Synthesis of Pd/SiO$_2$ Nanobeads for Use in Suzuki Coupling Reactions by Reverse Micelle Sol–gel Process

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Abstract Pd/SiO$_2$ nanobeads containing tiny Pd clusters with a diameter of about 2 nm were prepared via a sol–gel process for SiO$_2$ by using a water-in-oil microemulsion with Pd complexes and subsequent hydrogen reduction by heat treatment. The Pd/SiO$_2$ nanostructures were employed in Suzuki coupling reactions with various substrates, and they served as good catalysts in these reactions.

Keywords Palladium nanoparticles · Silica coating · Suzuki coupling · Bifunctional catalyst · Microemulsion

1 Introduction

Pd-catalyzed Suzuki coupling reactions have been carried out many types of organic syntheses and a significant number of synthetic transformations for obtaining pharmaceutical and natural products [1]. However, it is difficult to carry out these reactions in industrial applications by using homogeneous catalysts such as soluble Pd complexes with phosphine ligands because of the recycling problem, even though these catalysts have high activity [2, 3]. Recently, heterogeneous catalysis in which Pd nanoparticles are supported on solid surfaces such as those of carbon and metal oxides has been studied with the aim of preventing the Pd leaching problem and increasing the activities of catalysts in carbon coupling reactions [4–7].

Metal–silica hybrid structures have been considered to be excellent heterogeneous catalytic systems because silica is stable, has pore structures that can be modified, facilitates easy surface modification, and is chemically inert [8–11]. Initially, metal nanoparticles were supported on mesoporous silica materials such as mesostructured cellular foam (MCF) and SBA-15 by various techniques including impregnation, inclusion, and deposition–precipitation [12–14]. However, the sizes of the supports are on the order of micrometers, and this has a negative impact on the reactant's diffusion. More recently, we reported well-designed metal hybrid nanocatalysts, which have silica supports whose sizes are in the nanometer range, such as a yolk-shell nanoreactor framework [15, 16]. It has been observed that metal–silica nanocomposites have high thermal stability and that they completely prevent particle aggregation/agglomeration. Even though the well-designed nanostructures have high stability and activity, they were not given preference over conventional catalysts, especially in industrial catalytic applications, because of the complicated fabrication process involving the separated particle synthesis. In the present study, we report the fabrication of Pd/SiO$_2$ nanobeads consisting of Pd nanoparticles (diameter: $\sim$2 nm) in porous silica beads (diameter: $\sim$20 nm) by the simple modification of the conventional impregnation and reduction methods. The developed Pd/SiO$_2$ nanobeads with the resulting morphology were successfully used in Suzuki coupling reactions with various substrates.

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2 Experimental Procedure

2.1 General Remarks

Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. and used as received. Reaction products were analyzed by ^{1}H NMR. ^{1}H NMR with spectra obtained on a Varian Mercury Plus spectrometer (300 MHz). Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard, unless otherwise indicated, and coupling constants in Hertz. Reaction products were assigned by comparison with the literature value of known compounds. The nanoparticles were characterized by high-resolution transmission electron microscopy (HRTEM; Philips F20 Tecnai operated at 200 kV, KAIST) and high-angle annular dark field transmission electron microscopy (HAADF–TEM; Hitachi HD-2300A operated at 200 kV; National Nanofabrication Center, NNFC, at KAIST). Samples were prepared by placing a few drops of the corresponding colloidal solutions on carbon-coated copper grids (Ted Pellar, Inc). X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX-RB (12 kW) diffractometer. The Pd loading amount was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; POLY SCAN 60 E). Nitrogen sorption isotherms were measured at 77 K using a BELSORP mini-II (BEL Japan Inc.). Before measurements, the samples were degassed in a vacuum at 423 K for at least 6 h.

