# Size-Controlled Synthesis of Palladium Nanoparticles on a Silica–Cyclodextrin Substrate: A Novel Palladium Catalyst System for the Heck Reaction in Water

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**S** *Supporting Information*

**ABSTRACT:** This study offers an example of using a silica–cyclodextrin (SCD) substrate for the capture of metal nanoparticles to prepare a novel nanocatalyst for catalytic organic reactions in water as a green solvent. Also, a simple and efficient method for the size control of palladium nanoparticles (PdNPs) using their immobilization on a SCD substrate was introduced. These new catalyst systems were fully characterized using some different techniques such as XRD, TEM, SEM, TGA, ICP, XPS, and FT-IR. The average size of immobilized PdNPs on silica $\alpha$-, $\beta$-, and $\gamma$-CD substrates were obtained (10, 3, and 5 nm, respectively). The immobilized PdNPs on the silica $\beta$-CD substrate (PdNP-S$\beta$CD) was recognized as the best one for the Heck reaction in aqueous media. It seems that the anchored CD moieties on the silica surface can prevent removal of PdNPs and also their aggregations. Moreover, this substrate can provide appropriate catalytic sites for reactions in aqueous media; therefore, the PdNP-S$\beta$CD catalyst showed high activity in the Heck reaction in aqueous media.



**KEYWORDS:** *Palladium nanoparticles (PdNPs), Cyclodextrin (CD), Silica–cyclodextrin (SCD), Heck reaction, Water*
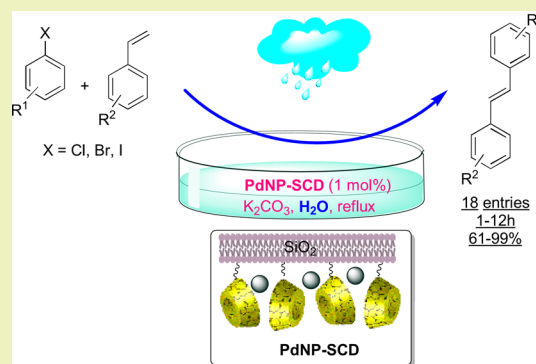
## INTRODUCTION

Palladium nanoparticle (PdNP) catalytic systems are well known as green catalysts because they are independent of ligand requirements and often possess capabilities of the recovery.[1−4] This class of Pd catalysts has been used for a large number of organic reactions.[5−15] However, the reactivity and stability of these catalyst systems are highly dependent on the substrates that are often used for the immobilization of PdNPs.[16,17] On the other hand, from the viewpoint of reactivity, PdNP catalyst systems with small particle size ranges of 1−10 nm are highly prefered. Thus, one of the most important objectives is to construct PdNPs as monodispersed and small.[18−22] While smaller-sized PdNPs are required, preparation becomes more demanding due to their affinity to aggregate and diminish surface tension.[23] For this reason, many research groups have focused their efforts on the preparation of monodispersed nanosized PdNPs by size-controlling methods.[24−26]

To control the size of PdNPs, different strategies such as solution-based synthesis, a seeding growth method, evaporation, pyrolysis, wet chemistry, and use of size-controlling supports have been used.[27−30] Among them, due to the simplicity of the procedure, the use of size-controlling supports is the most popular and efficient method,.[31,32] One of the size-controlling supports are porous structures, which provide cavities for confining PdNPs in a controlled manner.[33−36] In these supports, the particle size is determined according to the size of cavities, and also resistance to agglomeration is achieved by isolated cavities in the solid matrix. The size of the cavities in these materials is a very important factor, and its reduction to very small dimensions restricts diffusion of bulky organic substrates to the internal catalytic active sites. On the other hand, by increasing the pore size, the dimension of nanoparticles (NPs) is increased, and as a result, the reactivity is decreased dramaticaly.[37]

Another approach to control the size of the NPs is the use of host materials such as cyclodextrins (CDs) and calixarenes.[38−40] These materials have the capablity to incorporate into the cavities of various inorganic and organic molecules, mainly via hydrophobic and van der Waals interactions.[41] With the development of nanoscience and nanotechnology, these materials have attracted extensive attention for the preparation of NPs.[42,43] For example, CDs have been used to capture PdNPs with catalytic applications. Nevertheless, the main problems with this catalytic system are ease of separation and release of PdNPs from the CD substrate into the reaction media. Another problem linked to this catalytic system is significant reduction of its performance during the first round of application.[44−48]

