Supporting information

Meso-Macroporous Organic Polymer Supported Homogeneously Dispersed Small Pd Nanoparticles by a Simple Ion-Exchange Approach for Heck Reaction

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Experimental Section

2.1 Chemicals

Triethylamine (≥99.0%, 500 mL), ethyl acetate (≥99.5%, AR, 500 mL), DMF (≥99.5%, AR, 500 mL), anhydrous ethanol (≥99.7%, AR, 500 mL), divinylbenzene(≥98%, 500 mL), 4-vinylpyridine (96%, 25 mL), iodobenzene (≥97.0%, 100 g), 4-iodonitrobenzene (98％, 25 g), 4-iodotoluene (99％, 25 g), 4-iodoanisole (97%, 25 g), bromobenzene (≥99.5%, 500 mL), 4-bromonitrobenzene (97％, 5 g), 4-bromotoluene (98％, 25g), 4-bromoanisole (98%, 50 mL), chlorobenzene (≥99.5%, 500 mL), 4-chloronitrobenzene (99％, 100 g), 4-chlorotoluene (98％, 25 g), 4-chloroanisole (98%, 25 g), styrene (≥99.0%, 500 mL) and ethyl acrylate (≥98.0%, 500 mL) were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. Ultrapure water (≥ 18.2 MΩ cm^{-1}) was used in all experiments.

2.2 Synthesis of MOP

The meso-macroporous organic polymer (MOP) was synthesized by a reported method [22, 26] and the detail procedure was as follows: divinylbenzene (2 mL) and 4-vinylpyridine (1 mL) were added into a solution containing 0.07 g of AIBN and 30 mL of ethyl acetate. After stirring at room temperature for 3 h, the mixture was hydrothermally treated at 100 °C for 24 h, followed by slow evaporation of the solvents. The obtained sample was designated as MOP.

2.3 Characterization

Fourier transform infrared (FT-IR) spectra were recorded between 4000-400 cm^{-1} on a Nicolet 5700 instrument. The powder X-ray diffraction (XRD) data were

operated on a XD-3 diffractometer with Cu Kα radiation (λ = 0.15418 nm, 40 kV/30 mA). The diffraction patterns were performed in the range of 10-80° with a step of 0.020 °/s. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB250xi spectrometer (Thermon Scientific), all binding energies were calibrated by using the C1s peak at 284.8 eV as a reference. The nitrogen adsorption and desorption isotherms were measured at 77 K under a Micro ASAP 2020 instrument. Transmission electron microscopy (TEM) was taken on JEOL JEM-2100 at 300 kV. Palladium content of the catalyst was measured by inductively coupled plasma (ICP) on PE5300DV analyzer.

2.4. Typical procedure for Heck reaction

Iodobenzene (1.02 g, 5 mmol), styrene (0.78 g, 7.5 mmol), NEt_3 (15 mmol), DMF (10 mL), n-dodecane (0.5 mL, internal standard) and Pd-catalyst (0.0174 mol% Pd respect to iodobenzene) were added into a reaction tube equipped with a magnetic stir bar under atmospheric condition. The resulting mixture was then stirred at 90 °C for a specialized time. The yield of the products was determined by GC and GC-MS.

The catalyst leaching experiments was carried out by stirring the same mixture above at 90 °C. After 2 hour, Pd/MOP-I was filtered from the hot reaction mixture. Then the filtrate was continued for 5 hours at the same condition. The reaction cycles were performed using Pd/MOP-I catalyst (100 mg) in the Heck reaction of iodobenzene (50 mmol) and styrene (75 mmol) at 90 °C for 6 h. After each cycle the catalyst was separated, washed with DI-water and ethanol 3 times respectively, and dried at 60 °C under vacuum overnight. Fresh reactants and solvent were then charged to the glass-reactor together with the recovered catalyst to carry out the next run reaction.