2.2 Chemicals

Disodium tetrachloropalladate (Na$_2$PdCl$_4$, >98 %) was purchased from TCI. Tetramethyl orthosilicate (TMOS, 98 %), Igepal CO-630 (polyoxyethylene (9) nonylphenylether (C$_2$H$_4$O)$_n$•C$_{15}$H$_{24}$O), and octadecyl trimethoxysilane (C$_{18}$TMS, 90 %) were purchased from Aldrich. Ammonium hydroxide (NH$_4$OH, 28 % aqueous solution) and cyclohexane (99.5 %) were purchased from Junsei. All chemicals were used as received without further purification.

2.3 Encapsulation of Pd(II) Complexes in Silica Matrix

In a 125 mL polypropylene (PP) bottle containing 50 mL of cyclohexane and 1.0 mL of NH$_4$OH solution (28 % aqueous solution), Na$_2$PdCl$_4$ (0.2 g, 0.68 mol) was added and completely mixed by sonication for 20 min. After sufficient stirring for 20 min and the subsequent addition of 8.0 mL of Igepal CO-630 to the mixture solution, a pale yellow sediment was formed at the bottom of the mixture solution. Then, 1.0 mL of TMOS and 1.0 mL of C$_{18}$TMS were simultaneously added and stirred at 200 rpm for 1 h. After 1 h, the products were precipitated by adding 15 mL

of methanol and centrifuging at 10,000 rpm for 30 min. The precipitates were washed by carrying out a repetitive dispersion/precipitation cycle in ethanol; then, the precipitates were dried with acetone. Finally, the Pd(II) complexes/SiO$_2$ were obtained as a yellowish powder.

2.4 Synthesis of Pd/SiO$_2$ Nanobeads

The yellowish Pd(II) complexes/SiO$_2$ powders were placed in a ceramic boat in a glass tube oven, and they were slowly heated at a ramping rate of 4 K/min up to 773 K under a hydrogen flow of 200 cc/min. In order to carry out complete reduction of the Pd(II) complexes to Pd(0) clusters and to remove organic moieties from the sample, the samples were allowed to stand at 773 K for 4 h under the continuous hydrogen flow. After the reduction, the resulting dark-brown Pd/SiO$_2$ powder was cooled to room temperature.

2.5 Suzuki Coupling Reactions by the Pd/SiO$_2$ Nanocatalysts

In order to create the optimal reaction conditions, the Pd/SiO$_2$ catalyst (2 mg, 1.5 μmol), aryl halide (1.57 mL, 15.0 mmol), phenylboronic acid (2.38 g, 19.5 mmol), DMF (10.0 mL), water (0.5 mL), and K$_2$CO$_3$ (4.15 g, 10.06 mmol) were added to a 25 mL stainless steel reactor. The mixture was stirred for 3 h at 200 °C. After the reaction, the Pd/SiO$_2$ nanobeads were separated from the clean solution by centrifugation. The reaction products were analyzed by ^{1}H NMR using Varian Mercury Plus (300 MHz). The chemical shifts were recorded in units of parts per million relative to tetramethylsilane as an internal standard, unless otherwise indicated, and the coupling constants were determined in units of Hertz.

3 Results and Discussion

Pd/SiO$_2$ nanobeads were synthesized in two simple steps, as shown in Scheme 1: (i) loading of the Pd(II) complexes into the silica bead using microemulsions and (ii) hydrogen reduction of Pd(II) complexes to Pd(0) clusters and the simultaneous generation of silica pores by heat treatment.

3.1 Catalyst Preparation and Characterization

The Pd^{2+} complexes were deposited inside the silica spheres by employing a modified version of the reverse micro-emulsion method [17, 18]. A water-in-oil microemulsion was prepared by mixing Igepal CO-630 as a nonionic surfactant, aqueous ammonia solution, and cyclohexane. Disodium tetrachloropalladate powder (Na$_2$PdCl$_4$) as a Pd precursor was added to the mixture solution containing the

