

Diffusion Induced Reactant Shape Selectivity Inside Mesoporous Pores of Pd@meso-SiO₂ Nanoreactor in Suzuki Coupling Reactions

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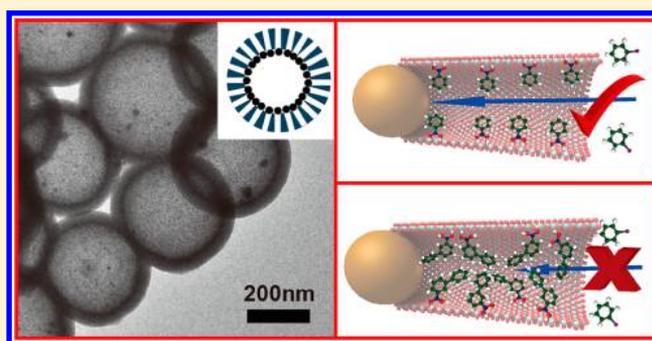
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S Supporting Information

ABSTRACT: Shape selectivity is one of the crown jewels of catalysis. It is frequently reported on microporous materials, mostly zeolite materials in gas phase reactions, but is rarely reported on mesoporous catalysts in liquid solution. Here we report reactant shape selectivity inside the mesoporous pores of Pd@meso-SiO₂ nanoreactor, which is a hollow composite with mesoporous silica walls and Pd nanoparticles residing at the inside pore mouths. The composite has structural features that resemble a nanoreactor and shows extremely high activity for Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. We observed sharp shape selectivity on phenylboronic acid. *N*-Butyl phenylboronic acid resulted in an 86% product yield, while *tert*-butyl phenylboronic acid resulted in a 0% product yield. We propose that nanoreactor feature of the catalyst and collective diffusion barrier induced by the preferential adsorption of bulky phenylboronic acid molecules account for these observations.



INTRODUCTION

Pd-catalyzed C–C coupling reactions, including the Suzuki reaction, the Heck reaction and the Sonogashira reaction, have been very successful methods in organic synthesis.^{1–6} Besides homogeneous Pd-based organometallic catalysts, various heterogeneous catalysts such as Pd particles or Pd supported composites are developed.^{1,7–10} In a recent communication, we produced a nanoreactor type catalyst that was composed of mesoporous silica (meso-SiO₂) hollow spheres and Pd nanoparticles residing inside the spheres.¹¹ The nanoreactor like catalyst showed excellent activity in Suzuki coupling reactions. Like many other related studies, shape selectivity was not considered possible in such mesoporous pores then.

Shape selectivity is one of the crown jewel in heterogeneous catalysis. Zeolite and zeolite-based catalysts have shown molecular shape selectivity in petrochemical process.^{12–14} However, these examples are all gas phase reactions within the uniform micropores of the zeolite type materials. There are very few reports on shape selectivity in liquid medium for organic synthesis.¹⁵ And mesoporous pores (2–50 nm) are too large for molecular shape selectivity.

In this study, we observed unprecedented sharp reactant shape selectivity in a series of Suzuki coupling reactions within the mesoporous pores of Pd@meso-SiO₂ nanoreactor-like catalyst. For a perfect example, *n*-butyl phenylboronic acid resulted in 86% yield (iodobenzene conversion), while *tert*-butyl phenylboronic acid resulted in 0% (iodobenzene

conversion). This is a clear example of reactant shape selectivity, and is observed within the mesopores in liquid. However, such shape selectivity is not the same molecular shape selectivity observed on zeolite. We propose that diffusion barrier caused by the nanoreactor features of the catalyst and preferential adsorption of bulky phenylboronic acid molecules account for these observations.

