

Supporting Information

Highly Efficient Heterogeneous Hydroformylation over Rh-Metallated Porous Organic Polymers: Synergistic Effect of High Ligand Concentration and Flexible Framework

Qi Sun, Zhifeng Dai, Xiaolong Liu, Na Sheng, Feng Deng, Xiangju Meng, and
Feng-Shou Xiao*

Experimental Section

Solvents were purified according to standard laboratory methods. THF was distilled over LiAlH₄, and DMF was distilled over CaH₂. Other commercially available reagents were purchased in high purity and used without further purification.

Synthesis of vinyl-functionalized dppe ligand monomer (4V-dppe).

1,2-bis(dichlorophosphino)ethane (15 mmol in 30 mL of THF) was added slowly at 0 °C to the (4-vinylphenyl)magnesium bromide solution, which was synthesized from 4-bromostyrene (60 mmol) and magnesium powder (70 mmol). After stirring at RT for 2 h, 50 mL of saturated NH₄Cl aqueous was added to quench the reaction. The organic phase was separated, and water phase was extracted with an excess of diethyl ether. The combined organic phase was washed with brine, dried over MgSO₄, filtered, and concentrated in vacuum. The obtained crude product was purified by silica gel chromatography (5%EtOAc/Petroleum ether) to afford a white solid. ¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ 7.21-7.30 (m, 16H), 6.54-6.62 (m, 4H), 5.63-5.67 (m, 4H), 5.14-5.17 (m, 4H), 2.70 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 23.88, 114.62, 126.28, 132.85, 132.95, 133.03, 136.39, 137.58, 137.98 ppm. ³¹P NMR (162

MHz): δ -13.42 (s, 1P) ppm.

Synthesis of vinyl-functionalized dppm ligand monomer (4V-dppm). 4V-dppm was synthesized similarly to the 4V-dppe, except that bis(dichlorophosphino)methane was used instead of 1,2-bis(dichlorophosphino)ethane. ^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ 7.33-7.27 (m, 16H), 6.71-6.64 (m, 4H), 5.77-5.23 (m, 4H), 5.27-5.24 (m, 4H), 2.7 (s, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 114.46, 126.10, 126.13, 126.16, 129.13, 134.05, 134.14, 134.25, 136.38, 136.41, 136.44, 136.50, 137.67, 143.63 ppm. ^{31}P NMR (162 MHz): δ -22.98 (s, 1P) ppm.

Synthesis of vinyl-functionalized dppb ligand (4V-dppb). 4V-dppb was also synthesized similarly to the 4V-dppe, except that 1,2-bis(dichlorophosphino)benzene was used to react with (4-vinylphenyl)magnesium bromide. ^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ 7.09-7.24 (m, 20H), 6.61-6.69 (m, 4H), 5.70-5.75 (m, 4H), 5.24 (t, 4H, $J=5.6\text{Hz}$) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 31.65, 114.64, 126.19, 126.22, 126.26, 126.72, 127.05, 132.94, 133.04, 133.14, 136.44, 138.02, 138.22, 138.25, 138.29 ppm. ^{31}P NMR (162 MHz): δ -14.98 (s, 1P) ppm.

Synthesis of POL-dppe. 2.0 g of vinyl-functionalized dppe monomer was dissolved in 20 mL of THF, followed by addition of 50 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave at 100 °C for 24 h. After evaporation of THF under vacuum, a solid monolith was obtained and denoted as POL-dppe.

Synthesis of nonporous polymeric dppe ligand (NPOL-dppe). The synthetic procedure is similar to that of the POL-dppe polymer, except that the polymerization was carried out under acetic ether as the solvent condition.

Synthesis of porous polymeric dppe ligand with poor swelling property (POL-dppe-PS). The synthetic procedure is similar to that of the POL-dppe polymer, except that 2.0 g of vinyl-functionalized dppe monomer was dissolved in 4 mL of

THF.

Synthesis of porous polymers with different dppe concentration (PDVB-*x*-dppe).

A series of porous polymers with different dppe concentration were prepared under the solvothermal conditions *via* copolymerizing of vinyl-functionalized dppe monomers with divinylbenzene monomers in different mass ratios. For example, 0.2 g of vinyl-functionalized dppe monomer, 1.8 g of divinylbenzene monomer and 50 mg of azobisisobutyronitrile (AIBN) were dissolved in 20 mL of THF. The mixture was transferred into an autoclave and maintained at 100 °C for 24 h. After evaporation of solvent, a white solid was obtained and denoted as PDVB-0.1-dppe.

Synthesis of Rh/POL-dppe catalysts. As a typical synthesis recipe, 1.0 g of the POL-dppe polymer was swollen in 40 mL of toluene for 30 min, followed by adding 5.1 mg of Rh(CO)₂(acac). After stirring at room temperature under N₂ atmosphere for 24 h, the mixture was filtrated and washed with an excess of toluene, and finally dried at 50 °C under vacuum. The obtained light yellow solid was denoted as Rh/POL-dppe with Rh loading at 2.0 wt.%.

Hydroformylation of olefins. Rh-based catalyst (12.8 mg containing 2.5 μmol of Rh), styrene (0.520 g), and toluene (10 mL) were added into a stainless steel autoclave (100 mL). After sealing and purging with syngas (CO/H₂ = 1:1) for 3 times, the pressure of syngas was adjusted to the desired value. Then the autoclave was put into a preheated oil bath and stirring at 80 °C for 18 h. After the reaction, the catalysts were taken out from the system by centrifugation and analyzed by gas chromatography (GC-1690 Kexiao Co., flame ionization detector and a Supelco γ-DEX 225 capillary column).

For each catalyst recycling, the catalysts were separated by centrifugation under N₂, washed with degassed toluene, and used directly for the next run.

Characterization

Nitrogen sorption isotherms at $-196\text{ }^{\circ}\text{C}$ were measured using Micromeritics ASAP 2020M and Tristar system. The samples were outgassed for 10 h at $100\text{ }^{\circ}\text{C}$ before the measurements. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultimate VI X-ray diffractometer (40 kV, 40 mA) using $\text{Cu K}\alpha$ ($\lambda=1.5406\text{ \AA}$) radiation. Scanning electron microscopy (SEM) image was performed using a Hitachi SU 1510. Transmission electron microscope (TEM) image was performed using a Hitachi HT-7700. X-ray photoelectron spectroscopy (XPS) spectra were performed on a Thermo ESCALAB 250 with $\text{Al K}\alpha$ irradiation at $\theta=90^{\circ}$ for X-ray sources, and the binding energies were calibrated using the C1s peak at 284.9 eV . Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was measured with a Perkin-Elmer plasma 40 emission spectrometer. ^1H NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from TMS at $\delta=0\text{ ppm}$, and J values are given in Hz. ^{13}C (100.5 MHz) cross-polarization magic-angle spinning (CP-MAS), and ^{31}P (161.8 MHz) MAS solid-state NMR experiments were recorded on a Varian infinity plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO_2 rotor. ^{31}P static solid-state NMR experiments were recorded on a Bruker Avance 500 spectrometer and $(\text{NH}_4)_2\text{HPO}_4$ was chosen as reference with ^{31}P chemical shift at 1.0 ppm .

