

## Electronic Supplementary Information

### Hydrogenation of levulinic acid to $\gamma$ -valerolactone over hydrophobic Ru@HCPs catalysts

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## **Experiment section**

### **Materials**

Levulinic acid,  $\gamma$ -valerolactone, and alpha-Angelica lactone were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. 4-hydroxyvaleric acid was supplied by Shanghai Macklin Biochemical Co., Ltd. Phenylphosphonic acid, 1, 3, 5-triphenylbenzene, phenylethyl alcohol, and diphenyl sulfoxide were purchased from TCI (Shanghai) Development Co., Ltd. Chlorobenzene, anhydrous  $\text{FeCl}_3$ , 1, 2-dichloroethane, and ethylbenzene were purchased from Sinopharm Chemical Reagent Co., Ltd. Ruthenium trichloride were obtained from CNMC Shenyang Research Institute of Nonferrous Metals Co., Ltd. Phenol and diphenylmethane was purchased from Innochem (Beijing) Co., Ltd. Methylbenzene was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Triphenylamine and dimethoxymethane was supplied by Energy Chemical. Tetrahydrofuran and methanol were purchased from Tianjin Damao Chemical Reagent Factory. Deionized water used in all experiments was obtained from a Milli-Q system (Millipore).

### **Synthesis of TPB-HCPs**

Triphenylamine (TPA, 0.0025 mol) and 1,3,5-triphenylbenzene (TPB, 0.00583 mol) were mixed with dimethoxymethane cross-linker (FDA, 0.06 mol) and dissolved in 1, 2-dichloroethane (DCE, 20 mL). Then, anhydrous  $\text{FeCl}_3$  (0.06 mol) was added rapidly under stirring. The mixture was heated at 45 °C for 5 h to form a network and then heated at 80 °C for 19 h to complete the condensation reaction and to produce a hierarchical porosity polymer. After washing the resulting solid product with methanol several times, until the filtrate liquor was nearly colorless. The product was Soxhlet extracted in methanol for 24 h followed by drying in a vacuum oven at 80 °C for 12 h.

### **Synthesis of EB-HCPs**

Triphenylamine (TPA, 0.0025 mol) and ethylbenzene (EB, 0.0175 mol) were mixed with dimethoxymethane cross-linker (FDA, 0.06 mol) and dissolved in 1, 2-dichloroethane (DCE, 20 mL). Then, anhydrous  $\text{FeCl}_3$  (0.06 mol) was added rapidly under stirring. The mixture was heated at 45 °C for 5 h to form a network and then heated at 80 °C for 19 h to complete the condensation reaction and to produce a hierarchical porosity polymer. After washing the resulting solid product with methanol several times, until the filtrate liquor was nearly colorless. The product was Soxhlet extracted in methanol for 24 h followed by drying in a vacuum oven at 80 °C for 12 h.

### **Synthesis of MB-HCPs**

Triphenylamine (TPA, 0.0025 mol) and methylbenzene (MB, 0.0175 mol) were mixed with dimethoxymethane cross-linker (FDA, 0.06 mol) and dissolved in 1, 2-dichloroethane (DCE, 20 mL). Then, anhydrous FeCl<sub>3</sub> (0.06 mol) was added rapidly under stirring. The mixture was heated at 45 °C for 5 h to form a network and then heated at 80 °C for 19 h to complete the condensation reaction and to produce a hierarchical porosity polymer. After washing the resulting solid product with methanol several times, until the filtrate liquor was nearly colorless. The product was Soxhlet extracted in methanol for 24 h followed by drying in a vacuum oven at 80 °C for 12 h.

### **Synthesis of DPM-HCPs**

Triphenylamine (TPA, 0.0025 mol) and diphenylmethane (DPM, 0.007 mol) were mixed with dimethoxymethane cross-linker (FDA, 0.06 mol) and dissolved in 1, 2-dichloroethane (DCE, 20 mL). Then, anhydrous FeCl<sub>3</sub> (0.06 mol) was added rapidly under stirring. The mixture was heated at 45 °C for 5 h to form a network and then heated at 80 °C for 19 h to complete the condensation reaction and to produce a hierarchical porosity polymer. After washing the resulting solid product with methanol several times, until the filtrate liquor was nearly colorless. The product was Soxhlet extracted in methanol for 24 h followed by drying in a vacuum oven at 80 °C for 12 h.

### **Synthesis of PA-HCPs**

Triphenylamine (TPA, 0.0025 mol) and phenylethyl alcohol (PA, 0.0175 mol) were mixed with dimethoxymethane cross-linker (FDA, 0.06 mol) and dissolved in 1,2-dichloroethane (DCE, 20 mL). Then, anhydrous FeCl<sub>3</sub> (0.06 mol) was added rapidly under stirring. The mixture was heated at 45 °C for 5 h to form a network and then heated at 80 °C for 19 h to complete the condensation reaction and to produce a hierarchical porosity polymer. After washing the resulting solid product with methanol several times, until the filtrate liquor was nearly colorless. The product was Soxhlet extracted in methanol for 24 h followed by drying in a vacuum oven at 80 °C for 12 h.

### **Synthesis of PH-HCPs**

Triphenylamine (TPA, 0.0025 mol) and phenol (PH, 0.0175 mol) were mixed with dimethoxymethane cross-linker (FDA, 0.06 mol) and dissolved in 1, 2-dichloroethane (DCE, 20 mL). Then, anhydrous FeCl<sub>3</sub> (0.06 mol) was added rapidly under stirring. The mixture was heated at 45 °C for 5 h to form a network and then heated at 80 °C for 19 h to complete the condensation

reaction and to produce a hierarchical porosity polymer. After washing the resulting solid product with methanol several times, until the filtrate liquor was nearly colorless. The product was Soxhlet extracted in methanol for 24 h followed by drying in a vacuum oven at 80 °C for 12 h.

### **Synthesis of Ru@HCPs**

Ru@HCPs were synthesized by the impregnation method: 50 ml of methanol and 500 mg of the HCPs support were added to a 100 ml flask and stirred for 2 h at room temperature. Then a certain amount of RuCl<sub>3</sub> methanol solution was added to the flask and stirred for 24 h. Finally, the solution was spun dry. The synthesized catalysts need to be placed in a quartz tube and reduced at 300°C for 2 h under continuous pure H<sub>2</sub> flow.

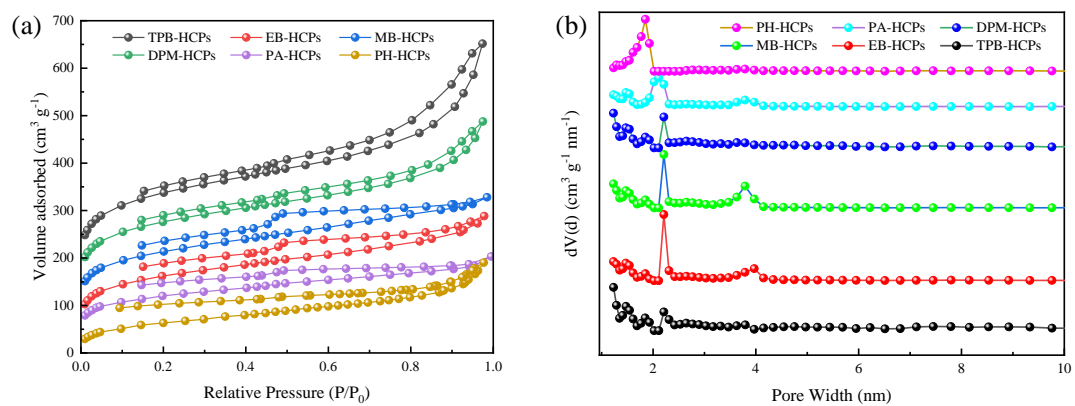
### **Characterization Methods**

X-ray photoelectron spectroscopy (XPS) was performed on a Thermofisher ESCALAB 250Xi spectrometer using AlK $\alpha$  radiation. The binding energies were calibrated using the C 1s level (284.8 eV) as the internal standard reference. Empyrean-100 powder diffraction system with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) was employed to record X-ray diffraction (XRD) of the obtained materials between 5° and 80° (40 kV, mA). The Ru leaching in the sample was detected by inductively coupled plasma–optical emission spectroscopy (ICP-OES) on a PerkinElmer ICP-OES 7300DV. N<sub>2</sub> adsorption/desorption isotherms were determined at 77 K on a Quantachrome Instrument, and the obtained materials were degassed under 300 °C before determination. Fourier transform infrared (FT-IR) spectra were measured in KBr media on a Bruker Tensor 27. The morphologies of the materials were examined by transmission electron microscopy (TEM) on the JEM-2100F electron microscope. Solid-state NMR spectra (CP/MAS <sup>13</sup>C-NMR) were obtained on a WB 400 MHz Bruker Avance II spectrometer. HR-TEM images and EDS Mapping were obtained on the FEI Talos F200X G2 and superX-G2. Water adsorption/desorption isotherms were collected at 298K on the BELSORP-maxII. Temperature programmed reduction (H<sub>2</sub>-TPR) was measured on a Micromeritics AutoChem II apparatus.