Scheme 1 The proposed procedures for the formation of encapsulated Pd/SiO$_2$ nanobead
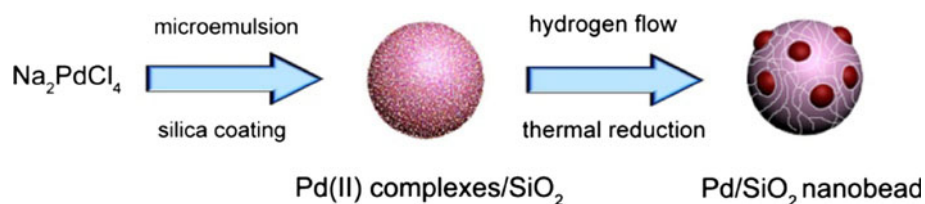
Fig. 1 **a** TEM and **b** HRTEM images of Pd(II) complexes/ SiO$_2$ beads. **c** XRD spectrum of Pd(II) complexes/SiO$_2$. The bars represent 20 nm (**a**) and 5 nm (**b**), respectively
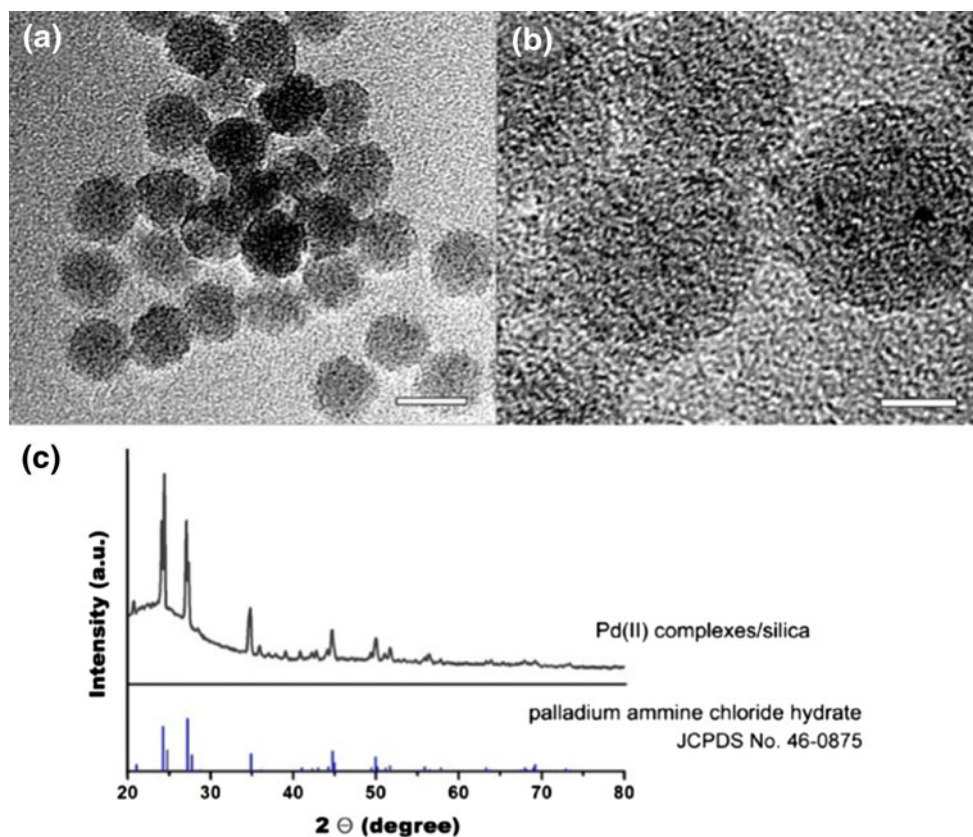

