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Fabrication of Hollow Palladium Spheres and Their Successful Application to the Recyclable Heterogeneous Catalyst for Suzuki Coupling Reactions

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The fabrication of uniform hollow spheres with nanometer-to-micrometer dimensions having tailored structural, optical, and surface properties has been intensively pursued in a wide range of applications.[1] These hollow spheres are used as photonic crystals, delivery vehicle systems, fillers, and catalysts. Various hollow spheres including carbons,[2] polymers,[3] metals,[4] and inorganic materials[5] have been synthesized by using spherical particles such as polystyrene beads or silica sol as a template.[6] Various procedures have been developed to fabricate these hollow spheres.[7]

Palladium-catalyzed cross-coupling reactions of aryl halides with arylboronic acids, often referred as Suzuki coupling reactions, are versatile methods for synthesizing unsymmetrical biaryls. The Suzuki coupling reactions have been applied extensively in the synthesis of natural products, nucleoside analogues, and pharmaceuticals.[8] Many palladium complexes have been used as homogeneous catalysts for these reactions.[9] Homogeneous catalytic systems generally exhibit better activity and selectivity than heterogeneous systems. For the large-scale applications in liquid-phase reactions, however, heterogeneous catalysts have many advantages over homogeneous counterparts, including easy removal from reaction mixtures and catalyst recyclability. Since the time of the early development of the Suzuki coupling reactions, heterogeneous catalysts, including Pd/C, have been used.[10] Recently many transition-metal nanoparticles have been utilized in various liquid-phase reactions because they have a characteristic high surface-to-volume ratio, and consequently a large fraction of the metal atoms are at the surface and available for catalysis.[11] Our research group reported the first heterogeneous Pauson−Khand catalysts using cobalt nanoparticles.[12] Nanoparticles of noble metals such as Pt and Pd have been used as catalysts for olefin hydrogenation,[13] and in carbon−carbon coupling reactions including the Heck and Suzuki reactions.[14] Here, we report on the fabrication of hollow spheres composed of palladium nanoparticles and their applications to heterogeneous Suzuki coupling reactions.

Scheme 1 shows the overall procedure used to synthesize the Pd hollow spheres. The uniform silica spheres were synthesized using the Stöber method.[15] The surfaces of the silica spheres were functionalized with mercaptopropylsilyl (MPS) groups by refluxing the silica spheres and mercaptopropyltrimethoxysilane ($HS(CH_2)_3Si(OCH_3)_3$) in toluene. The palladium precursor, palladium acetylacetonate ($Pd(acac)_2$) was then adsorbed onto the surfaces of these MPS-functionalized silica spheres. The resulting Pd^{2+}-adsorbed-MPS-functionalized silica spheres were heated at 250 °C for 3 h to obtain Pd metal-coated spheres. The CO generated in situ from the thermal decomposition of acetylacetonate seems to act as the reductant.

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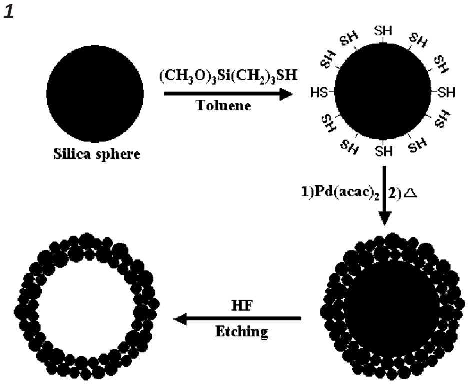
Scheme 1



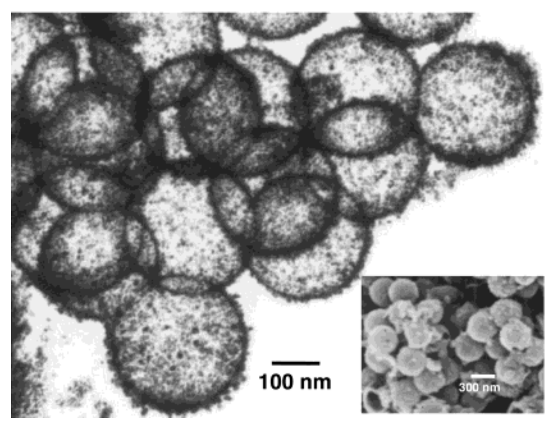


Figure 1. Transmission electron micrograph and scanning electron micrograph (Inset) of hollow palladium spheres.