The kinetic profiles of the consecutive runs were performed as follows: Iodobenzene (10.2 g, 50 mmol), styrene (7.8 g, 75 mmol), NEt_3 (150 mmol), DMF (100 mL), n-dodecane (5 mL, internal standard) and Pd-catalyst (0.0174 mol% Pd respect to iodobenzene, 100 mg) were added into a reaction tube equipped with a

magnetic stir bar under atmospheric condition. An aliquot (50 uL) was removed every 2 hour and diluted with diethyl ether. GC analysis (1 uL autoinjection) indicated that the maximum yield of product was reached within 8 h. After each cycle the catalyst was separated, washed with DI-water and ethanol 3 times respectively, and dried at 60 ^{o}C under vacuum overnight. Fresh reactants and solvent were then charged to the glass-reactor together with the recovered catalyst to carry out the next run reaction.

Tables

Table S1. Textural properties of MOP, MOP-I and Pd/MOP-I

Sample	S_{BET} ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pd loading (wt %) / ICP
MOP	486	0.414	-
MOP-I	132	0.300	-
Pd/MOP-I	115	0.284	1.70

Table S2. The summary of supported Pd nanoparticles catalysts for Heck Reaction for iodobenzene with styrene

Sample	Particle size of Pd NPs (nm)	Pore size (nm)	BET (m^2/g)	T (^oC)	t(h)	Yield (%)	TON [a]	TOF (h^{-1}) [b]	Ref.
Pd/SiO_2	7			135	4	88	629	157.25	7
Pd/CNCs	4.8	-	-	40	3	99	70	23.33	8
Pd/RGO–IL	7	2		130	6	92	244	40.67	9
Pd/MOF-3	2.8	-	-	80	24	98	163	6.8	10
Pd/ZIF-67-50	6	-	-	120	6	78	867	144.5	11
$Pd/ZnFe_2O_4$	-	24.1	75	120	12	65	542	90.3	12
Pd/NHC-MOP	3-5	0.7-1.3	610	130	1	99	99	99	13
Pd/PS-IL(Cl)	4-6	-	-	100	6	42	210	35	14
PdNPs/ZIF-8	3-5		197	95	0.5	85	0.85	1.7	S1
Pd/ZPGly	10	-	-	120	3	82	860	286.67	S2
Pd/pAT	2-5	-	-	100	8	90	1200	150	S3
PdNPs@NHC@ZIF-8	Ultra small	2.1	758	110	0.75	94	1250	1666.67	S4
Pd/Nano-sized SiO_2-g-PAAm	-	-	-	85	30	100	10000	333.33	S5
Pd-imine@MNPs/Cs	20.5	-	-	-	-	75	-	5.7×10^4	S6
Pd(0)/met/GO	14	-	-	110	1	96	960	960	S7
PdcNPs/ $C@Fe_3O_4$	10-15	-	-	100	12	99	135	11.25	S8
Pd@PANI	2	-	-	100	0.5	88	1466.67	2933.33	S9
Pd/CNCs	4.8	-	-	40	5	92.5	65.5	13.1	S10
Pd/MOP-I	2.4±0.2	30-90	115	90	6	97.3	5560	926.67	This work

[a] TON = Molars of product / Molars of catalyst

[b] TOF(h^{-1}) = TON/Reaction time (hours)

Table S3. ICP-OES results of all recycle runs for Pd/MOP-I and filtrate solution

Sample	Pd loading of Pd/MOP-I (wt %)	Pd content of filtrate solution (ppm)
1st	1.70	＜0.1
2nd	1.72	＜0.1
3rd	1.69	＜0.1
4th	1.69	＜0.1

