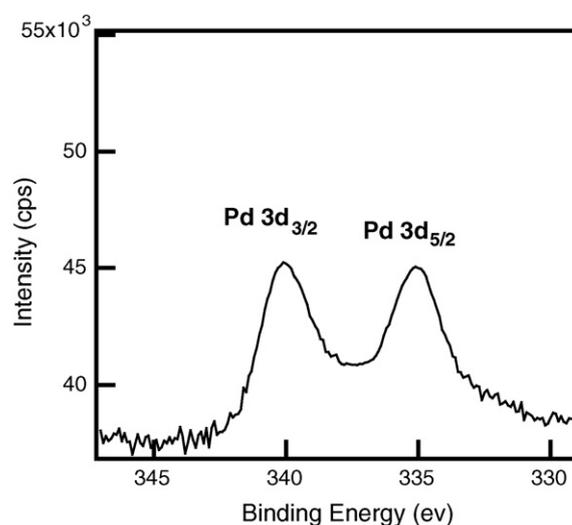

Fig. 2. XPS spectrum of Pd/SBA sample.

has major diffraction peaks at $2\theta = 40.1°$ (1 1 1) and $46.7°$ (2 0 0), which were not found in the wide-angle XRD pattern of Pd/SBA (Pd content: 0.1 mol%) even after the catalytic reaction (Fig. 4), further proving that reduced palladium was highly dispersed as amorphous and extremely small nano-colloids in the mesoporous silica material.

FT-IR data shown in Fig. 5 clearly support the chemical modifications of the matrix and the Pd reductive process. The original SBA-15 showed adsorption bands at $960\,cm^{-1}$, which is attributable to Si–O stretching of the Si–OH groups. On the other hand, when it was modified with trimethoxysilicane $(CH_3O)_3SiH$, this peak almost disappeared and two peaks at about 2240 and $880\,cm^{-1}$ evolved. These additional peaks can be assigned as Si–H stretching and bending vibrations, respectively. This proved that, during the treatment of SBA-15 with trimethoxysilane, a reaction between $(CH_3O)_3SiH$ and SiOH groups occurred, resulting in the creation of Si–H on the inner and outer surfaces of the mesoporous material. It was this Si–H group that reduced the Pd^{2+} ions to form the metal colloids on the surface of the silica matrix.

As a primary measurement for the physical properties, nitrogen physisorption was conducted for system analysis before and after Pd loading. Fig. 4 shows the nitrogen adsorption/desorption
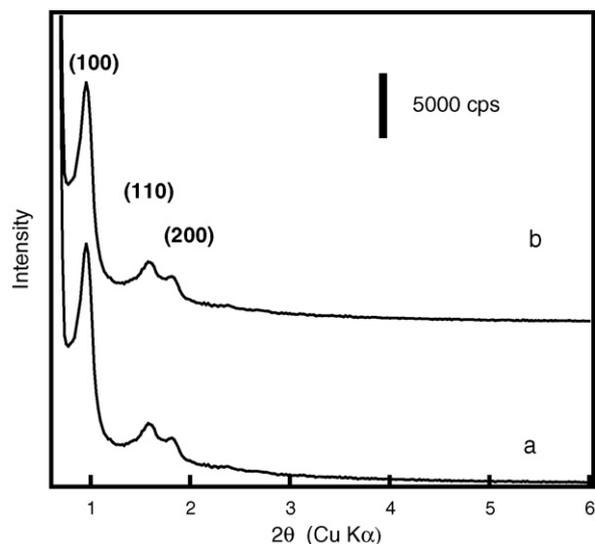

Fig. 1. TEM images of Pd-SBA catalyst before (a and b) and after (c) catalytic reaction.

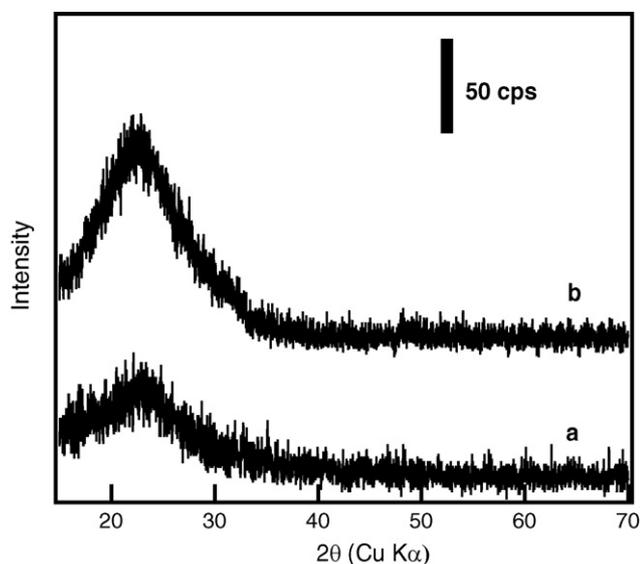Fig. 3. Small-angle XRD patterns of (a) SBA-15 and (b) Pd/SBA.

