Supporting information for

Palladium Nanoparticles in Carbon Thin Film Lined SBA-15 Nanoreactors: Efficient Heterogeneous Catalysts for Suzuki-Miyaura Cross Coupling Reaction in Aqueous Media

*Jian Zhi, Depeng Song, Zhiwen Li, Xia Lei, Aiguo Hu**

Experimental

Materials

All the reactions and manipulations were carried out under Nitrogen atmosphere with the use of standard Schlenk technique. Tetrahydrofuran and triethylamine were distilled over Na or Calcium hydride under nitrogen prior to use. Other reagents used in the reactions were analytically pure and used as received. A 10 mM H_2PdCl_4 aqueous solution was prepared by completely dissolving 44.5 mg $PdCl_2$ in 25 ml of 20 mM HCl in a boil water bath. All chromatographic purifications were performed on silica-gel (200-300 mesh) using the indicated solvent systems. Detailed synthesis of enediyne molecules can be found in our recently published paper.[1]

Characterization

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in chloroform-*d* ($CDCl_3$) on an Ultra Shield 400 spectrometer (BRUKER BIOSPIN AG, Magnet System 400 MHz/54 mm). Powder X-ray diffraction patterns (XRD) of the samples were obtained by Bruke D8 Focus diffractometer with a graphite-monochromatized Cu Kα radiation (λ = 0.15405 nm). The size and morphology of the samples were investigated by using a transmission electron microscope (TEM, JEOL, JEM-2010) with EDX analysis (Oxford INCA EDS) operated at 200 kV. Raman analyses were performed on an inVia+Reflex Raman spectrometer (Renishaw, 514 nm). The palladium contents of the samples were determined by ICP-AES on a Thermo Elemental IRIS 1000 instrument. Nitrogen adsorption/desorption isotherms were measured at 77 K with an adsorption apparatus on a Quanta Nova 2000 instrument. The surface area of the samples was determined from the Brunauer-Emmett-Teller (BET) equation and pore volume, from the adsorption branches of the isotherms with use of the Barrett-Joyner-Halanda (BJH) method. Gas chromatography (GC) was performed on GC-3010A (Shanghai Institute of Computer and Technology) with Agilent HP-5 column.

Synthesis of SBA-15[2]

Triblock copolymer Pluronic P123 (5 g) was dissolved in deionized water (160 g) and 12M HCl (26.5 ml) at 40 °C under stirring. Then tetraethoxysilane (TEOS, 10.4 g) was added into the solution. The resulting mixture was stirred at 40°C for 24 h, and then aged at 100 °C for 24 h without stirring. After filtration and drying, the polymer template P123 was removed by calcination at 550 °C for 4 h. For activation, as-synthesized SBA-15 was dispersed in piranha solution (H_2SO_4:H_2O_2=7:3, volume ratio) with 30 min sonication, and heated at 90 °C for 24 h. The resulting mixture was centrifuged (9500 rpm, 15 min) and rinsed with deionized water to neutrality and then washed with anhydrous ethanol repeatedly to obtain a white powder (activated SBA-15).

Synthesis of SBA-15$^{©}$

Immobilization of enediyne containing imine inside SBA-15. Following our recently published procedure with minor modification,[1] enediyne containing imine (1.54 g), of anhydrous ethanol (20 ml) and anhydrous $MgSO_4$ (3 g) were mixed in 50 ml Schlenk flask, and then activate SBA-15 (1.21 g) was added. After stirred for 40 h under nitrogen atmosphere at 85 °C, the resulting mixture was centrifuged (9500 rpm, 15 min) and rinsed with anhydrous ethanol repeatedly to obtain a pale yellow powder.

Bergman Cyclization inside the channels. Bergman cyclization reactions were performed under vacuum in a sealed glass tube with enediyne grafted SBA-15 inside and diphenyl ether outside as reflux bath (259 °C) for 8 h. The resulting light brown powder was rinsed with deionized water repeatedly to remove the residual $MgSO_4$. After drying, dark brown powder was obtained.

Carbonization. The carbonization was performed in a tube furnace with a continuous hydrogen/argon (10/90) flow. The brown powder obtained in the previous step was heated in the furnace while the temperature was increased to 300 °C at a rate of 2 °C min^{-1}, maintaining for 2 h, and then increased to 750 °C, maintaining for 1 h to obtain a black powder.

Synthesis of Pd@SBA-15

Pd@SBA-15 was synthesized by a simple impregnation method as that for Pd@SBA-15$^{©}$. The Pd loading on the sample was 3.5 wt% based on ICP-AES analysis.