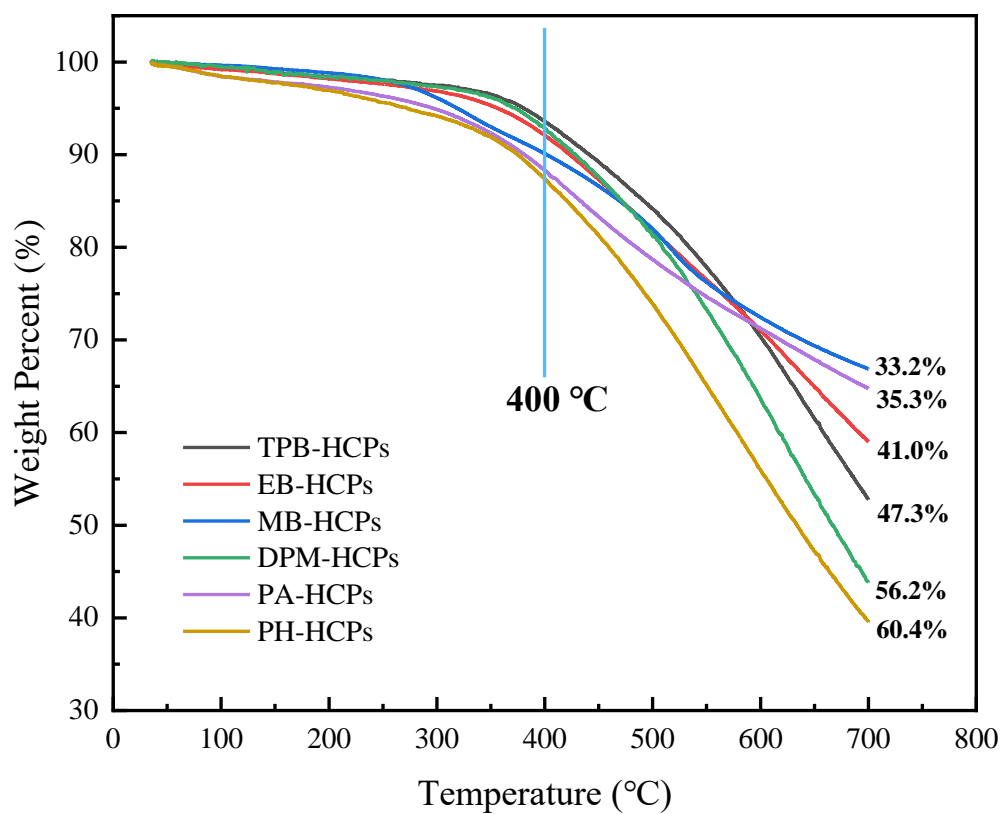
### **Hydrogenation procedures and product analysis**

The hydrogenation of LA was performed in a 60 mL autoclave. Typically, 10 mL of water as the solvent, 2.5 mmol of LA, and 15 mg of catalyst were added into the autoclave. The reactor was closed tightly, which was then flushed with hydrogen to remove air, and the H<sub>2</sub> pressure was regulated to

1.0 MPa before the reaction. The autoclave then was heated up to the reaction temperature under stirring at 500 rpm. After the reaction finished, the reactor was cooled to room temperature. Chlorobenzene was added as an internal standard. The final liquid products were identified by Agilent 7890 N GC/5973 MS detector and quantitated by Agilent 7890 A GC equipped with a CP-Volamine (30.0 m × 0.320 $\mu$ m) and flame ionization detector.