**Scheme 1. Synthetic Route for Preparation of SCD Substrates**[a]
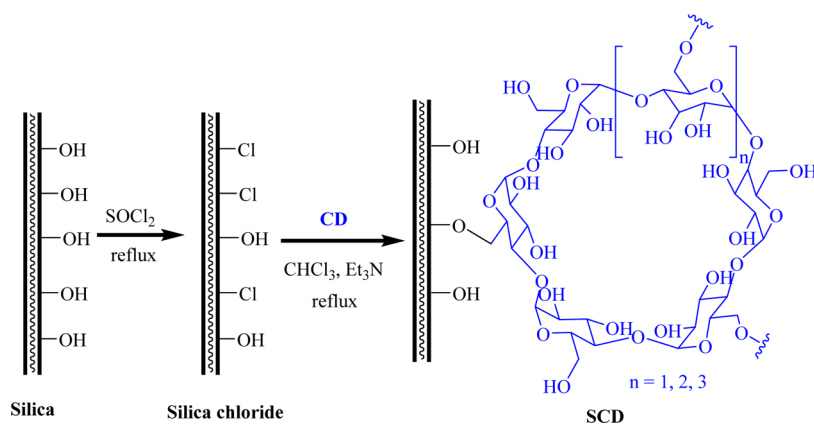


[a]n = 1, silica α-CD substrate (SαCD); n = 2, silica β-CD substrate (SβCD); and n = 3, silica γ-CD substrate (SγCD).
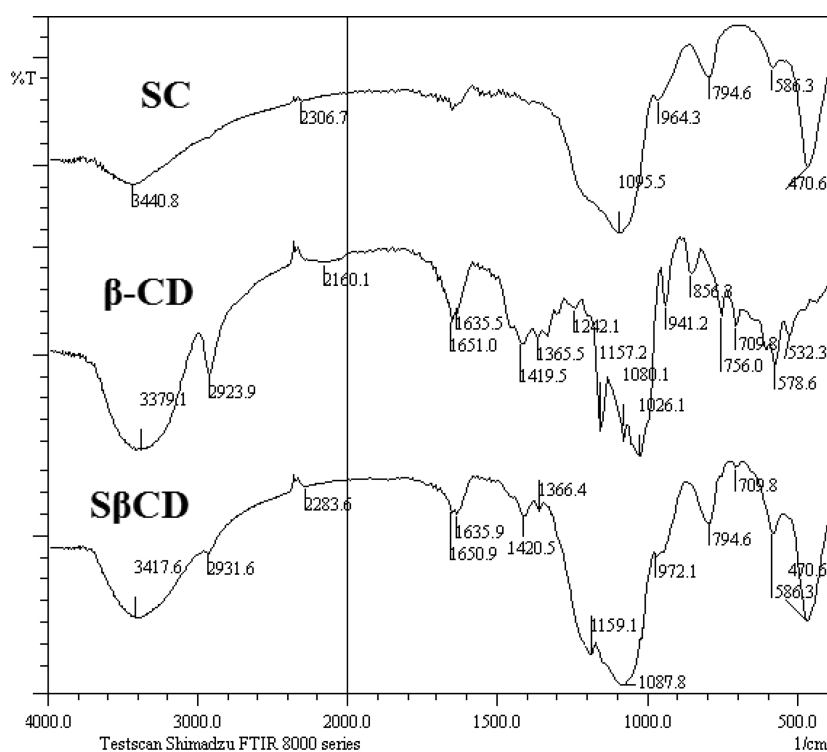


**Figure 1.** Comparison between the FT-IR spectra of SC, β-CD, and SβCD substrate.

In continuation of our previous study,[49] herein, we disclosed that the grafting of CD moieties to the silica support has resulted in the production of a porous organic−inorganic hybrid material with specific microporous cavities. These cavities not only can control the size of NPs but also could play important roles to stabilize them and provide efficient routes for conducting the starting materials in catalytic sites in order to increase the reaction rates.

This substrate was used for immobilization of PdNPs in the size range of 1−10 nm in order to obtain a heterogeneous catalyst system for Pd-catalyzed reactions. In this study, the catalytic performance of the immobilized PdNPs on the silica−cyclodextrin substrate (PdNP-SCD) was evaluated in the Heck reaction in aqueous media.

## ■ EXPERIMENTAL SECTION

**General.** Chemicals were purchased from Fluka and Aldrich chemical companies and used without further purification. Silica chloride was produced based on the previous procedure.[49] The known products were characterized by comparison of their spectral and physical data with those reported in the literature. $^1$H (250 MHz) and $^{13}$C NMR (62.9 MHz) spectra were recorded on a Bruker Avance spectrometer in CDCl$_3$ and DMSO-$d_6$ solutions with tetramethylsilane (TMS) as an internal standard. X-ray diffraction (XRD, D8, Advance, Bruker, axs) and FT-IR spectroscopy (Shimadzu F T-IR 8300 spectrophotometer) were employed for characterization of the catalysts and products. ICP analysis was determined, using an inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro). The scanning electron micrograph (SEM) for the NTDSS catalyst was obtained by SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV). Transmission electron microscopy (TEM) was obtained using a TEM apparatus (CM-10-Philips, 100 kV) for characterization of the catalysts. Melting points were determined in open capillary tubes in a

Barnstead electro-thermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates. Column chromatography was carried out on columns of silica gel 60 (70−230 mesh)

**Preparation of SCD Substrate.** To a magnetically stirred mixture of silica chloride (5 g) in $CHCl_3$ (30 mL), CD (0.3 mmol) and triethyl amine (0.4 mL) were added and refluxed for 12 h. Subsequently, the mixture was filtered and washed with chloroform (3 mL × 10 mL) and water (3 mL × 10 mL). After drying in the oven at 100 °C for 4 h, the SCD substrate was obtained as a white powder.

**Preparation of PdNP-SCD Catalyst.** To a mixture of the silica−cyclodextrin substrate (2 g) in absolute ethanol (20 mL), palladium acetate (0.12 g, 0.52 mmol) was added and stirred for 24 h at rt. Then, the mixture was filtered and washed with ethanol (3 mL × 10 mL) and diethyl ether (2 mL × 10 mL). After drying in a vacuum oven at 80 °C for overnight, the PdNP-SCD catalysts were obtained as dark solids.

**General Producer for the Heck Reaction in the Presence of PdNP-SβCD Catalyst.** In a typical experiment, to a mixture of aryl halide (1 mmol), styrene (1.2 mmol), and $K_2CO_3$ (2 mmol) in 2 mL water, a PdNP-SβCD catalyst (0.04 g, 1.0 mol %) was added and heated in an oil bath at the refluxing temperature of water for the time specified in Table 6. The reaction was followed by TLC. After completion of the reaction, the mixture was cooled to room temperature and filtered, and the remaining solid was washed with dichloromethane (3 mL × 5 mL) in order to separate the catalyst. After extraction of dichloromethane from water, the organic extract was dried over $Na_2SO_4$. The products were purified by column chromatography (hexane/ethyl acetate) to obtain the desired purity. The purity and identity of the previously described products were confirmed by ^{1}H NMR, ^{13}C NMR, mass spectroscopy, and elemental analysis (Supporting Information).