Catalytic reaction

Kinetic study for Suzuki-Miyaura coupling reaction

Bromobenzene (0.8 mmol), phenylboronic acid (1.0 mmol) and tetrabutyl ammonium bromide (TBAB, 0.5 mmol) were added to a suspension of Pd catalyst (0.08 mol%) in aqueous K_2CO_3 solution (2.4 mmol, 5 ml). After this mixture was degassed for several times, the internal standard tetrahydronaphthalene (0.25 mmol, for GC analysis) was added. The reaction mixture was stirred at 80°C under N_2 atmosphere. Every 15 minutes, an aliquot of reaction mixture (~ 200 μl) was sucked out with degassed syringe, filtered and washed with brine and diethyl ether. The organic phase was subjected for GC analysis.

Determination of Pd leaching from Suzuki-Miyaura coupling reaction

After the Pd catalyzed coupling reaction, the reaction mixture was hot filtered through celite, washed with deionized water and diethyl ether. An aliquot of the filtrate (10 ml) was boiled with concentrated HNO_3 and then subjected for ICP-AES analysis.

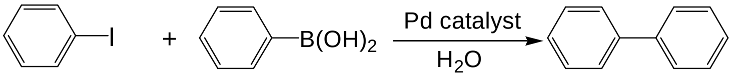
Catalyst recycle and reusing for Suzuki-Miyaura coupling reaction

The coupling reaction was performed with iodobenzene and phenylboronic acid under the same reaction condition as described above. Each time, the catalyst was isolated from the reaction mixture at the end of the reaction, washed with water and diethyl ether, and then dried at 100 °C under vacuum. The dried catalyst was then reused in the next run.

Table S1. Nitrogen adsorption-desorption analysis of SBA-15, SBA-15$^{©}$ and Pd@SBA-15$^{©}$

sample	BET surface area (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)
SBA-15[2]	850	89	1.17
SBA-15$^{©}$	265	35	0.27
Pd@SBA-15$^{©}$	256	34	0.29

Table S2. Catalyst reusing experiments for Pd@SBA-15©[a].

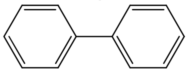


run	**1st**	**2nd**	**3rd**	**4th**	**5th**
Yield(%)[b]	99	98	95	97	96

[a] Reaction conditions: iodobenzene (0.8 mmol), phenylboronic acid (1.0 mmol), K_2CO_3 (2.4 mmol), tetrabutyl ammonium bromide (TBAB, 0.5 mmol), and palladium catalyst (0.08 mol%), 80 °C, 1 h, under N_2. [b] Determined with GC.

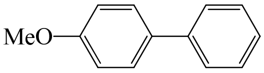
Analytical data for compounds

Biphenyl



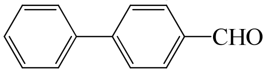
The product was obtained as white crystal. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.53 (d, 4 H), 7.42 (m, 4 H), 7.35 (t, 2 H).

4-Methoxybiphenyl



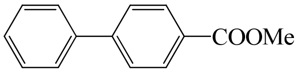
The product was obtained as white solid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.56-7.52 (m, 4H), 7.44-7.39 (m, 2H), 7.31 (t, 1H), 6.98 (d, 2H), 3.86 (s, 3H).

[1,1'-biphenyl]-4-carbaldehyde



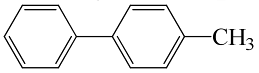
The product was obtained as white crystal. ^{1}H NMR ($CDCl_3$, δ, ppm): 10.01 (s, 1H), 7.97 (d, 2H), 7.79 (d, 2H), 7.66 (d, 2H), 7.51 (t, 2H), 7.45 (t, 1H).

methyl [1,1'-biphenyl]-4-carboxylate



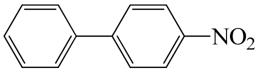
The product was obtained as white crystal. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.12 (d, 2H), 7.68-7.62 (m, 4H), 7.47 (t, 2H), 7.40 (t, 1H), 3.94 (s, 3H).

4-methyl-1,1'-biphenyl



The product was obtained as white solid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.85-7.80 (m, 2H), 7.61 (d, 2H), 7.53 (d, 2H), 7.45 (d, 2H), 7.37 (t, 1H), 2.42 (s, 3H).

4-nitro-1,1'-biphenyl



The product was obtained as brown oil. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.32 (d, 2H), 7.78 (d, 2H), 7.64 (d, 2H), 7.54-7.47 (m, 3H).