EXPERIMENTAL SECTION

Synthesis of Carbon Nanospheres. Glucose (4.5 g) was dissolved in 30 mL water to form a clear solution and then transferred into a 40 mL Teflon-sealed autoclave. The autoclave was maintained at 190 °C for 4 h. The products were separated by centrifugation, followed by washing three times using water and ethanol and finally oven-dried at 80 °C for further use.¹⁶

Loading Pd Nanoparticles onto the Carbon Nanosphere To Form Pd/C. In a typical process, 100 mg carbon nanosphere was dispersed in 50 mL distilled water and stirred for 10 min as part A. 0.1 g SnCl₂ was dissolved in 20 mL 0.02 M HCl solution as part B. Parts A and B were mixed together under stirring for 10 min. Then the suspension was centrifuged. After washing with distilled water five times, the precipitate was dispersed in 50 mL distilled water. Then 372 μL of 0.0564 M

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PdCl₂ was added into it. Ten min later, 10 mL of 0.15 M sodium formate solution was added following stirring for 5 h. After centrifugation and washing with distilled water five times, the precipitate was dried at 60 °C for 12 h.⁷

Production of Pd@mesoporous SiO₂ Nanoreactor.

The Pd/C composite obtained from last step was first dispersed in the solution containing 40 mL of H₂O, 30 mL of ethanol, 0.15 g of CTAB and 568 μL of NH₃·H₂O with ultrasonic for 20 min. Then 150 μL of TEOS was added and the mixture was vigorously stirred for 6 h. The precipitate was harvested after centrifugation and washed with distilled water and with ethanol for three times, then dried at 60 °C for 6 h. Then the product was calcined at 400 °C in N₂ flow for 2 h then in air atmosphere for 6 h to remove carbon sphere, CTAB template and other organic species. The finally obtained Pd@mesoporous SiO₂ product was further employed as nanoreactor for Suzuki cross-coupling reaction. The production route of catalyst B was same as Catalyst A except Pd loading varied to 0.4 wt %. The catalyst C was produced by stabbing and grinding Pd@mesoporous SiO₂ nanoreactor (catalyst A) intentionally with a mortar for 30 min.

Suzuki Cross-Coupling Reaction. First, 10 mg of catalyst, 0.5 mmol of substituted iodobenzene, 1 mmol of substituted phenylboronic acid, 1 mmol of K₂CO₃, and 0.5 mmol of pentamethylbenzene (as internal standard for HPLC analysis) were added to 10 mL of ethanol under stirring. The reaction was taken at reflux (ca. 78 °C). A certain amount of the reaction mixture was collected at special time during reaction. The mixture was separated quickly by centrifugation, and the liquid was analyzed by HPLC.

Characterization and Measurements. Transmission electron microscopy (TEM) was carried out on a JEOL 1011F electron microscope running at 100 kV. Nitrogen adsorption–desorption isotherms was obtained on Quantachrome Autosorb AS-1. The conversions of reagent were measured using HPLC (shimadzu LC-10 AVP Plus). Theoretical calculations were performed by using dispersion-corrected density functional theory (DFT-D) provided by the DMol3 code. We used the standard parameter set of Grimme without any parameter optimization. The atomic orbitals were represented by a double-numeric-quality basis set with d-polarization functions (DNP). All of the calculations were all-electron ones and were performed with an extra-fine mesh. A self-consistent field procedure was used with a convergence criterion of 10⁻⁵ au on the energy and electron density.

RESULTS AND DISCUSSIONS

Figure 1 showed the structure of the nanoreactor type catalyst and its TEM image. As illustrated in Figure 1a, TEM images of the catalyst with various magnification showed hollow sphere structures with black Pd nanoparticles dispersed onto the inside wall of the spheres. Figure 1c and HRTEM image (Figure 1d) showed that the Pd nanoparticles with sizes of about 2–10 nm were densely and uniformly distributed on the inside wall of SiO₂ nanosphere. There were likely many Pd nanoparticles with the diameter of less than 2 nm that were not very visible in the TEM image. The Pd nanoparticles were indeed uniformly distributed on the inside surface of SiO₂, because they were first uniformly deposited onto the surface of carbon spheres, and were then coated with silica shell. We believed that the distribution of the Pd nanoparticles did not change during the silica coating. The silica shell added difficulty to observe these smaller Pd nanoparticles by TEM. Moreover, Pd nanoparticles