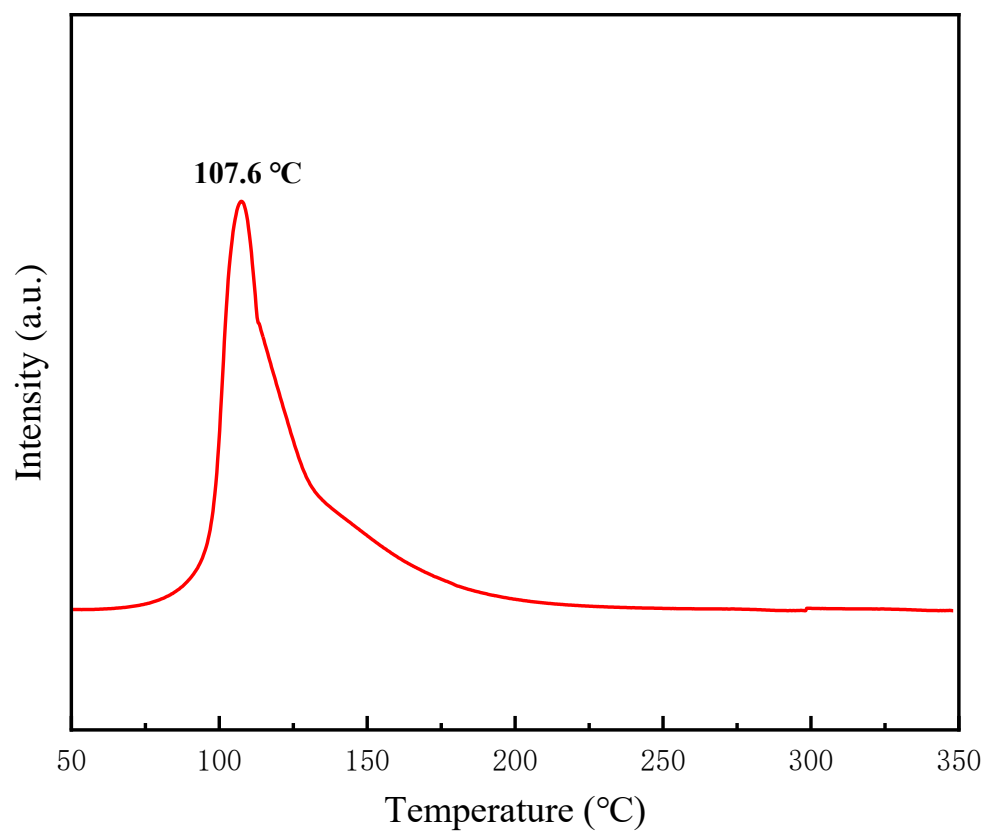


**Fig. S1 (a) N<sub>2</sub> adsorption/desorption isotherms and (b) pore size distribution of different HCPs.**

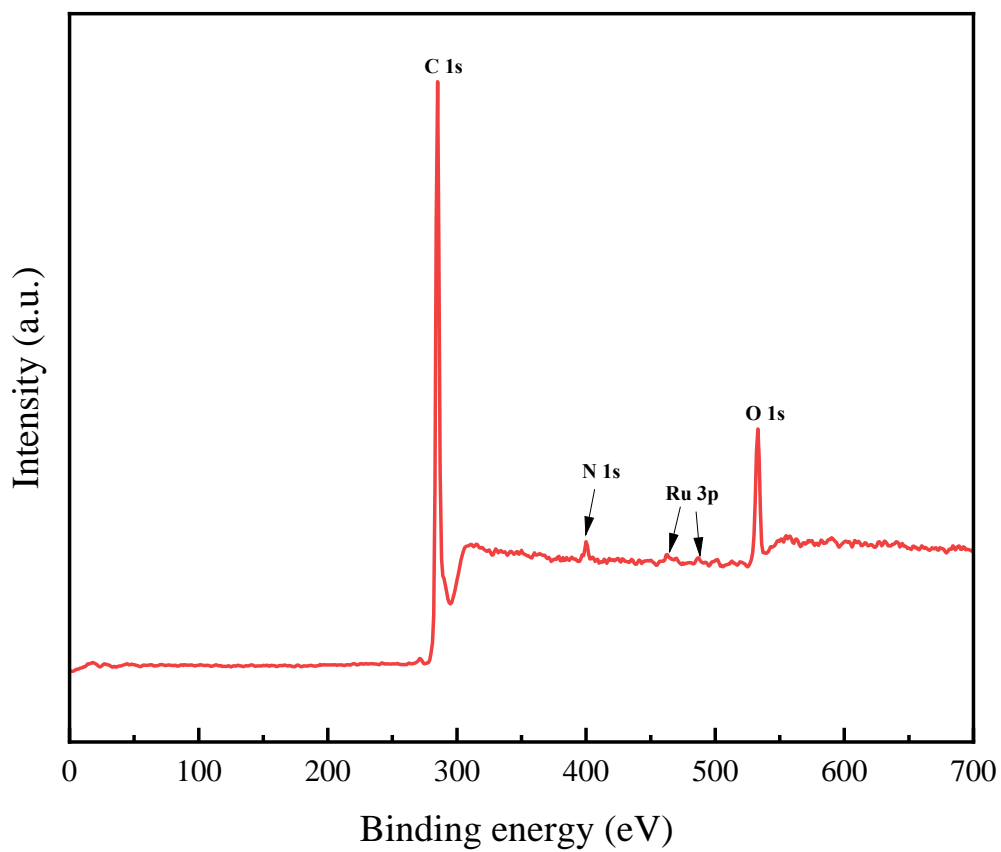


**Fig. S2 Thermal stability of different supports. TGA curves of TPB-HCPs, EB-HCPs, MB-HCPs, DPM-HCPs, PA-HCPs, and PH-HCPs.**

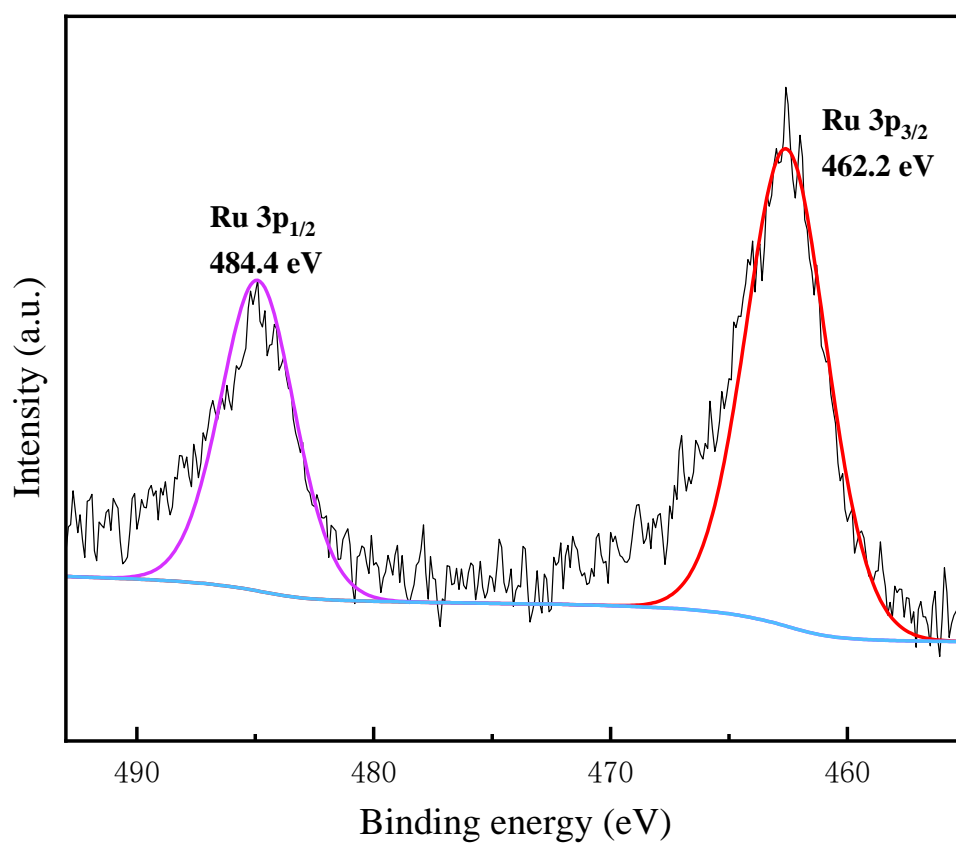




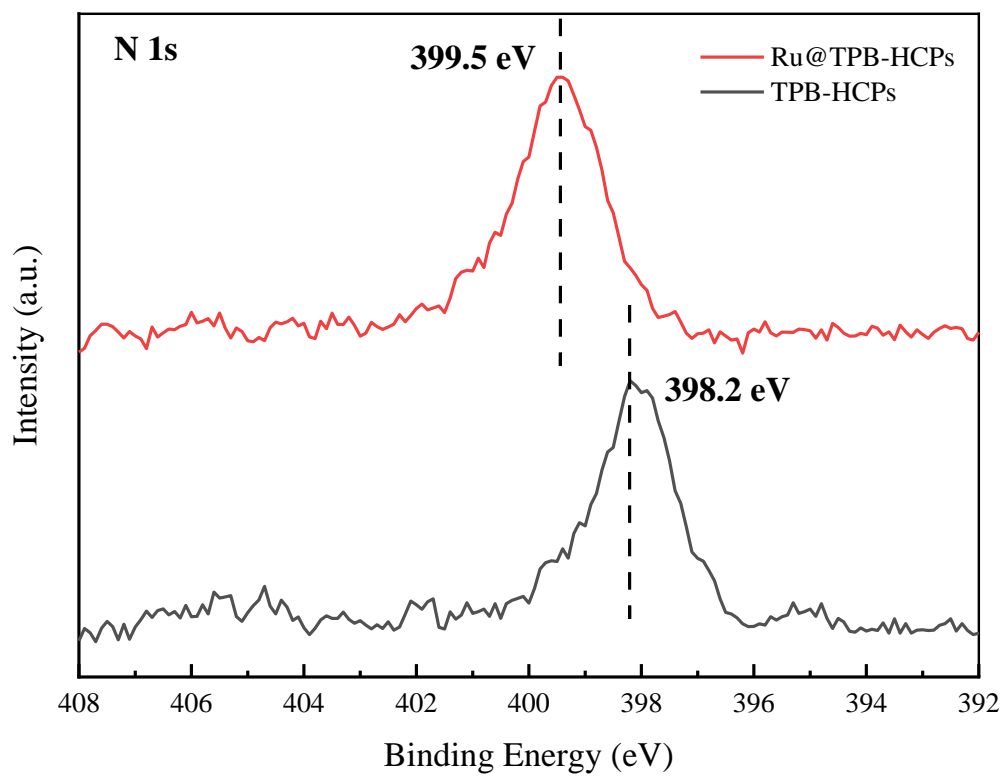
**Fig. S3 H<sub>2</sub>-TPR profiles of the Ru@TPB-HCPs catalyst.**