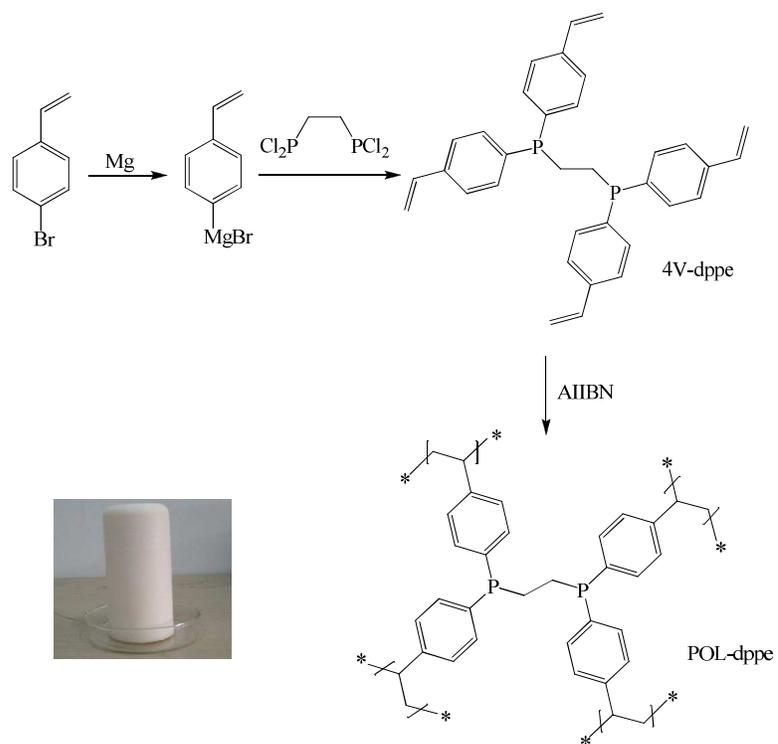


Figure S1. Synthesis of POL-dppe polymer.

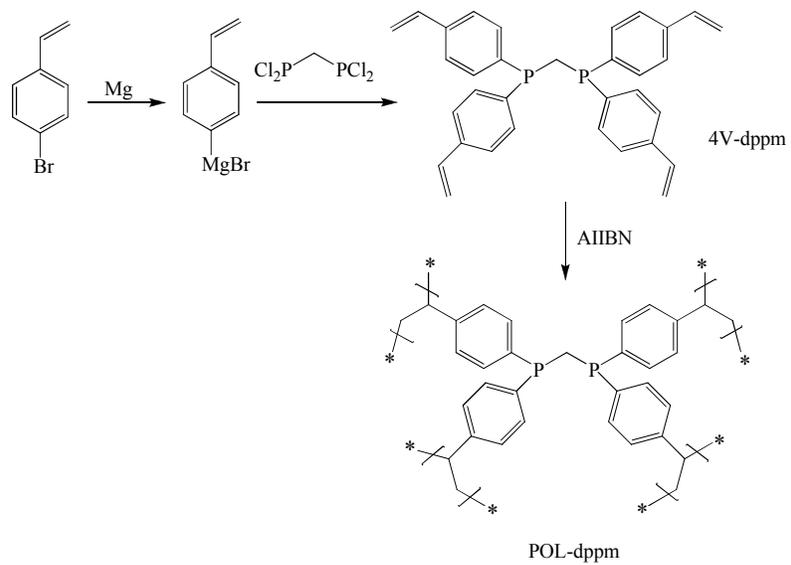


Figure S2. Synthesis of POL-dppm polymer.

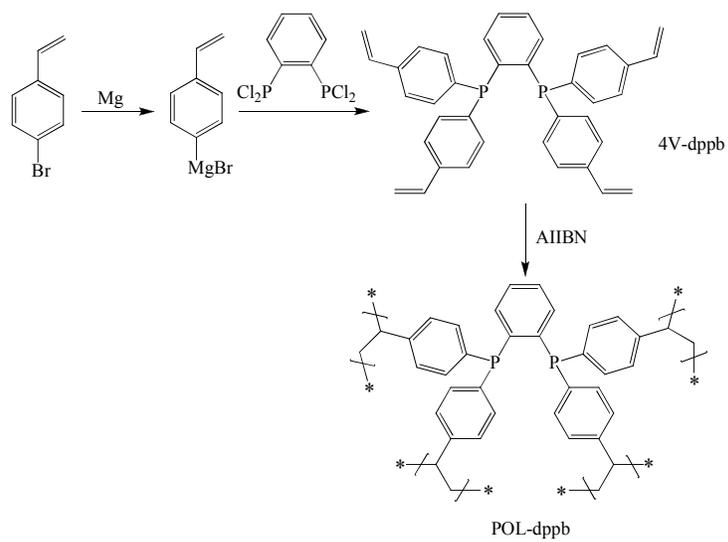
