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Synthesis of Pd-supported Nanosized Mesoporous Silica as a Spherical Nanocatalyst for Suzuki–Miyaura Coupling Reaction

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Nanosized mesoporous silica spheres with an average diameter of approximately 50 nm have been used as a catalyst support of active Pd nanoparticles, which was found to be highly efficient for Suzuki–Miyaura cross coupling compared to submicrosized or microsized conventional mesoporous silicas.

Mesoporous molecular sieve materials have attracted a great deal of attention because of their thermal/chemical stability, tunable pore structures (2–10 nm), and easy functionalization with silane coupling agents. They have opened new possibilities as exclusively promising support materials, especially for applications in catalysis, adsorption, and materials science.[1] In order to expand their inherent properties, the modification of mesoporous structures, such as diameter, geometry, and morphology, has been intensively pursued, and the catalytic performance has also been tuned by using such nanostructured mesoporous silica materials.[2] However, the high aspect ratio of highly ordered mesoporous channels often suffers from serious mass-transport limitation toward active sites located within mesopores, which severely circumvents their industrial applications.[3] In order to improve the above problems, the hierarchical combination of different pore sizes, such as meso/macroporous materials, has been developed recently, which enable easy access to active sites owing to the additionally introduced macroporous structures.[4]

In this study, we synthesized nanosized mesoporous silica spheres with a diameter of ca. 50 nm having worm-hole type short mesostructures, which was utilized as promising catalyst support for Pd nanoparticles. It is expected and herein demonstrated that the nanosized mesoporous silica spheres expose more active sites compared to conventional mesoporous silicas and consequently promote Suzuki–Miyaura coupling without the mass-transport limitations.

The nanosized mesoporous silica sphere with the size of about 50 nm (MS-S-50) was prepared according to a literature procedure via sol–gel method using polyalcohol triethanolamine instead of the common NaOH base.[5] To investigate the size effect of the mesoporous silica supports, we also prepared larger mesoporous silica nanosphere with the size of about 500 nm (MS-S-500) and typical bulky mesoporous silica particle (MS-B).[6] The deposition of Pd (0.5 wt %) was performed by simple ion exchange from aqueous [Pd(NH$_3$)$_4$Cl$_2$] solution.[7] The choice of Pd as catalytically active metal is motivated by its versatility and efficiency for a wide range of functional group transformations and for carbon–carbon bond-forming reactions.[8]

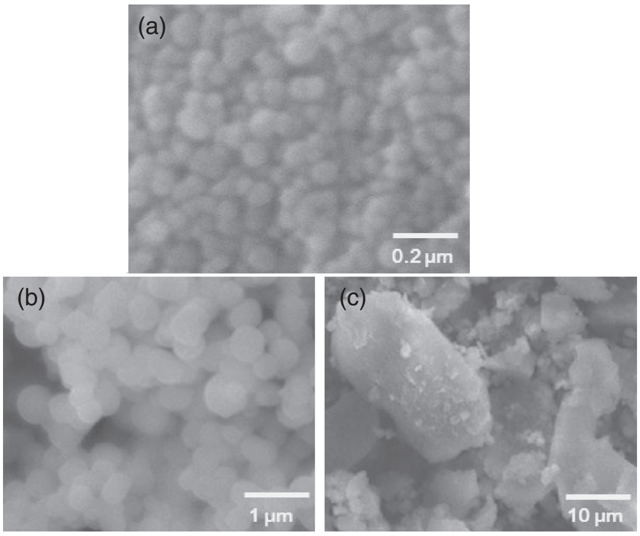
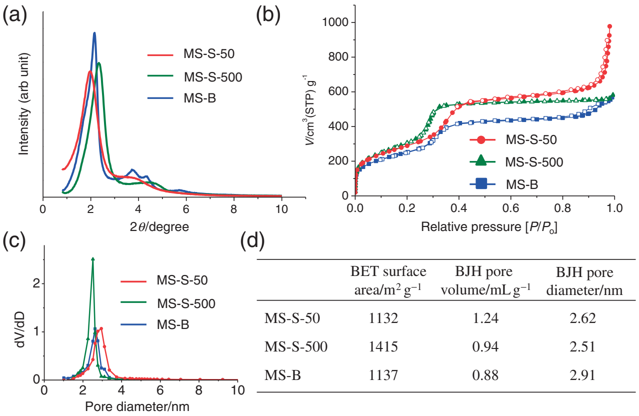


Figure 1. SEM images of (a) MS-S-50, (b) MS-S-500, and (c) MS-B.