Fig. 4. Wide-angle XRD patterns of Pd/SBA before (a) and after (b) catalysis.
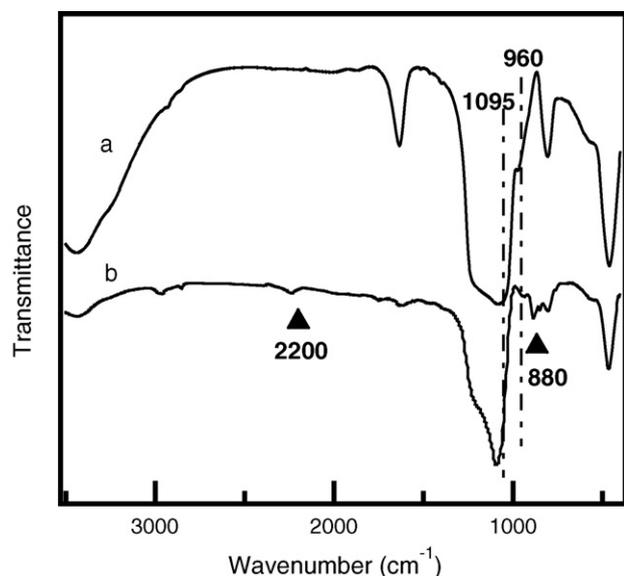

Fig. 5. FT-IR spectra for samples of (a) SBA-15 and (b) H/SBA.

Fig. 6. Nitrogen adsorption/desorption isotherms of (a) SBA-15, (b) H/SBA and (c) Pd/SBA.

isotherms for SBA-15, H/SBA and Pd/SBA. All of the samples exhibited type IV isotherms with a H1-type broad hysteresis loop, corresponding to typical large-pore mesoporous materials with 1D cylindrical pore channels. Capillary condensation of nitrogen caused a sudden step increasing in nitrogen uptake in the typical relative pressure (P/P_0) range of 0.6–0.8 for all samples studied, suggesting well-defined mesoporous structure with uniform pore diameters. The pore parameters of samples are summarized in Table 2. The decrease in BET surface area, BJH pore volume and average pore size, together with the increased thickness of pore wall, can be attributed to the incorporation of Pd nano-colloids

in/on SBA-15. In just similar manner to our previous studies [15a], under the *in situ* reduction condition (Si–H groups as reductant), the BET surface area and BJH pore volume caused only limited decrease after the metal incorporation. In this case, BET surface area decreased from 608 to 514 m^2/g and BJH pore volume from 0.971 to 0.679 cm^3/g. This suggests that the incorporated Pd did not block the pore and only occupied a very limited space. Accordingly, all the pore channels of the host silica remained open. This property is very important for catalytic applications. Only under that condition, the guest molecules can be easy to diffuse into the host mesoporous silica and access catalyst nano-particles for reactions to be catalyzed (Fig. 6).

The mesoporous Pd/SBA material catalyzed the Mizoroki–Heck carbon–carbon coupling reaction (Scheme 1). The catalytic activity of this material was investigated with activated and non-activated aryl halides, with styrene and methyl acrylate as the vinyl substrate. All the reactions were conveniently carried out in a reactor in air. The yields for the aryl halides with respect to reaction time, amount of catalyst used and TOF values all showed that the Pd/SBA catalyst has an excellent activity for Mizoroki–Heck carbon–carbon coupling reactions. Compared with other palladium catalysts supported on mesoporous silicas [14,15], this material showed very efficient catalytic activities, and only about 1/10 to 1/20 amount of Pd catalyst was needed to reach the same conversion under the same reaction conditions (Table 1). This property may be related to the dispersing behavior of the palladium in the matrix. The aggregation of Pd particles, and also the continuous/dense coating of Pd colloids on supports should be responsible for the relatively low TOF values for the reactions in the previous reports [14,15]. In the present synthesis, the surfactant template of the silica matrix was directly eliminated by calcination resulting in significantly lower amount of Si–OH groups on the surface, compared with that by solvent extraction [15a]. Thus, after modified with Si–H group, much less palladium ions were reduced to Pd colloids on the pore or outer surfaces than those in mesoporous silica with template removed by

Table 2
Pore structure parameters of SBA-15, H/SBA and Pd/SBA composite.