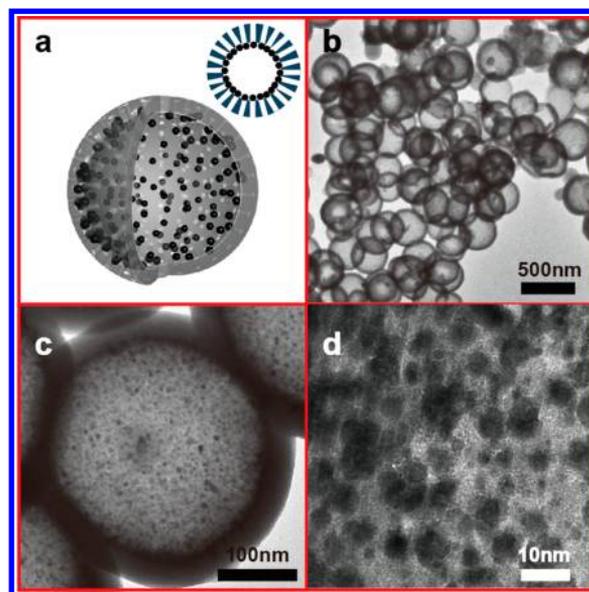


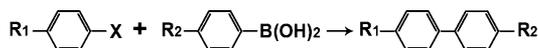
Figure 1. (a) Schematic illustration of Pd@meso-SiO₂ nanoreactor composite. (b and c) TEM images of Pd@meso-SiO₂ nanoreactor composite in different magnification. (d) HRTEM of Pd@meso-SiO₂ nanoreactor.

were partially embedded into the inner wall of the mesoporous SiO₂ layer. Such embedment added much stronger binding to anchor the Pd nanoparticles. During TEM observations, we did not observe any movement of Pd nanoparticles (which usually move around by electron beam if their attachments to the substrate were weak), suggesting that Pd nanoparticles are not movable in the nanoreactor. The HRTEM image of the used catalyst (shown in Supporting Information, Figure S3) showed no significant difference with fresh catalysts.

Supporting Information, Figure S1, showed a BET surface area of 1123 m² g⁻¹ and a BJH pore size distribution around 2.1 nm for the composite. Reactions are confined within the mesopores, and reactants and products must diffuse through the 2 nm mesopores, which are only about 40 nm long. High surface area meso-SiO₂ can adsorb reagents, thus enrich the reactants around the catalyst and promote the reactions. Such nanoreactor features enable the catalyst to be extremely active in Suzuki cross-coupling reaction, as 99.5% yield is obtained in 3 min. Such embedment structure will indeed lower the fraction of Pd surface that was accessible for catalysis (roughly 50%). However, the confinement effect within the mesopores as well as high surface area of silica pores may enhance the activity of those accessible Pd surface. The turnover frequency (TOF) was calculated to be 0.74 s⁻¹. This TOF value was quite satisfying comparing with many other Pd catalysts.¹¹

As show in Table 1, the presence of the carboxyl group and especially the location of the carboxyl group have profound effect on the reaction. With nearly 100% yield for unsubstituted phenylboronic acid, the reaction yield between *p*-carboxyphenylboronic acid and iodobenzene (run 2) decreased to 67.2%, while the *o*-carboxyphenylboronic acid resulted in a yield of 0% (run 4). In a series of control experiments, same set of reactions were carried out using commercial Pd/C catalyst (10% Pd loading). All phenylboronic acids showed similar reactivity, resulting in approximately 90% yield in 30 min, as shown in Supporting Information, Table S1. Thus, the near zero conversion with *o*-carboxyphenylboronic acid was not entirely due to the spatial restriction effect observed on homogeneous