	BET surface area/m^2 g^{-1}	BJH pore volume/mL g^{-1}	BJH pore diameter/nm
MS-S-50	1132	1.24	2.62
MS-S-500	1415	0.94	2.51
MS-B	1137	0.88	2.91

Figure 2. (a) Low-angle XRD patterns, (b) N$_2$ adsorption–desorption isotherms, (c) BJH pore size distribution, and (d) structural parameters of three samples.

SEM images of the prepared three samples are shown in Figure 1. As expected, MS-S-50 and MS-S-500 are found to be uniform-sized nanospheres with the particle sizes of 50 and 500 nm throughout the image area, respectively. In the case of the MS-B, bulky and nonuniform microsized particles are observed. The mesoporous structure was characterized by small-angle XRD patterns and N$_2$ adsorption–desorption measurements. Figure 2a shows the small-angle XRD of three samples, which exhibits a sharp diffraction peak associated with (100) reflection, suggesting the formation of hexagonally packed mesoporous structure. The diffraction pattern of MS-B can be assuming typical MCM-41 material.[9] The diffraction patterns of MS-S-50 and MS-S-500 show moderate peaks at around 3–4.5

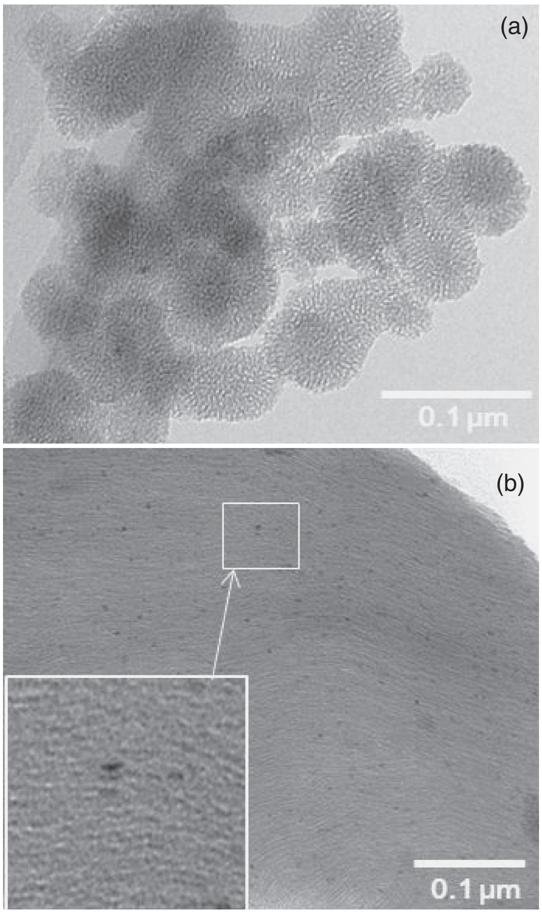


Figure 3. TEM images of (a) Pd/MS-S-50 and (b) Pd/MS-B.

and 3.5–5.5°, respectively, and the intensity associated with (100) reflection is relatively lower than that of MS-B. This indicates that the regularity of the mesopores was slightly diminished in MS-S-50 and MS-S-500, presumably due to the smaller size of the nanosphere.[10] Because of the low level of Pd loading, the peaks attributable to the Pd lattice could not be confirmed by wide-angle XRD analysis. N_2 adsorption–desorption isotherms of the samples show typical type IV isotherms without significant hysteresis loop (Figure 2b). At the relative pressure range from 0.2 to 0.4, the isotherms exhibit a sharp inflection indicative of capillary condensation inside the mesopores. The pore diameter calculated by Barrett–Joyner–Halenda (BJH) method (Figure 2c), Brunauer–Emmett–Teller (BET) surface area, and total pore volume of MS-S-50, MS-S-500, and MS-B are shown in Figure 2d. Apparently, all samples possess high surface area, large pore volume, and uniform pore structures regardless of the total sizes.

