Electronic Supplementary Material (ESI) for Nanoscale.

Insights into Surface Properties of Oxides on Catalytic Activity of Pd for C—C Coupling Reactions

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Experimental Section

All chemicals (AR, grade) were used as received, except where otherwise noted. Water used in all experiments was purified with a resistivity of 18.2 MΩ cm. All glasswares were thoroughly washed by aqua regia (a volume ratio of 1:3 of concentrated nitric acid and hydrochloric acid) to avoid any possible contamination.

Synthesis of Porous Nanorods of Ceria (PN-CeO_2)

PN-CeO_2 was synthesized by our previously reported method[1], which involved a two-step hydrothermal method. Briefly, a mixture of 1.367 g of $Ce(NO_3)_3 \cdot 6H_2O$ and 19.2 g of NaOH in 70 mL of water was treated with hydrothermal process at 100 °C for 24 h in a Pyrex bottle to obtain nonporous $Ce(OH)_3/CeO_2$ nanorods. Subsequently, the *PN*-CeO_2 was synthesized by hydrothermal treatment on nonporous $Ce(OH)_3/CeO_2$ nanorods in a stainless autoclave at various temperatures (160, 180 and 200 °C) for 12 hours.

Synthesis of Pd/ *PN*-CeO_2 Catalysts

Pd/*PN*-CeO_2 catalysts with a 3 wt% metal loading was prepared by a modified deposition-precipitation method.[2, 3] Typically, 50 mg of *PN*-CeO_2 was suspended in 5 mL of Na_2PdCl_4 solution (2.92×10^{-3} mM) at room temperature for 1 h. After adding 200 mg of urea, the solution was heated to 80 °C and kept for 4 hours under vigorous stirring. Then, the reaction was cooled to room temperature and 5 mL of $NaBH_4$ ice solution (0.56 mg/mL) was added. The reaction was continued for another 1 hour at room temperature. Finally, the Pd/*PN*-CeO_2 black solid was washed for 4 times with distilled water and dried overnight at 60 °C.

Synthesis of Pd Nanocatalysts on other Supports

Pd/TiO_2, Pd/activated carbon, Pd/nonporous nanorods CeO_2, Pd/octahedrons CeO_2 and Pd/cubes CeO_2 were synthesized by the same methods except the *PN*-CeO_2 was replaced. The Pd loading was controlled at 3 wt%.

Characterization of the Catalysts

The phase evolution of as-synthesized nanostructures was monitored by powder X-ray diffraction (XRD). The XRD patterns with diffraction intensity versus 2θ were recorded in a Shimadzu X-ray diffractometer (Model 6000) using Cu Kα radiation. Transmission electron microscopy (TEM) studies were conducted on a Hatchie HT-7700 field-emission transmission electron microscope with an accelerating voltage of 120 kV. Raman measurements were carried out on LabRAM HR800 (Horbia Jobin Yvon) at 514 nm. The surface area was measured by N_2 physisorption (Micromeritics, ASAP 2020 HD88) based on the Brunauer-Emmet-Teller (BET) method. X-ray photoelectric spectra (XPS) were acquired using a Thermo Electron Model K-Alpha with Al Kα as the excitation source. The dispersion of Pd was calculated from CO chemisorption by using pulses of a gas mixture containing 10% CO in He at room temperature. A given amount of CO (0.05 mL) was introduced in a pulse per 5 min until the intensity of the peak reached a constant value. Fourier transform infrared (FT-IR) analysis of the samples was taken on a Thermo Scientific Nicolet 6700 Fourier transform infrared spectroscopy. All of the samples were mixed with KBr and pressed to a thin plate for measurement.

CO_2 Temperature-Programmed Desorption (CO_2-TPD) Measurements

CO_2-TPD was carried out using a quartz fixed-bed micro-reactor. For a typical measurement, 150 mg of catalysts were pretreated in Ar at 300 °C for 0.5 h. Then, a gas mixture of 10 vol% CO_2/Ar (40 mL min^{-1}) was absorbed by catalysts for 0.5 h at 100 °C. After the excess CO_2 was removed using Ar (40 mL min^{-1}). The temperature-programmed procedure occurred from 100 °C to 800 °C with a ramping rate of 10 °C min^{-1}. The production of CO_2 was monitored by using a mass spectrometer (QIC-20, HIDEN).