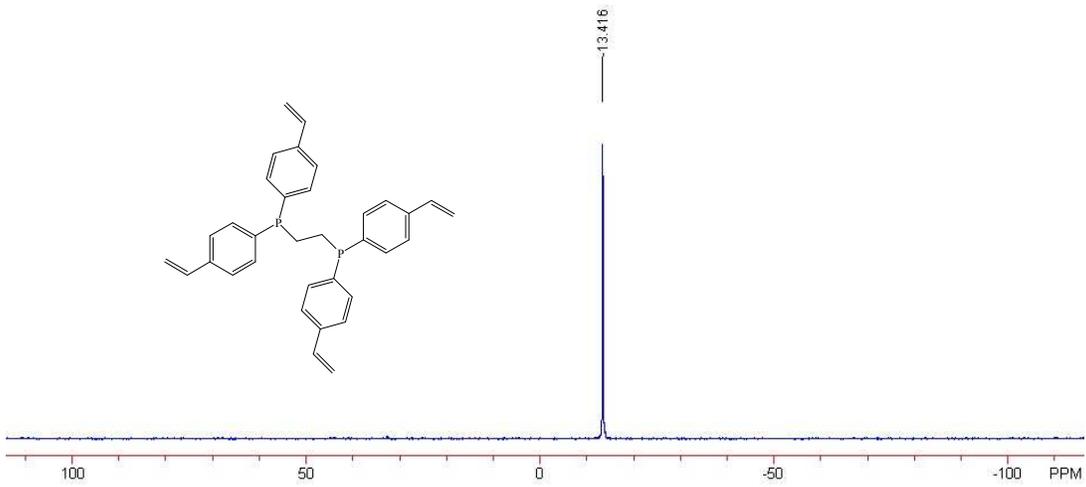
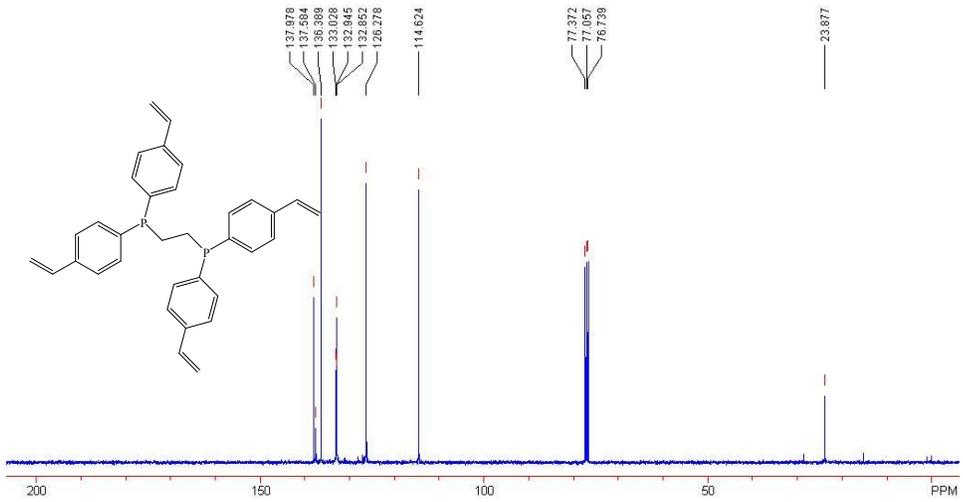
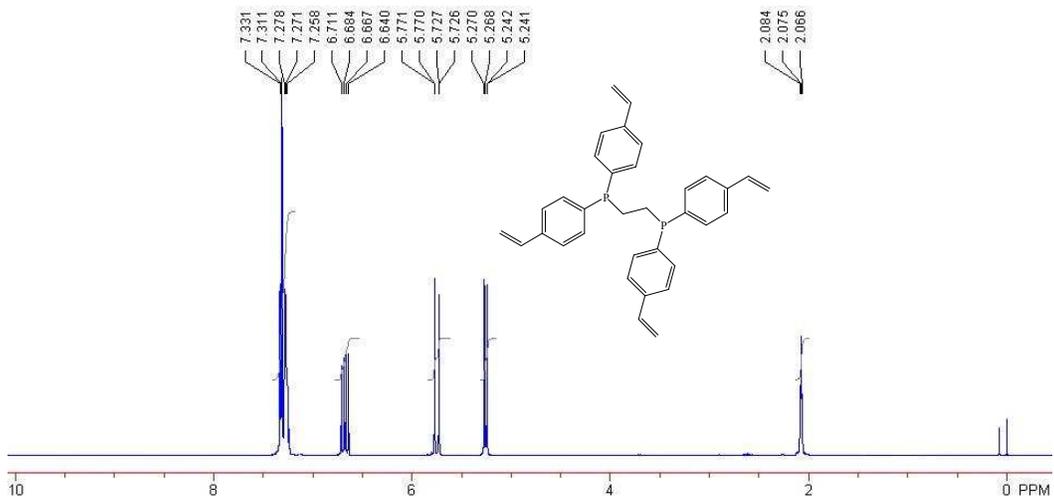
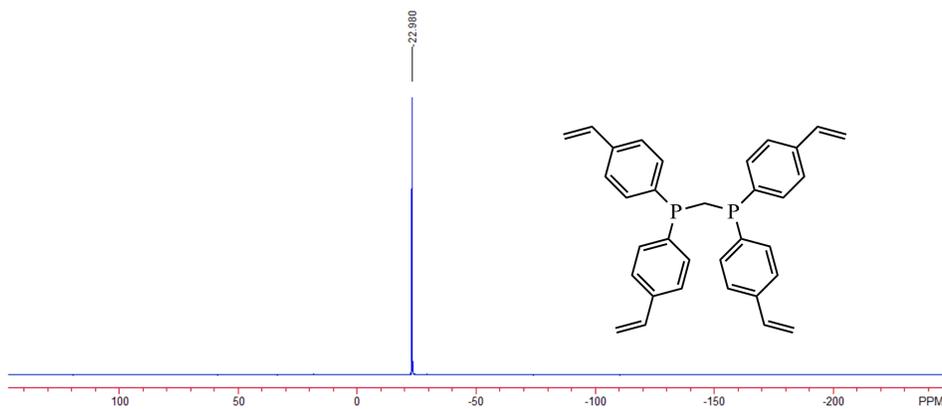
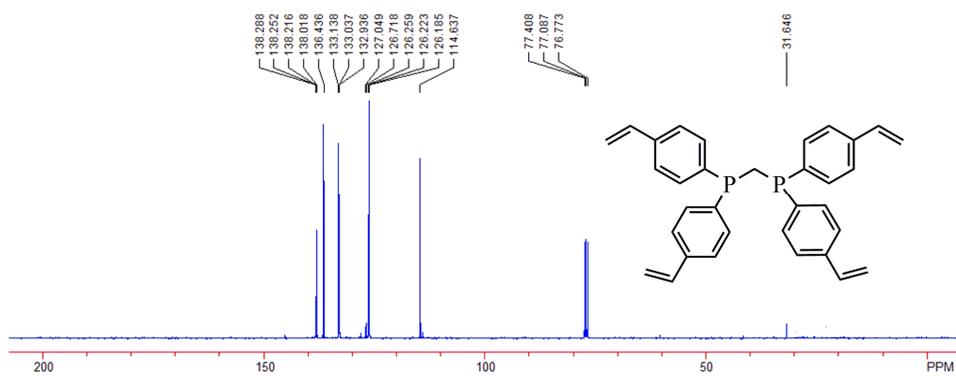
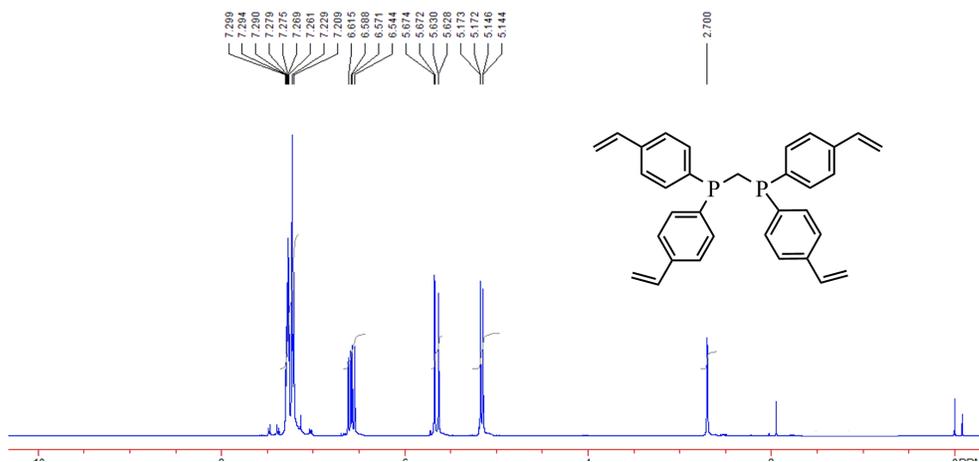