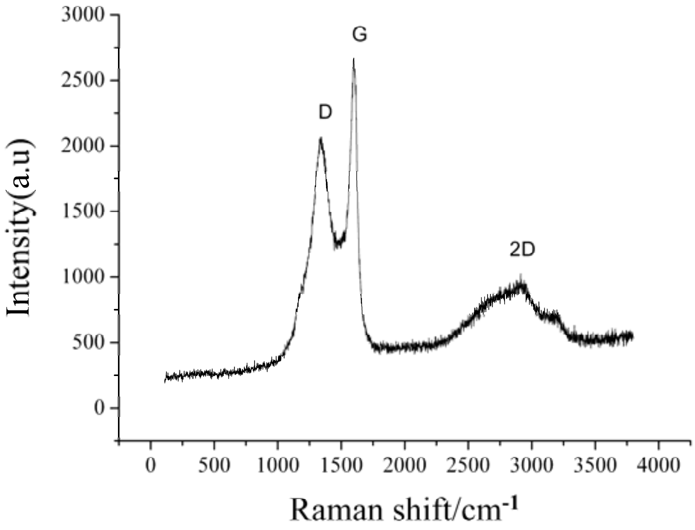


Figure S1 . Raman spectra of SBA-15$^{©}$

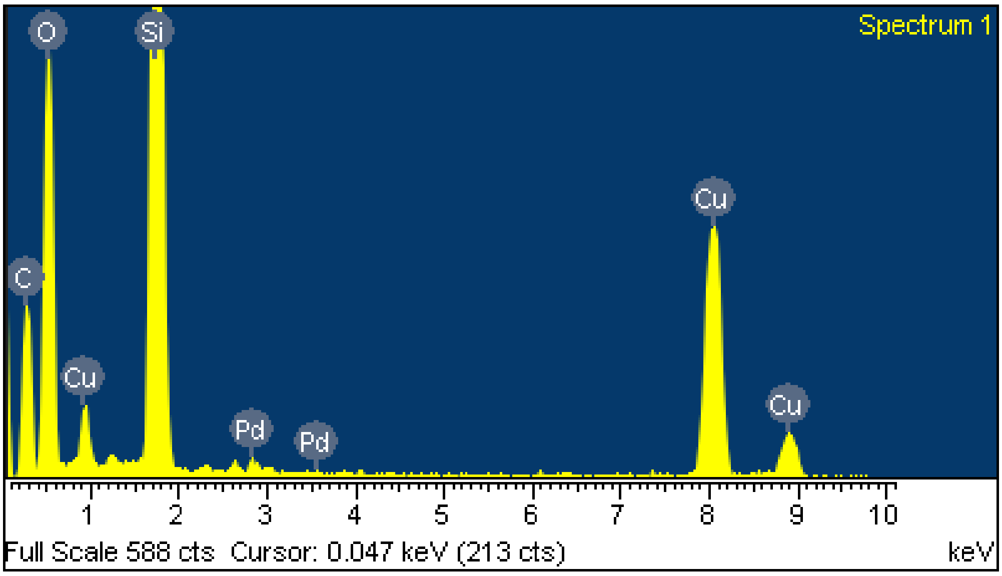


Figure S2. EDS spectrum of Pd@SBA-15$^{©}$.

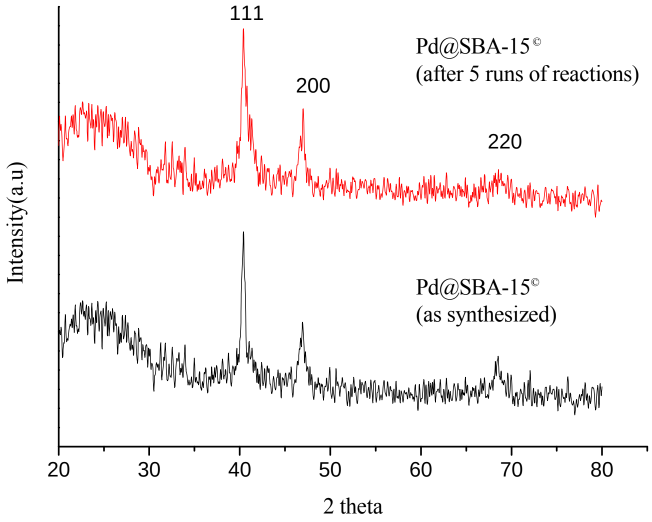


Figure S3. Wide angel XRD patterns for Pd@SBA-15© catalysts recorded before and after catalytic reaction.

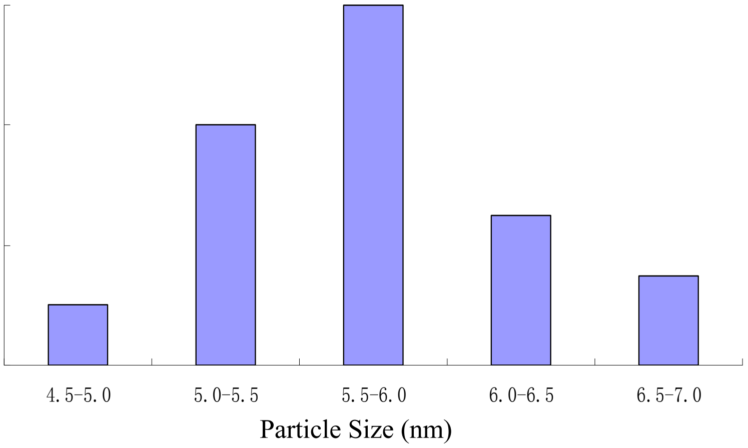


Figure S4. Pd particle size distribution of Pd@SBA-15© as measured with TEM.