Table 1. Suzuki Reaction^a of *p*-, *m*- and *o*-Carboxyphenylboronic Acid and Iodobenzene Catalyzed by Pd@meso-SiO₂ Nanoreactor



Run	Reagent 1	Reagent 2	Time	Conversion
1			3 min	99.5 %
2			3 min	67.2 %
3			3 min	59 %
4			3 h	trace

^aReaction conditions: 80 °C, ethanol (10 mL), iodobenzene (0.5 mmol), phenylboronic acid (1 mmol), K₂CO₃ (1 mmol), and catalyst (10 mg).

catalyst.¹⁷ These findings prompted us to explore the possibility of shape selectivity on this catalyst.

Sharp shape selectivity was observed for phenylboronic acid. With a systematic approach, we chose different substituting groups on phenylboronic acid. The side groups on phenylboronic acid showed dramatic effect on the reaction rate as shown in Table 2. For example, phenylboronic acid with *n*-

Table 2. Suzuki Reaction^a of Substituted Phenylboronic Acid and Iodobenzene Catalyzed by Pd@meso-SiO₂ Nanoreactor

Run	Reagent 1	Reagent 2	Time	Conversion
1			5 min	85.9 %
2			5 h	trace
3			3 h	trace
4			3h	trace
5			3 min	86.3 %

^aReaction conditions: 80 °C, ethanol (10 mL), iodobenzene (0.5 mmol), phenylboronic acid (1 mmol), K₂CO₃ (1 mmol), and catalyst (10 mg).

butyl groups (run 1) showed a decent reaction rate (iodobenzene conversion reached 86% in 5 min.); while for phenylboronic acid with *tert*-butyl group (run 2); the conversion was nearly zero after 5 h.

Furthermore, no iodobenzene conversion was observed for reaction 3 and 4 in Table 2. These results indicated that large substituting groups on phenylboronic acid would block the Suzuki reaction on this nanoreactor-like catalyst. Note that 1-naphthalenylboronic acid resulted in an 86.3% conversion in 3 min. This seemingly odd result is significant for elucidating the

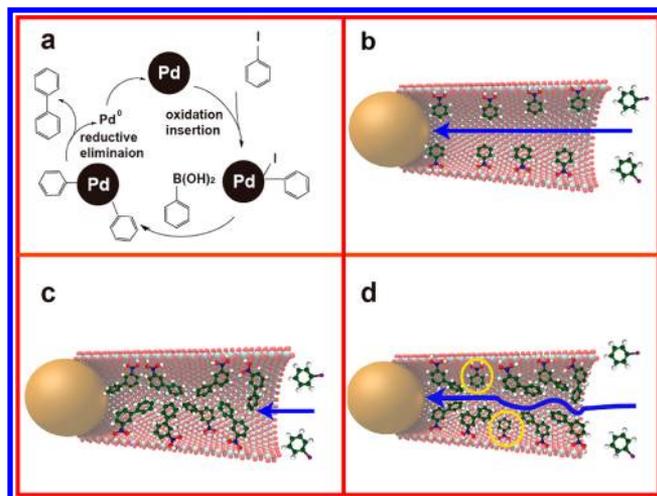
origin of the shape selectivity on this catalyst, and will be discussed later.

Again in control experiments, the same series of reactants in Table 2 resulted in similar iodobenzene conversion of nearly 90% using commercial Pd/C catalyst as shown in Supporting Information, Table S1. The conversions of substituted phenylboronic acid and iodobenzene catalyzed by Pd/C were controlled to be approximately 90% with different reaction time, indicating the substitute groups affected the reaction rate substantially. However, results from Pd/C catalyst confirmed that all these reactions can be catalyzed by Pd nanoparticles, and no shape selectivity was observed on Pd/C catalyst. The apparent shape selectivity observed on Pd@meso-SiO₂ nanoreactor was due to the structural feature of the catalyst.