Figure S3. Synthesis of POL-dppb polymer.





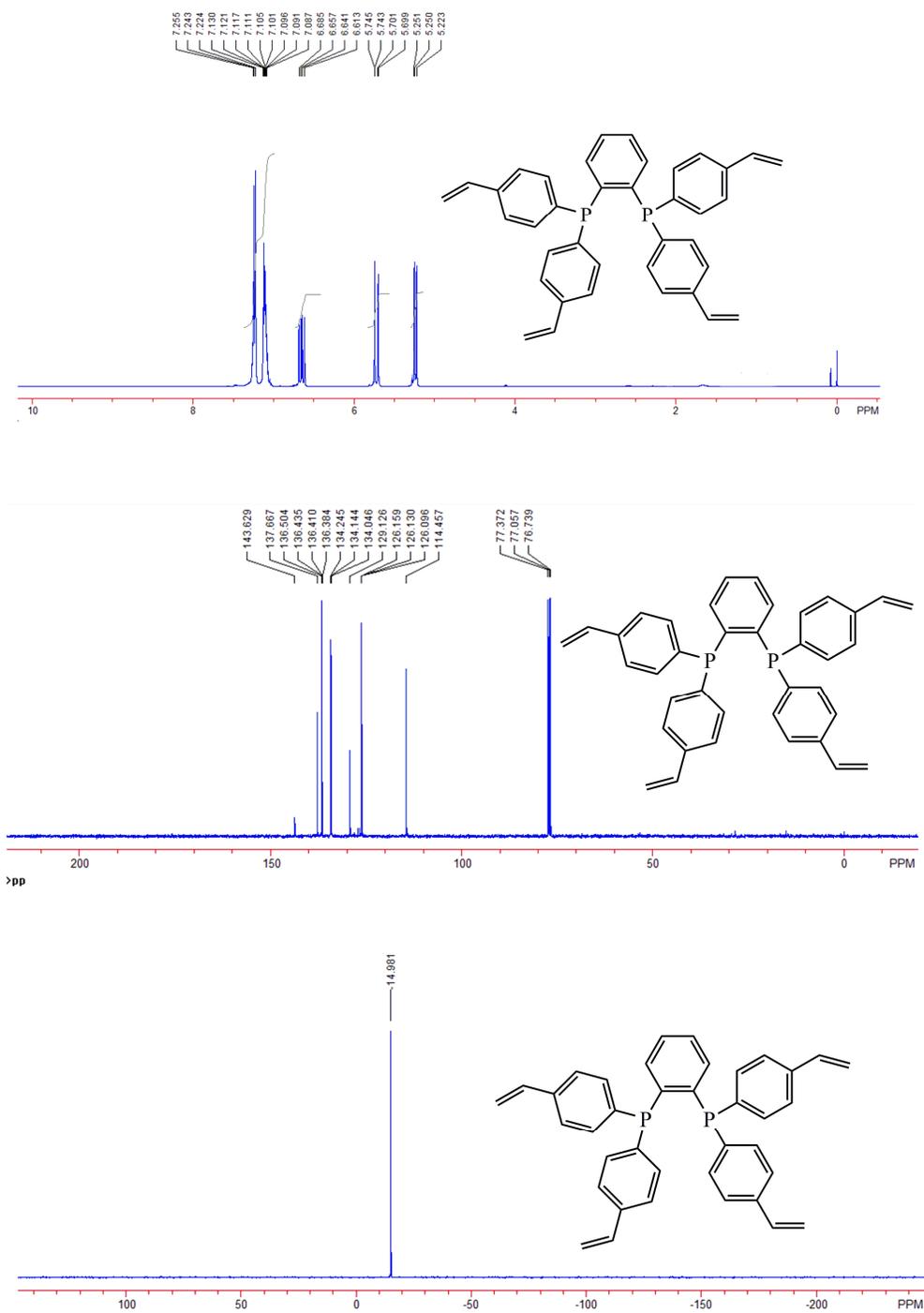


Figure S4. Liquid NMR spectra of vinyl-functionalized diphosphine ligands

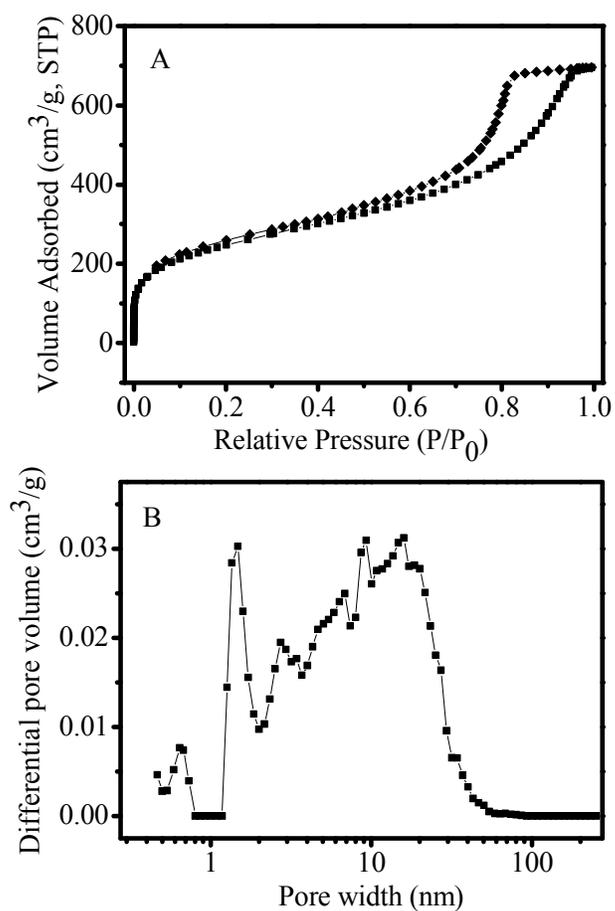


Figure S5. (A) Nitrogen sorption isotherms and (B) Pore size distribution of the POL-dppm polymer. Pore size distribution was calculated by the nonlocal density functional theory method (NLDFT).

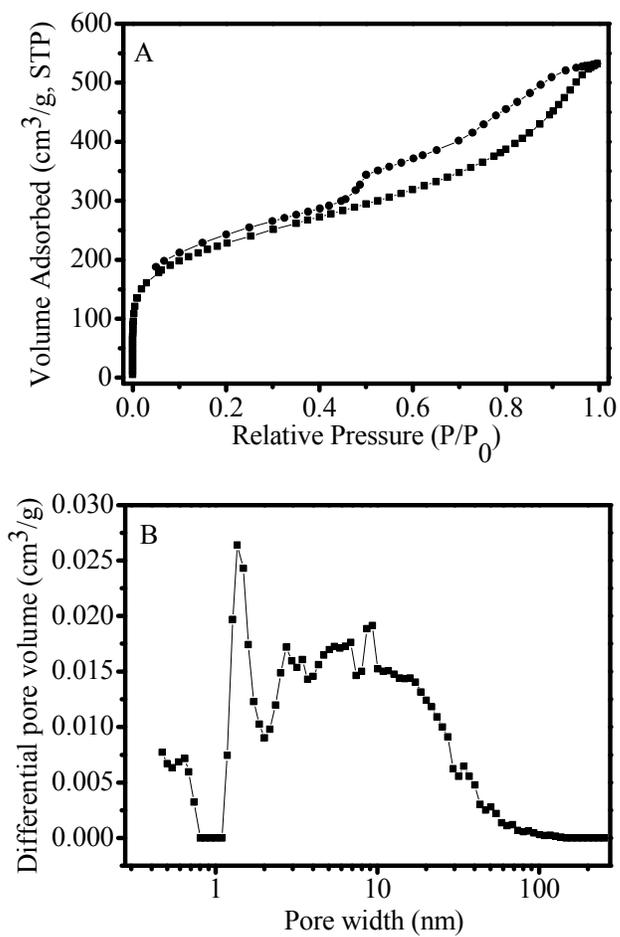


Figure S6. (A) Nitrogen sorption isotherms and (B) Pore size distribution of the POL-dppb polymer. Pore size distribution was calculated by the nonlocal density functional theory method (NLDFT).

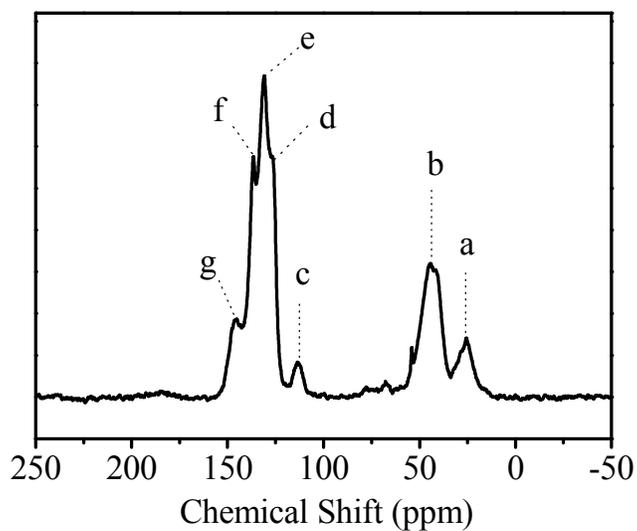
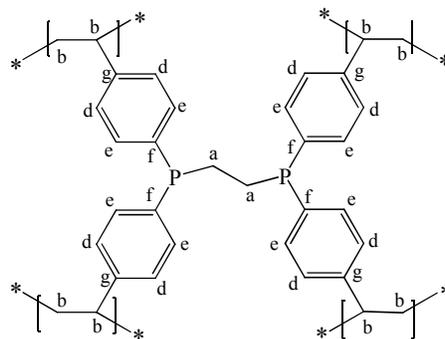


Figure S7. ^{13}C MAS NMR spectrum of the POL-dppe polymer. The strong peak of b and relatively weak peak of c are assigned to the polymerized and un-polymerized vinyl groups, respectively, indicating that the POL-dppe has a high degree of the polymerized framework.

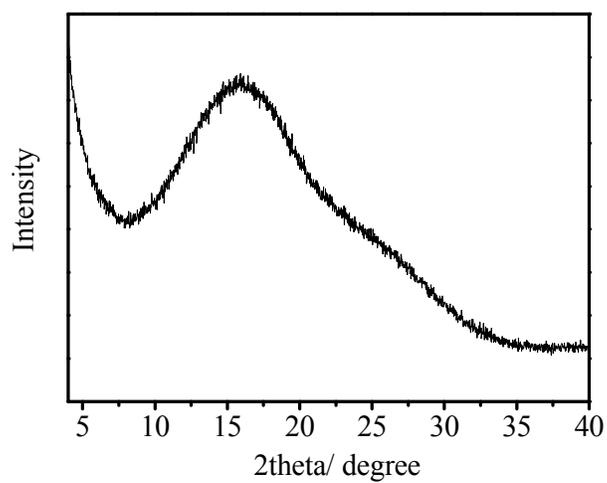


Figure S8. XRD pattern of the POL-dppe polymer. The broad peak ranged from 10 to 35°, indicating the amorphous nature of the sample.

