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Pd nanoparticles embedded in mesoporous carbon: A highly efficient catalyst for Suzuki-Miyaura reaction

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ABSTRACT

Mesoporous carbon functionalized with Pd nanoparticles (Pd@MC) was synthesized via one-pot method using SBA-15, furfuryl alcohol and $PdCl_2$ as a template, a carbon source and a palladium source, respectively. The HRTEM image shows that Pd nanoparticles are homogeneously distributed on the surface of nanoporous carbon whereas the XPS spectrum of the catalyst indicates that Pd exists in the form of Pd (0). With a low loading of the catalyst (2 mol% Pd), Pd@MC shows a high conversion (100%) and selectivity for the desired product (>95%) in the Suzuki-Miyaura reactions of acyl halides with phenylboronic acid under a mild reaction condition. The catalyst was found to be highly active and no leaching in the reaction is observed. The catalyst can further be recycled for up to three times without loss of reactivity.

1. Introduction

Suzuki-Miyaura reaction is one of the most important carbon-carbon bond forming reactions and has been widely used in industrial organic synthesis [1,2]. Traditionally, this reaction is promoted by catalysts based on Pd which is a precious metal. Researches on enhancing the efficiency of Pd catalyst and its recyclability have been quite challenging [3–5]. Typically, Pd can be supported on polymeric and inorganic carrier in order to enhance the dispersion and the recycling capability of Pd. However, inorganic supports are generally preferred due to their high stability as the polymeric supports are normally easy to swell under the reaction conditions which significantly affects the catalytic properties [2–5]. Corma et al. and Štěpnička et al. immobilized various Pd complexes onto the mesoporous silica supports with different structures and pore diameters for various organic reactions including Mizoroki–Heck and Suzuki coupling reaction [6–8]. Although mesoporous silicas are excellent supports for these noble metal complexes, they suffer from poor stability and recyclability. Carbon nanomaterials are also widely employed as supports for the noble metal catalysts. Especially, the carbon-supported Pd catalyst for the Suzuki-Miyaura reaction has made great progress over the decades [9–11]. Among the carbon nanomaterials, mesoporous carbon support has received much attention in the recent years as it is found to be an ideal support to load a huge amount of highly dispersed Pd nanoparticles for catalytic Suzuki-Miyaura reaction [12,13]. In most cases, impregnation method is used to support Pd on the surface of the mesoporous carbon which involves the adsorption of Pd ions onto the surface of the pre-prepared carbon support followed by the thermal decomposition or reduction of adsorbed Pd species. These several steps significantly alter the shape of the nanoparticles and lead to agglomeration and limit the efficiency of the catalysts.

In order to achieve Pd nanocatalyst with a high activity, selectivity and stability, there are several challenging aspects to be considered for these preparation process: how to control the morphology of Pd nanoparticles and their dispersion on the carbon surface; how to enhance the interaction between the carrier and Pd in order that the latter is not easy to leach during the catalytic reaction and thus realizing Pd catalyst recycling [3–5,12]. Recently, a novel method for preparing metal nanoparticles has aroused interest [14–19]. Compared with the traditional impregnation preparation method with multi-step process, this method is a “one step” one and can simultaneously provide the carbon support and the metal nanoparticles which are embedded in the carbon skeleton itself. By this method, metal nanoparticles may be uniformly distributed on the surface of the support, and the nanoparticle is not easy to grow bigger during the reaction. It is expected that the high dispersion of the catalyst without much agglomeration of the nanoparticles offer a high activity and selectivity

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for the catalysts. However, to the best of our knowledge, the "one-step" preparation of Pd supported on a carbon support for Suzuki-Miyaura reaction is rarely reported [19,20]. In this paper, we report a one-pot method to prepare new mesoporous carbon embedded with Pd nanoparticles using SBA-15, furfuryl alcohol and $PdCl_2$ as template, carbon source and palladium source, respectively. The Pd nanoparticles are attached in the skeleton of the mesoporous carbon which show a high reactivity and selectivity in the Suzuki-Miyaura reaction of aryl halides and phenylboronic acid. The catalyst is found to be highly stable and can be reused up to three times without loss of activity.

2. Experimental

2.1. Chemicals and materials

Reagents in the experiment were of analytical grade, used directly without further treatment. Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (EO20PO70EO20) with an average molecular weight of 5500, $PdCl_2$ (99%), Furfuryl alcohol, (≥98%). Phenyl boronic acid (95%), 2-bromo-toluene (99%), 4-bromoanisole (>99%), 4-bromo- phenol (99%), 4-bromobenzaldehyde (99%), and 4′-bromoacetophenone (98%) were purchased from Sigma Aldrich.