## ■ RESULTS AND DISCUSSION

**Synthesis and Characterization of SCD Substrates.** As shown in Scheme 1, the SCD substrate was prepared in a two-step process. First, silica was converted to silica chloride, and subsequently, it was reacted with CD to obtain SCD substrates. Silica chloride was prepared according to the procedure in the literature.[49]

After preparation of the SCD substrates, they were characterized using various techniques such as FT-IR, TGA, EDX, and elemental analysis. As a model, a comparison between the FT-IR spectra of silica chloride (SC), β-CD, and the silica-β-CD (SβCD) substrate is shown in Figure 1. This comparison reveals some absorption bands in the SβCD substrate that are present in both silica and β-CD.

In the SβCD spectrum, the peaks positioned at around 2932, 16051, 1636, 1420, 1366, 1159, 1972, and 710 cm$^{-1}$ are related to the bonds in β-CD in the structure of the SβCD substrate. The observed shift in the absorptions of these peaks is associated with the chemical bond formed between the β-CD and silica. The bond formation between silica and β-CD can change the electron density around the chemical bonds. The comparison between the FT-IR spectra shows that the SβCD substrate was generated according to our procedure. The thermal gravimetric analysis (TGA) curves of the SβCD substrate is depicted in Figure 2.

As shown in Figure 2, the TGA curves of the SCD substrates show a ~4.0% weight loss within a temperature near 100 °C, which is due to the loss of adsorbed water molecules. Further, it shows a ~5% weight loss at 220−450 °C, which is due to the decomposition of grafted CD. The high temperature for CD removal indicates high thermal stability for the SCD substrates because CD is covalently bonded to silica. Also the elemental analysis of the synthesized SCD substrates demonstrates the presence of carbon and hydrogen atoms, which confirm the
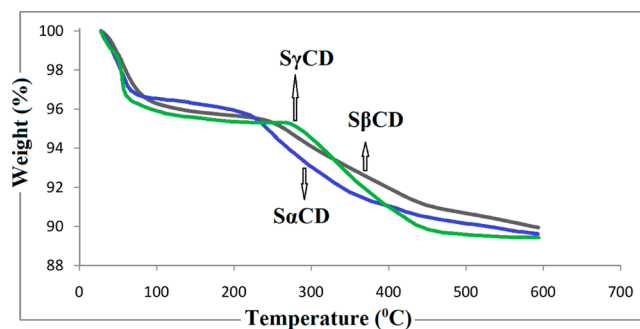


**Figure 2.** Typical TGA curve of the SCD substrates.

presence of CD on the silica surface. The results of TGA and elemental analysis are shown in Table 1.

**Table 1. Results of TGA and Elemental Analysis**

| entry | weight loss in TGA (%) | C in CHNS (%) | mmol/g CD | w/w (%) |
|---|---|---|---|---|
| SαCD | ~4.8 | 2.25 | 0.052 | 5.0 |
| SβCD | ~4.7 | 2.31 | 0.046 | 5.2 |
| SγCD | ~4.9 | 2.37 | 0.041 | 5.3 |

According to the data in Table 1, it can be concluded that about 5% of CD is grafted to the silica surface based on our procedure (Supporting Information). The EDX spectrum (Figure 3) of SβCD also shows the elements, including C, O, and Si, that are present in the structure of this material.

**Preparation and Characterization of Palladium Nanoparticle Catalysts Based on SCD Substrate.** After the synthesis and characterization of SCD substrate, we decided to immobilize the PdNPs on the substrates in order to prepare heterogeneous palladium catalysts for application in palladium-catalyzed reactions. Thus, palladium acetate was reduced to PdNPs using the method of alcohol reduction on a SCD substrate as a green process (Scheme 2).[49−51]

In order to study the immobilization of the PdNPs on a SCD substrate, they were characterized using TEM, SEM, and XRD techniques. The TEM images of PdNP-CD catalysts are depicted in Figure 4. Also, the SEM images of the PdNP-CD catalysts are shown in Figure 5. The SEM images show the presence of metal NPs on the surface of substrate. According to the SEM image, the size of the silica particles are in the range of a micrometer.

According to the TEM images and histogram (Figure 4), the average diameters of the particles are estimated to be 3, 5, and 10 nm for PdNP-SβCD, PdNP-SγCD, and PdNP-SαCD, respectively. The TEM images of the catalysts (Figure 4) show that the near spherical PdNPs were produced during the preparation process. In Table 2, we show a comparison between the obtained size of PdNPs in PdNP-SβCD, PdNP-SγCD, and PdNP-SαCD substrates and upper and base aperture of CDs.

The work of Liu and Antunes research groups showed that in the presence of CD the PdNPs can be produced in an average size of 3.2 nm (when $NaBH_4$ was used as a reducing agent) and 2.7−5.6 nm (by use of the alcohol reduction method), respectively.[45,46] Also, Bedford et al. reported that modified silica can form stable, catalytically active PdNPs with diameters of 3−6 nm.[52] These studies demonstrated that both silica and CD can affect the size of produced PNPs in the presence of
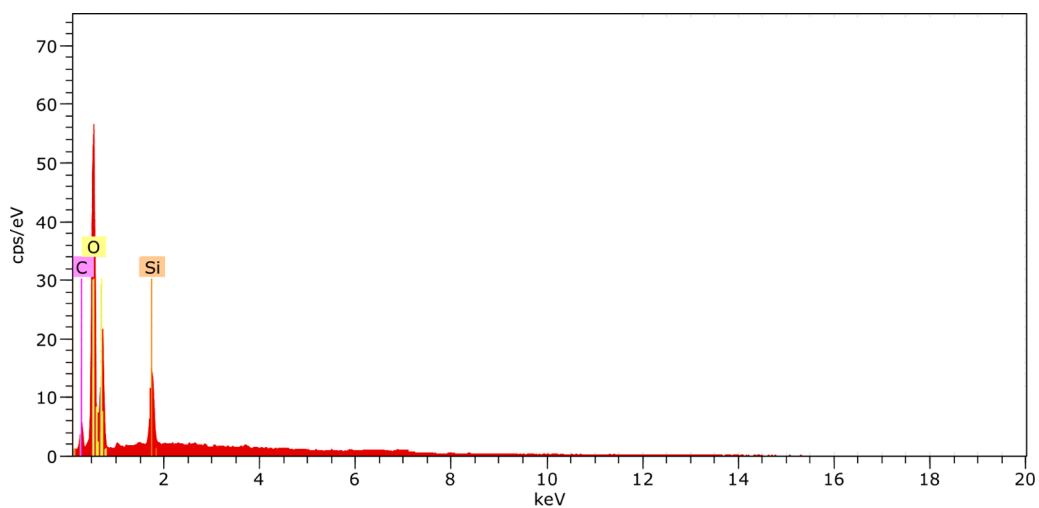
**Figure 3.** EDX spectrum of the S*β*CD substrate.