Figures

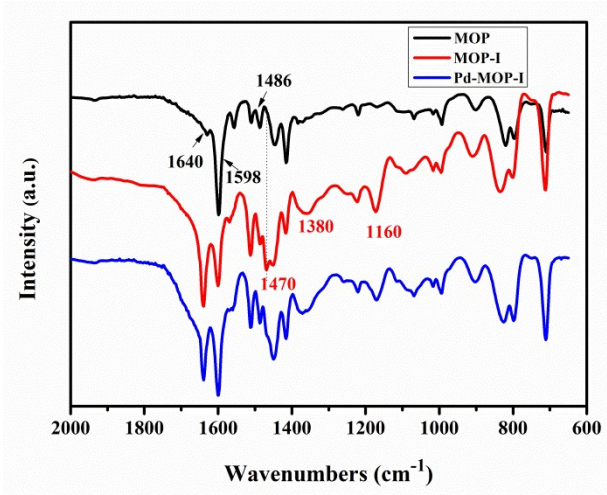

Fig. S1. FT-IR spectra of MOP, MOP-I and Pd/MOP-I

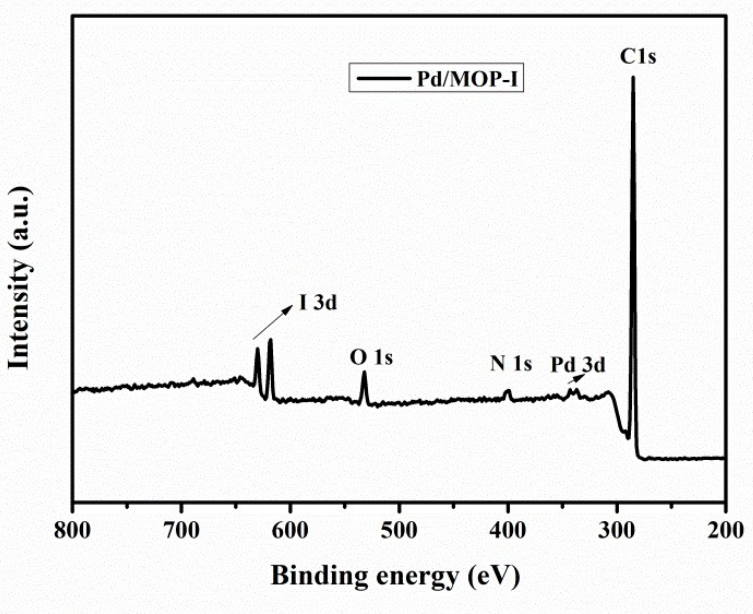

Fig. S2. The survey XPS spectra of Pd/MOP-I

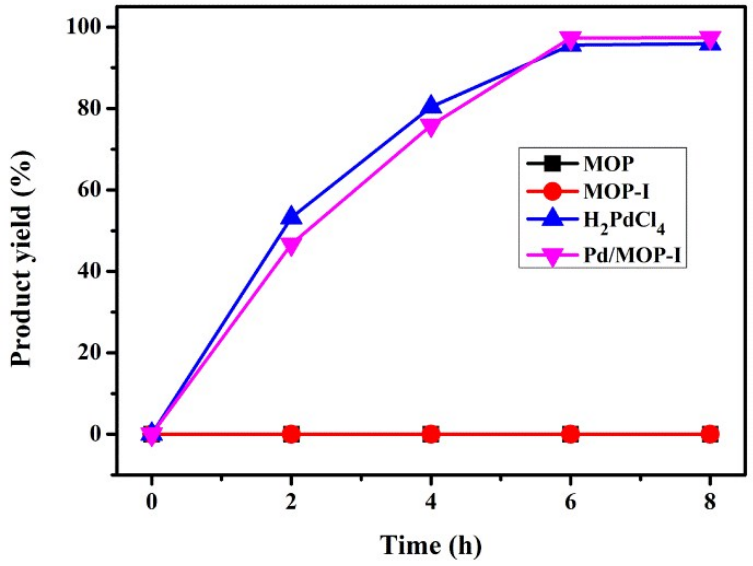

Fig. S3. The Heck reaction of iodobenzene with styrene catalyzed by Pd/MOP-I and control samples.