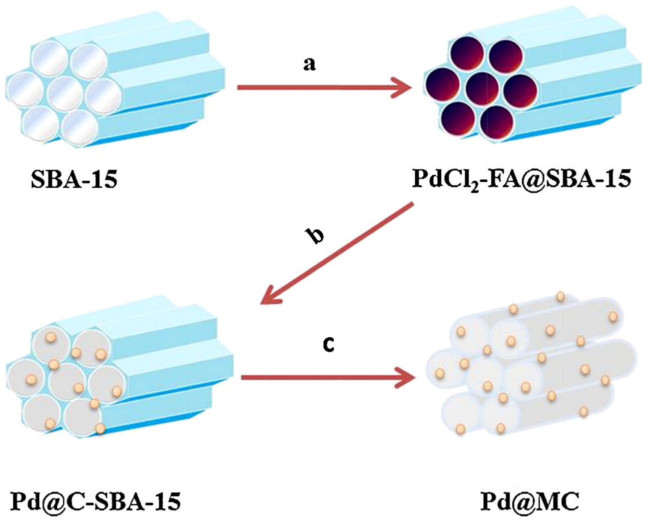
2.2. Synthesis of mesoporous carbon embedded with Pd nanoparticles (Pd@MC)

In a typical synthesis, 4 g poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) ($EO_{20}PO_{70}EO_{20}$) was dispersed in deionized water (30 g) and dilute hydrochloric acid (120 ml, 2 M), and then the mixture was stirred at room temperature for 5 h to produce a colloidal solution. Subsequently, tetraethyl orthosilicate (TEOS, 9 g) was added to the solution under stirring. The solution was aged for 24 h at 40 °C and then transferred into an autoclave for 48 h at 150 °C. Hydrothermal reaction products were collected and milled into a fine powder, and then the powder was calcined in a muffle furnace at 540 °C for 48 h to give SBA-15 [21].

The Pd@MC was synthesized by a modified one-pot method [14]. SBA-15 (1 g) was degased at 250 °C under vacuum for 6 h to remove the water adsorbed on the surface of SBA-15. Then furfuryl alcohol (1.6 g, 16.3 mmol) and $PdCl_2$ (50 mg, 0.28 mmol) in 2 ml of ethanol were mixed thoroughly. The mixture was heated at 40 °C in a vacuum over (vacuum level ~ -0.1 MPa) for 24 h. Then it was heated to 80 °C and kept at the same temperature for 24 h under nitrogen. The mixture was continued to be heated to 150 °C and retained for another 8 h. The collected solid was heated to 900 °C with a heating rate of 5 °C/min in a tubular furnace in nitrogen atmosphere, and maintained at this temperature for 5 h. Finally, the obtained black powder was treated with a 2 M NaOH solution at 80 °C for 2 h to remove the template. The solid was collected by filtration and dried under vacuum to give Pd@MC.

2.3. Characterization

TEM images were obtained with a JEOL-3000F. X-ray photoelectron spectra were collected on Kratos Axis Ultra Meter (AlKα, 1253.6 eV). Pd content was measured by Varian Vista-Pro ICP-OE. ^1H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in chloroform-*d*3. Conversion and product yield of the reaction were obtained from Shimadzu GC-2010 with an autosampler. The column is Agilent HP-Ultra 1 (25 m × 0.2 mm × 0.33 μm). Split ratio is 50:1, the temperature of vaporization chamber is 270 °C, and the temperature of FID detector is 270 °C.



Scheme 1. Synthesis of Pd@MC. (a) adsorption of carbon and Pd sources, (b) polymerization and carbonization and (c) removal of the SBA-15 silica template.

2.4. Catalytic Suzuki-Miyaura reaction by Pd@MC

4 mg of Pd@MC catalyst (2 mol%), 0.5 mmol of aryl halides, and 0.55 mmol of phenyl boronic acid were added into a pressure-resistant reaction tube. Then, 1 mmol of Na_2CO_3 and 4 ml water–ethanol (v/v = 1:1) were added into the tube. The tube was sealed and the mixture was stirred at 80 °C for 1 h. The catalyst was separated through a short column (silica gel). The pure product was obtained after removal of solvents by rotary evaporation. Finally, the product was purified by column chromatography (silica, hexane/ethyl acetate) if it is necessary. The structures of the pure products was confirmed by ^1H NMR spectra. The conversion and the yield were tested by gas chromatograph (Shimadzu GC-2010).