Ullmann C-C Coupling Reaction

In a 25 mL Schlenk flask, bromobenzene (0.5 mmol), glucose, base (1.5 mmol) and catalysts (5 mg) mixed with 4 mL solvent. The reaction was carried out at 90 ºC under continuous stirring for desired time. Then, 0.25 mmol dodecane was added and the mixture was extracted with 12 mL ethyl acetate. After purification on a microcolumn filled with silica gel, the product was analyzed by GC-MS and GC (Agilent 7890A GC and 597C MS with HP-5MS column).

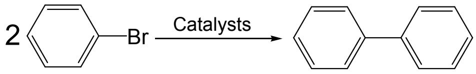
Suzuki C-C Coupling Reaction

In a typical experiment for Suzuki C-C coupling reaction, bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), base (1.5 mmol) and catalysts (5 mg) were added to 4 mL solvent in a 25 mL Schlenk flask. The reaction mixture was stirred at 90 ºC for desired time. The products were extracted with 12 mL ethyl acetate. Dodecane was used as the internal standard. After purification on a microcolumn filled with silica gel, the products were analyzed by GC-MS and GC.

Heck C-C Coupling Reaction

Bromobenzene (0.5 mmol), styrene (0.6 mmol), base (1.5 mmol) and catalysts (5 mg) mixed with 4 mL solvent in a 25 mL Schlenk flask. The reaction mixture was stirred at 120 ºC for desired time. Similar to the purification process of Suzuki coupling reaction, the products of Heck coupling reaction were analyzed by GC-MS and GC.

Table S1. Optimization of reaction conditions for Ullmann C-C coupling reaction[a]



Entry	Base	Solvent (DMF:H_2O)	Glucose (mg)	Time (h)	Yield (%)[b]
1	Et_3N	0:1	50	8	53.7[c]
2	NaOH	0:1	50	8	9.0[c]
3	K_2CO_3	0:1	50	8	37.6[c]
4	Et_3N	1:1	50	8	25.5[c]
5	Et_3N	1:0	50	8	0[c]
6	Et_3N	0:1	100	8	100
7	Et_3N	0:1	50	8	83.0[d]
8	Et_3N	0:1	100	6	99.2
9	Et_3N	0:1	100	4	93.4

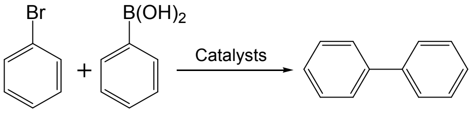
[a] Unless otherwise noted, the reaction conditions are: bromobenzene (0.5 mmol), base (1.5 mmol) and catalysts (5 mg), 4 mL of solvent, 90 ℃.

[b] Isolated yield of bromobenzene, determined by GC.

[c] With bromobenzene (1 mmol) and base (3 mmol).

[d] With 3 mmol Et_3N.

Table S2. Optimization of reaction conditions for Suzuki C-C coupling reaction[a]

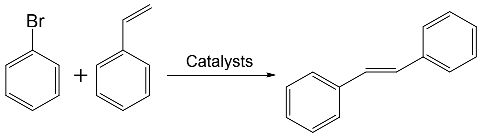


Entry	Base	Solvent (DMF:H_2O)	Time (h)	Yield(%)[b]
10	-	5:2	14	<5
11	K_2CO_3	5:2	14	>95
12	K_2CO_3	5:2	6	82.6
13	K_2CO_3	0:4	6	<5, by-product
14	K_2CO_3	1:3	6	60.5, by-product
15	K_2CO_3	1:1	6	99.4
16	K_2CO_3	3:1	6	73.4
17	K_2CO_3	4:0	6	-
18	K_2CO_3	1:1	2	99.1
19	K_2CO_3	1:1	1	72.3

[a] Unless otherwise noted, the reaction conditions are: bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), K_2CO_3 (1.5 mmol) and catalysts (5 mg), 4 mL of solvent, 90 ºC.

[b] Isolated yield of bromobenzene, determined by GC.

Table S3. Optimization of reaction conditions for Heck C-C coupling reaction[a]



Entry	Base	Solvent (DMF:H_2O)	Time (h)	Temperature (°C)	Yield(%)[b]
20	Et_3N	1:1	14	90	35.9
21	K_2CO_3	1:1	14	90	35.6
22	Et_3N	1:1	14	90	32.2[c]
23	Et_3N	1:1	24	90	45.6
24	Et_3N	1:0	24	90	0
25	Et_3N	0:1	24	90	31.6
26	Et_3N	1:1	8	120	21.2
27	Na_3PO_4	1:1	8	120	46.5
28	K_2CO_3	1:1	8	120	63.7
29	K_2CO_3	1:1	14	120	90.3

[a] Unless otherwise noted, the reaction conditions are: bromobenzene (0.5 mmol), styrene (0.6 mmol), base (1.5 mmol) and catalysts (5 mg), 4 mL of solvent.

