

*Supporting Information for*

**An efficient and ultrastable single-Rh-site catalyst on porous organic  
polymer for heterogeneous hydrocarboxylation of olefins**

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## Experiment section

### Materials

All solvents were purified according to the standard laboratory methods. Other reagents were of analytical grade and used as purchased without further purification unless otherwise stated. Cyclohexene, cyclopentene, 1-hexene, 1-octene, 1-phenylethanol, cyclohexanecarboxylic acid, *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H<sub>2</sub>O), 1,3-dimethyl-2-imidazolidinone (DMI), triethanolamine (TEOA) were purchased from Shanghai Macklin Biochemical Co., Ltd. Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>, Rh(CO)<sub>2</sub>(acac) and 4-bromostyrene were purchased from J&K Chemical Ltd. Acetic acid, propionic acid, cyclohexyl acetate, cyclohexyl iodide, cyclopentyl iodide, cyclopentanecarboxylic acid, heptanoic acid, 2-methylhexanoic acid, nonanoic acid and SBA-15 were purchased from Aladdin Co., Ltd. RhCl<sub>3</sub>·nH<sub>2</sub>O with metal loading of 37 wt.% was purchased from Johnson Matthey (Shanghai) Chemicals Ltd. The coarse coconut shell activated carbon (AC) of 40-60 mesh, purchased from Tangshan United Carbon Technology Co., was washed with deionized water (353 K) till the electrical conductivity of washing water was below 20 μs/cm, and afterwards dried at 393 K for 12 h. Al<sub>2</sub>O<sub>3</sub> was purchased from Gongyi Tengfei Co., Ltd. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was dried with molecular sieves and distilled before used. Tetrahydrofuran (THF) was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. Methyl iodide (CH<sub>3</sub>I) and Iodoethane (CH<sub>3</sub>CH<sub>2</sub>I) was purchased from Shandong West Asia Chemical Industry Co., Ltd. Toluene and dioxane were obtained from Sinopharm Chemical Reagent Co., Ltd. Magnesium powder and azodiisobutyronitrile (AIBN) were purchased from Sigma-Aldrich. PCl<sub>3</sub>, n-hexane and anhydrous ether were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd.

### Catalyst characterization

Nitrogen sorption isotherms were measured by a Quantachrome Autosorb-1 system at 77 K. Scanning electron microscopy (SEM) was carried out on a JSM-7800F. Transmission electron microscopy (TEM) was performed using a JEM-2100

device. Thermogravimetric analysis (TGA) was obtained on a NETZSCH STA 449F3 thermal analyzer. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were gained by using a JEM-ARM200F STEM/TEM instrument. Powder X-ray diffraction (XRD) data were obtained using a PANalytical EMPYREAN. Solid-state  $^{13}\text{C}$  and  $^{31}\text{P}$  MAS NMR spectra were gained on a Bruker Avance 600 AV device. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Thermo ESCALAB 250XI instrument. Water contact angle (WCA) was carried out on a KRUSS DSA100. Inductively coupled plasma optical emission spectrometer (ICP-OES) was measured using a PerkinElmer apparatus Optima 7300 DV.

### **Preparation of catalysts**

POPs and PIPs: POPs were synthesized according to the synthesis process of the POL-PPh<sub>3</sub> in our previous work<sup>1</sup> and we denoted the porous organic polymer synthesizing from the thermal polymerization of trivinyl-functionalized PPh<sub>3</sub> as POPs in this work. Below are the synthesis procedures of POPs and the main synthesis steps were displayed in the **Scheme S1**.

Synthesis of 3V-PPh<sub>3</sub> monomer: Under the argon atmosphere and in the ice water bath, 0.5 g magnesium powder and 10 mL of anhydrous ether were added into a 100 mL three-necked round bottom flask and stirred for 2 h. Then the mixed solution 1 (4 g 4-bromostyrene in 10 mL of anhydrous ether) and mixed solution 2 (6 g PCl<sub>3</sub> in 10 mL of anhydrous ether) were added into the mentioned flask successively and stirred for 2 h respectively, followed by stirring for another 0.5 h after adding 10 mL water. The primary production was obtained after the extraction of the mixture with 90 mL of anhydrous ether, filtration and rotary evaporation. After the purification by silica gel chromatography (5% EtOAc/Petroleum ether) and recrystallization with n-hexane, the white solid 3V-PPh<sub>3</sub> monomer was obtained.