2.5. The recycled experiment for Pd@MC

The catalyst Pd@MC (8 mg, 2 mol%), 4 - acetyl-bromobenzene (1 mmol, 100 mg) and phenylboronic acid (1.1 mmol, 133 mg) were added to a mixture of Na_2CO_3 (2 mmol, 212 mg) and 8 ml water–ethanol (v/v = 1:1) in a pressure-resistant reaction tube and then the tube was sealed. The mixture was stirred at 80 °C for 1 h. The mixture was then transferred to a centrifugation tube and centrifuged at a speed of 5000 rpm/min for 15 min. The supernatant was carefully removed with a pipette and a small amount of ethanol was added to the tube for washing the residue. The washing step was repeated three times. Then, the separated catalyst was used in the reaction for the next run.

3. Results and discussion

The preparation process of the catalyst is illustrated in Scheme 1. The process consists of three steps. First, an ethanol solution of palladium chloride and furfuryl alcohol was adsorbed into the channels of the dehydrated SBA-15. In this step, the dehydrated SBA-15 is a template, while palladium chloride and furfuryl alcohol is the source for palladium and carbon, respectively. The second step for the catalyst preparation is very important for controlling the morphology and its dispersion over the porous channels of the support. During this step, furfuryl alcohol was polymerized first and then gradually carbonated. The melting point of palladium chloride is about 680 °C, thus below this temperature palladium chloride is solid which was embedded into the formed polymer. When the temperature exceeds the melting point of palladium chloride, Pd

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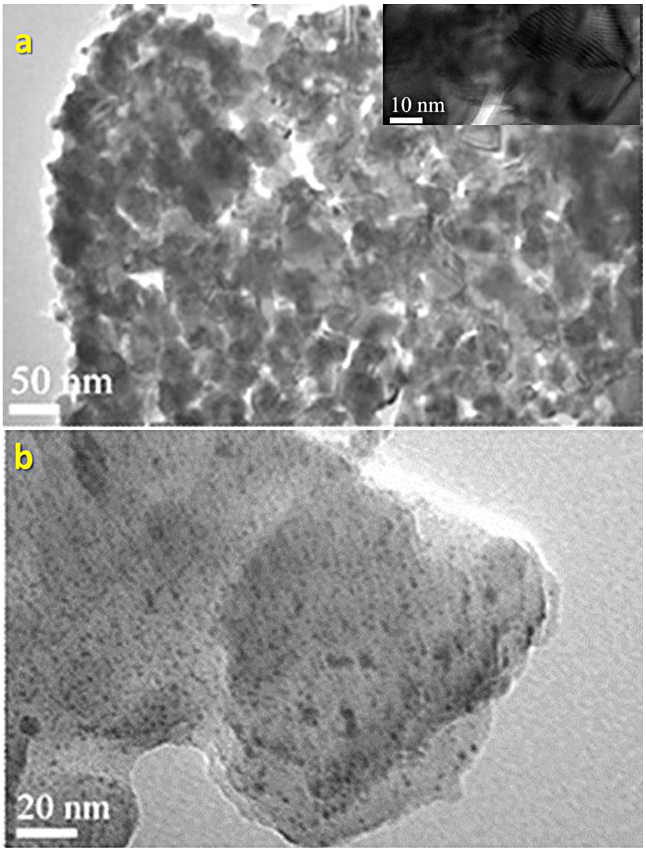

Fig. 1. TEM images of Pd@MC. Scale bar: (a) 50 nm; (b) 20 nm.

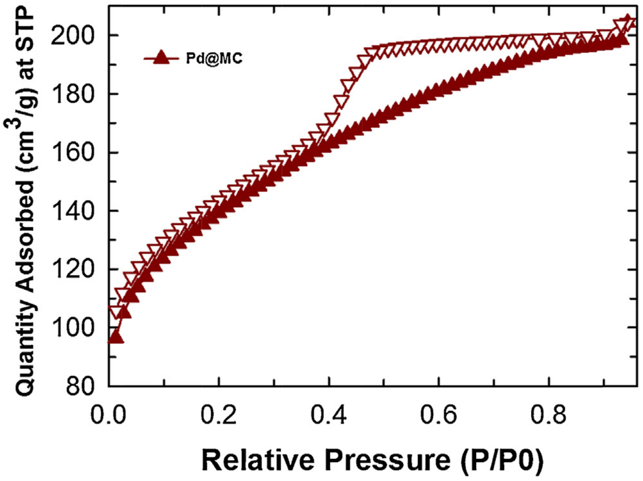

Fig. 2. Nitrogen adsorption–desorption isotherm of Pd@MC.