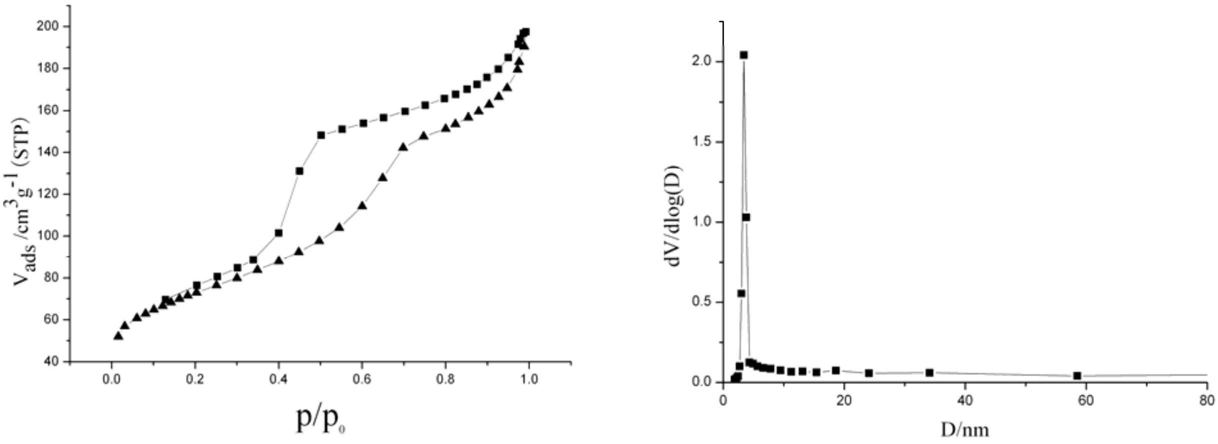


Figure S5. Nitrogen adsorption isotherms at 77 K (left) and pore-size distribution curves (right) of Pd@SBA-15©.

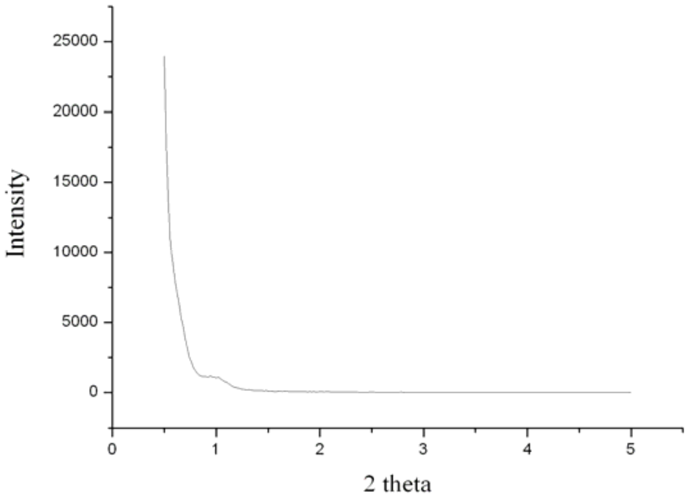


Figure S6. Small angel XRD pattern for Pd@SBA-15©.

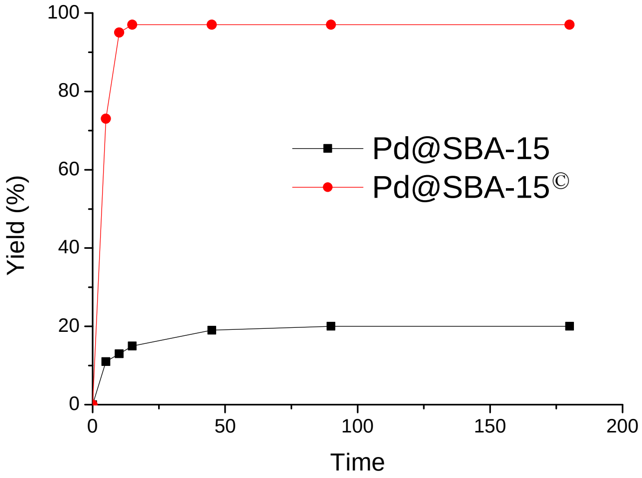


Figure S7: Kinetic profiles for the coupling reaction between bromobenzene and phenylboronic acid catalyzed by Pd@SBA-15© and Pd@SBA-15.

Reference

1. X. Yang, Z. Li, J. Zhi, J. Ma and A. Hu, *Langmuir*, 2010, **26**, 11244-11248.
2. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548-552.