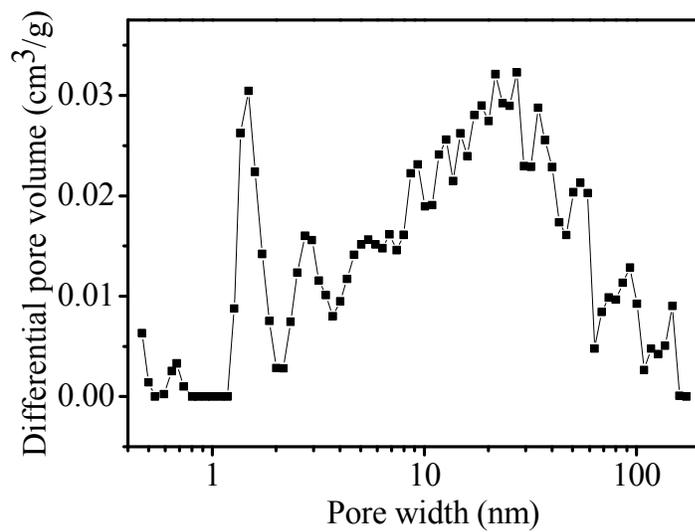


Figure S9. Pore size distribution of the POL-dppe polymer calculated from non-local density functional theory (NLDFT). This result indicates that the presence of hierarchical porosity in the sample.

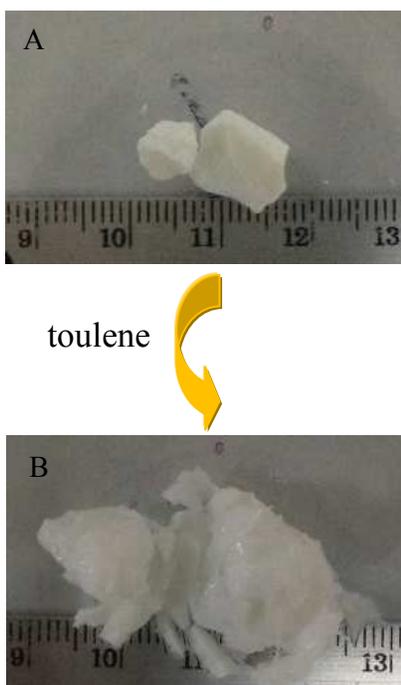


Figure S10. Photographs of POL-dppe polymer before (A) and after (B) addition of toluene solvent. These photographs indicate that the POL-dppe is remarkably swollen after the addition of the toluene solvent, which is due to the flexible dppe ligand framework.

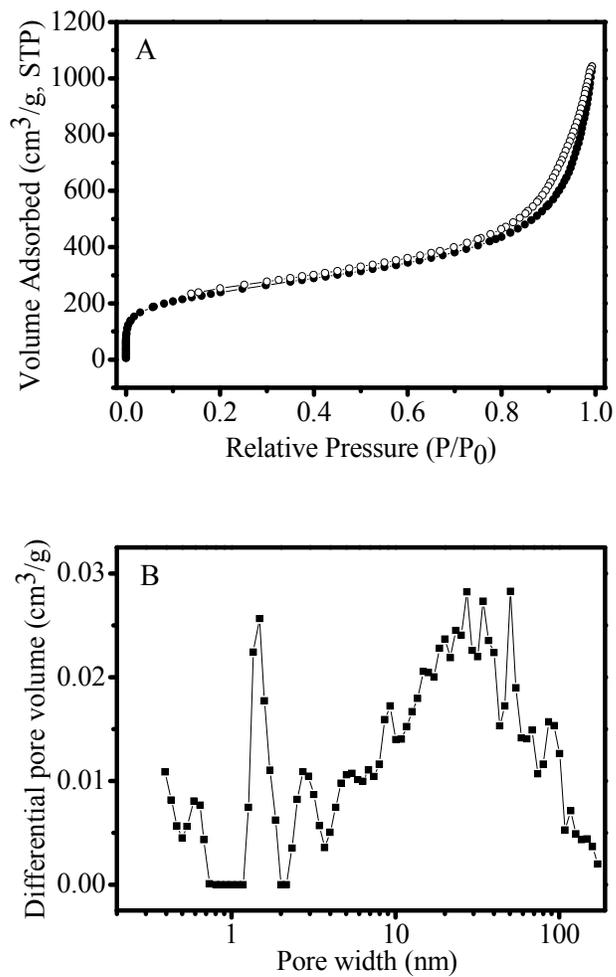


Figure S11. (A) Nitrogen sorption isotherms and (B) Pore size distribution of the Rh/POL-dppe catalyst (Rh loading at 2.0 wt.%), calculated from the nonlocal density functional theory method (NLDFT). These results indicate that after metalation with Rh species, the sample still has high surface and hierarchical porosity.

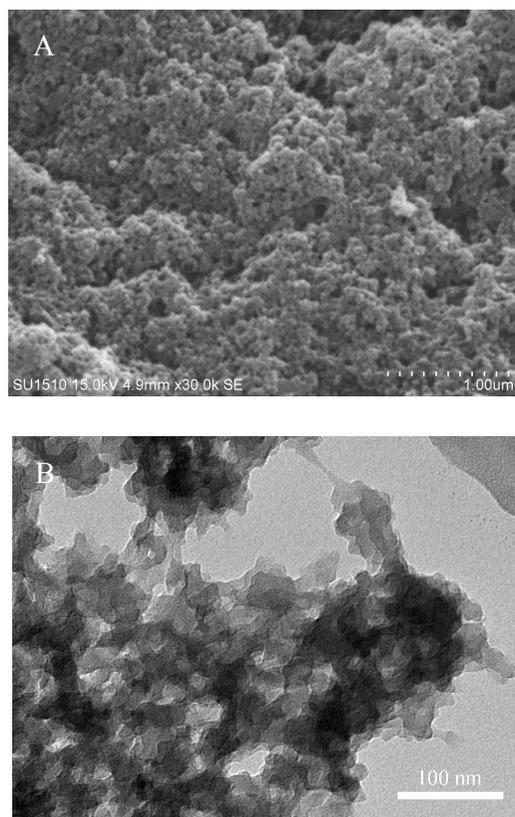


Figure S12. (A) SEM and (B) TEM images of the Rh/POL-dppe catalyst (Rh loading at 2.0 wt.%). These two images confirm the presence of hierarchical porosity in the sample.

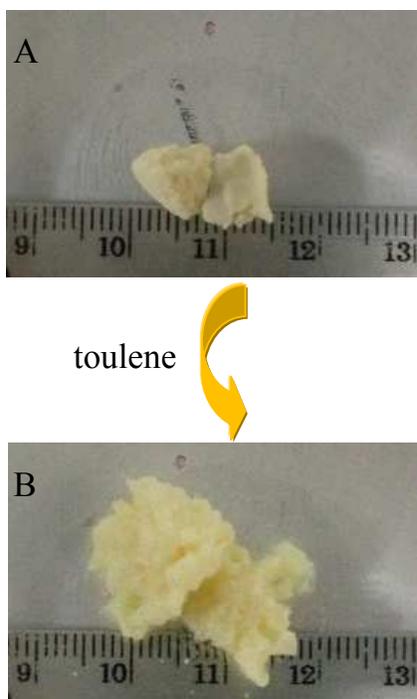


Figure S13. Photographs of Rh/POL-dppe catalyst (Rh loading at 2.0 wt.%) before (A) and after (B) addition of toluene solvent. The photographs indicate that the Rh/POL-dppe is remarkably swollen after addition of the toluene solvent, which is due to the flexible dppe ligand framework.