microemulsion, and it was completely dissolved by sonication. After sonication for 20 min, a pale yellow sediment was observed at the bottom of the mixture; this indicates the formation of the tetraammine Pd(II) chloride complex. The formation of silica spheres and encapsulation of Pd(II) complexes were simultaneously initiated by adding TMOS as a silica precursor and adding C$_{18}$TMS as a porogen in order to introduce irregular pores after calcination. Igepal CO-630 and ammonia were used as the reaction media for the formation of the microemulsion and as a catalyst for the decomposition of TMOS, respectively. After the mixture solution was stirred at room temperature for 1 h, the yellow product comprising Pd(II) complexes/SiO$_2$ beads was obtained by centrifugation. The TEM image in Fig. 1a shows spherical Pd(II) complexes/SiO$_2$ nanobeads with an average diameter of 19 $\pm$ 1 nm. In the case of direct irradiation with the electron beam during the TEM measurement, the Pd(II) complex loaded in silica beads appeared as a few dark dots on the image, as shown in Fig. 1b, because the high-energy

electrons can reduce Pd(II) complexes to Pd clusters. The XRD spectrum of Pd(II) complexes/SiO$_2$ beads in Fig. 1c corresponds to that of tetragonal Pd ammine chloride hydrate (JCPDS No. 46-0875).

The Pd(II) complexes/SiO$_2$ beads were calcined at 773 K for 4 h under hydrogen atmosphere. By heat treatment under a hydrogen flow, the Pd ammine chloride hydrate complex in the silica matrix was reduced [19], and this led to the formation of tiny Pd clusters. The TEM image in Fig. 2a clearly shows the dark spots that indicate the presence of Pd clusters, and the inset presents the size distribution of Pd NPs verifying that an average diameter of Pd NPs measured from TEM images is 1.7 $\pm$ 0.3 nm. In the HAADF–TEM image (Fig. 2b), the "tiny" Pd particles are observed as white spots. The HRTEM image in Fig. 2c shows the single-crystalline nature of Pd nanoclusters. The distance between adjacent lattice fringe images was measured to be 0.224 nm, which matches that in the case of (111) planes in face-centered cubic (fcc) Pd. The XRD

Fig. 2 a TEM, **b** HAADF–TEM, and **c** HRTEM images of Pd/SiO$_2$ nanobeads. **d** XRD spectrum of Pd/SiO$_2$ beads. The inset images of **a** and **c** show a histogram of Pd NP size distribution and single Pd/SiO$_2$ nanobead, respectively. The bars represent 20 nm (**(a)**, **(b)**), 5 nm (inset of (**c**)), and 2 nm (**c**), respectively
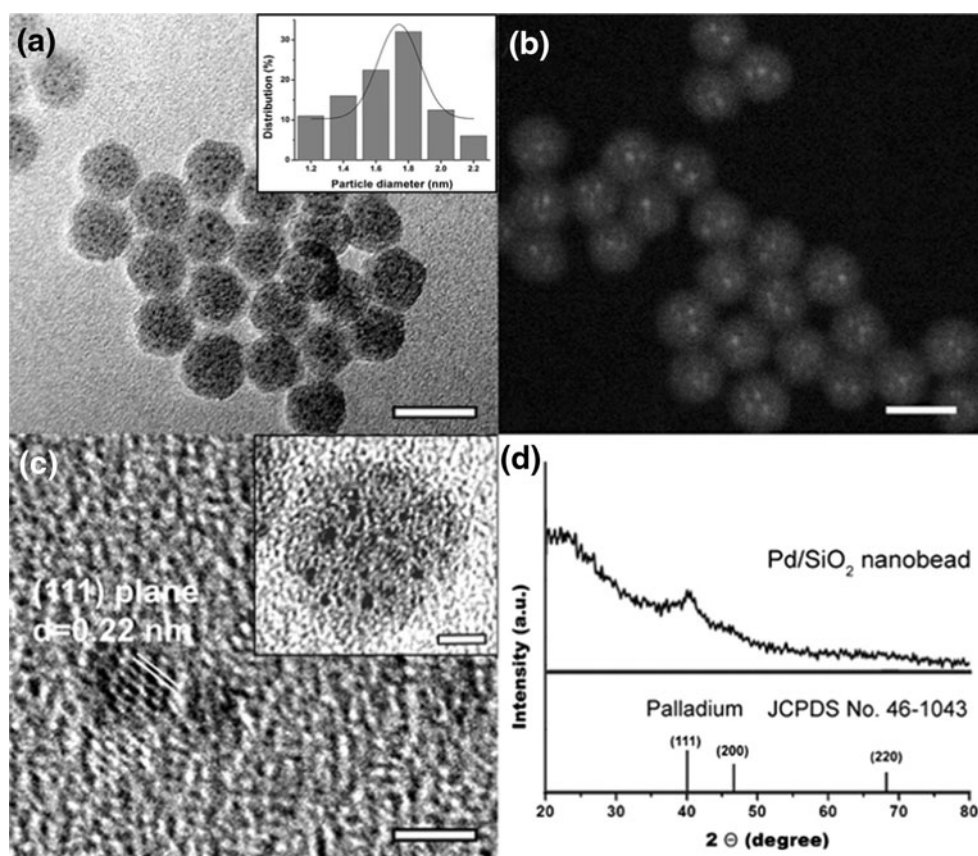
Table 1 Optimization of reaction condition for Suzuki reaction of bromobenzene with phenylboronic acid