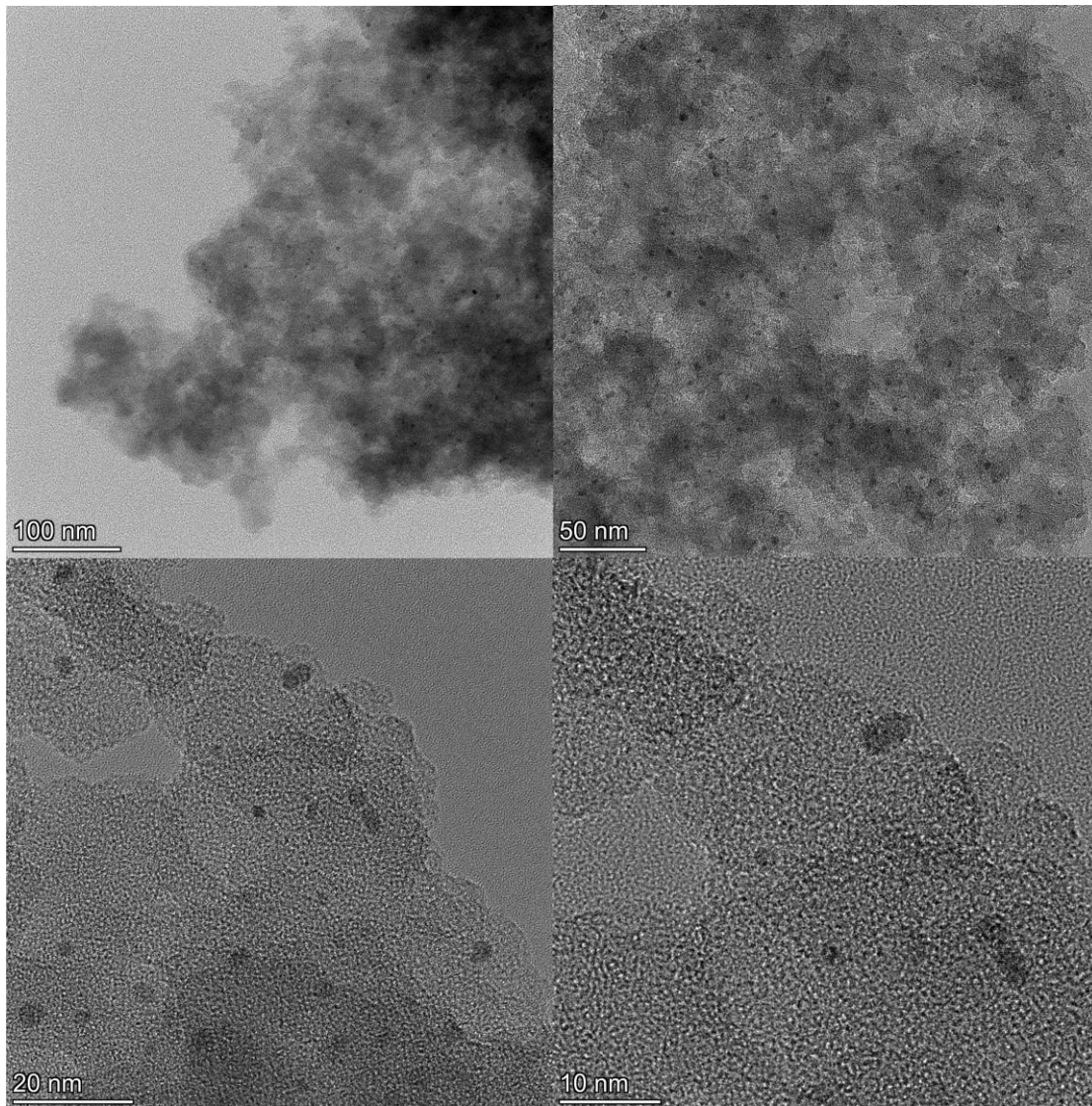
**Fig. S4 XPS survey of the Ru@TPB-HCPs catalyst.**



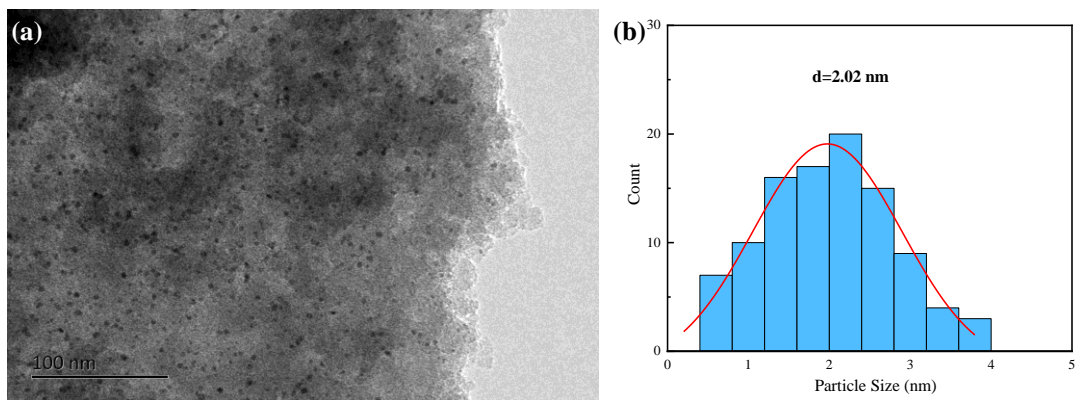
**Fig. S5 Ru 3p XPS spectra of the Ru@TPB-HCPs catalyst.**



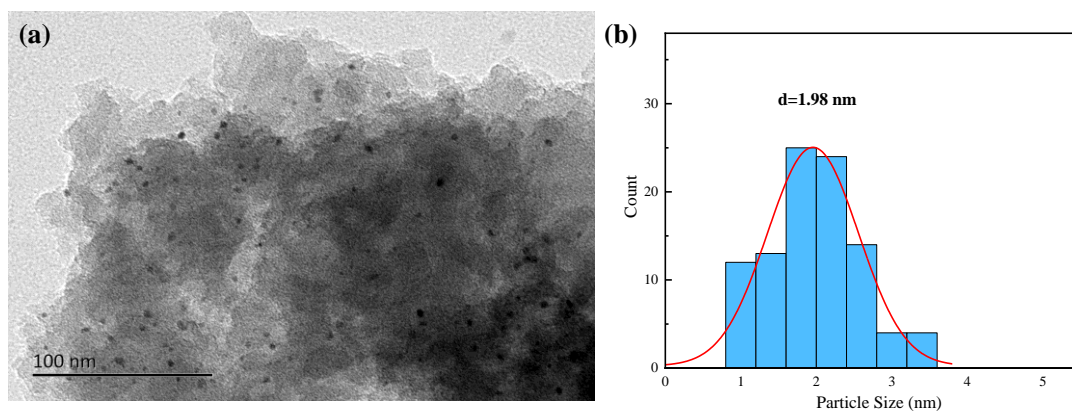
**Fig. S6 XPS spectra of the N 1s region for TPB-HCPs and Ru@TPB-HCPs.**



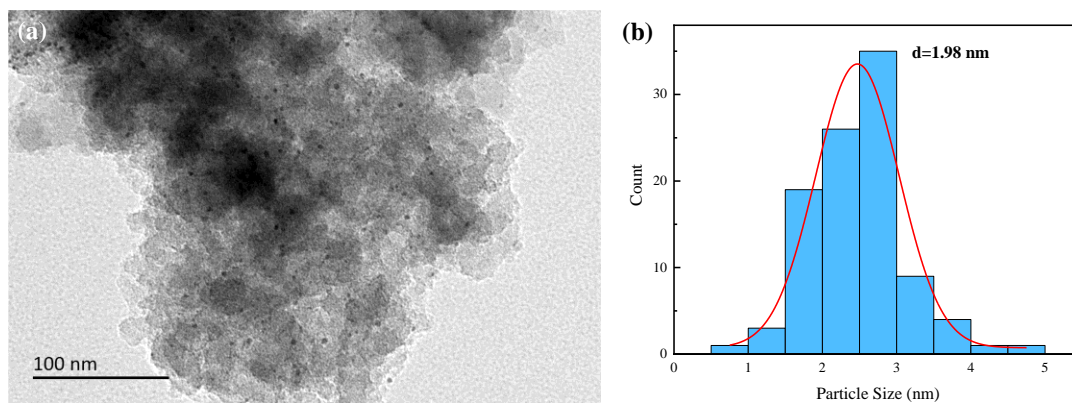
**Fig. S7 TEM images the Ru@TPB-HCPs catalyst.**