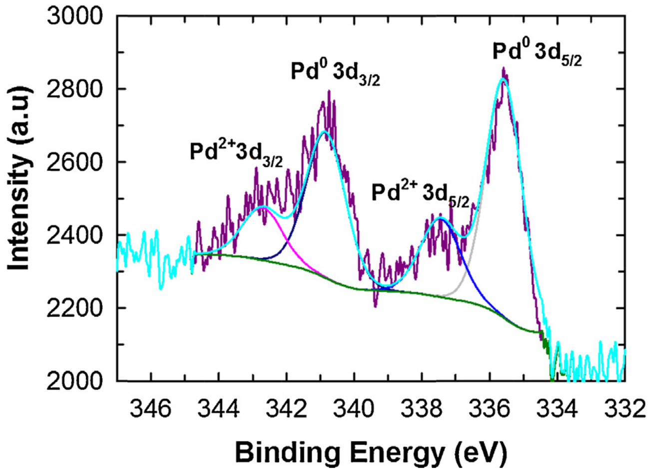

Fig. 3. XPS spectrum of Pd@MC.

nanoparticles were generated by the decomposition of palladium chloride. As the temperature was raised to 900 °C, the polymer was carbonated and the nanocomposite was formed. The size of the Pd nanoparticles was limited by the channels of SBA-15 and the carbon skeleton which can separate the Pd nanoparticles. As a result, Pd particles can be formed with small size and the agglomeration of these nanoparticles can easily be avoided. Therefore, in this sense, the second step can be so-called “one-pot” step and simultaneously obtain the catalyst and the support. The third step for the preparation of the catalyst is the removal of the SBA-15 template from the silica/carbon nanocomposite using the sodium hydroxide solution at 80 °C in order to obtain an embedded Pd catalyst, Pd@MC.

The size and the distribution of the embedded Pd nanoparticles were obtained by transmission electron microscopy (TEM). The highly dispersed Pd nanoparticles on the porous carbon is clearly confirmed by TEM. As shown in Fig. 1b, the pores of the nanoporous are filled with a large number of Pd nanoparticles which appear as dark spherical particles inside the pores of the nanoporous carbons and are uniformly distributed on the pore channels of the carbon support. The size of the particles is very small and is almost similar to the pore diameter of the nanoporous carbon support. In addition, the particles are highly crystalline which are important for the coupling reaction (Fig. 1a inset). However, wide angle XRD pattern of Pd@MC shows that some of the particles are quite large and formed either on the external surface or in the wall structure (Fig. 1S). It should be noted that although the pores of the carbon are clearly visible, some of the pores are damaged by the carbonization and the NaOH treatment. Therefore, the formed mesoporous carbon is not completely ordered after the template is removed. The textural parameters of the Pd@MC were obtained by nitrogen adsorption-desorption measurement. Fig. 2 shows the nitrogen-adsorption desorption isotherm of the Pd@MC. The sample exhibits a type IV isotherm with a broad capillary condensation step at a higher relative pressure, which indicates the presence of disordered mesopores in the samples. The specific surface area of the Pd@MC is 489 m^2/g which is smaller than that of the pure mesoporous carbon. This could be due to the fact that the sample contains a huge amount of Pd nanoparticles which increases the density of the sample.

The nature and the oxidation state of the Pd nanoparticles embedded in the mesoporous carbon were studied by XPS spectroscopy. Fig. 3 shows the XPS spectrum of Pd nanoparticles embedded in mesoporous carbon support. In order to know the oxidation state of the Pd nanoparticles, the Pd 3d binding energy region was deconvoluted into four peaks with binding energies of 335.6, 337.5, 340.9 and 342.7 eV. The two peaks in the Pd 3d spectrum centered at 340.9 and 335.6 eV are very sharp with a huge intensity. These peaks are assigned to Pd^0 $3d_{3/2}$ and Pd^0 $3d_{5/2}$ respectively. The other two minor peaks centered at 342.7 and 337.5 eV are attributed to Pd^{2+} $3d_{3/2}$ and Pd^{2+} $3d_{5/2}$ respectively [22,23]. The percentage of the Pd nanoparticles with different oxidation state is calculated from the relative areas of the Pd^0 and Pd^{2+} peaks. The ratio of Pd (0) content to Pd (II) content is about 3:1, which indicates that Pd species in the catalyst are mainly in zerovalent form. This is quite interesting because of the fact that the one-pot method allows the nanoporous carbon to reduce most of the Pd ions into the Pd nanoparticles that are nicely embedded on the carbon wall structure. The Pd content was also measured by ICP and the results showed that the content is about 22.6 wt%.