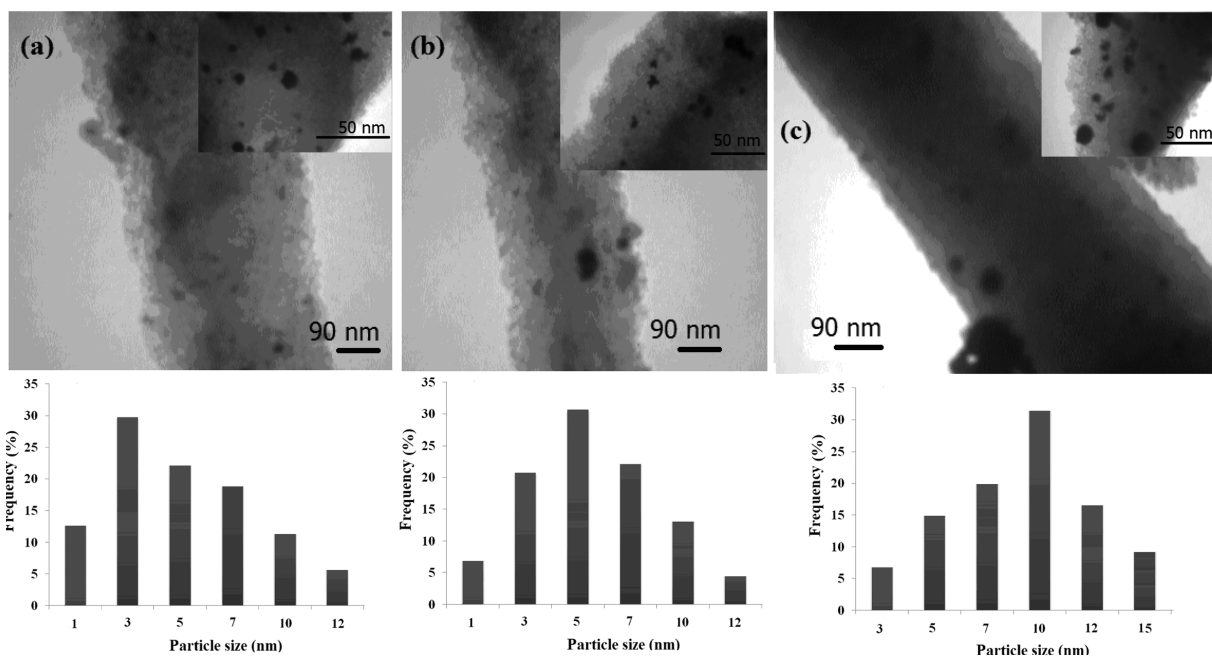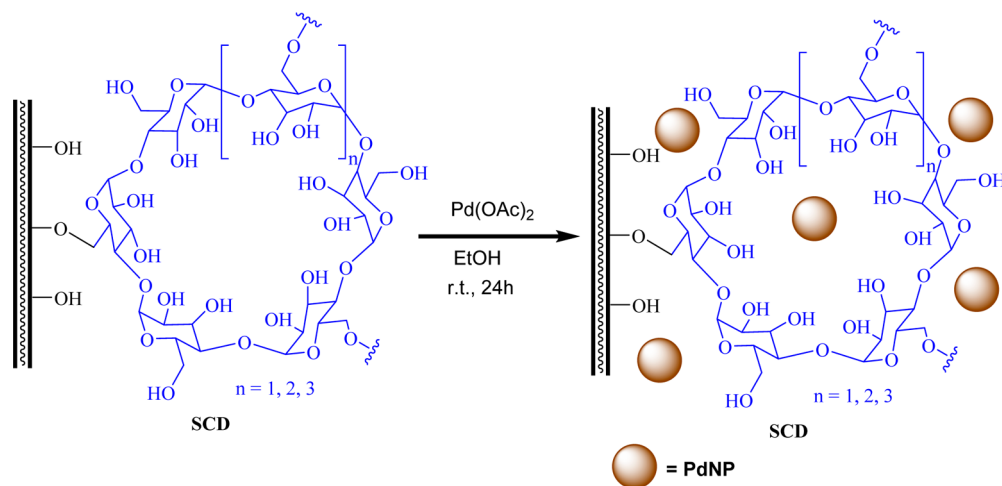**Scheme 2. Reduction of Pd(II) to Pd(0) on SCD Substrate Using EtOH**