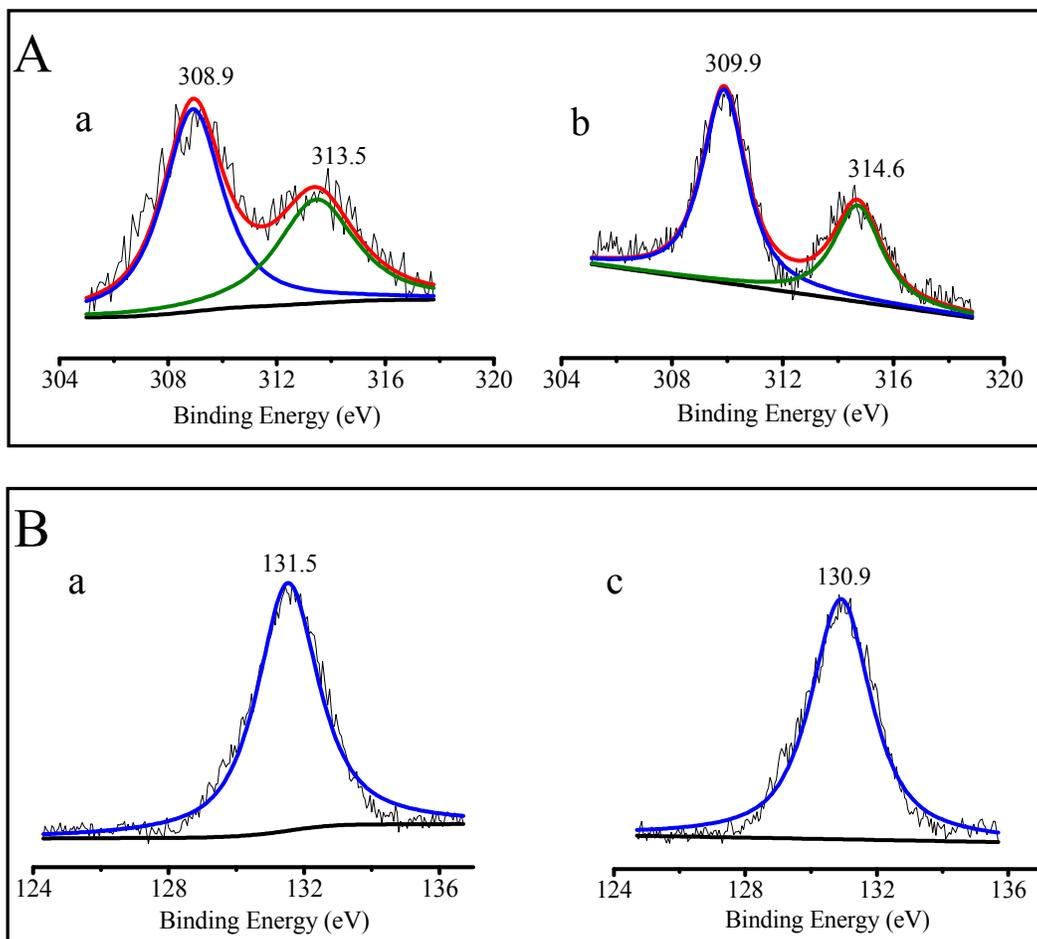


Figure 14. (A) Rh3d and (B) P2p XPS spectra of (a) Rh/POL-dppe and (b) Rh(CO)₂(acac), and (c) POL-dppe samples. Rh/POL-dppe gives the values of Rh3d_{5/2} and Rh3d_{3/2} at 308.9 and 313.5 eV, which are obviously lower than those (309.9 and 314.6 eV) of Rh(CO)₂(acac). Simultaneously, the P2d binding energy of the Rh/POL-dppe exhibits relatively higher value (131.5 eV) than that (130.9 eV) of the POL-dppe. These results indicate that the interaction between POL-dppe and Rh species occurs in the Rh/POL-dppe catalysts.

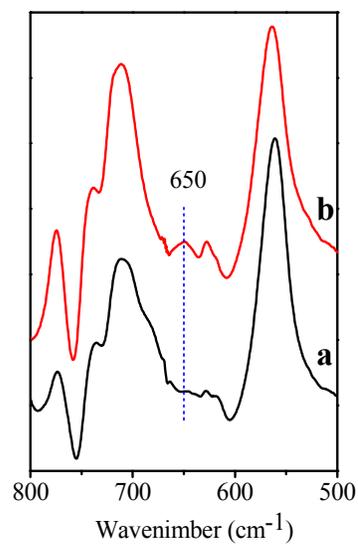


Figure S15. IR spectra of (a) POL-dppe and (b) Rh/POL-dppe. The appearance of band at 650 cm⁻¹ in Rh/POL-dppe is associated to the characteristic peak of P-Rh-P.

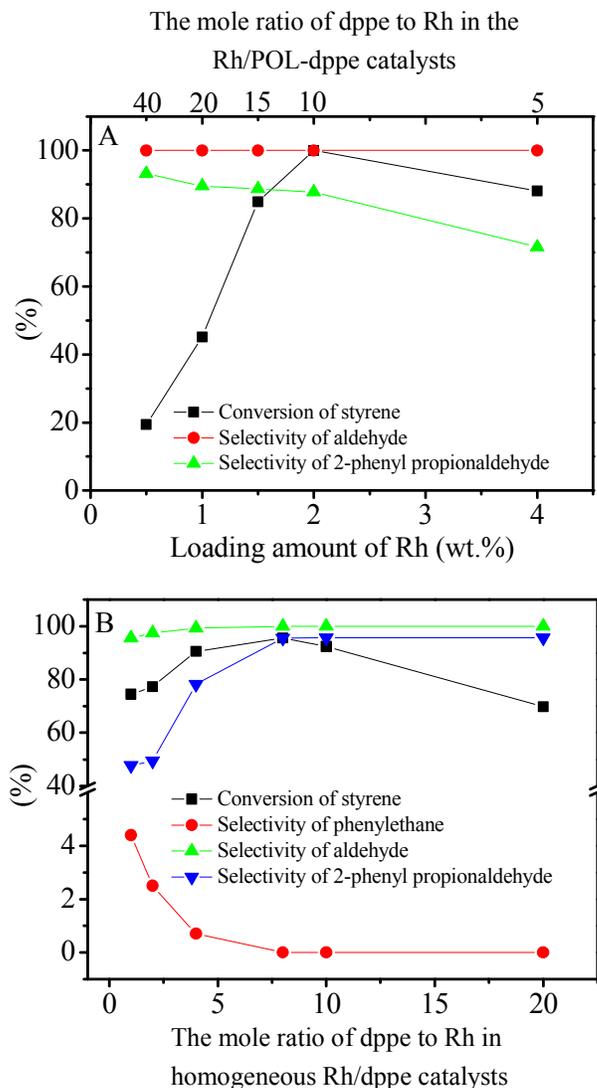


Figure S16. Dependences of catalytic activities and selectivities in the hydroformylation of styrene on the dppe/Rh ratios over (A) Rh/POL-dppe heterogeneous and (B) dppe/Rh homogeneous catalysts. Reaction conditions: styrene (5.0 mmol), toluene (10 mL), 80 °C, CO/H₂ = 1:1 (1.0 MPa), S/C=2000, and 18 h. For the Rh/POL-dppe heterogeneous catalyst, when the Rh loading from 0.5 to 2.0 wt.% (correspondingly, the molar ratio of dppe to Rh from 40 to 10), the conversion of the reaction significantly increase along with the branched aldehyde selectivity is slightly decrease; when the Rh loading from 2.0 to 4.0 wt.% (correspondingly, the molar ratio of dppe to Rh from 10 to 5), the conversion and branched aldehyde selectivity are decreased. For the Rh/dppe homogeneous catalysts, it is observed similar phenomena.

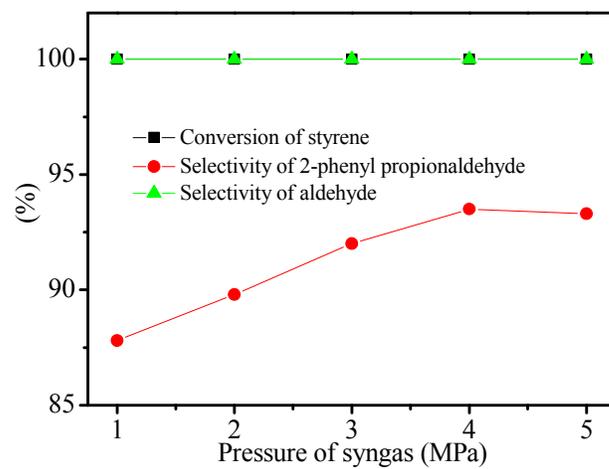


Figure S17. Dependences of catalytic activity and selectivity on the pressure of syngas in hydroformylation of styrene over the Rh/POL-dppe catalyst (Rh loading at 2.0 wt.%). Reaction conditions: styrene (5.0 mmol), toluene (10 mL), 80 °C, S/C=2000, and 18 h.

