



# Palladium supported on mesoporous silica via an in-situ method as an efficient catalyst for Suzuki–Miyaura coupling reactions



Peiyu Wang<sup>a,\*</sup>, Guoheng Zhang<sup>a</sup>, Liwei Liu<sup>a</sup>, Haiyan Jiao<sup>a</sup>, Xiaoyan Deng<sup>a</sup>, Xiaoping Zheng<sup>b</sup>

<sup>a</sup> Key Laboratory for Electronic Materials of the State National Affairs Commission of PRC, Northwest University for Nationality, Lanzhou, Gansu 730030, China

<sup>b</sup> Lanzhou City University, Lanzhou 730070, China

## ARTICLE INFO

### Article history:

Received 20 October 2013

Received in revised form 29 March 2014

Accepted 18 July 2014

Available online 21 July 2014

### Keywords:

A. Composites

A. Mesoporous materials

D. Catalytic properties

## ABSTRACT

Palladium-containing SBA-15 (Pd/SBA-15) was synthesized via an in situ approach. In this procedure, the hydrophobic solvent ( $\text{CHCl}_3$ ) was used as a transport medium to inject the Pd precursor (Pd (acetylacetonate)<sub>2</sub>) directly into the inner core of the surfactant micelles. The resulting nanocomposite with 1.46 wt% Pd loading was achieved with highly dispersed and uniform palladium nanoparticles. The Pd/SBA-15 nanocomposite exhibited excellent catalytic activities and reuse ability in air for the Suzuki–Miyaura coupling reactions.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Palladium-catalyzed cross coupling reactions, such as the Suzuki–Miyaura reaction, have become the standard methodologies for the synthetic organic chemists to construct biaryl units [1–3]. Although homogeneous Pd catalysts have gained enormous relevance, industrial applications of these reactions remain challenging, because the homogeneous catalysts require the use of ligands, which are often not easy to handle. In addition, the removal of the catalysts from reaction mixtures and products is difficult in most cases, which is a drawback especially when these reactions are applied in the pharmaceutical field. To overcome these problems, the substitution of heterogeneous catalysts has been developed. A number of materials, such as mesoporous silicas [4–7], polystyrene spheres [8], carbon [9,10], montmorillonite [11], graphene [12], zeolites [13] and MOF [14] have been employed as solid supports for Pd catalysts. Among these cases, low catalytic efficiencies were typically found, which led to low turnover numbers (TON) and high Pd loadings (1–10 mol%). Furthermore, the reported coupling reactions were mostly carried out in organic solvents which are volatile, toxic and dangerous. Thus, from both an economic and a green chemistry point of view, the development of highly efficient heterogeneous catalysts to

facilitate cross coupling reactions in aqueous media is highly desirable [1,2].

Mesoporous silicas possess larger surface area, uniform pore structure and inert environment for immobilization of transition metal nanoparticles; it has become an excellent carrier for many metal nanoparticles [15]. Thus, the incorporation of such nanomaterials inside the pore channels of mesoporous silica is of great interest. Among many methods, in situ formation of palladium nanoparticles inside the pore channels of ordered mesoporous silica represents a new progress in the confinement of nanosized metal in the channels of mesoporous silica [16–18].

In comparison to other mesoporous silica, SBA-15 exhibits larger pores, thicker walls, and higher hydrothermal stability [19]. In this work, we prepare well-dispersed palladium nanoparticles predominately inside the pores of SBA-15 via an in situ method according to our recently published paper [18]. A 1.46 wt% Pd loading was achieved without the loss of pore ordering. The catalytic activity of the Pd/SBA-15 was investigated by Suzuki–Miyaura reactions.

## 2. Experimental

Triblock poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) copolymer Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , MW = 5800) was from Aldrich, hydrochloric acid (HCl), tetraethoxysilane (TEOS), chloroform ( $\text{CHCl}_3$ ), 4-tert-butyltoluene, phenylboronic acid, aryl bromide and potassium carbonate were all purchased

\* Corresponding author. Tel.: +86 931 4872644.  
E-mail address: [wangpy03@126.com](mailto:wangpy03@126.com) (P. Wang).

from Shanghai Reagent Factory Two Company. Pd(acetylacetonate)<sub>2</sub> (Pd(acac)<sub>2</sub>) was from Shanghai July Chemical Co., Ltd. All chemicals were used as received without any purification. The deionized water was used in all experiments.

### 2.1. Preparation of Pd/SBA-15 nanocomposite

A somewhat modified synthesis of Ha and co-workers was employed [20]. The triblock copolymer EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> (2 g) was dissolved in 64 g water and stirred separately for 5 h at 35 °C. Subsequently, 1 ml 3 wt/V%, 2 ml 3 wt/V%, 2 ml 3 wt/V% Pd(acac)<sub>2</sub>/CHCl<sub>3</sub> solution were added and stirred for 1 h at 35 °C in a sealed container. 4.5 ml of TEOS was dispersed in 3.2 g of an HCl aqueous solution (pH 2), and hydrolysis was performed under vigorous stirring at 35 °C for 1 h and a transparent solution was formed, which was dropped immediately into the template solution. The combined mixture was stirred at 35 °C for 2 h in a sealed container. The solid product was filtrated quickly and placed in an autoclave at 100 °C for 48 h. The resulting sample was then washed with water three times and dried at room temperature. The dried sample was calcined at 400 °C for 6 h and then reduced by H<sub>2</sub> gas at 300 °C for 2 h, the resulting sample was denoted as S-1, Pd/SBA-15 and S-2. The SBA-15 was synthesized as above procedure without the Pd(acac)<sub>2</sub>/CHCl<sub>3</sub> solution adding for comparison. For comparison of the catalytic activity in Suzuki–Miyaura reactions, the other sample (WI) by the wetness impregnation method was also prepared. The SBA-15 (1.0 g) was added to a solution of PdCl<sub>2</sub> (0.025 g) in water (5 ml) and stirred for 24 h at room temperature. The mixture was dried 60 °C for 24 h and reduced by H<sub>2</sub> gas at 300 °C for 2 h.