**Figure 4.** TEM images of immobilized PdNPs on modified silica by (a) *β*-CD, (b) *γ*-CD, and (c) *α*-CD with the corresponding histogram.
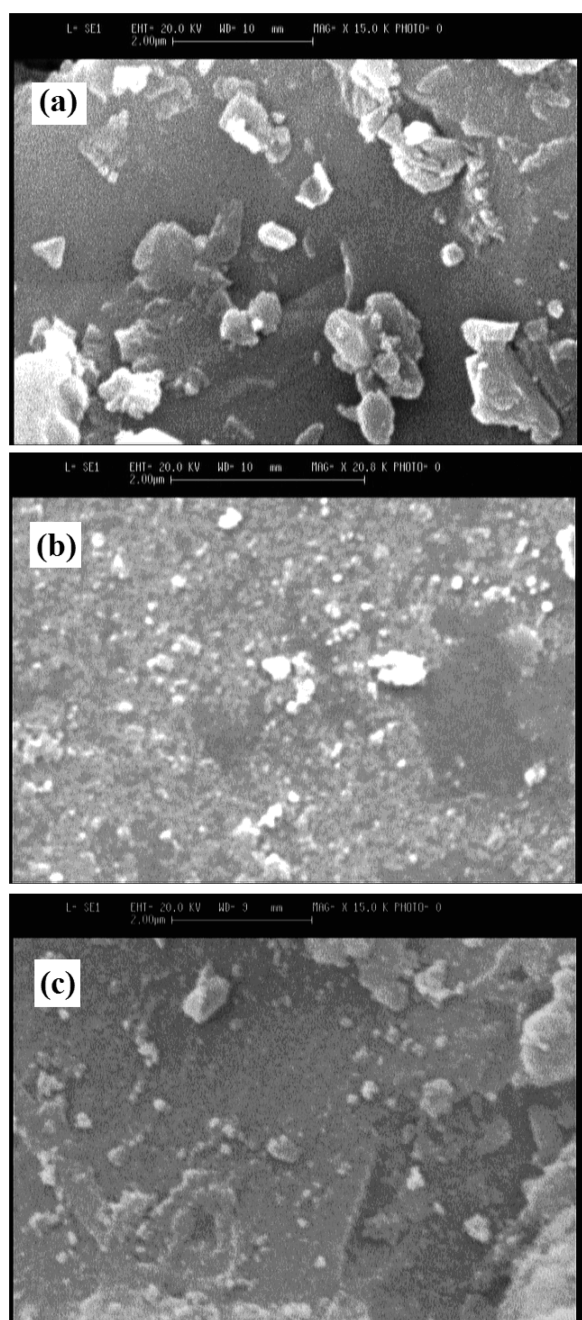
**Figure 5.** SEM image of (a) PNP-SαCD, (b) PNP-SβCD, and (c) PNP-SγCD with magnification of 2 μm.

**Table 2. Comparison between Average Size of PdNPs of SCD Substrates and Upper and Base Aperture of CDs**

| catalyst | PdNPs size (nm) | upper aperture size of CD (nm) | base aperture size of CD (nm) |
|---|---|---|---|
| PdNP-SαCD | 10 | 1.37 | 0.57 |
| PdNP-SβCD | 3 | 1.53 | 0.78 |
| PdNP-SγCD | 5 | 1.69 | 0.95 |
| PdNP-SSS | 8 | – | – |

these materials. However, when CD is covalently connected to the silica surface, we have a new material containing both the cavity of CD and porosity of silica. Thus, we cannot expect that the SCD substrate acts in a manner similar to each of them during stabilization of PNPs. We believe that the CD moieties

on the surface of silica can enhance the capturing and stabilization character of the silica surface. On the basis of the fact that changing the type of CD results in variation of the average size of PNPs, it is suggested that this substrate can be used as a size-controlling support. As shown in Table 2, for SαCD, the size of PdNPs is about 10 nm, and on the basis of the previously reported catalyst system (PdNPs on silica–starch substrate; PdNP-SSS),[49] this result shows that the size of the CD cavity has no significant effect on the size control of PdNPs. It seems that the SαCD substrate can stabilize PdNPs using its hydroxyl group the same as the silica–starch substrate. However, the size of the PdNPs in PdNP-SβCD and PdNP-SγCD revealed that the cavity size in these CDs has an important role in the size control of synthesized PdNPs. For β-CD with a smaller cavity, the size of the particles is less than γ-CD. As the size of the cavities in β-CD and γ-CD is about 1 nm, some of the PdNPs are formed in the range of 1 nm. Thus, it is possible to capture some particles in the CD cavities. However, the porous nature of the silica and the hydroxyl group of grafted CD moieties on the silica is also influence the size control of the PdNPs.

The XRD pattern of the catalysts (Figure 4) shows that PdNPs exist on the SCD substrates. The strongest peaks of the XRD pattern correspond to SiO₂, and other peaks are indexed as the (111), (200), (220), and (311) planes of the PdNPs.[49] According to the XRD spectrum (Figure 6), a sharp peak of
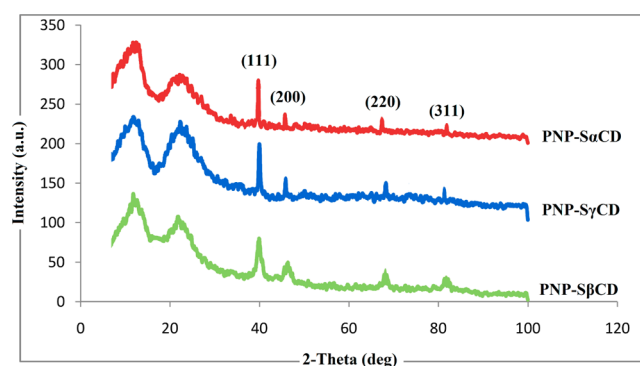


**Figure 6.** XRD spectra of the PdNP-SCD catalysts.

PNPs is observed at ~2 θ = 40°. The size of the PNPs was also determined from the X-ray line broadening using the Debye–Scherrer formula[49] given as $D = 0.9\, L/\beta \cos(\theta)$, where $D$ is the average crystalline size, $L$ is the X-ray wavelength used, $\beta$ is the angular line width at half-maximum intensity, and $\theta$ is Bragg's angle. For $\theta = 20°$, $L = 1.06$ Å. The obtained $\beta$ value is based on XRD spectra. The average size of the PdNPs on the SCD substrates were estimated, and results are shown in Table 3. These values are in good agreement with data obtained from the TEM image.