Synthesis of polymer POPs: Under the argon atmosphere and room temperature, 1 g 3V-PPh<sub>3</sub> was dissolved in the 10g THF, followed by adding 25 mg azodiisobutyronitrile (AIBN). After the absolute dissolution, the mixed solution was

transferred into a 50 mL autoclave placed at the oven with 100 °C for 24 h. POPs was obtained after cooled to the room temperature and dried under vacuum at 60 °C for 6 h.

PIPs was synthesized by adding 1.5 g POPs, 3.9 g CH<sub>3</sub>I and 40 mL acetic acid into a 100 mL autoclave under magnetic stirring at 120 °C for 16 h. After evaporation of acetic acid under vacuum, a yellow solid of PIPs was obtained.

Rh<sub>1</sub>/POPs, Rh<sub>1</sub><sup>I</sup>/POPs and Rh<sub>1</sub><sup>II</sup>/POPs: Rh<sub>1</sub>/POPs was prepared as the following procedures. Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub> (0.0191 g) was dissolved in 30 mL of CH<sub>2</sub>Cl<sub>2</sub> in a 50 mL three-necked round bottom flask under argon atmosphere, followed by a 20 min stirring to obtain a homogeneous solution. Then 1.0 g POPs was introduced into the round bottom flask and the resulting mixture was stirred under argon atmosphere at room temperature for another 24 h. The Rh<sub>1</sub>/POPs was obtained by filtrating, washing with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and drying under vacuum at 60 °C. The Rh<sub>1</sub><sup>I</sup>/POPs and Rh<sub>1</sub><sup>II</sup>/POPs were obtained by using 0.0254 g Rh(CO)<sub>2</sub>(acac) and 0.0271g RhCl<sub>3</sub>·nH<sub>2</sub>O (37 wt.% metal content) instead of Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub>, respectively.

Rh/AC and Rh<sup>II</sup>/AC: Rh/AC and Rh<sup>II</sup>/AC were prepared by impregnation using the coarse coconut shell activated carbon (AC, BET surface area 1054 m<sup>2</sup>/g) of 40-60 mesh as supports and Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub>, RhCl<sub>3</sub>·nH<sub>2</sub>O as the precursors, respectively. For Rh/AC, 0.0191 g Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub> was dissolved in 30 mL of ultra-pure water and stirred for 20 min to get the precursor solution. Then 1.0 g AC was added into the solution followed by drying at 90 °C for 3 h, 120 °C for 4 h and calcined at 300 °C for 4 h under argon atmosphere finally. For Rh<sup>II</sup>/AC with mononuclear carbonyl group of Rh, the preparation methods were followed by our previous work (except for the 0.0271 g RhCl<sub>3</sub>·nH<sub>2</sub>O and 1.0 g AC).<sup>2</sup>

Rh/Al<sub>2</sub>O<sub>3</sub>: 0.0191 g Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub> was dissolved in 30 mL of ultra-pure water and stirred for 20 min to get the precursor solution. Then 1.0 g Al<sub>2</sub>O<sub>3</sub> (BET surface area 174 m<sup>2</sup>/g) was added into the solution under magnetic stirring. After mixing for 9 h at

room temperature, the solution was dried at 80 °C using a rotary evaporator. Then the catalyst was calcined at 500 °C for 3 h.

Rh/SBA-15: 0.0191 g  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  was dissolved in 30 mL of ultra-pure water and stirred for 20 min. Then 0.1173 g triethanolamine (TEOA) (TEOA:Rh molar ratio of 8:1) was added into the solution under stirring for 30 min. The Rh precursor solution was injected via a syringe pump (10 mL/hr) into a 30 mL suspension of SBA-15 support (1.0 g, BET surface area 703  $\text{m}^2/\text{g}$ ) under stirring. After mixing for 12 h, the solution was dried at 80 °C using a rotary evaporator. Then the catalyst was calcined in flowing air at 450 °C for 4 h.