[b] Isolated yield of bromobenzene, determined by GC.

[c] With 10 mg catalytic.

Table S4. Catalytic activity test of Pd nanocatalysts on various supports for C-C coupling reactions

Catalysts	**Ullmann coupling reaction** [a]	**Suzuki coupling reaction** [b]	**Heck coupling reaction** [c]
	Yield (%) [d]	**Yield (%)** [d]	**Yield (%)** [d]
Pd/activated carbon	16.0	50.3	Trace
Pd/TiO_2	82.7	61.9	37.2
Pd/PN-CeO_2-160	93.4	72.3	90.3
Pd/nonporous nanorods CeO_2	77.2	63.0	67.6
Pd/octahedrons CeO_2	48.8	44.9	66.3
Pd/cubes CeO_2	78.2	63.7	72.9

[a] **Reaction conditions:** bromobenzene (0.5 mmol), glucose (100 mg), Et_3N (1.5 mmol) and catalysts (5 mg), H_2O (4 mL), 90 ºC and 4 h.

[b] **Reaction conditions:** bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), K_2CO_3 (1.5 mmol) and catalysts (5 mg), 4 mL of solvent, V(DMF:H_2O) of 1:1, 90 ºC and 1 h.

[c] **Reaction conditions:** bromobenzene (0.5 mmol), styrene (0.6 mmol), K_2CO_3 (1.5 mmol) and catalysts (5 mg), 4 mL of solvent, V(DMF:H_2O) of 1:1, 120 ºC and 14 h.

[d] Yield of bromobenzene, determined by GC.

Table S5. Catalytic activity test of Pd/*PN*-CeO_2 catalysts for C-C coupling reactions

Catalysts [e]	**Ullmann coupling reaction** [a]	**Suzuki coupling reaction** [b]	**Heck coupling reaction** [c]
	Yield (%) [d]	**Yield (%)** [d]	**Yield (%)** [d]
PN-CeO_2-160	93.4	72.3	90.3
PN-CeO_2-180	89.3	74.0	75.4
PN-CeO_2-200	80.1	63.7	55.3

[a] **Reaction conditions:** bromobenzene (0.5 mmol), glucose (100 mg), Et_3N (1.5 mmol) and catalysts (5 mg), H_2O (4 mL), 90 ºC and 4 h.

[b] **Reaction conditions:** bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), K_2CO_3 (1.5 mmol) and catalysts (5 mg), 4 mL of solvent, V(DMF:H_2O) of 1:1, 90 ºC and 1 h.

[c] **Reaction conditions:** bromobenzene (0.5 mmol), styrene (0.6 mmol), K_2CO_3 (1.5 mmol) and catalysts (5 mg), 4 mL of solvent, V(DMF:H_2O) of 1:1, 120 ºC and 14 h.

[d] Yield of bromobenzene, determined by GC.

[e] *PN*-CeO_2-160, -180 and -200 were obtain from hydrothermal dehydration at 160, 180 and 200 ºC, respectively.

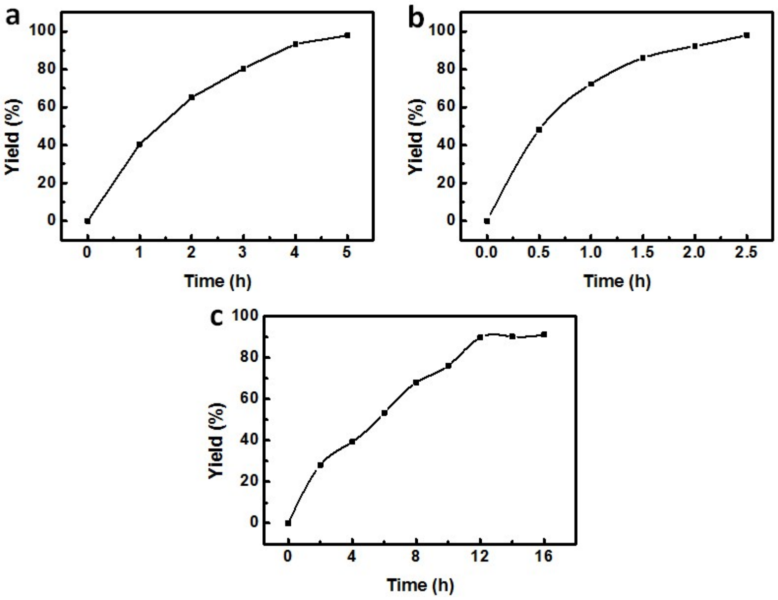


Figure S1. The kinetic studies of (a) Ullmann, (b) Suzuki and (c) Heck coupling reactions with Pd/*PN*-160-CeO_2 catalysts, respectively.