	SBA-15	H/SBA	Pd/SBA
Surface areas (m^2/g)	645	608	515
Pore diameter (nm)	7.65	7.01	6.48
Pore volume (cm^3/g)	1.06	0.97	0.68
Thickness of pore wall (nm)	2.46	2.76	3.27.
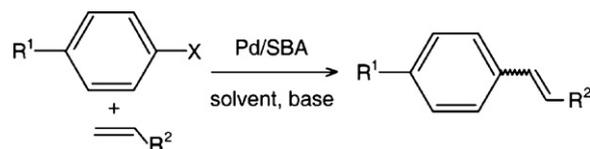
Scheme 1. Heck coupling.
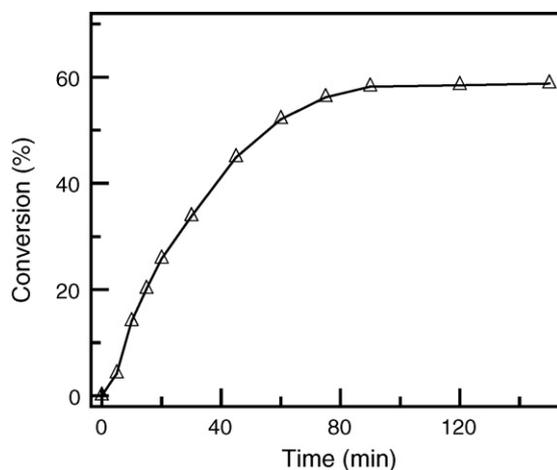
Fig. 7. Time conversion plot for the Mizoroki–Heck reaction between methyl acrylate and bromobenzene under the presence of 0.002 mol% Pd as catalyst in form of Pd/SBA.

Table 3
Reuse properties of Pd/SBA for the reaction between styrene with bromobenzene.

State	Conversion (%)	Selectivity (%)[a]
1st	57.2	95
2nd	56.9	94
3rd	56.6	95
4th	54.6	96
5th	55.1	95
6th	54.1	91

[a] Selectivity = mole of coupling product/mole of reactant converted.

extraction. These metal colloids only can exist as isolated islands or even isolated single atoms both on the inner and outer surface due to the extremely low Pd amount and extraordinarily high surface area of the matrix. This kind of structure is responsible for the especially high catalytic efficiency for Mizoroki–Heck reactions. Also in this supported heterogeneous catalyst, the evenly dispersed catalyst species keep high surface-to-volume ratio. On the other hand, appropriate spaces among catalytic species make them simultaneously interact with reactants and promote the catalytic process.

Fig. 7 shows the time conversion of the C–C coupling reaction between methyl acrylate and bromobenzene. The kinetics investigation indicated that an instant rapid reaction occurred when catalyst was added into the reaction mixture. The coupling conversion increased with the prolongation of the reaction time. After 120 min 57% conversion and 91% selectivity were obtained on as little as 0.002 mol% Pd catalyst. The catalyst deactivation did not occur in the reaction. The elemental analysis showed that there was less than 0.08 ppm Pd in the reaction mixture in all the Mizoroki–Heck reactions by ICP due to a very low amount of Pd colloids leached into the solution during reaction. The palladium content on the support after reaction was also checked by ICP, 98% of the colloids were retained in SBA-15 matrix. The materials showed very high stability against leaching of the active species into the liquid phase under the given reaction conditions. This feature is important for a heterogeneous catalyst system.

Another important issue concerning the use of a solid catalyst is its reusability. To gain insight into this issue, the Pd/SBA catalyst recycling studies were also performed by using the reaction between styrene with bromobenzene, by recycling and then reusing the material under the same conditions. Before reuse, the solid was separated from the reaction medium by filtration, washed with THF and finally dried at 80 °C. Table 3 shows the reused activity

over six times, the activity of Pd/SBA shows little decrease during reuse. Meanwhile, it still retained relatively high activity and could be used more times. The relatively stable conversion showed that immobilized catalyst could be repeatedly used without apparent decrease in its catalytic activity.

4. Conclusions

In conclusion, a heterogeneous catalyst system Pd/SBA, with extremely low Pd loading amount of 0.1 mol%, had been successfully prepared by directly *in situ* reduction method. The palladium ions were evenly reduced to form metal colloids which existed as isolated islands on both the inner and outer surfaces. With extremely low used amount (0.002 mol%) of Pd as the catalyst, extraordinarily high catalytic activity and TOF values for Mizoroki–Heck reactions were achieved, and during the reactions, the catalyst kept high surface-to-volume ratios. The large and open pore network, ultrahigh surface area and highly dispersed catalyst species made it one of the most active heterogeneous catalysts for Mizoroki–Heck reactions. The catalyst species showed very high stability against leaching from the support and can be recycled for repeated use.

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