In-situ Synthesize High Dispersed Catalytic Active Sites to Enhance the Catalysis Performance

Ting Suo, Xiang Shi, Xiaoxuan Zhang*, Shizhong Luo*, and Ruirui Yun*

The Key Laboratory of Functional Molecular Solids Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, 214001, China

Corresponding author: Ruirui Yun

E-mail: ruirui58@ahnu.edu.cn; shzhluo@ahnu.edu.cn

S1. Materials and Instrumentation

All chemicals were from commercial and used without further purification: Cobalt (Il) nitrate hexahydrate (Aladdin, AR, 99%), Zinc(Il) nitrate hexahydrate (Aladdin, AR, 99%), ethanol (Sinopharm Chemical Reagent Co., Ltd., AR, ≥99.7%), methanol (Sinopharm Chemical Reagent Co., Ltd., AR, ≥99.7%), deionized water (resistance 18.25 M Ω·cm) from Millipore system , Poly(vinyl pyrrolidone) (PVP, Sigma, MW ~58000), (2-methylimidazole (MelM, Aladdin, AR, 98%),Tannic acid (TA, AR, ≥95%)

Scanning electron microscopy (SEM) was carried out with Hitachi 8100, o perating voltage: 5 kV. Powder X-ray diffraction (PXRD) data were collected a t room temperature using Cu Kα radiation (λ=1.5418 Å) with a SmartLab X-ra y diffractometer and step size 0.02° in the range of 5 to 80° on the voltage of 45 kV with the current of 200 mA and counting time is 4′37″. Transmission e lectron microscopy (TEM) observations were obtained on a Hitachi HT7700 ins trument at an electron accelerating voltage of 100 kV. JEOL-2011 was subjecte d to high-resolution transmission electron microscopy (HR-TEM). Meanwhile, th e BET adsorption isotherms of the samples at 77 K were determined with a Micrometrics ASAP 2020. The post-reaction products were analyzed and identif ied by Thermo gas-mass spectrometer (GC-MS). X-ray photoelectron spectrosco py (XPS) measurements were carried out on a thermal high-performance electro n spectrometer ESCALAB 250. The excitation source was monochromate Al Kα (h v=1486.6 eV). The XPS deconvolution analysis was performed on Avantage soft.

The preparation of samples for SEM analysis: 3 mg sample was dispersed i n ethanol and ultrasonic for a few minutes, and then the dispersed sample was dropped on the copper sheet for SEM analysis.

The preparation of samples for TEM analysis： 3 mg sample was dispersed in ethanol and ultrasonic for a few minutes, and then the dispersed sample was dropped on the copper mesh for TEM analysis.

The samples preparation for surface area and porosity measurements： 100 mg sample has put into the quartz sample tube, and then the sample was degassed at 80 °C for 3-5 hours by vacuum pump. After the degassing is complete, the nitrogen was refilled and weighed again for testing.

S2. Preparation of samples

Synthesis of Co-PVP: All the chemicals were directly used after purchase without further purification. In a typical synthesis, Co-precursor prisms was prepared as the previous report with some modifications. In brief, 1 g of Poly(vinyl pyrrolidone) (PVP, MW~58000) and 2.199 mmol Cobalt (Il) nitrate hexahydrate (0.64g) were added to 200mL ethanol and mixture was stirred by magnetic stirrer. Then the homogenous dissolved solution was heated 85 °C for 4 h under refluxing conditions. Then the product was centrifuged at 10000 rpm and purified by washing hot ethanol (70°C) several times to remove the attached PVP on the surface. The purified light pink product was dried in a vacuum oven at 70 °C overnight.

Synthesis of HN-ZIF-67: In total, 5.2 g of 2-MIm was dissolved into 150 mL of methanol and heated in an oil bath at 110°C as solution A. 20 mg of the above Co precursors prisms was dispersed into 10 mL of methanol as the solution B. Then, solution B was quickly injected into solution A and subsequently heated at 110 °C under refluxing conditions for 30 min. The obtained purple products were separated through centrifugation and washed with methanol for 3 times, and dried in a vacuum drying oven at 80 °C overnight. the ZIF-67 hollow prisms were obtained.

Synthesis of ZIF-8 nano-cube (NC): ZIF-8-NC was synthesized and developed according to literature report. In brief, 2.924 mmol Zinc(Il) nitrate hexahydrate $(Zn(NO_3)_2 6H_2O$, 0.87 g)was dispersed in a 30 mL deionized water, the resulting mixture was named as solution A. 0.1658mol 2-Methylimidazole (2-MIm,13.62 g) and 20 mg hexadecyl trimethyl ammonium bromide(CTAB) was dissolved in 200 mL deionized water., which was stirred to obtained the completely dispersed mixture was named as solution B. After stirring for 5 min, respectively, and then solution B was subsequently quickly added to solution A. The resultant suspension was transferred into a 25 mL Teflon-lined stainless-steel autoclave for 6 h at 120 °C. The precipitate was

collected by centrifugation and washed with the mixed solution of ethanol and deionized water several times and dried in vacuum at 80 °C for overnight. After grinding, white powder was obtained.