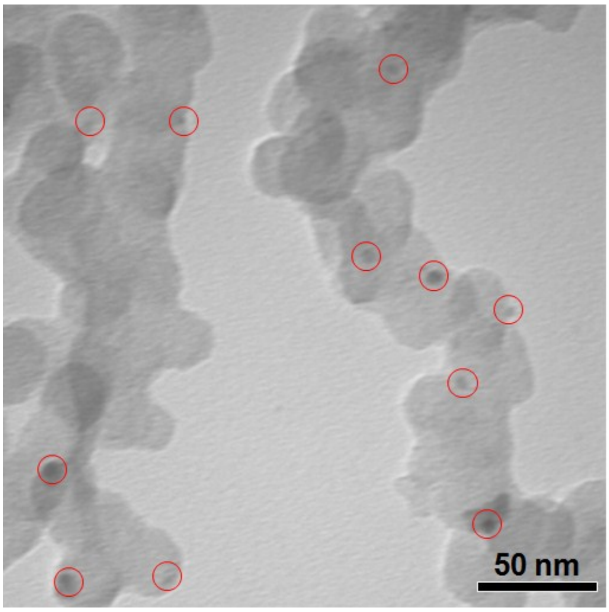


Figure S2. TEM image of Pd/activated carbon.

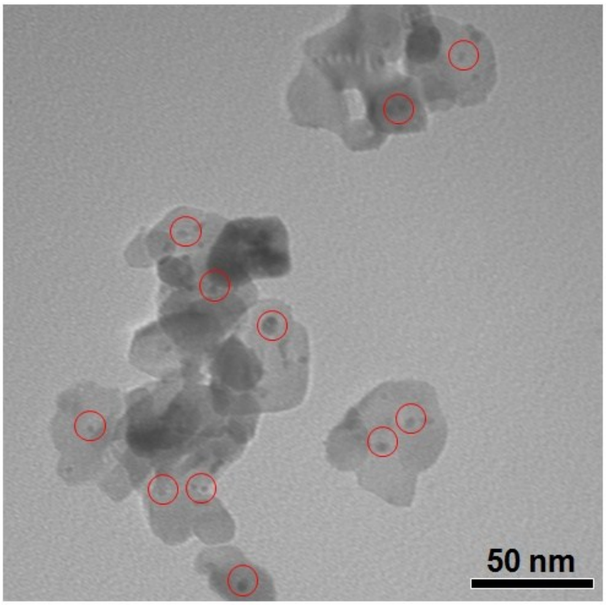


Figure S3. TEM image of Pd/TiO_2.

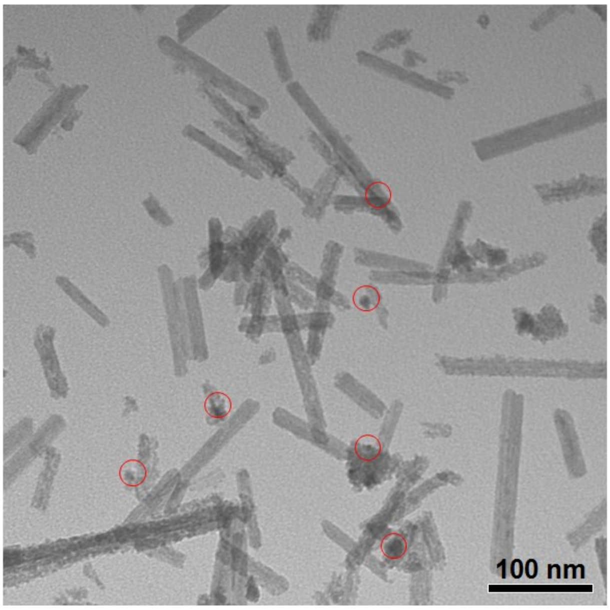


Figure S4. TEM image of Pd/nonporous nanorods CeO_2.