Entry	Cat. (mol%)	Temp. (°C)	Time (h)	Solvent	Conv. (%)[a]
1	0.01	200	3	DMF	22
2	0.01	200	5	DMF	38
3	0.5	200	1.5	DMF:H$_2$O(10:0.5)	83
4	0.01	200	3	DMF:H$_2$O(10:0.5)	>99
5	0.005	200	3	DMF:H$_2$O(10:0.5)	65

[a] Determined by ^{1}H NMR spectra. K$_2$CO$_3$ (2.0 equiv.) was used as a base

spectrum of Pd/SiO$_2$ beads in Fig. 2d is similar to that of bulk Pd (JCPDS No. 46-1043; space group, *Fm-3 m*). The broad peak at $2\theta = 40.1°$ reflects entirely regular and small Pd single-crystalline domain sizes; by using the value of the full-width half-maximum of the (111) peak and the Debye–Scherrer equation, the domain sizes were calculated as 2.8 nm. The small irregular pores in the silica matrix were simultaneously generated via heat treatment by removing the long alkyl carbon chains of C$_{18}$TMS [20]. To evaluate the porosity of silica nanobeads, a N$_2$ sorption experiment was conducted at 77 K. The resulting
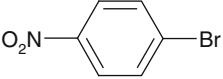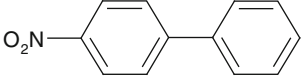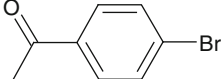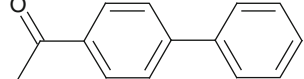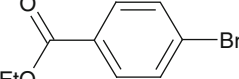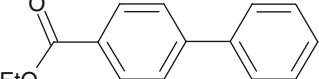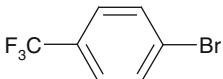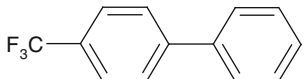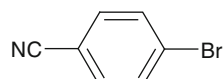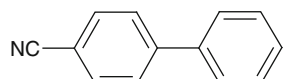
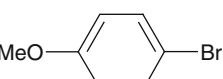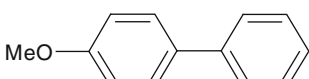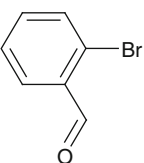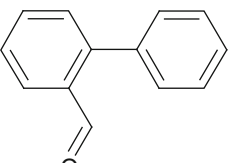Brunauer–Emmett–Teller (BET) surface area and total pore volume were calculated to be 203 m^2/g and 0.56 cm^3/g, respectively. The load of Pd in Pd/SiO$_2$ nanobeads was measured to be 8.27 wt % by ICP-AES.