TEM images of Pd/MS-S-50 and Pd/MS-B are shown in Figure 3. Short-range ordered worm-hole mesopore channels are observed in the nanospherical MS-S-50 samples. The Pd nanoparticles are also spherical morphology with the average diameter of 2.6 nm. On the other hand, the bulk MS-B exhibited long-range ordered mesopore channels with the deposited Pd nanoparticles. The average diameter of Pd nanoparticles was determined to be ca. 2.8 nm, and a small fraction of the particles is slightly cylindrical morphology along the mesopore channels.

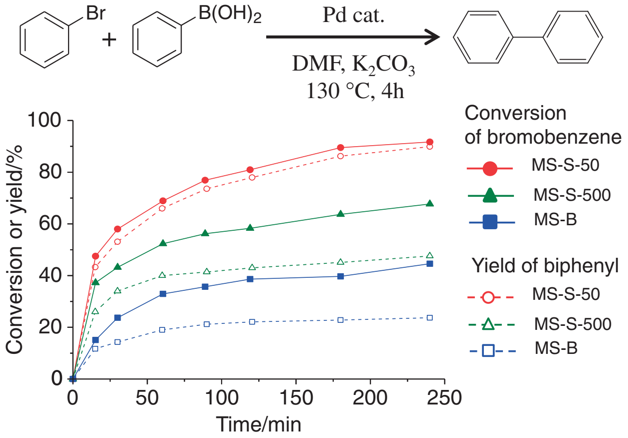


Figure 4. Time course of Suzuki–Miyaura coupling.

The catalytic activity of three samples was first evaluated in the hydrogenation of nitrobenzene to aniline in the presence of atmospheric molecular hydrogen. It was proven that the catalytic activity was almost independent of the employed Pd catalysts; the yields of aniline after 1 h were 63, 62, and 61% for Pd/MS-S-50, Pd/MS-S-500, and Pd/MS-B, respectively. The material balance between aniline and the nitrobenzene after the reaction agreed reasonably well (Figure S1[12]), showing that the deposition of the organic compounds in the nanoparticles was avoided because of their small size relative to the mesopore channels. It is well known that hydrogenation is generally believed to be a structure-insensitive reaction and the catalytic activity only dependent on the number of exposed surface metal species,[11] thus indicating that the mean diameter of the deposited Pd nanoparticles is almost the same for three Pd catalysts.

In contrast, a drastic change in potential catalytic activities was observed for the Suzuki–Miyaura reaction of bromobenzene with phenylboronic acid to produce biphenyls in the presence of potassium carbonate as a base. The kinetics are shown in Figure 4. It is found that there is strong correlation between catalytic activity and mesoporous silica particle size. The Pd/MS-S-50 catalyst with smallest particle size showed the highest catalytic activity, while Pd/MS-B significantly retarded the reaction. The high catalytic activity of the Pd/MS-S-50 can be ascribed to the short-range ordered worm-hole mesopore channels, which suppress the deposition of products and salts formed during the catalytic reaction and provides ease of further access of reactants to the catalytically active Pd nanoparticles. On the other hand, the saturation of the products and salt within a confined pore space may become prominent as the size of catalyst supports increases and restrict the diffusion of reactants. This result can be supported by the difference of material balance in the Suzuki–Miyaura coupling reaction: the values of conversions and yields are almost the same during the course of reaction using MS-S-50, while significant inconsistences were observed in the case of MS-S-500 and MS-B. This indicates that the larger coupling product, biphenyl, generated within the mesoporous channel could not come out from the inside pore and that the bromobenzene and phenylboronic acid could not approach the Pd nanoparticle. Vide supra, no differences in catalytic activity as well as reasonable agreement of material balance in the hydrogenation of the smaller nitrobenzene can also support the above assumption.

In summary, the catalytic activities of Pd-supported mesoporous silica materials with varied particle sizes are investigated. It was demonstrated that there is strong correlation between the size of mesoporous silica support and catalytic activity in the case of Suzuki–Miyaura reaction to produce larger size of coupling product. Controlling of morphology of the catalyst support is one of the most important keys to construct efficient catalyst, and further extension to other catalytic reactions is now under investigation in our laboratory.

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