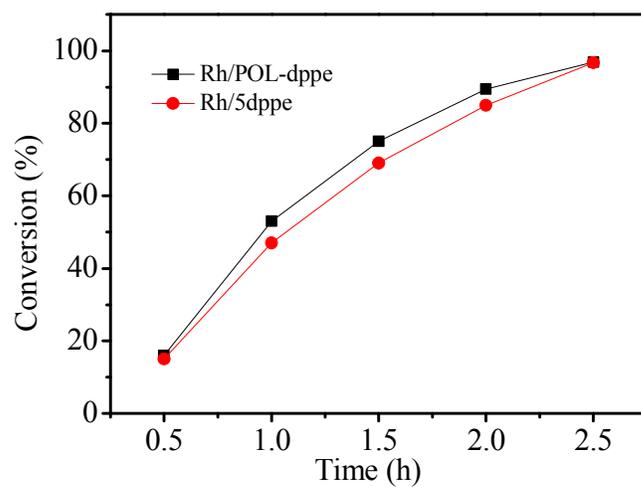


Figure S18. Plots of GC conversion (%) versus time for hydroformylation of 1-octene using Rh/POL-dppe and Rh/5dppe as catalysts under identical conditions. Reaction conditions: 1-octene (5.0 mmol), toluene (10 mL), 90 °C, CO/H₂=1:1 (2.0 MPa), S/C=2000.

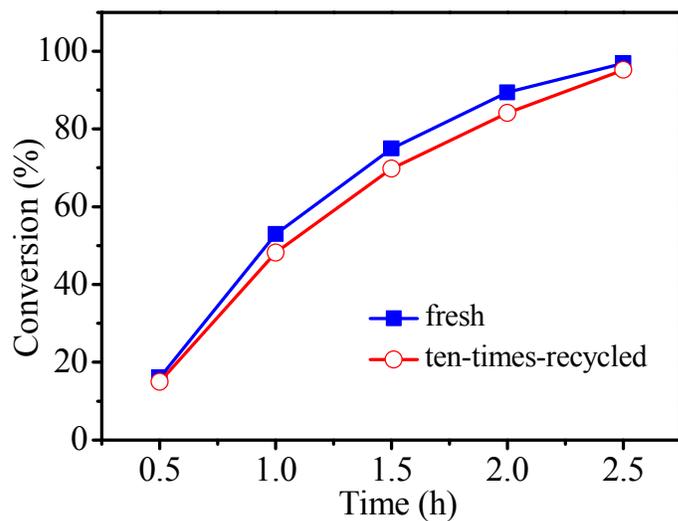


Figure S19. Plots of GC conversion (%) *versus* time for hydroformylation of *n*-octene using fresh Rh/POL-dppe and ten-times-recycled Rh/POL-dppe as catalysts under the same conditions. Reaction conditions: *n*-octene (5.0 mmol), toluene (10 mL), 90 °C, CO/H₂=1:1 (2.0 MPa), Rh/POL-dppe (0.05 mol% based on Rh species), S/C=2000, and Rh loading amount at 2.0 wt.%.

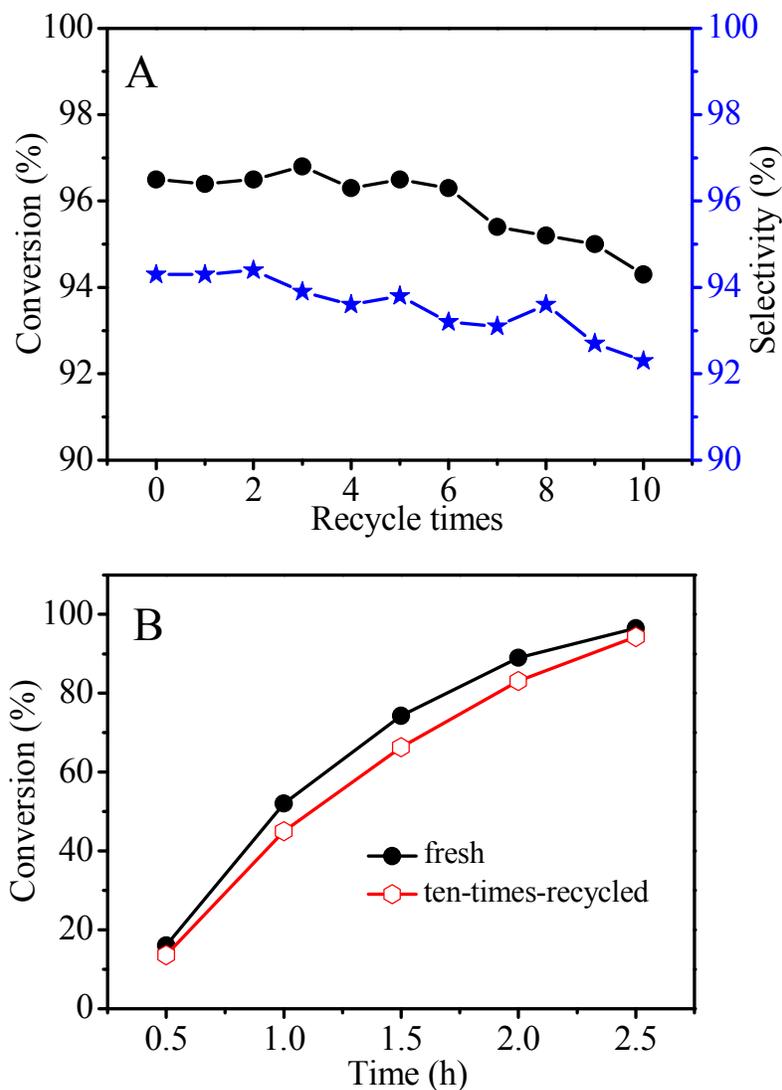


Figure S20. (A) Recycling tests of the Rh/PDVB-0.8-dppe catalyst for hydroformylation of *n*-octene; (B) Plots of GC conversion (%) versus time for hydroformylation of *n*-octene using fresh Rh/PDVB-0.8-dppe and ten-times-recycled Rh/PDVB-0.8-dppe as catalysts under the same conditions. Reaction conditions: *n*-octene (5.0 mmol), toluene (10 mL), 90 °C, CO/H₂=1:1 (2.0 MPa), Rh/PDVB-0.8-dppe (0.05 mol% based on Rh species), S/C=2000, and Rh loading amount at 2.0 wt.%.