### **Catalyst test**

All the reactions were carried out using zirconium autoclave (150 mL of inner volume) reactor equipped with a magnetic stirrer. In a typical run, Rh catalyst (0.15g, Rh content = 1.0 wt.%), *p*-TsOH·H<sub>2</sub>O (1.0 mmol), acetic acid (100 mmol), olefin (5.7 mmol), CH<sub>3</sub>I (2.77 mmol) and ultra-pure water (30 mmol) were successively added into the reactor. The autoclave was sealed, pressure tested and cautiously purged three times with 1.0 MPa carbon monoxide (CO). Then the reactor was pressurized with 1.0 MPa CO at room temperature and the reaction mixture was stirred and heated to 180 °C. After 16 h, the autoclave was cooled down to room temperature by an ice-water bath and then carefully vented. The liquid product was analyzed by gas chromatography equipped with an HP-FFAP column (length = 30 m, diameter = 0.32 mm) and a flame ionization detector. The column was isothermally at 35 °C for 3 min, then heated to 150 °C at 8.5  $\text{min}^{-1}$  and to 240 °C at 10  $\text{min}^{-1}$ . 1-phenylethanol was used as an internal standard for GC analysis to give a conversion of olefins and yield of products.

### **Recycle and leaching experiments**

For the recycle experiments, the following procedure was followed. After the reaction, the spent Rh<sub>1</sub>/POPs catalyst was obtained by centrifugation. The solid

catalyst was washed thoroughly with solvents acetic acid and dichloromethane in turn. It would be reused in the next run after dried under vacuum at 65 °C for 6 h.

Metal leaching experiment was conducted in a way of hot filtration to make sure that Rh<sub>1</sub>/POPs catalyst worked as a real heterogeneous way. A typical reaction was stopped abruptly at 180 °C after 4 h with a yield of 28% and then the hot reaction mixture separated from the solid catalyst continued to react in the reactor for another 12h.

### **Water adsorption tests**

POPs and PIPs were dried under vacuum at 90 °C for 24 h prior to the water adsorption tests. 0.5 g sample was wrapped by 450 mesh gauze and immersed into 80 mL water in a 100 mL beaker for 48 h at room temperature, a sufficient time for adsorption saturation. Then, the sample was taken out, wiped off the excess water on the surface with a filter paper and weighed finally.