Synthesis of HP-C: Tannic acid (150 mg) was dissolved in 20 mL of water, and an appropriate amount of KOH was added to adjust the PH value to approximately 8. The precursors ZIF-8 nano-cube was dipped in a tannic acid solution for approximately for hours until the white color turned green. The precipitate was collected by centrifugation and washed with the deionized water several times and dried in vacuum at 80 °C.

Synthesis of HP@ZIF-67-C: 35 mg of ZIF-8 nano cube-TA ,118 mg of cobalt nitrate hexahydrate and 150mg of polyvinylpyrrolidone (PVP; MW~58000) was dissolved in 10 mL of methanol (solution A), The obtained dispersion was stirred at room temperature for 12 h. 133 g of 2-methylimidazole and an amount of triethylamine solution was dissolved in 10 mL of methanol (solution B). Solution B was mixed with solution A at room temperature under ultrasonication (solution C). Then, the solution C was stirred at room temperature for 24 h, The precipitate was obtained via centrifugation and washed with methanol several times. Finally, the purple precipitate was dried in an oven at 60 °C.

Synthesis of HP-P: Tannic acid (50 mg) was dissolved in 3mL of water, and an appropriate amount of KOH was added to adjust the PH value to approximately 8. The precursors Co-PVP was dipped in a tannic acid solution for approximately for hours until the pink color turned brown. The precipitate was collected by centrifugation and washed with the deionized water several times and dried in vacuum at 80°C.

Synthesis of HP@ZIF-67-P: 35 mg of HP-P ,118 mg of cobalt nitrate hexahydrate and 150mg of polyvinylpyrrolidone (PVP; MW~58000) was dissolved in 10 mL of methanol (solution A), The obtained dispersion was stirred at room temperature for 12 h. 133 g of 2-methylimidazole and an amount of triethylamine solution was dissolved in 10 mL of methanol (solution B). Solution B was mixed with solution A at room temperature under ultrasonication (solution C). Then, the solution C was stirred at room temperature for 24 h, The precipitate was obtained via centrifugation and washed with methanol several times. Finally, the purple precipitate was dried in an oven at 60 °C.

S3. The reduction of variety of nitro compounds:

A series of catalytic hydrogenation reactions of aromatic nitro compounds were carried out in a 25 mL glass reaction bottle with high pressure resistance and a collector constant temperature heating magnetic stirrer. Typically, 0.196mmoL substrate, 2 mL ethanol solution, 3 mL hydrazine hydrate and 10 mg catalyst were filled react-ion bottle, and then quickly transferred to a heat-collecting thermostatic magnetic stirrer, which could be heated, and reacted at room temperature for 20 min. Following the reaction, 2 mL of supernatant was taken and 2 mL of ethyl acetate was added for extraction. The supernatant was diluted twice with ethanol and then the conversion rate and selectivity were tested by GC-MS with n-dodecane as the internal standard.