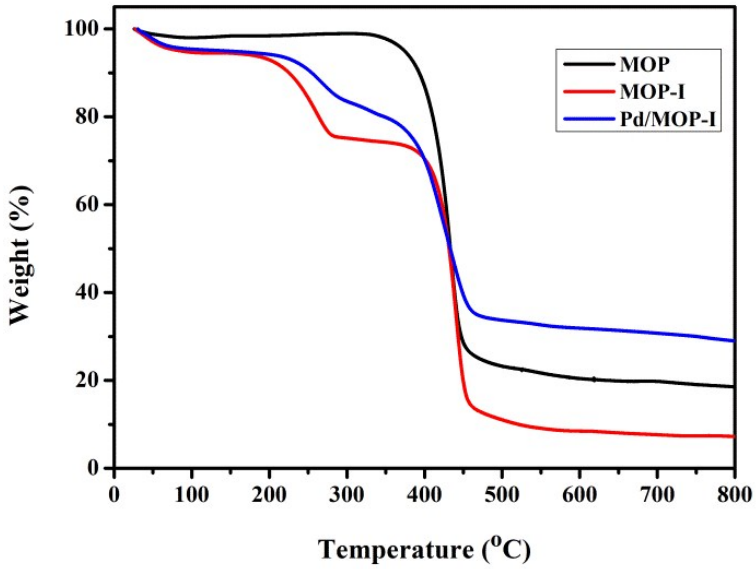

Fig. S4. TG analysis curves of MOP, MOP-I and Pd/MOP-I.

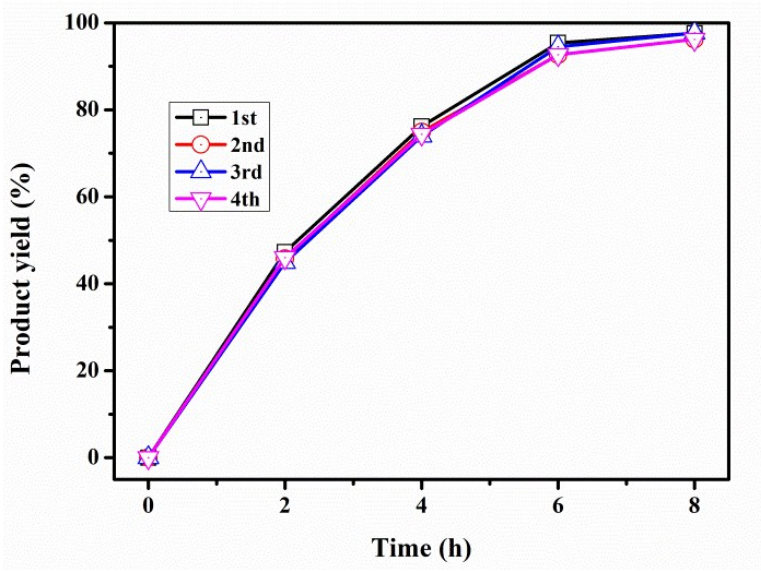

Fig. S5. The kinetic profiles of the consecutive runs of Pd/MOP-I.

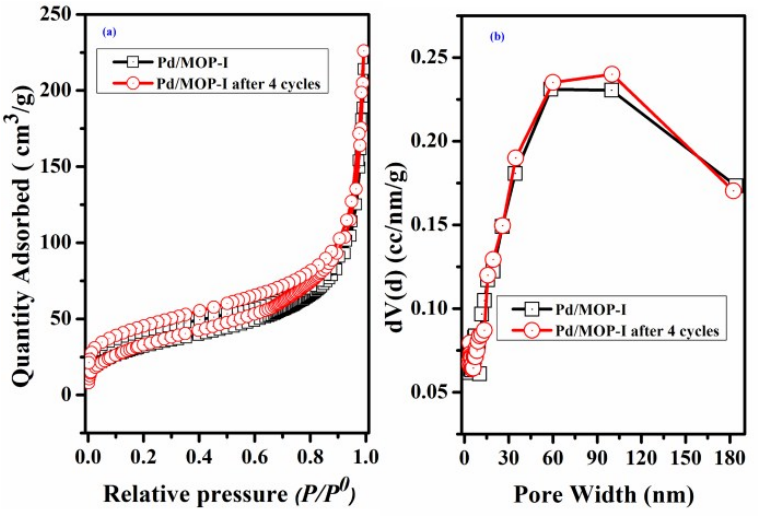

Fig. S6. N_2 adsorption-desorption isotherms and pore size distributions of fresh Pd/MOP-I and after 4 recycles

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