**Fig. S8 (a) TEM images and (b) the distribution of particle size of the Ru@EB-HCPs catalyst.**

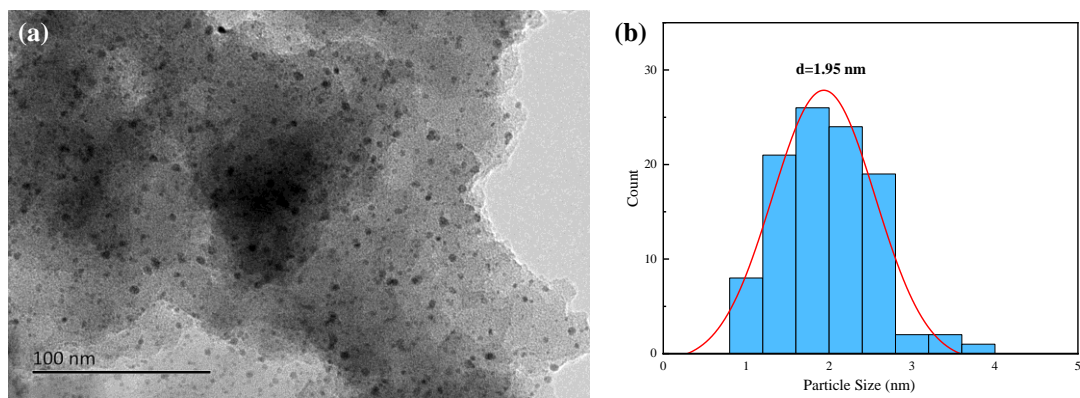


**Fig. S9 (a) TEM images and (b) the distribution of particle size of the Ru@MB-HCPs catalyst.**

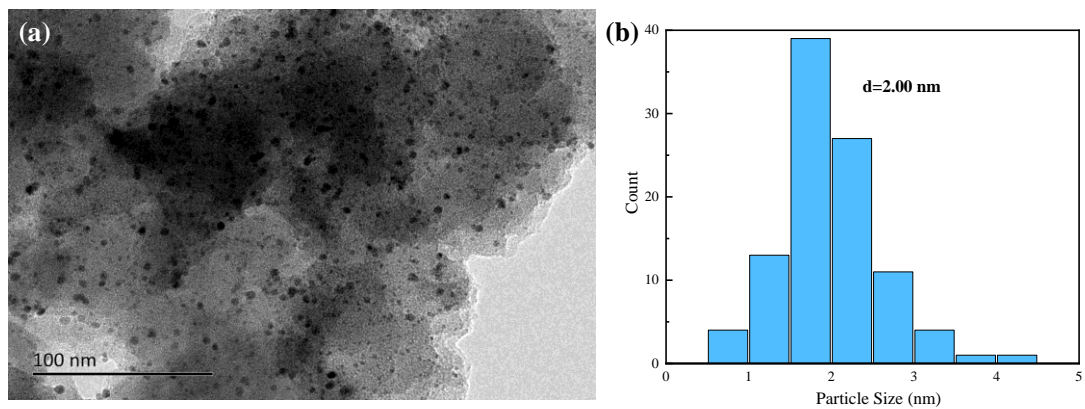


**Fig. S10 (a) TEM images and (b) the distribution of particle size of the Ru@DPM-HCPs catalyst.**

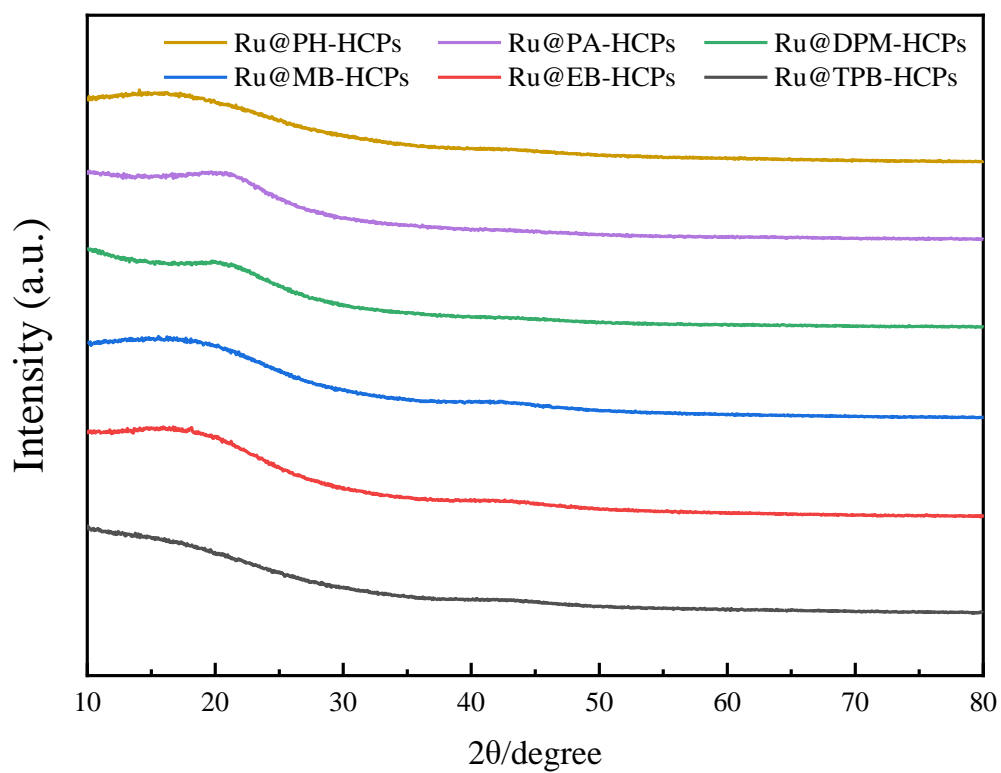




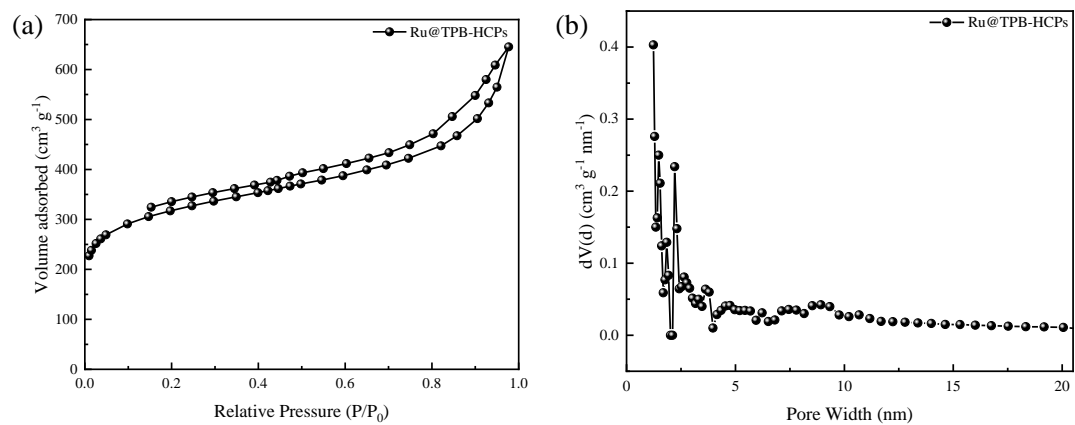
**Fig. S11 (a) TEM images and (b) the distribution of particle size of the Ru@PA-HCPs catalyst.**



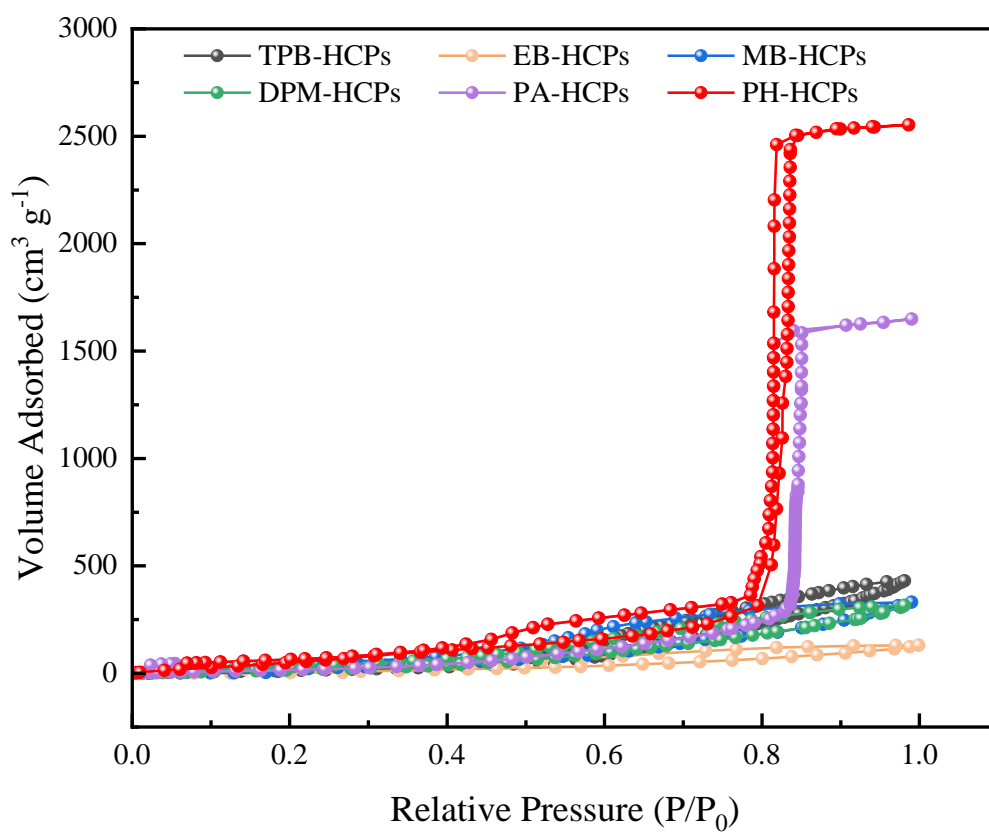
**Fig. S12 (a) TEM images and (b) the distribution of particle size of the Ru@PH-HCPs catalyst.**