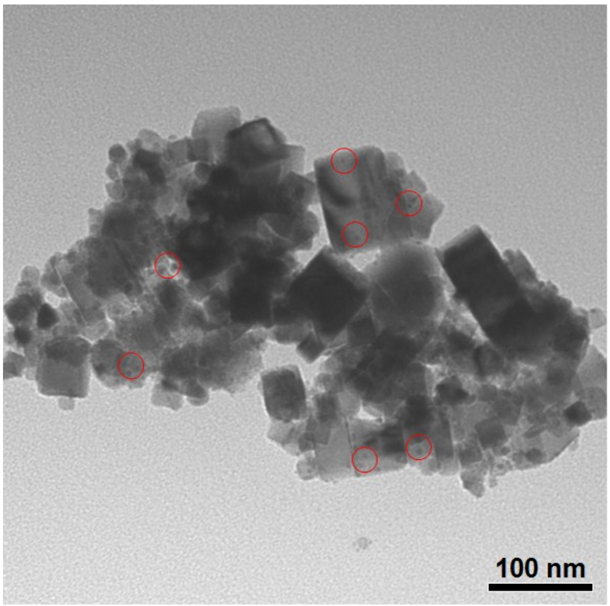


Figure S5. TEM image of Pd/cube CeO_2.

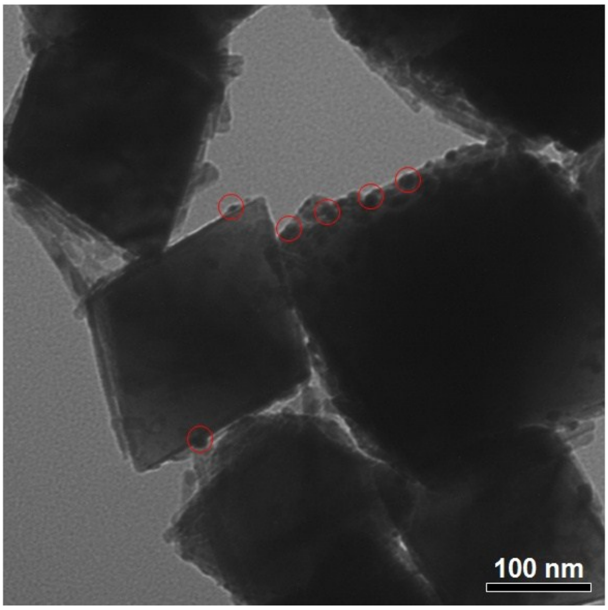


Figure S6. TEM image of Pd/octahedron CeO_2.

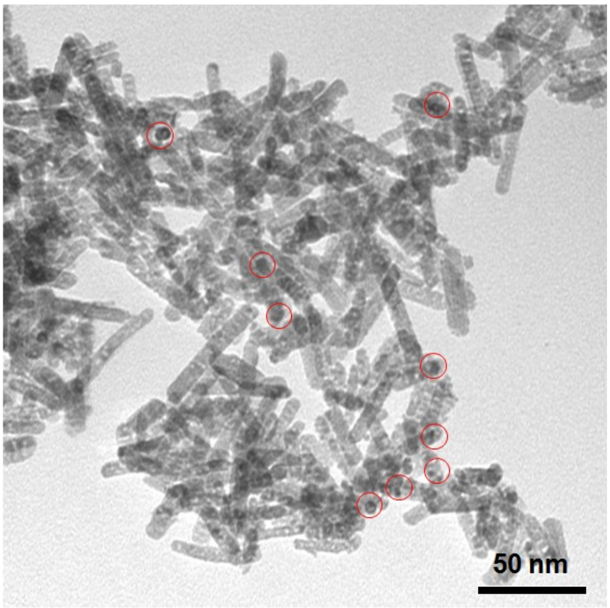


Figure S7. TEM image of Pd/*PN*-CeO_2-180.

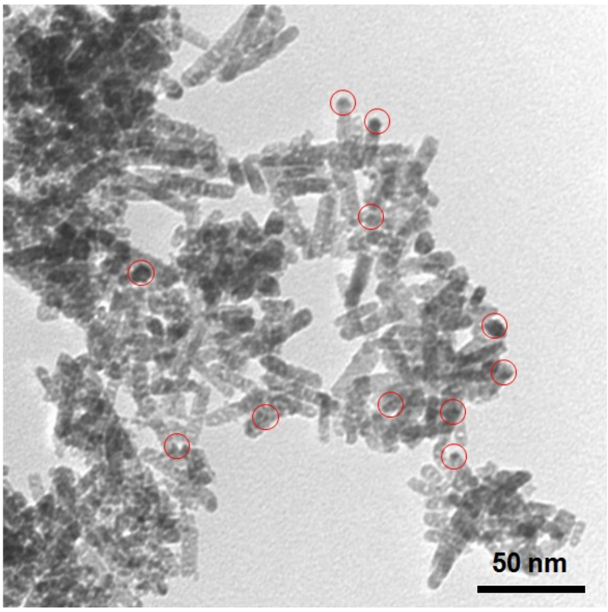


Figure S8. TEM image of Pd/*PN*-CeO_2-200.