**Table 3. Estimated PNP Size Based on XRD Using Debye–Scherrer Formula**

| catalyst | $\beta$ (mm) | PNPs size (nm)[a] | PNPs size (nm)[b] |
|---|---|---|---|
| PNP-SαCD | 0.85 | 12 | 10 |
| PNP-SβCD | 2.5 | 4 | 3 |
| PNP-SγCD | 1.4 | 7 | 5 |

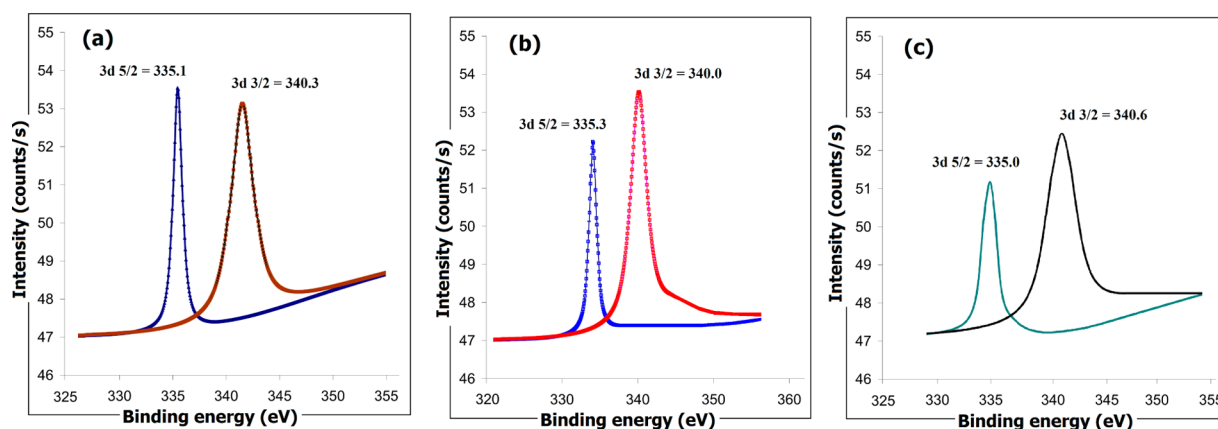[a]Based on XRD. [b]Obtained based on TEM and particle analyzer.

**Figure 7.** XPS analysis of (a) PNP-SγCD, (b) PNP-SβCD, and (c) PNP-SαCD catalyst.

The chemical oxidation state of the Pd in PNP-SCD catalysts was analyzed using XPS (Figure 7). The XPS spectra reveal that we have only Pd(0) on the SCD substrate. The binding energy (BE) values of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ in palladium catalysts at about 335 and 340 eV, respectively, are assigned to the Pd(0) species. Also, the reason for the change in binding energy of the catalysts by change of substrate can be attributed to the type of PdNPs dispersion on the substrate surface and also the interaction between Pd and other elements in the substrate.[53−55]

Also, to verify the Pd content in the catalysts, they were treated with concentrated HCl and HNO₃ (3/1 ratio of HCl and HNO₃) to digest the Pd species and then were analyzed by ICP analysis. The Pd content was estimated to be 22.5 ppm (22.5 mg L$^{-1}$; 2.25% w/w), 22.8 ppm (22.8 mg L$^{-1}$; 2.28% w/w), and 22.6 ppm (22.6 mg L$^{-1}$; 2.26% w/w) for PdNP-SγCD, PdNP-SβCD, and PdNP-SαCD catalysts, respectively.

**Heck Reaction Catalyzed by PdNP-SCD Catalysts in Water.** Water is a safe, benign, green, and cheap solvent compared with other solvents for organic transformations.[56] The use of water as a solvent in the Heck reaction is of importance to develop greener manufacturing protocols. However, common uses of water as a solvent in the Heck reaction is restricted because of the insolubility of starting materials and catalyst "in water".[57−59] In one strategy, some of the Heck reactions have been conducted "on water", but these reactions also have their limitations.[60] To overcome these constraints, there are some strategies that facilitate the use of water as a solvent for the Heck reaction such as use of water-dispersible Pd catalysts and solid-supported Pd catalysts with hydrophobic surfaces.[49,61−63] Previously, we reported that when silica is modified with starch it provides suitable catalytic sites for reactions in aqueous media.[49] The PdNP-SSS catalyst was successfully used in the Heck and copper-free Sonogashira reactions. In this study, we applied the PdNP-SCD catalysts in the Heck reaction in order to evaluate their catalytic activity and compare it with the PdNP-SSS catalyst in the viewpoint of reactivity.

To evaluate the catalytic reactivity of the PdNP-SCD catalysts, the Heck reaction between bromobenzene (**1a**) and styrene (**2a**) was selected as a simple model substrate (Scheme 3). The optimized conditions for the PdNP-SSS catalyst was PdNP-SSS (1.2 mol %), H₂O (2 mL), K₂CO₃ (2 mmol), and reflux conditions.[49]

Comparison of Heck reaction catalyzed by PdNP-SCD and PdNP-SSS catalysts under optimum conditions demonstrated

**Scheme 3. Simple Model Reaction for PdNP-SCD Catalyst Evolution**
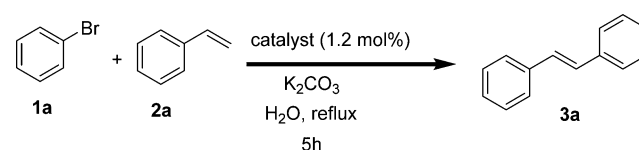


that the PdNP-SβCD catalyst was better than the other; therefore, it was selected as the best tested catalyst for the Heck reaction in water in this study (Table 4). These interesting results encouraged us to continue the optimization studies using PdNP-SβCD as the best tested catalyst.