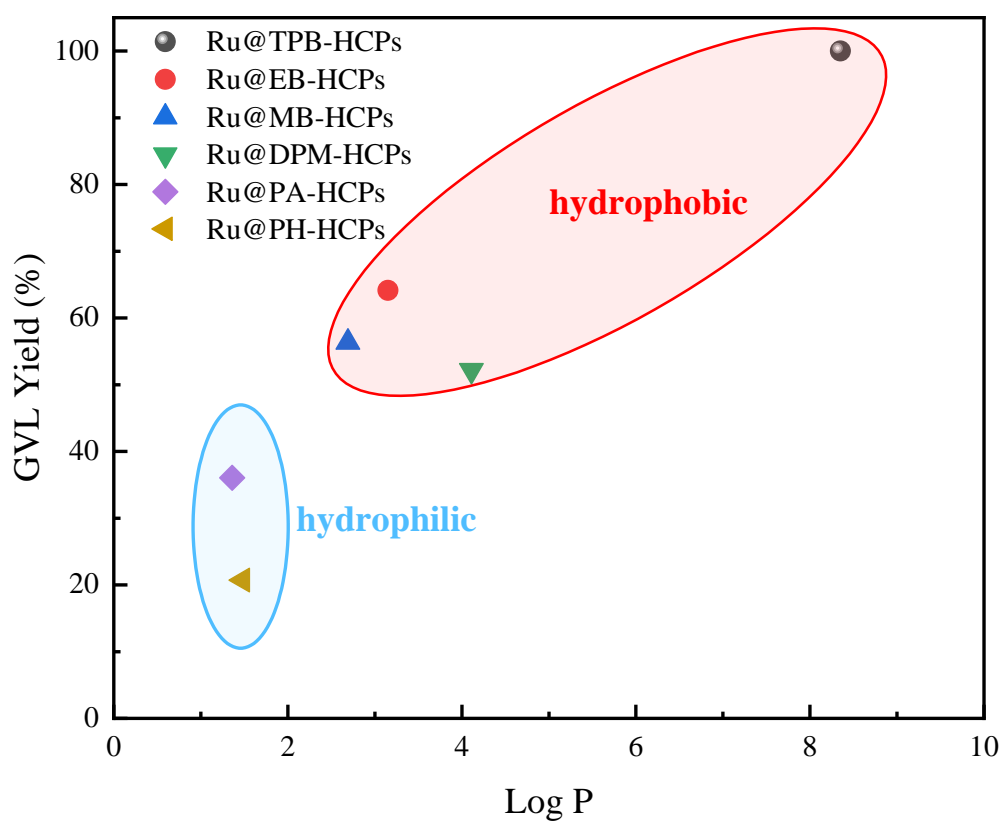
**Fig. S13 XRD spectra of different Ru@HCPs catalysts.**



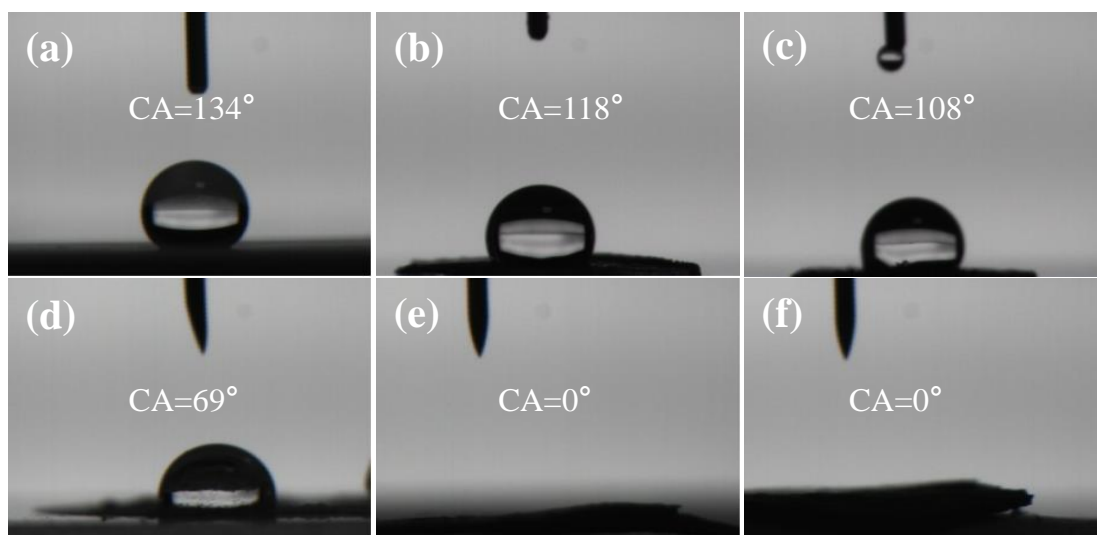
**Fig. S14 (a) N<sub>2</sub> adsorption/desorption isotherms and (b) pore size distribution of the Ru@TPB-HCPs catalyst.**



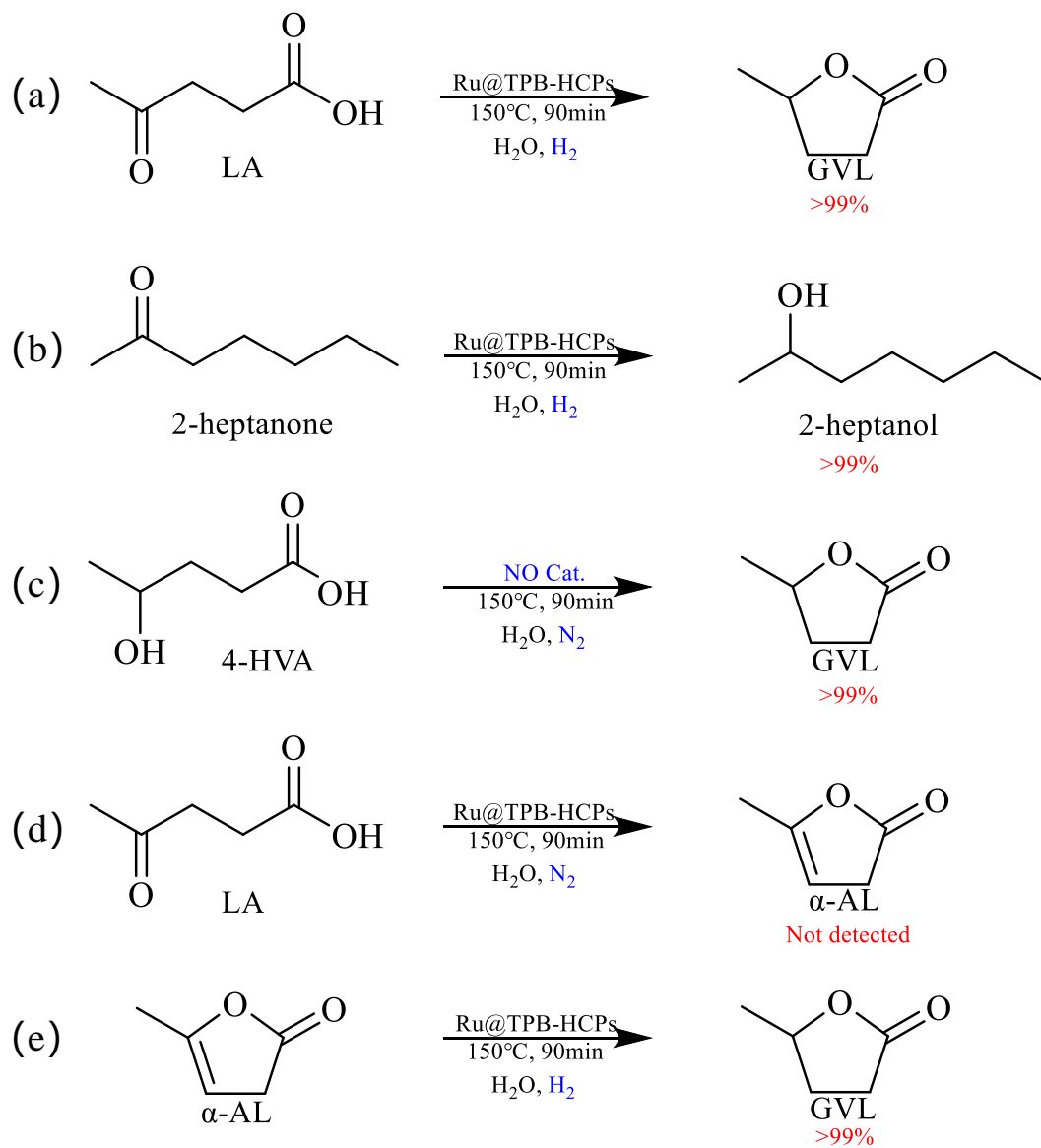
**Fig. S15** Water adsorption tests of different HCPs supports.