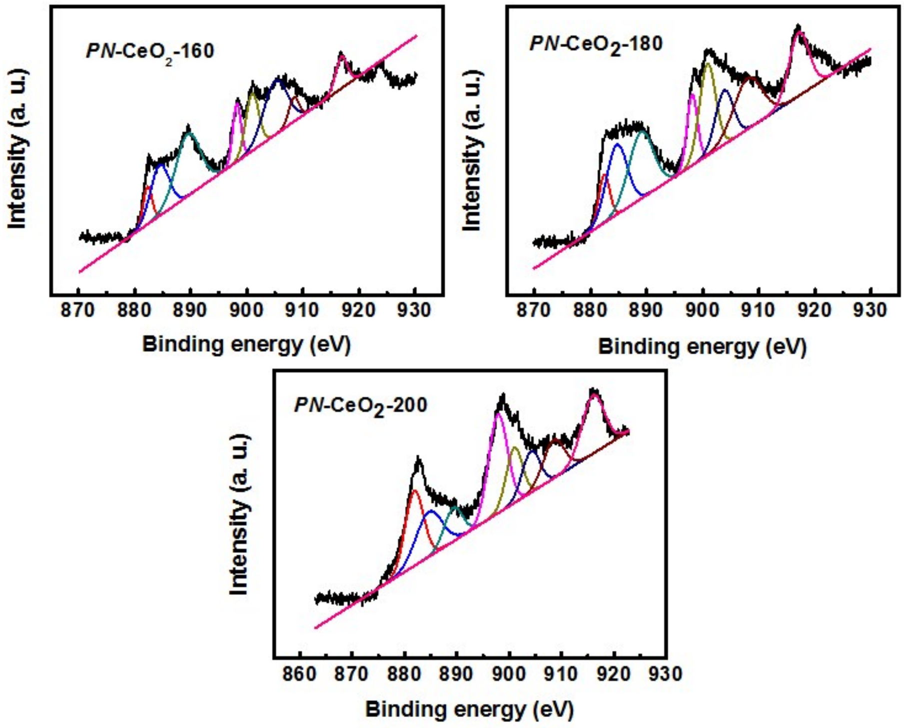


Figure S9. The XPS analysis of *PN*-CeO_2-160, *PN*-CeO_2-180 and *PN*-CeO_2-200.

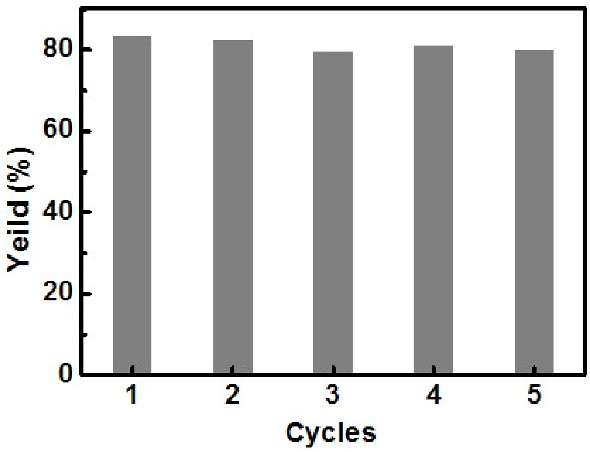


Figure S10. The reusability of Pd/*PN*-160-CeO_2 catalysts for C-C coupling reactions. Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), K_2CO_3 (1.5 mmol) and catalytic (10 mg), 4 mL of solvent, V(DMF:H_2O) of 1:1, 90 °C and 0.5 h.

Reference:

1. J. Li, Z. Zhang, Z. Tian, X. Zhou, Z. Zheng, Y. Ma and Y. Qu, *Journal of Materials Chemistry A*, 2014, **2**, 16459.
2. A. Hugon, L. Delannoy and C. Louis, *Gold Bulletin*, 2008, **41**, 127.
3. P. Christopher, H. Xin and S. Linic, *Nature chemistry*, 2011, **3**, 467.