**Table 4. Comparison of Heck Reaction Catalyzed by PdNP-SCD and PdNP-SSS Catalysts in Water**[a]

| entry | catalyst (mol %) | yield of **3a** (%)[b] |
|---|---|---|
| 1 | PdNP-SαCD (1.1) | 89 |
| 2 | PdNP-SβCD (1.1) | 95 |
| 3 | PdNP-SγCD (1.1) | 92 |
| 4 | PdNP-SSS (1.2) | 92 |

[a]Reaction conditions: bromobenzene (1 mmol) and styrene (1.2 mmol), K₂CO₃ (2 mmol), H₂O (2 mL), catalyst (0.05g), and reflux. Reaction time: 5 h. [b]Isolated yield.

To optimize the amount of PdNP-SβCD catalyst, different experiments were accomplished (Table 5).

As shown in Table 5, with increasing the amount of catalyst, the yield of product remained unchanged (entry 1). Furthermore, as a result of reducing the amount of catalyst, a decrease in the yield of product was observed (Table 5, entries 3 and 4). Thus, the simple system including PdNP-SβCD (40

**Table 5. Optimization of Catalyst Quantity**[a]

| entry | PdNP-SβCD | | time (h) | yield of **3a** (%)[b] |
|---|---|---|---|---|
| 1 | 60 mg | ~1.4 mol % | 5 | 97 |
| 2 | 50 mg | ~1.1 mol % | 5 | 96 |
| 3 | 40 mg | ~1.0 mol % | 5 | 95 (96)[c] |
| 4 | 30 mg | ~0.8 mol % | 5 | 91 (94)[c] |

[a]Reaction conditions: bromobenzene (1 mmol), styrene (1.2 mmol), K₂CO₃ (2 mmol), H₂O (2 mL), catalyst, and reflux. [b]Isolated yield. [c]Reaction yield after 12 h.

mg, 1.0 mol %), $H_2O$ as solvent, and reflux temperature of water was chosen as the optimized reaction conditions.

To determine the scope of this protocol, various stilbenes were synthesized under the optimized conditions, and the results are summarized in Table 6. The results in Table 6 reveal

**Table 6. Synthesis of Stilbenes in the Presence of PdNP-SβCD Catalyst in Water[a]**

| entry | R | X | Y | product | time (h) | yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | H | Cl | Ph | 3a | 12 | 75 |
| 2 | H | Br | Ph | 3a | 5 | 96 |
| 3 | H | I | Ph | 3a | 2 | >99 |
| 4 | 4-OMe | Cl | Ph | 3b | 12 | 67 |
| 5 | 4-OMe | Br | Ph | 3b | 7 | 92 |
| 6 | 4-OMe | I | Ph | 3b | 2 | 97 |
| 7 | 4-CN | Cl | Ph | 3c | 12 | 81 |
| 8 | 4-CN | Br | Ph | 3c | 4 | 96 |
| 9 | 4-CN | I | Ph | 3c | 1 | >99 |
| 10 | H | Cl | 4-OMe-Ph | 3b | 12 | 68 |
| 11 | H | Br | 4-OMe-Ph | 3b | 5 | 90 |
| 12 | H | I | 4-OMe-Ph | 3b | 2 | 97 |
| 13 | H | Cl | 4-F-Ph | 3d | 12 | 77 |
| 14 | H | Br | 4-F-Ph | 3d | 5 | 95 |
| 15 | H | I | 4-F-Ph | 3d | 1.5 | >99 |
| 16 | 2-Me | Cl | Ph | 3e | 15 | 61 |
| 17 | 2-Me | Br | Ph | 3e | 8 | 89 |
| 18 | 2-Me | I | Ph | 3e | 3 | 92 |

[a]Reagents and conditions: aryl halide (1 mmol), alkene (1.2 mmol), $K_2CO_3$ (2 mmol), PdNP-SβCD (40 mg), $H_2O$ (2 mL), and reflux.
[b]Isolated yields.

that PdNP-SβCD is an active and efficient catalyst for the Heck reaction in water. All of the products were obtained in *trans* form, demonstrating good *trans* selectivity for the PdNP-SβCD catalyst in Heck reaction. The reaction condition is quite broad with respect to the substrates examined, providing the desired stilbenes with good to excellent yields. As clearly shown in Table 6, the PdNP-SβCD catalyst can be used for aryl halides with electron-withdrawing and electron-donating groups. Moreover, sterically hindered aryl halides can be used under the same reaction conditions.

For sensible application of this heterogeneous catalyst, its level of reusability was investigated using the model reaction under optimized conditions. The recycled catalyst could be reused at least five times without any treatment in its catalytic activity (Table 7).