$$W_a = \frac{m_2 - m_1}{m_0} \times 100\%$$

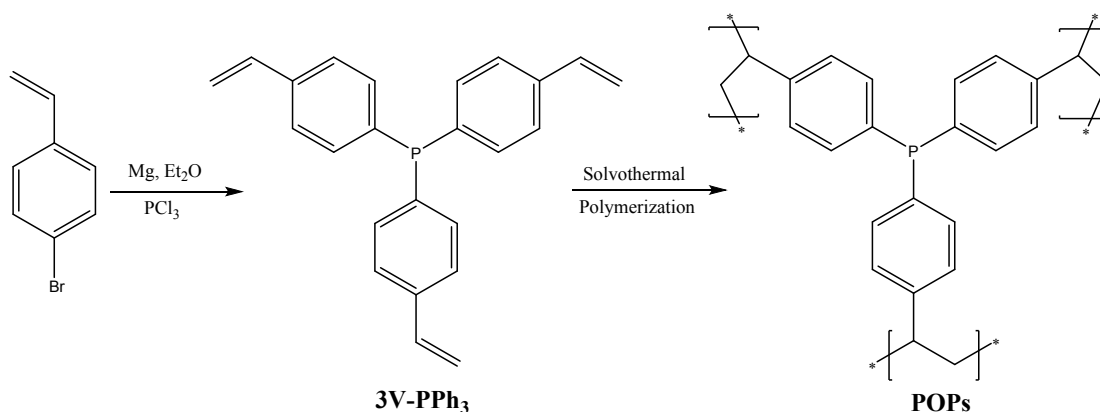
$W_a$ : water adsorption ratio

$m_0$ : the net mass of samples, namely 0.5 g

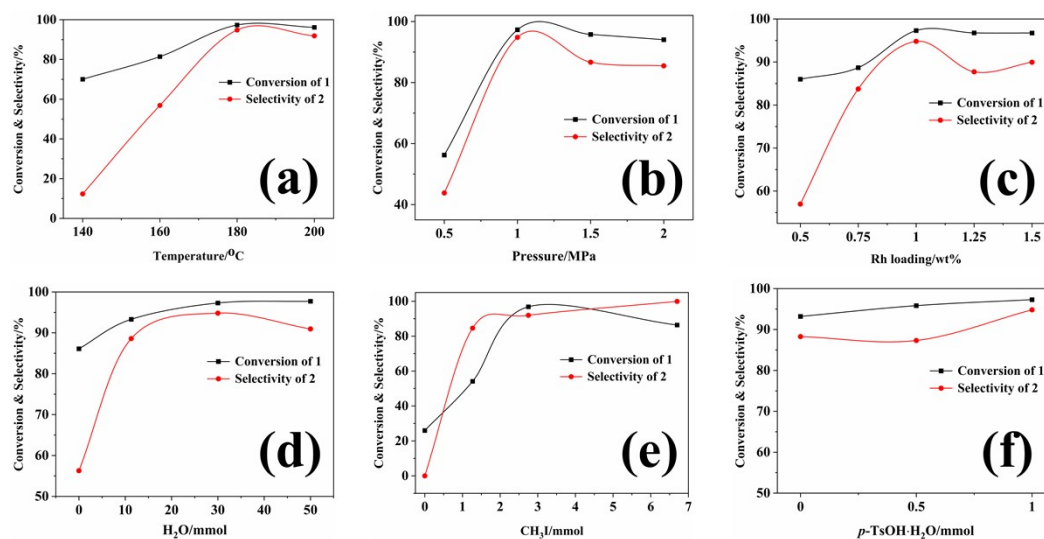
$m_1$ : the mass of samples before adsorption tests