**Fig. S16** Catalytic activity of different wettability catalysts. The wettability of HCPs is represented by the monomer's Log P value.

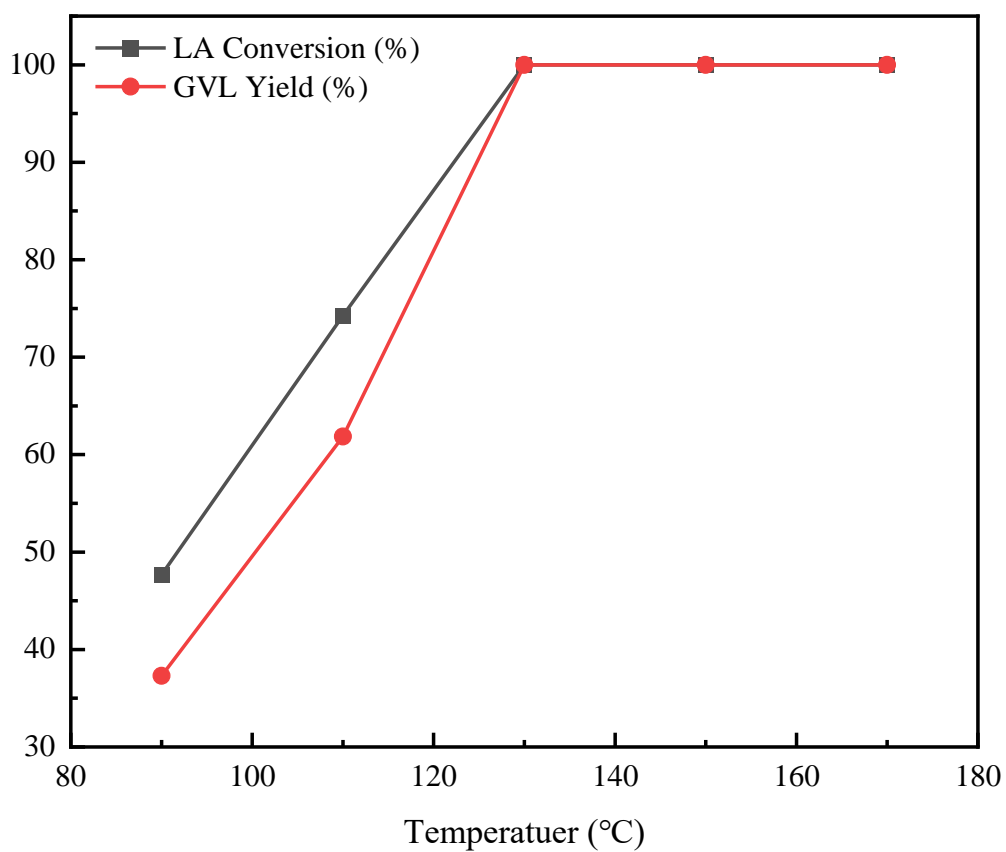


**Fig. S17** Water contact angle images of different supports: (a) TPB-HCPs, (b) EB-HCPs, (c) MB-HCPs, (d) DPM-HCPs, (e) PA-HCP, and (f) PH-HCPs.