**Table 7. Reusability of PdNP-SβCD Catalyst in the Heck Reaction in Water[a]**

| entry | yield of product (%) | recovery of PdNP-SβCD (%) |
|---|---|---|
| fresh | 96 | >99 |
| 1 | 95 | 99 |
| 2 | 93 | 98 |
| 3 | 93 | 98 |
| 4 | 91 | 97 |
| 5 | 90 | 96 |

[a]Reaction conditions: PdNP-SβCD (0.1 g), $K_2CO_3$ (4.0 mmol), $H_2O$ (4 mL), bromobenzene (2.0 mmol), and ethyl acrylate (2.4 mmol)

Because leaching of the PdNPs from the support makes the catalyst inactive, a stability study of a PdNP catalyst is necessary. Thus, leaching of PdNPs from the SCD support was checked. After five times of reuse, we checked the Pd content of the PdNP-SβCD catalyst using ICP analysis, and the results showed that less than 2% of Pd was lost. In an experiment where the reaction between bromobenzene with styrene was completed, hot filtration had been accomplished, and the ICP analysis of the aqueous solution showed less than 1 ppm of Pd. Considering these results, it can be concluded that there is a small amount of Pd species leaching from the support. These results are in good agreement with the catalytic activity of the PdNP-SβCD after each recovery. Also, to confirm that the reaction conditions have not had a significant effect on the stability of our catalyst system, we conducted a reaction in which the SβCD substrate was used under optimized conditions ($K_2CO_3$, refluxing water, 12 h), and then it was analyzed by elemental analysis to determine the amount of lost CD from the silica surface. This percent of C was 2.26, demonstrating that about 2.1% of CD was lost from the silica surface. Thus, although occurrences (such as dehydration, hydrolysis) may happen for the SCD substrate during the reaction, these changes do not have significant effect on the stability of the substrate. To study the effects of Hg(0) on the catalytic activity of the PNP-SβCD catalyst, the following test was accomplished. A solution of iodobenzene (1.0 mmol) styrene (1.2 mmol), $K_2CO_3$ (2 mmol), and Hg(0) (400 equiv to total palladium content) in water (2 mL) was magnetically stirred at a refluxing temperature of water. Then, the catalyst (containing 1 mol % Pd) was rapidly added, and the reaction was monitored by GC. It was established that the PNP-SβCD catalyst preserves its activity in the Heck reaction in the presence of a large amount of Hg(0) (Hg/Pd, 400:1) (2 h, 96% of 3a). The high activity of catalyst even in the presence of Hg(0) confirms that the PNP-SβCD catalyst is not a precatalyst for the formation of exposed PdNPs.[64]

To compare the efficiency of our catalyst with some of the reported catalysts for the Heck reaction, we have tabulated the results of these catalysts for the synthesis of compound 3a in Table 8. As shown in Table 8, our catalyst is superior to some of the previously reported catalysts in terms of reaction condition, reaction time, and yield.

## ■ CONCLUSIONS

In conclusion, SCD is introduced as a new size-controlling support for capture of metal NPs. This porous organic–inorganic hybrid material with specific microporous cavities can prevent the release of NPs from a silica surface. In this regard, a SCD substrate was used as size-controlling support for immobilization of PdNPs with average sizes of 3, 5, and 10 nm for SβCD, SγCD, and SαCD substrates, respectively. Among the synthesized PdNP-SCD catalysts, PdNP-SβCD was recognized as the best one. As the catalytic activity of the PdNP-SβCD catalyst was evaluated in the Heck reaction in water, a significant activity was observed. By use of PdNP-SβCD as the catalyst, the Heck products were obtained in high yields under green conditions. The PdNP-SβCD acts as a heterogeneous catalyst, and it can be recovered for six runs without significant loss in its activity.

1183

dx.doi.org/10.1021/sc5000122 | ACS Sustainable Chem. Eng. 2014, 2, 1177−1186

**Table 8. Comparison of Results of Synthesis of Compound 3a Using SBSAN Catalyst with Those Obtained by Reported Catalysts**
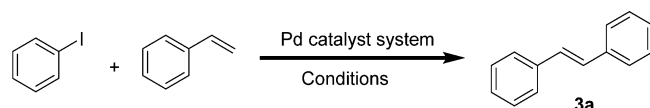


| entry | catalyst and conditions | time (h) | yield (%) | ref |
|---|---|---|---|---|
| 1 | Pd(OAc)$_2$ (1.0 mol %), H$_2$O, 90 °C | 24 | 20 | – |
| 2 | Pd(OAc)$_2$ (1.0 mol %), β-CD (0.05 g, 5.0 mol %), H$_2$O, 90 °C | 24 | 80 | – |
| 3 | PdNP-SβCD (1.0 mol %), K$_2$CO$_3$, H$_2$O, 90 °C | 2 | 98 | this work |
| 4 | Pd-αHPCD (0.02 mol %), K$_2$CO$_3$, H$_2$O, 80 °C | 24 | 96 | 45 |
| 5 | PS-PdONPs (1.5 mol %), Et$_3$N, H$_2$O, 80 °C | 20 | 14 | 65 |
| 6 | cellulose−Pd, n-Bu$_3$N, H$_2$O, 90 °C | 6 | 98 | 66 |
| 7 | PS-co-PMAA-IDA-Pd (0.1 mol %), K$_2$CO$_3$, H$_2$O, 90 °C | 8 | 10 | 67 |
| 8 | RaMe-b-CD-modified Pd/C (0.1 mol %), H$_2$O, Et$_3$N, 100 °C | 24 | 29 | 40 |
| 9 | Pd-MPTA-1, K$_2$CO$_3$, H$_2$O, reflux | 6 | 92 | 68 |
| 10 | Pd-LHMS-3, triethanol amine, reflux, 383 K | 10 | 85 | 69 |

## ASSOCIATED CONTENT

### Ⓢ Supporting Information
Copies of $^1$H- and $^{13}$C-NMR spectra and spectral data for the synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

## ABBREVIATIONS
SCD, silica−cyclodextrin; PdNPs, palladium nanoparticles; CD, cyclodextrin; SαCD, silica α-cyclodextrin; SβCD, silica β-cyclodextrin; SγCD, silica γ-cyclodextrin; XRD, X-ray diffraction; TEM, transmission electron microscopy; SEM, scanning electron micrograph; TGA, thermal gravimetric analysis; XPS, X-ray photoelectron spectroscopy; FT-IR, Fourier transform infrared; ICP, inductively coupled plasma; SC, silica chloride

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