Above results established interesting shape selectivity by this nanoreactor like catalyst. In Suzuki reaction, it poses strict shape activity for phenylboronic acid; even *n*-butyl and *tert*-butyl group substitution on phenylboronic acid has totally different result. This is unprecedented case of reactant shape selectivity, and it occurs in liquid phase within the mesopores. However, unlike gas phase shape selectivity in zeolites, the shape selectivity could not have occurred at molecular level on this catalyst. We initially speculated that the shape selectivity might be originated from the size of the products. However, the diameter of the mesoporous was relatively uniform with an average value of 2.1 nm and the maximum size of 3-biphenylboronic acid; *tert*-butyl-phenylboronic acid, phenylboronic acid and iodobenzene are 1.12, 0.95, 0.74, and 0.63 nm, respectively. They were significantly smaller than the mesopores. Moreover, the diameter of product 4-*tert*-butyl biphenyl and 3-phenyl biphenyl are 1.23 and 1.29 nm (both below 2 nm), respectively, both of which should also be able to diffuse through the mesoporous pores. Diffusion is more likely the key factor.

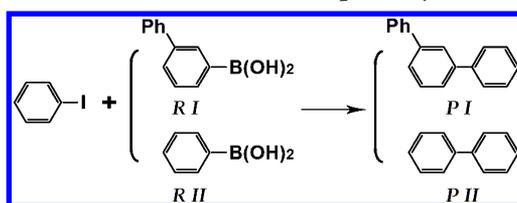
We propose that this is a new type of shape selectivity, which is induced by the collective diffusion barriers from reactants adsorbed in the mesopores. The well-established catalytic cycle of Suzuki reaction is depicted in Scheme 1a,¹⁸ which requires that both iodobenzene and phenylboronic acid to be around the same catalytic site during the catalytic cycle. This may not always be possible inside the confined space of mesoporous channel of the nanoreactor like catalyst. Reagents and products have to diffuse through the mesoporous; thus, diffusion becomes the key factor in this catalytic system. Phenylboronic acids tend to bind with hydroxyl group through hydrogen bonds.¹⁹ In this study, phenylboronic acid molecules were absorbed preferentially on the surface of SiO₂ mesoporous pores, so that the surface of the mesopores was covered with phenylboronic acid molecules. With phenylboronic acid, a substantial part of the pores was still open, allowing the diffusion of the reactants and products, as shown in Scheme 1b. However, with 3-biphenylboronic acid, the adsorbed molecular layer occupied most of the pores, causing overwhelming diffusion barrier for Suzuki reactions. As shown in Scheme 1c, ensemble of these adsorbed 3-diphenylboronic acids created a collective diffusion barrier. Table 2 showed that seemingly bulky 1-naphthalenylboronic acid had decent conversion (entry 5). This apparently odd result actually agreed well with the diffusion barrier mechanism. When being adsorbed inside the mesopores, the naphthalene rings lay parallel to the pores (see Figure S2 in the Supporting Information); thus, the diffusion barrier from 1-naphthalenylboronic acid was close to phenylboronic acid, leading to similar conversions.

Scheme 1. (a) Catalytic Cycle of Suzuki Reaction, (b) Schematic View of Suzuki Reaction between Phenylboronic Acid and Iodobenzene, (c) Schematic View of Suzuki Reaction between 3-Biphenylboronic Acid and Iodobenzene Being Inhibited by the Diffusion Barrier, and (d) Schematic View of Suzuki Reaction between 3-Diphenylboronic Acid, Phenylboronic Acid, and Iodobenzene



A very interesting result was observed when a mixture of 3-biphenylboronic acid and phenylboronic acid were used in the Suzuki reaction (the combined amount of two phenylboronic acids was kept at 1.0 mmol). On the basis of molecular shape selectivity assumption, we initially expected that phenylboronic acid would be converted; while 3-biphenylboronic acid would not. However, as shown in Table 3, experimental data indicated