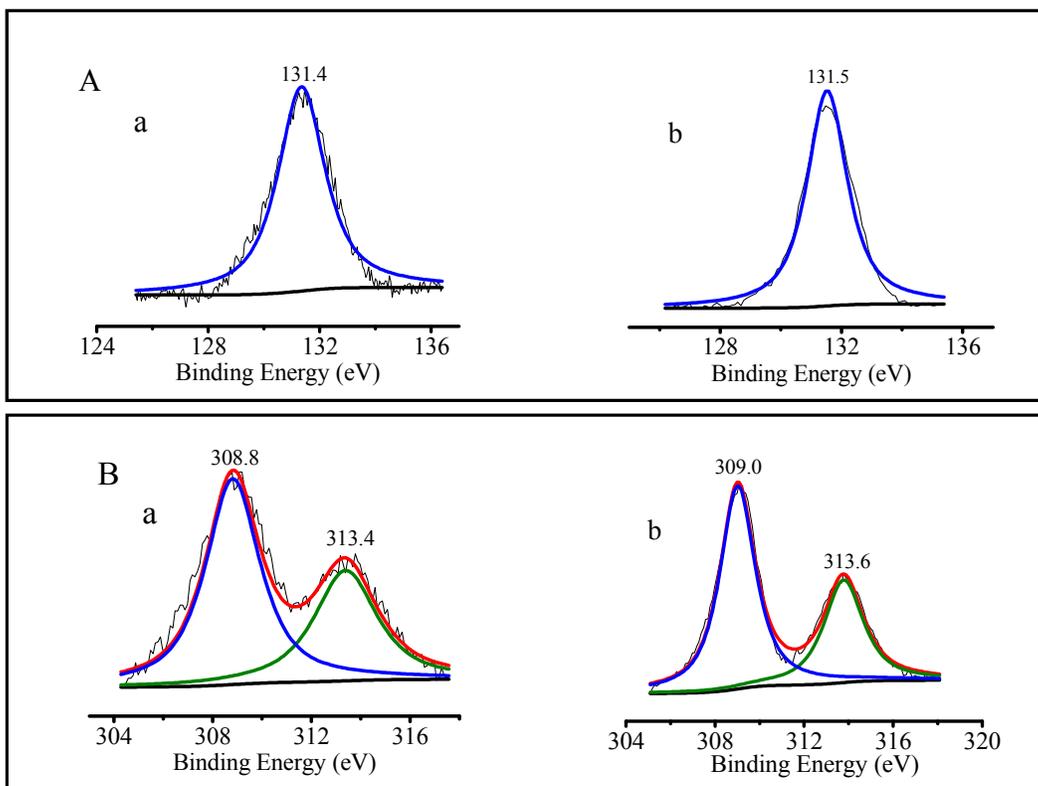
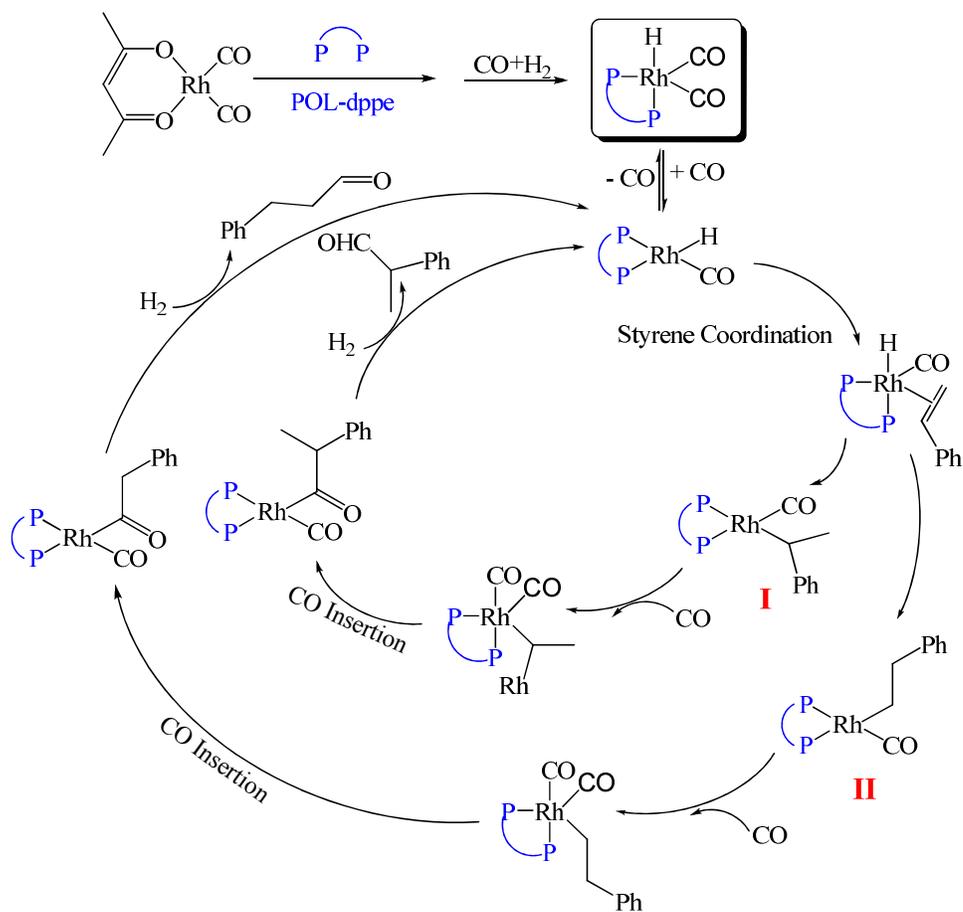
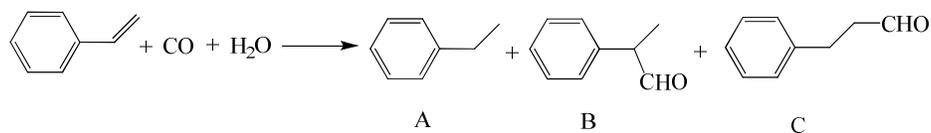


Figure S21. (A) P2p and (B) Rh3d XPS spectra of (a) Rh/NPOL-dppe and (b) Rh/POL-dppe-PS. XPS spectra reveal that the binding energies of P2p and Rh3d in Rh/NPOL-dppe and Rh/POL-dppe-PS are similar to those of Rh/POL-dppe (Figure S21), suggesting their similar bonding nature of Rh species with the dppe moieties.



Scheme S1. Possible mechanism for Rh/POL-dppe catalyzed hydroformylation of styrene.

Table S1. Effect of the temperature on the catalytic performance in the hydroformylation of styrene over the Rh/POL-dppe catalyst.^a



Entry	Time (h)	Temperature (°C)	Conv. (%)	Select. (%)		
				A	B	C
1	10	110	100	0	72.5	27.5
2	18	50	26.7	0	95.3	4.7
3	48	50	51.3	0	94.9	5.1
4	18	60	54.3	0	90.7	9.3
5	18	70	95.7	0	88.8	11.2

^a Reaction conditions: styrene (5.0 mmol), toluene (10 mL), 80 °C, CO/H₂ = 1:1 (1.0 MPa), S/C=2000, and Rh loading at 2.0 wt.%.

Table S2. Recycles of the Rh/POL-dppe catalyst in hydroformylation of *n*-octene.^a

Entry	Conv.(%)	Paraffin (%) ^b	Iso-olefins (%) ^b	Aldehydes (%) ^b
0	96.9	0	0.7	99.3 (n/i=2.46)
1	96.7	0	0.7	99.3 (n/i=2.45)
2	96.5	0	0.8	99.2 (n/i=2.45)
3	97.0	0	1.0	99.0 (n/i=2.43)
4	96.3	0	1.1	98.9 (n/i=2.44)
5	96.7	0	1.1	98.9 (n/i=2.43)
6	96.1	0	1.2	98.8 (n/i=2.44)
7	95.3	0	1.4	98.6 (n/i=2.43)
8	95.4	0	1.4	98.6 (n/i=2.44)
9	94.8	0	1.5	98.5 (n/i=2.42)
10	95.2	0	1.3	98.7 (n/i=2.43)

^aReaction conditions: *n*-octene (5.0 mmol), toluene (10 mL), 90 °C, CO/H₂ = 1:1 (2.0 MPa), Rh/POL-dppe (0.05 mol%); S/C=2000, and 2.5 h; ^b Selectivity.

Table S3. Textural parameters of Rh/PDVB-*x*-dppe samples.

x^a	S_{BET} (m ² /g)	Pore volume (cm ³ /g)
0.1	679	0.55
0.2	746	0.69
0.4	744	1.19
0.8	1011	1.30

^a x stands for mass ratios of vinyl-functionalized dppe monomer to the DVB monomer.

Table S4. Catalytic performance in hydroformylation of styrene over various catalysts.^a

Entry	Catalyst	Conv.(%)	Aldehydes (%) ^b	Branched aldehyde (%) ^c
1	4.0 wt.%Rh/POL-dppe + dppe ^d	98.6	>99.5	91.8
2	2.0 wt.%Rh/POL-dppe	>99.5	>99.5	87.8
3	4.0 wt.%Rh/POL-dppe	88.1	>99.5	71.6
4	Rh/5dppe ^e	94.3	>99.5	84.6

^a Reaction conditions: styrene (5.0 mmol), toluene (10 mL), 80 °C, CO/H₂ = 1:1 (1.0 MPa), S/C=2000, and 18 h; ^b Aldehydes selectivities; ^c Branched aldehyde selectivities; ^d additional soluble dppe ligands were added to make the ratio of dppe moieties to Rh species in the resulting catalytic system at 10; ^e homogeneous catalytic system with dppe/Rh ratio at 5.