$m_2$ : the mass of samples after adsorption tests

## **Results and discussion**

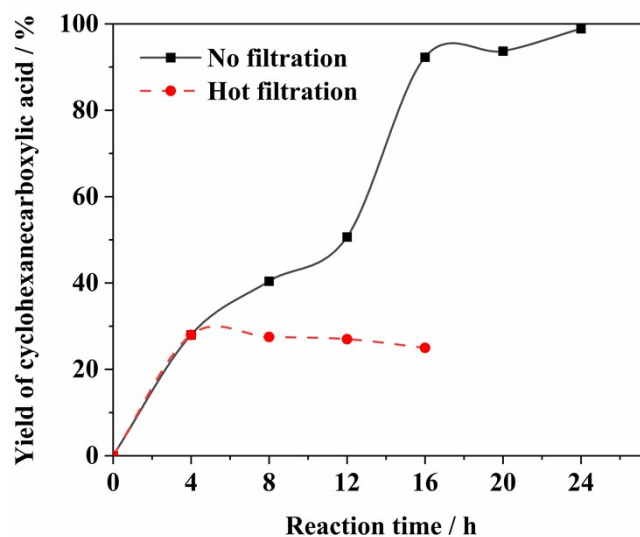


**Scheme S1** Synthesis of POPs.

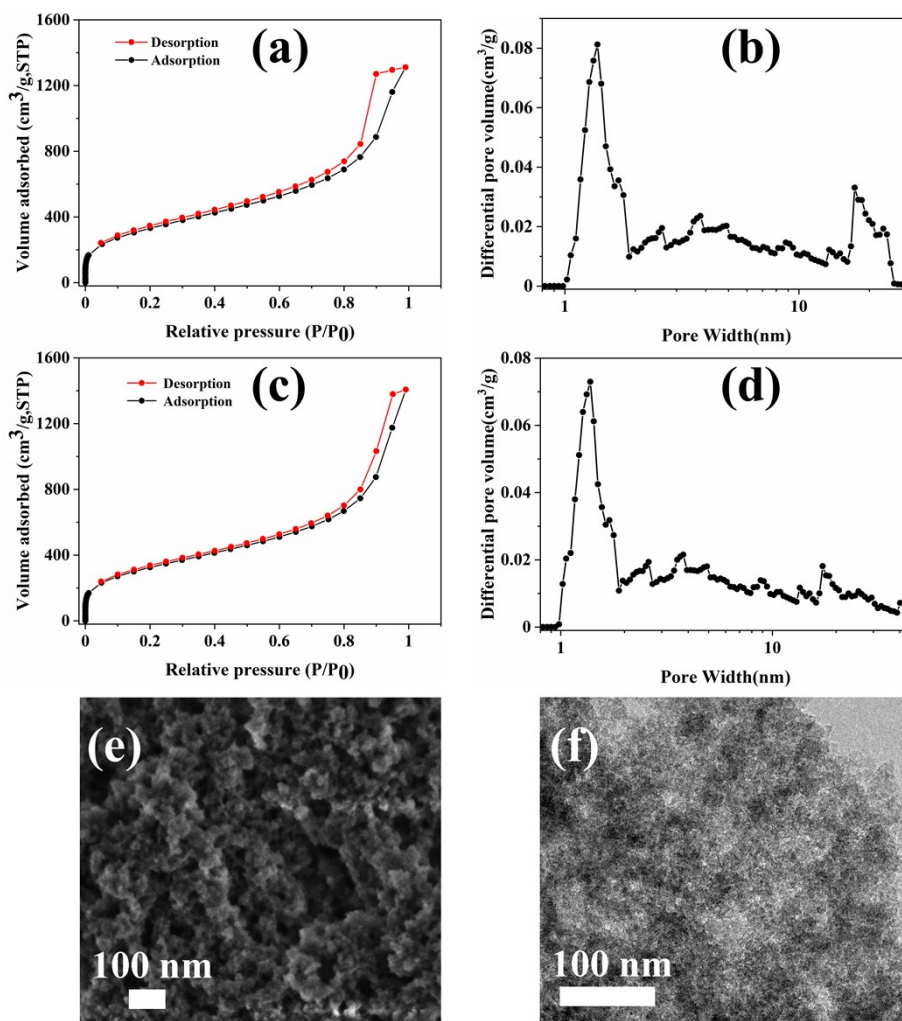


**Figure S1** The optimization of parameters of (a) temperature, (b) pressure of CO, (c) Rh weight loading, dosage of the (d) water, (e) CH<sub>3</sub>I and (f) *p*-TsOH·H<sub>2</sub>O.<sup>a</sup>

<sup>a</sup> Reaction conditions: (a) Catalyst (0.15 g, Rh content = 1.0 wt.%), *p*-TsOH·H<sub>2</sub>O (1.0 mmol), acetic acid (100 mmol), cyclohexene (5.7 mmol), CH<sub>3</sub>I (2.77 mmol) and ultra-pure water (30 mmol), 1.0 MPa (CO at room temperature), 16 h. (b) Catalyst (0.15 g, Rh content = 1.0 wt.%), *p*-TsOH·H<sub>2</sub>O (1.0 mmol), acetic acid (100 mmol), cyclohexene (5.7 mmol), CH<sub>3</sub>I (2.77 mmol) and ultra-pure water (30 mmol), 180 °C, 16 h. (c) Catalyst (0.15 g), *p*-TsOH·H<sub>2</sub>O (1.0 mmol), acetic acid (100 mmol), cyclohexene (5.7 mmol), CH<sub>3</sub>I (2.77 mmol) and ultra-pure water (30 mmol), 1.0 MPa (CO at room temperature), 180 °C, 16 h. (d) Catalyst (0.15 g, Rh content = 1.0 wt.%), *p*-TsOH·H<sub>2</sub>O (1.0 mmol), acetic acid (100 mmol), cyclohexene (5.7 mmol) and CH<sub>3</sub>I (2.77 mmol), 1.0 MPa (CO at room temperature), 180 °C, 16 h. (e) Catalyst (0.15 g, Rh content = 1.0 wt.%), *p*-TsOH·H<sub>2</sub>O (1.0 mmol), acetic acid (100 mmol), cyclohexene (5.7 mmol) and ultra-pure water (30 mmol), 1.0 MPa (CO at room temperature), 180 °C, 16 h. (f) Catalyst (0.15 g, Rh content = 1.0 wt.%), acetic acid (100 mmol), cyclohexene (5.7 mmol), CH<sub>3</sub>I (2.77 mmol) and ultra-pure water (30 mmol), 1.0 MPa (CO at room temperature), 180 °C, 16 h.