Table 3. Conversion of RI (3-Biphenylboronic Acid) and RII (Phenylboronic Acid) at a reaction time of 10 min, with the initial ratio of 3-Biphenylboronic Acid to Phenylboronic Acid at 20:1, 10:1, 5:1, and 1:1, Respectively^a



run	RI:RII ratio	total conversion, %	PI:PII ratio
1	20:1	7	2:1
2	10:1	17.5	5:3
3	5:1	30	5:4
4	1:1	50	1:1

^aReaction conditions: 80 °C, ethanol (10 mL), iodobenzene (0.5 mmol), the sum of phenylboronic acid (1.0 mmol), K₂CO₃ (1.0 mmol), and catalyst (10 mg).

that even the presence of a small amount of phenylboronic acid enabled both phenylboronic acid and 3-biphenylboronic acid to be converted and the reaction rate increased substantially with higher phenylboronic acid content. On the other hand, the reaction between smaller molecules (phenylboronic acid) and iodobenzene were still favored. For example, with 3-biphenylboronic acid to phenylboronic acid ratio at 20:1, the number of converted 3-biphenylboronic acid was only two times that of phenylboronic acid molecules. Note in these series

of experiments, the amount of the iodobenzene was only half of that of two phenylboronic acids combined.

The diffusion barrier mechanism can explain these findings. Assuming that phenylboronic acid and 3-biphenylboronic acid have the same affinity with the mesopores, the adsorption layer of phenylboronic acid should reflect the mole composition of phenylboronic acid and 3-biphenylboronic acid. As showed in Scheme 1d, with even small number of phenylboronic acid molecules, the significantly smaller size of phenylboronic acid molecules will substantially lower the diffusion barrier by creating sinuous path pathways for the reactants and products. Such a sinuous pathway might be functional with relatively larger pores on the catalysts, leading to low conversions for both phenylboronic acid and 3-biphenylboronic acid, and smaller phenylboronic acid will be favored.

The diffusion barrier mechanism relied on the critical nanoreactor feature of the catalyst; i.e., all reactions were limited within the mesopores. In the normal catalyst (designated as catalyst A) the entrance to the void space of the catalyst was blocked by Pd nanoparticles at the inner ends of the mesopores, as shown in Figure 2a. Suppose reactants

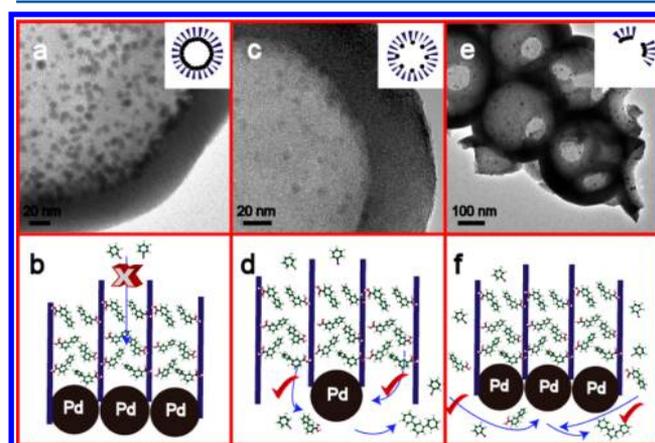
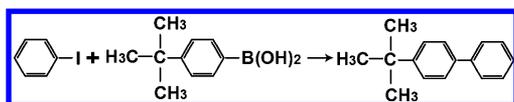


Figure 2. (a, c, e) TEM of catalyst A, B, C; (b) Diffusion barrier in catalyst A; (d, f) How the reaction can proceed in catalyst B and catalyst C.

could somehow enter the inner space of the hollow nanoreactor, then there would be no space restriction. The inner space was several hundreds nanometers in diameter, which was too large for any shape selectivity. This was the reason why no shape selectivity was observed on commercial Pd/C catalyst. In control experiments, two more catalysts were designed to confirm this.