The final step involves the removal of the silica template by treating the Pd-coated silica spheres with 10 M HF to produce hollow Pd spheres (*Extreme caution*!).[16] The structure of the hollow Pd spheres was investigated by powder X-ray diffraction (XRD) and electron microscopy. The XRD pattern of the material revealed a metallic fcc Pd crystal structure. The scanning electron microscopic (SEM) image of the Pd spheres, shown by the inset in Figure 1, revealed that nearly monodisperse 300-nm sized spherical particles were produced. The transmission electron microscopic (TEM) image (Figure 1) showed that the individual particles were composed of an empty core with a uniform shell of 15 nm. Shell thickness can be controlled by varying the amount of adsorbed Pd precursor. The TEM image at high magnification showed that the shell is composed of ∼10 nm Pd nanoparticles. The BET surface area of the Pd spheres was measured to be 64 $m^2\ g^{-1}$, which is much larger than the value of 8.3 $m^2\ g^{-1}$ calculated for the surface of dense spheres.

The Suzuki coupling reaction of iodothiophene and phenylboronic acid was used as a test reaction. The cross-coupling reactions were carried out using 3 mol % Pd catalyst in ethanol

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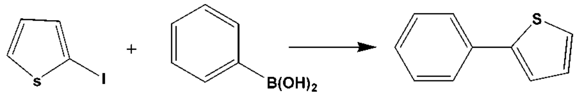
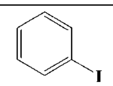
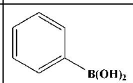
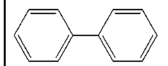
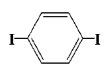
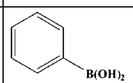
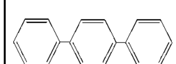
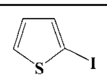
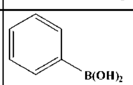
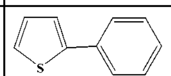
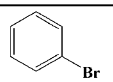
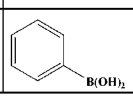
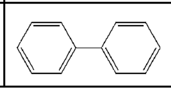
Table 1. Suzuki Cross Coupling Reactions Using Hollow Pd Spheres as Catalyst[a]



entry	catalyst	yield (%)[b]
1	Pd spheres	97
2	first recycle	95
3	second recycle	95
4	third recycle	96
5	fourth recycle	98
6	fifth recycle	95
7	sixth recycle	96[c]

[a] Reaction conditions: 10 mg of hollow Pd spheres (3 mol %), 3 mmol iodothiophene, 6 mmol phenylboronic acid, 12 mmol K_3PO_4, and 50 mL of EtOH under reflux, 3 h, 78 °C. [b] Yield obtained from GC. [c] Isolated yield.

Table 2. Suzuki Cross-Coupling Reaction for Various Substrates[a]

Entry	Aryl halide	Boronic acid[b]	Time (h)	Product	Yield (%)[c]
1			3		99
2			24		96
3			3		97
4[d]			24		90

[a] Reaction conditions: 10 mg of hollow Pd spheres (3 mol %), 3 mmol aryliodide, 6 mmol phenylboronic acid, 12 mmol K_3PO_4, and 50 mL of EtOH under reflux. [b] 12 mmol of phenylboronic acid was used for diiodobenzene. [c] Isolated yield. [d] 50-mg hollow Pd sphere (15 mmol %) was used for bromobenzene.

under reflux conditions. Table 1 shows that the Pd spheres are highly active for this reaction, in addition, the catalyst can be recycled and reused seven times without losing its catalytic activity (entry 2−7). The high surface area of Pd spheres resulting from the nanoparticular nature of the shell is responsible for the high catalytic activity. Earlier studies by other research groups reported that Pd nanoparticles used in Suzuki coupling reactions were agglomerated after one cycle, resulting in a loss of catalytic activity.[17] Heterogeneous catalysts often suffer extensive leaching of the active metal species during reactions and eventually lose their catalytic activity. To our surprise, these catalysts maintained their catalytic activities even after seven recycles. In addition, simple filtering can retrieve the catalyst from the reaction pot. Elemental analysis of the filtrate after the reaction demonstrated no leaching of Pd, which is very important when Pd catalysts are used for pharmaceutical production. Recently, the de Vries group demonstrated the recycling of $Pd(OAc)_2$ catalyst for Heck reactions.[18] Table 2 shows that hollow Pd spheres are active catalysts for the reaction of various aryliodides and phenylboronic acid (entry 1−3). When arylbromides were used as reactant, instead of aryliodides, 5 times more Pd catalyst was required to achieve a similar yield (entry 4). The reaction with aryl chloride did not proceed, showing that the Pd shell is not active enough to catalyze the reaction.

In conclusion, we have synthesized palladium hollow spheres using silica spheres as a template. The hollow Pd spheres showed good catalytic activities in Suzuki cross coupling reactions and can be reused many times without loss of catalytic activity.

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Supporting Information Available: The detailed synthetic procedure for hollow Pd spheres (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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