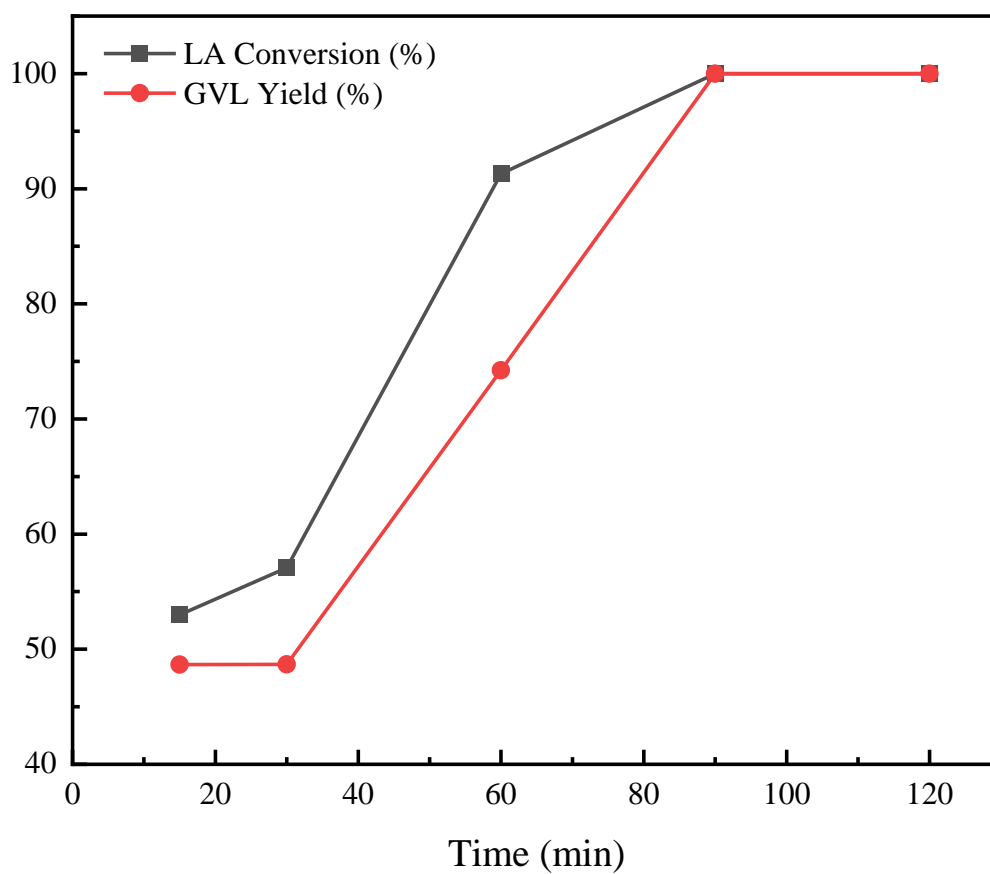
**Fig. S18 Control experiments.**





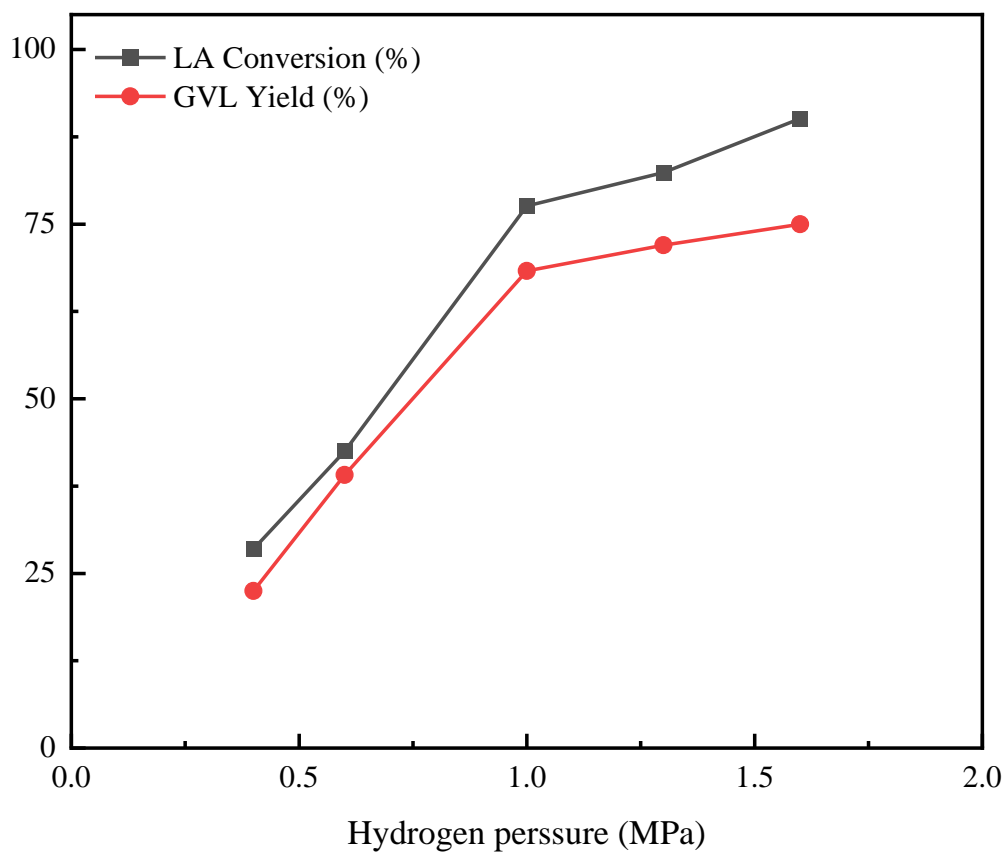
**Fig. S19 Conversion of LA to GVL at different reaction temperatures over Ru@TPB-HCPs catalyst.**

Reaction Condition: 2.5 mmol LA, 10 ml water, 1 MPa H<sub>2</sub>, 15 mg catalyst, 120 min.



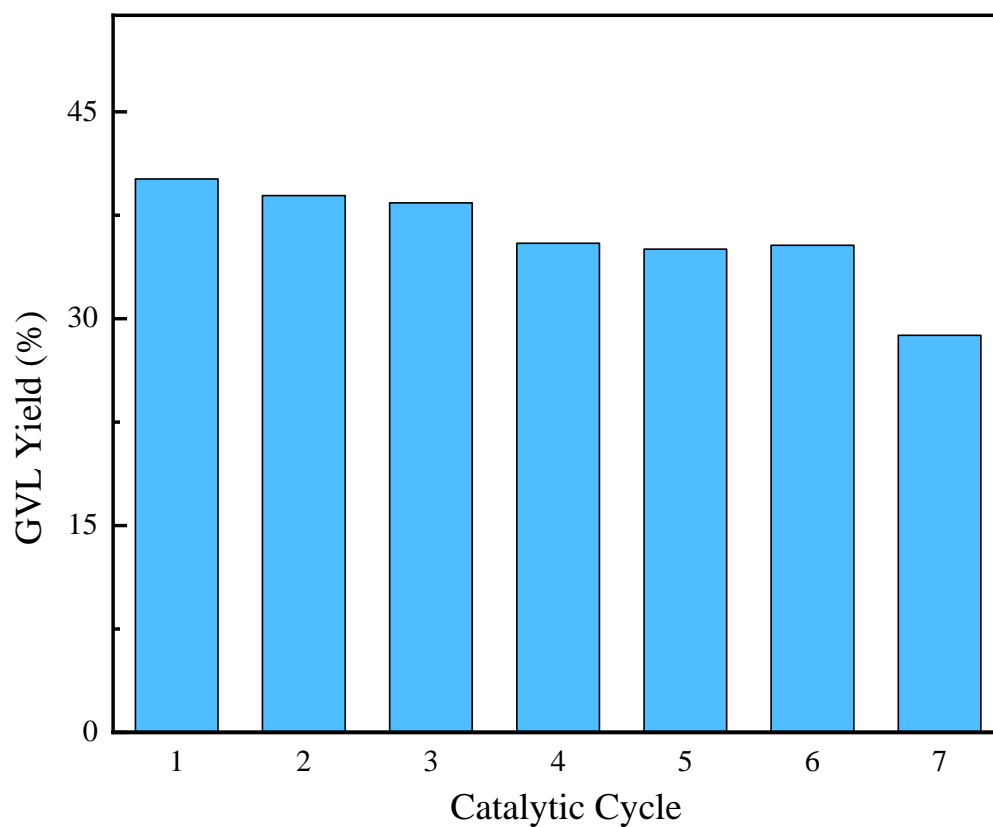
**Fig. S20 Conversion of LA to GVL at different reaction time over Ru@TPB-HCPs catalyst.**

Reaction Condition: 2.5 mmol LA, 10 ml water, 1 MPa H<sub>2</sub>, 15 mg catalyst, 130 °C.



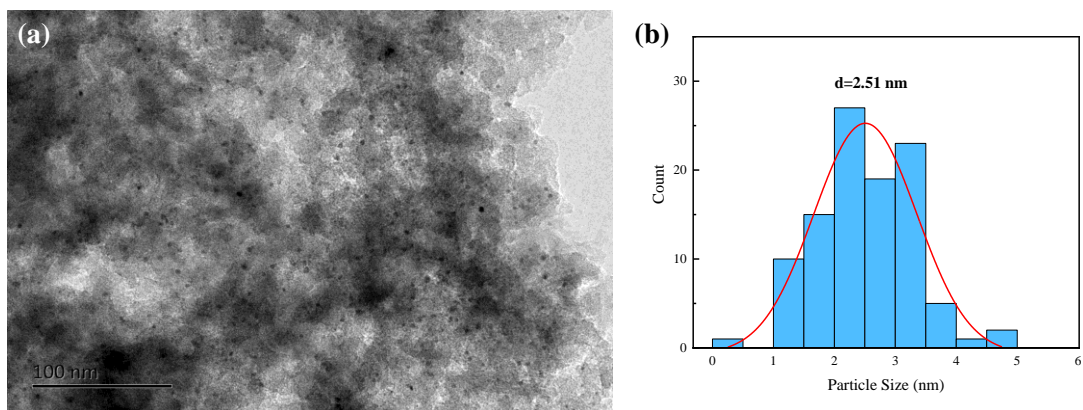
**Fig. S21 Conversion of LA to GVL at different H<sub>2</sub> pressure over Ru@TPB-HCPs catalyst.**

Reaction Condition: 2.5 mmol LA, 10 ml water, 15 mg catalyst, 130 °C, 60 min.



**Fig. S22 Stability tests of the Ru@TPB-HCPs catalyst.**

Reaction conditions: 2.5 mmol LA, 10 mL water, 1 MPa H<sub>2</sub>, 15 mg catalyst, 150 °C, 15 min.



**Fig. S23 (a) TEM images and (b) the distribution of particle size of the used Ru@TPB-HCPs catalyst.**

**Table S1. Composition and Porosity of different HCPs.**

Entry	Support	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{p}}^{\text{b}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$D_{\text{p}}^{\text{c}}$ (nm)
1	TPB-HCPs	1137	0.98	1.23
2	EB-HCPs	619	0.47	2.21
3	MB-HCPs	729	0.50	2.21
4	DPM-HCPs	926	0.73	1.23
5	PA-HCPs	416	0.31	2.11
6	PH-HCPs	289	0.32	1.84

<sup>a</sup> Surface area calculated from nitrogen adsorption isotherms at 77 K using the multipoint BET equation.

<sup>b</sup> Pore volume calculated from nitrogen adsorption isotherms at 77 K and  $P/P_0 = 0.99$ .

<sup>c</sup> Pore width calculated from nitrogen adsorption isotherms at 77 K using the NLDFT model.

**Table S2. Comparison of Catalytic activity of different catalysts.**

Catalyst	Ru (wt %)	Log P	water adsorption values (cm <sup>3</sup> g <sup>-1</sup> )	LA Conversion (%)	GVL Yield (%)
Ru@TPB-HCPs	0.71	8.35	430	>99	>99
Ru@EB-HCPs	0.54	3.15	131	74.5	64.1
Ru@MB-HCPs	0.63	4.14	331	67.1	56.3
Ru@DPM-HCPs	0.49	2.69	312	66.7	52.2
Ru@PA-HCPs	0.74	1.36	1650	46.1	36.1
Ru@PH-HCPs	0.69	1.48	2553	20.8	20.7

Reaction Condition: 2.5 mmol LA, 10 ml water, 1 MPa H<sub>2</sub>, 15 mg catalyst, 150 °C, 120 min.