Catalyst B had much less Pd loading at 0.4 wt %, comparing to 4 wt % for catalyst A. From TEM images in Figure 2a, we believed that the Pd nanoparticles would block all inner ends of the mesoporous channels in catalyst A; and in catalyst B (Figure 2c), the sparse distribution of Pd nanoparticles left many channels unblocked. The reactants could thus diffuse into the inner space of the nanoreactor for unrestricted reaction, as depicted in Figure 2d. As shown in Table 4, reaction using *tert*-butyl phenylboronic acid could proceed almost completely in 5 min using catalyst B, while trace conversion was observed on catalyst A.

Another catalyst, catalyst C was simply prepared by intentionally breaks the catalyst A through grinding (Figure 2e). Some of the sphere-shaped nanoreactors were then broken, so that the original inner hollow space of the catalyst

Table 4. Suzuki Reaction^a Catalyzed by Catalysts A, B, and C

catalyst	time	conversion
A	5 h	trace
B (1/10 Pd loading)	5 min	95.6%
C (broken catalyst)	10 min	70.3%

^aReaction conditions: 80 °C, ethanol (10 mL), iodobenzene (0.5 mmol), phenylboronic acid (1.0 mmol), K₂CO₃ (1.0 mmol), and catalyst (10 mg).

was directly exposed. As shown in Table 4, catalyst C also exhibited decent activity similar to that of the commercial Pd/C catalyst.

The shape selectivity observed in this work may also provide strong support for heterogeneous catalysis in Suzuki reaction. Several studies have shown that Pd-catalyzed C–C coupling reaction, including Suzuki reaction, Heck reaction, and Sonogashira reaction can be catalyzed by Pd solid particles.^{20–24} However, many researchers maintained that these reactions were in fact catalyzed by leached soluble Pd atoms or molecular complexes even when Pd solid particles were used, while palladium nanoparticles were only acting as reservoirs of molecular complexes.^{18,25–28} If Suzuki reaction is exclusively a homogeneous catalytic process, shape selectivity can hardly occur since the molecular Pd species will be able to diffuse out of the channels, and into the bulk solution, where no space restriction is applied. Our previous report has shown that Pd leaching is mostly prevented by the nanoreactor feature of the catalyst.¹¹ Combining the lack of Pd leaching and the observed shape selectivity in this work, we propose that Suzuki reaction can be catalyzed at the surface of Pd nanoparticles.

CONCLUSIONS

In summary, we observed unprecedented sharp reactant shape selectivity in Suzuki cross-coupling reactions on Pd@meso-SiO₂ catalyst. The diffusion barrier caused by the nanoreactor features of the catalyst and the preferential adsorption of bulky phenylboronic acid were the key reasons for the observed shape selectivity. Although the largest molecular diameter is smaller than the pore size of SiO₂, the preferential adsorption of bulky phenylboronic acid molecules would decrease the free space inside the mesopores and cause overwhelming diffusion barrier for other reactants and products. The overall reaction was consequently limited. A combined experimental and computational study on the molecular dynamics would offer better understanding of the phenomenon. A combined experimental and computational study on the molecular dynamics would offer better understanding of the phenomenon. For future work, we will optimize the pore size of the mesopores and expand this catalyst to other noble metal catalyzed reactions, and employing synchrotron beamline base techniques to elucidate the chemistry within the mesoporous channels.

ASSOCIATED CONTENT

Supporting Information

Nitrogen adsorption–desorption isotherm of the catalyst, reactions result tables of control experiment results by Pd/C, schematic view of Suzuki reaction for 1-naphthaleneboronic

acid and iodobenzene, TEM and HRTEM of 0.4 wt % Pd@meso-SiO₂ nanoreactor, and used 4 wt % Pd@meso-SiO₂. 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.

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