### 2.2. Catalytic studies

A typical experimental procedure was as follows: a mixture of aryl bromide (10.0 mmol), phenylboronic acid (13.0 mmol), potassium carbonate (18.0 mmol), the catalyst (0.04 mol% with respect to palladium), and 4-*tert*-butyltoluene (500 mg) as an internal standard for gas chromatograph (GC) analysis were stirred in water (3 ml) at 80 °C. Every 15 min, an aliquot of reaction mixture (~100 μl) was sucked out with degassed syringe, filtered and washed with brine and diethyl ether. After completion, the reaction mixture was diluted with water (20 ml) and extracted with ether (3 × 20 ml). The combined extract was washed with brine (2 × 20 ml) and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, ethyl acetate-hexane: 1:9) to obtain the desired products. The products were confirmed by comparing the <sup>1</sup>H and <sup>13</sup>C NMR and mass spectral data with authentic samples. The Pd concentration was measured with inductively coupled plasma atomic emission spectrometry (ICP-AES). The recycling test was performed with bromobenzene and phenylboronic acid under the same reaction condition as described above. Each time, the catalyst was isolated from the reaction mixture at the end of the reaction, washed with water and diethyl ether, and then dried at 100 °C under vacuum. The dried catalyst was then reused in the next run.

### 2.3. Instruments

The Pd content of synthesized materials was estimated using a Thermo IRIS advantage the inductively coupled plasma atomic emission spectrometer (ICP-AES). The powder X-ray diffraction patterns of the synthesized materials were collected on a Rigaku D/Max-2400 X-ray diffractometer using Cu K<sub>α</sub> radiation. Surface area was measured by nitrogen adsorption at –196 °C using NOVA 2000e surface area and pore size analyzer. The transmission electron microscopy (TEM) observations of the nanocomposite were carried out on a JEM 2010 operating at an acceleration voltage of 200 kV. CO chemisorption measurements were taken at 25 °C using a homemade pulse flow system. Prior to measurements, samples were subjected to a pretreatment involving exposure to hydrogen flow for 1 h at 300 °C, then the sample was cooled down to room temperature in pure N<sub>2</sub> stream. CO was pulsed at room temperature over the reduced catalyst until the TCD signal from the pulse was constant. A stoichiometry of CO/Pd = 1/1 [21–23] and a Pd surface density of 1.27 × 10<sup>19</sup> atoms/m<sup>2</sup> was used for calculations [24].

## 3. Results and discussion

### 3.1. Structure of nanocomposite

The Pd loading of S-1, Pd/SBA-15, S-2 and WI were 0.83, 1.46, 3.01 and 1.41 wt%. In this in-situ method, above 85% of the palladium is incorporated into SBA-15 (Table 1), avoiding losses of this expensive metal during the synthesis. Molecular assembly template was employed as a hydrophobic carrier to provide the compatible environment for the hydrophobic compounds. The hydrophobic solvent (CHCl<sub>3</sub>) was used as a transport medium to inject the Pd precursor (Pd(acetylacetonate)<sub>2</sub>) directly into the inner core of the surfactant micelles. One inherent advantage of using template micelles as a carrier is its strict selectivity of metal nanoparticles only being charged into the channels [18,25,26]. Furthermore, the orientations of pores have no effect on the distribution of the nanoparticles in the channels of mesoporous silica.

Fig. 1 shows the low-angle XRD patterns of SBA-15, S-1, Pd/SBA-15, S-2 and WI. The main diffraction peaks of SBA-15 with 2θ = 0.81°, 1.38°, and 1.61° are shown in Fig. 1. The d-spacing ratios of three peaks are 1 : 1/√3 : 1/2; these three diffraction peaks can be indexed as (1 0 0), (1 1 0), and (2 0 0) diffractions associated with highly ordered mesoporous silica SBA-15 with a two-dimensional hexagonal symmetry (space group p6mm) [19]. In comparison to SBA-15, S-1, and Pd/SBA-15 show low-angle XRD patterns similar to that of SBA-15. Obviously, the hexagonal ordered structures are retained well indicating that the introduction of Pd into SBA-15 does not collapse the mesoscopic order of a two-dimensional hexagonal structure. In this method, higher loadings (3.01 wt%, S-2 sample) also cause a decrease in pore ordering. It is clearly visible in small angle X-ray diffraction (Fig. 1). For sample S-2 with 3.01 wt % Pd, one broad (1 0 0) peak could be observed and the (1 1 0) and (2 0 0) reflections almost invisible even magnified by five times. However, the Pd loading also causes a slightly increase of the (1 0 0)

**Table 1**  
Synthesis condition and characterization of palladium containing SBA-15 materials.

Sample	Concentration of solution (wt/V%)	Amount of solution (ml)	Measured <sup>a</sup> Pd loading (wt%)	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
SBA-15	0	/	/		0.91
S-1	3	1	0.83	530	0.83
Pd/SBA-15	3	2	1.46	400	0.82
S-3	6	2	3.01	380	0.77
WI	/	/	1.41	370	0.65

<sup>a</sup> Measured Pd loading determined by the ICP-AES.

Download English Version:

<https://daneshyari.com/en/article/1488044>

Download Persian Version:

<https://daneshyari.com/article/1488044>

[Daneshyari.com](https://daneshyari.com)