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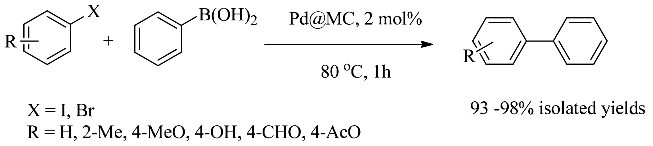

Scheme 2. Suzuki-Miyaura reaction of aryl halides and phenylboronic acid catalyzed by Pd@MC.

Table 1
Suzuki-Miyaura reactions catalyzed by Pd@MC.[a]

Entry	X	R	Conversion (%)[b]	Yield (%)[c]
1	I	H	100	100 (98)
2	Br	H	100	100 (98)
3	Br	4-MeO	100	100 (96)
4	Br	4-CHO	100	100 (98)
5	Br	4-OH	100	95 (97)
6	Br	2-Me	100	95 (93)
7	Br	4-AcO	100	96 (96)
8[d]	Br	4-AcO	100	99 (95)
9[e]	Br	4-AcO	100	98 (95)
10[f]	Br	4-AcO	100	97 (93)

[a] Reaction conditions: acyl halides 0.5 mmol, phenylboronic acid 0.55 mmol, Na_2CO_3 (or K_2CO_3) 1 mmol, $Et_2OH:H_2O = 2$ ml:2 ml as solvent. Catalyst 4 mg (2 mol%), and 80 °C for 1 h.

[b] Determined by GC.

[c] Yield based on GC and column chromatograph (silica, Hex/Ethyl acetate as eluent), yields in parenthesis are isolated yields.

[d] The first recycle.

[e] The second recycle.

[f] The third recycle.

The Pd@MC catalyst was then applied to the Suzuki-Miyaura reaction of aryl halides and phenylboronic acid with a low amount of catalyst loading (2 mol%) at 80 °C (Scheme 2 and Table 1). It was found that the catalyst showed a high reactivity and selectivity for all substrates regardless of iodobenzene or bromo halides with electron-withdrawing group and electron donating group (Table 1, Entry 1–7). All of the catalytic reactions can be completed within 1 h, the conversion of each reaction was 100% and the lowest selectivity was more than 95%. It is worth noting that the TOF values for the reactions are about 50 h^{-1}. The excellent performance of Pd@MC is due to the uniformity of the Pd catalyst and the strong interaction between the catalyst and the support [18]. The embedded Pd nanoparticles may be limited by carbon support and not easy to grow bigger during the reaction, which also contributes to the high activity and selectivity of the reaction. After the reaction, the ICP result of the filtrate showed that the Pd concentration in the filtrate is less than 0.1 ppm, which indicated that the catalyst is stable and there is no Pd leaching during the reaction. The catalyst can be easily separated by means of filtration or centrifugation. The reuse experiment of the recovered catalyst (Table 1, Entry 8–10) shows that Pd@MC can be recycled for three times and the activity and selectivity of the catalyst remain substantially unchanged.

4. Conclusions

We demonstrated that Pd catalyst can be embedded on the pore channels of the mesoporous carbon by one-pot method. Since Pd is uniformly embedded in the carbon skeleton, Pd has a strong interaction with the carrier and the catalyst exhibits excellent catalytic properties in the Suzuki-Miyaura reactions of acyl halides and phenylboronic acid under a mild reaction condition. The embedded catalyst was stable and can be recycled at least three times without loss of activity. This method is currently being extended to prepare embedded Pd nanoparticles for activating acyl chlorine in our group. We believe that our work may also provide a facile and efficient method to prepare non-Pd metal catalyst supported on mesoporous carbon.

Supporting Information. ^1H NMR spectra (Figs. S2–S7) of the products are attached in the supporting information.

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2014.08.038.

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