3.2 Catalytic activity

The Pd/SiO$_2$ catalyst was employed in the Suzuki coupling reaction of bromobenzene with phenylboronic acid. The systematically optimized reaction conditions are presented in Table 1. The reaction time and catalyst amounts affected the conversion rates. By utilizing a small amount of water in dimethylformamide (DMF), the reactivity of Pd/SiO$_2$ catalysts was increased further (Table 1, entry 3). The optimized reaction was carried out using K$_2$CO$_3$ as a base at 200 °C. When the catalyst was used at a concentration of 0.01 mol % with respect to the substrate amount, bromobenzene was completely converted to biphenyl within 3 h (Table 1, entry 4). Even when the concentration of the catalyst was 0.005 mol %, a satisfactory conversion of 65 % was achieved.

Recently, direct fabrications of Au–Pd core–shell heterostructures and catalysts for Suzuki coupling reaction under mild reaction conditions (reflux at 80 °C, 0.5 h) have been reported [21]. This can be a good example of the Suzuki reaction using various types of Pd metals. This will

Table 2 Pd/SiO$_2$ catalyzed Suzuki coupling reaction of various substrates with phenyl boronic acid

Entry	Substrate	Product	Conv. (%) [a]
1	O$_2$N—⟨⟩—Br	O$_2$N—⟨⟩—⟨⟩	82
2	MeCO—⟨⟩—Br	MeCO—⟨⟩—⟨⟩	82
3	EtO(O)C—⟨⟩—Br	EtO(O)C—⟨⟩—⟨⟩	66
4	F$_3$C—⟨⟩—Br	F$_3$C—⟨⟩—⟨⟩	59
5	NC—⟨⟩—Br	NC—⟨⟩—⟨⟩	100
6	MeO—⟨⟩—Br	MeO—⟨⟩—⟨⟩	53
7	o-OHC-C$_6$H$_4$-Br	o-OHC-C$_6$H$_4$-C$_6$H$_5$	100

[a] Determined by ^{1}H-NMR spectra. K$_2$CO$_3$ (2.0 equiv.) was used as a base

help us to review the reaction to the mild reaction conditions and understand the behaviors of catalysts. The coupling reaction between iodobenzene and phenylboronic acid to form biphenyl was performed. In the case of using our Pd/SiO$_2$ nanobeads, 73 % yield was found under the same conditions. The lower activity of Pd/SiO$_2$ nanobeads than Au–Pd core–shell heterostructures (91 % yield) can explained by their effective high-index surface facets.

The substrate scope of the Pd/SiO$_2$-catalyzed Suzuki coupling reaction of aryl bromides is summarized in Table 2. From the table, it is clear that this reaction can be extended to a wide variety of substituted aryl bromides (Table 2, entries 1–7). In our catalytic system, both bromobenzenes and chlorobenzenes, which include either electron-withdrawing substituents such as NO$_2$, COMe, COOEt, CF$_3$, and CN or electron-donating ones such as OMe, were readily coupled with arylboronic acids in moderate yields. Reactions of various aryl bromides

including electron-rich and electron-deficient substrates proceeded readily, and various functional groups were tolerated in the reaction. High reactivity with excellent yield was also observed in the production of biaryls via the coupling of activated o-bromobenzaldehyde with phenyl-boronic acid (Table 2, entries 7). Furthermore, the reaction with electron-rich 4-methoxyphenylboronic acid proceeded readily to afford the corresponding 4-methoxybiphenyl in a high yield (100 %).

4 Conclusions

Pd/SiO$_2$ nanobeads consisting of tiny Pd clusters with a diameter of about 2 nm were prepared via a sol–gel process for silica by using a water-in-oil microemulsion with Pd complexes and subsequent hydrogen reduction along with heat treatment. The Pd/SiO$_2$ catalyst was used as a

high-temperature catalyst in Suzuki coupling reactions of various aryl bromides with phenylboronic acids. One important factor affecting the yield of the reaction is the superior chemical reactivity of the nanoparticles. The present result indicates that transition-metal nanoparticles can be used as catalysts for a wide variety of organic transformations.

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