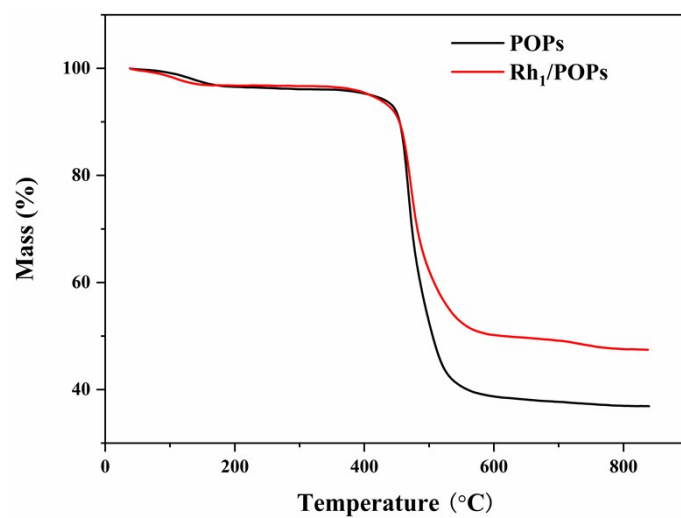


**Figure S2** Hot filtration tests for  $\text{Rh}_1/\text{POPs}$  catalyst in hydrocarboxylation of cyclohexene.

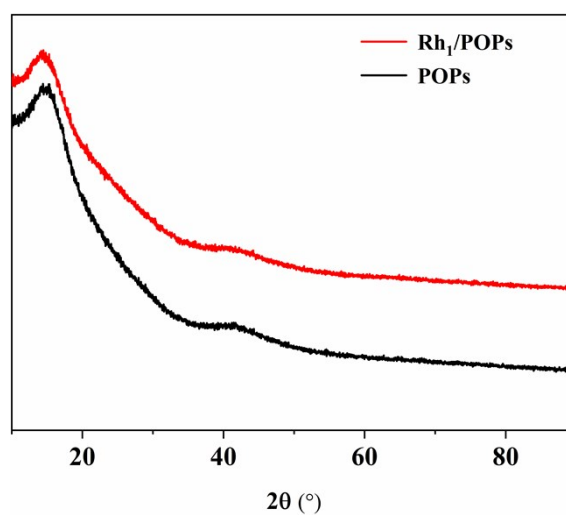


**Figure S3** (a)  $\text{N}_2$  sorption isotherms and (b) pore size distributions of POPs (c)  $\text{N}_2$  sorption isotherms and (d) pore size distributions of  $\text{Rh}_1/\text{POPs}$ , (e) SEM and (f) TEM images of  $\text{Rh}_1/\text{POPs}$ .

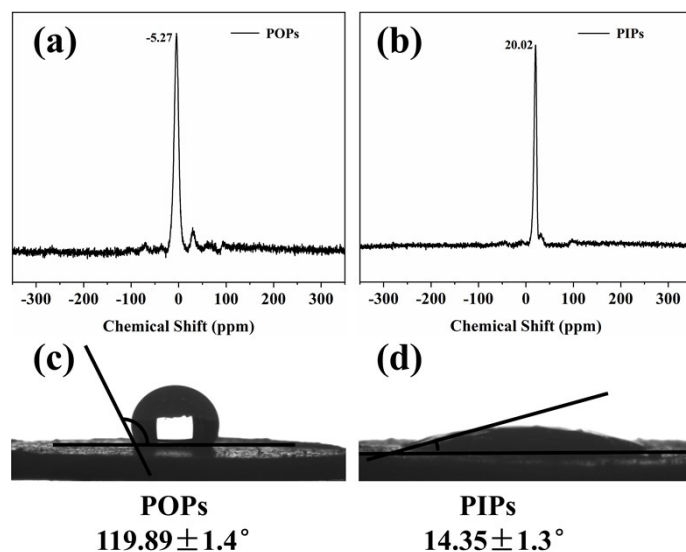




**Figure S4** TG curves of POPs (black) and Rh<sub>1</sub>/POPs (red).



**Figure S5** The XRD patterns of POPs (black) and Rh<sub>1</sub>/POPs (red).



**Figure S6** Solid-state <sup>31</sup>P NMR spectrum of (a) POPs and (b) PIPs. Water droplet (3 μL) images and water contact angle measurements on (c) POPs and (d) PIPs.

**Table S1** The Rh loading of fresh and spent Rh<sub>1</sub>/POPs catalysts analyzed by ICP-OES.

Samples	Rh loading	
	(wt.%)	(mmol/gcat)
Fresh Rh <sub>1</sub> /POPs	0.99	0.0966
Spent Rh <sub>1</sub> /POPs	0.96	0.0931

**Table S2** The water adsorption ratio of POPs and PIPs.

Samples	$W_a$ (%)
POPs	540
PIPs	1446

## References

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2. S. Feng, X. Song, Y. Liu, X. Lin, L. Yan, S. Liu, W. Dong, X. Yang, Z. Jiang and Y. Ding, *Nat. Commun.*, 2019, **10**, 5281.