S4. The characterization of the samples
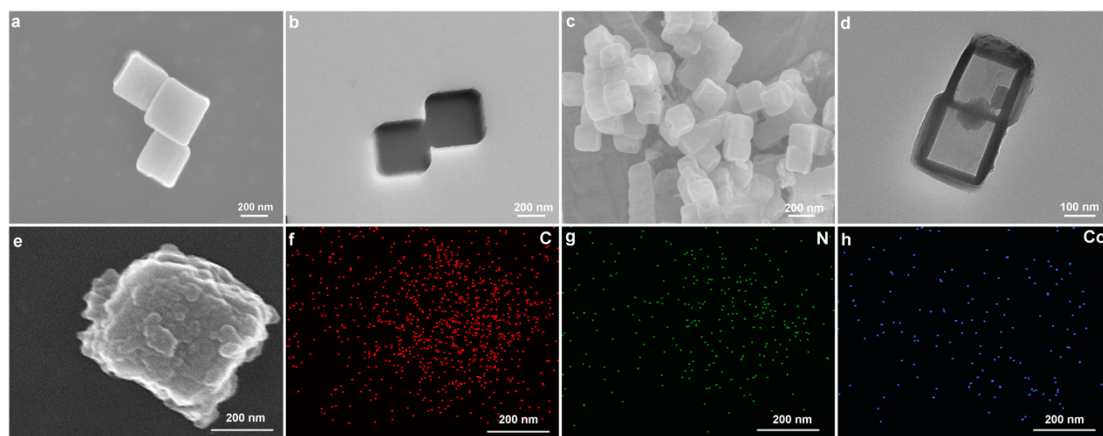
Figure S1. a) and b) SEM and TEM images of ZIF-8-NC; c) and d) the SEM and TEM images of HP-C; e) and f~ h the SEM images of HP@ZIF-67-C) scanning electron microscope，SEM）image and corresponding energy-dispersive spectroscopy (EDS) elemental mapping of C, N, Co.
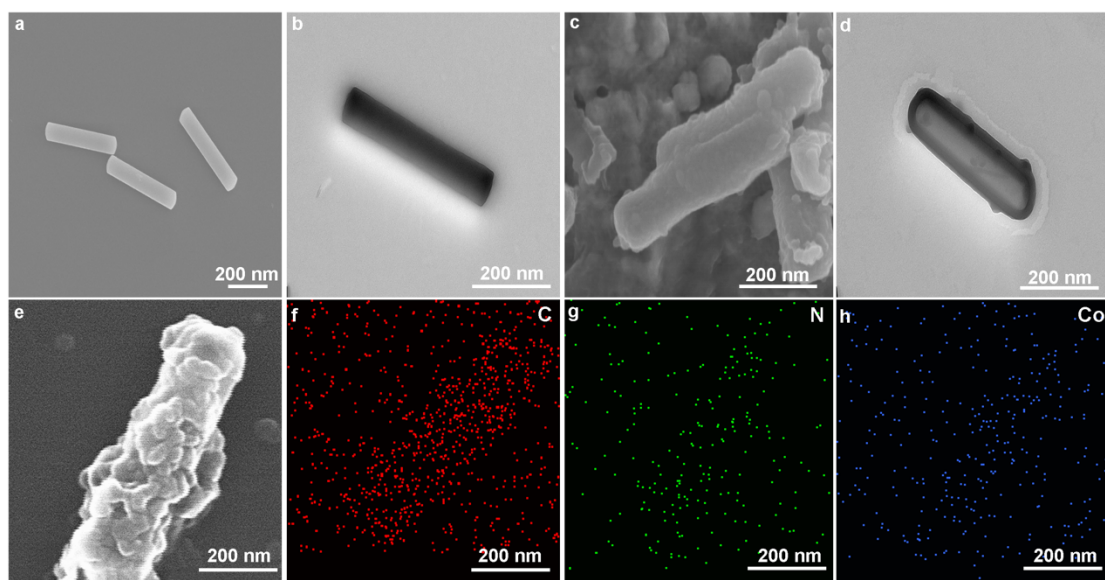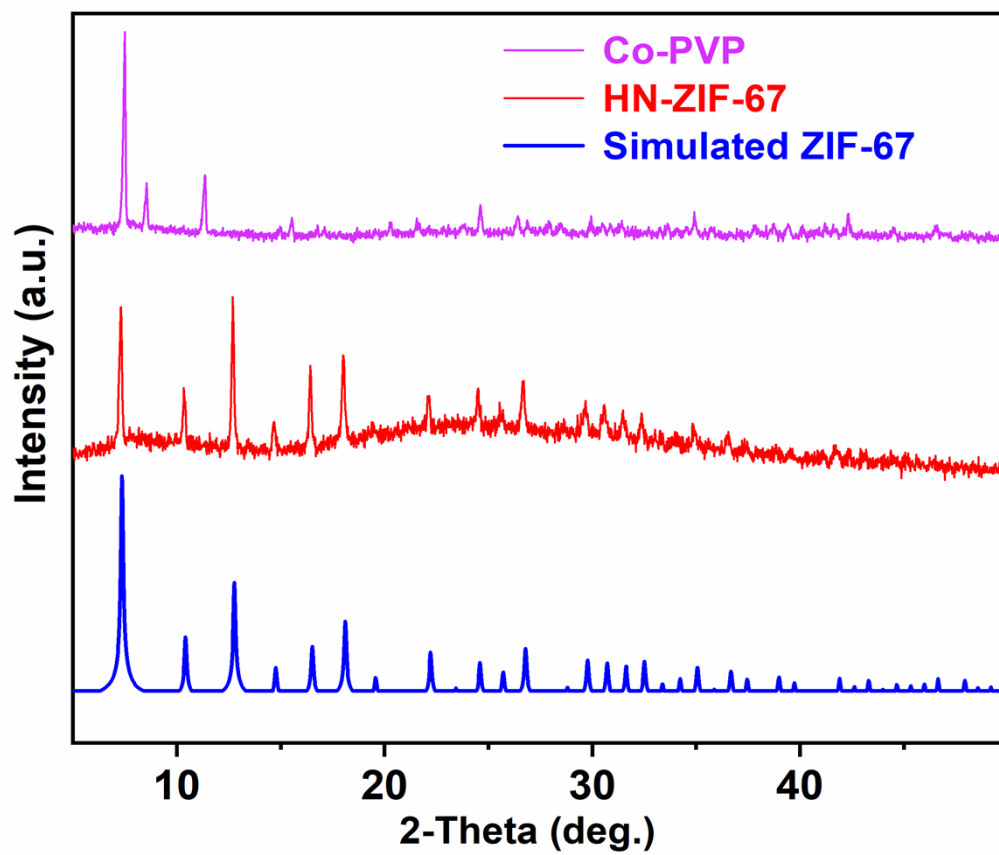
Figure S2. a) and b) SEM and TEM images of Co-PVP; c) and d) the SEM and TEM images of HP-P; e) and f~ h the SEM images of HP@ZIF-67-P) scanning electron microscope，SEM）image and corresponding energy-dispersive spectroscopy (EDS) elemental mapping of C, N, Co.

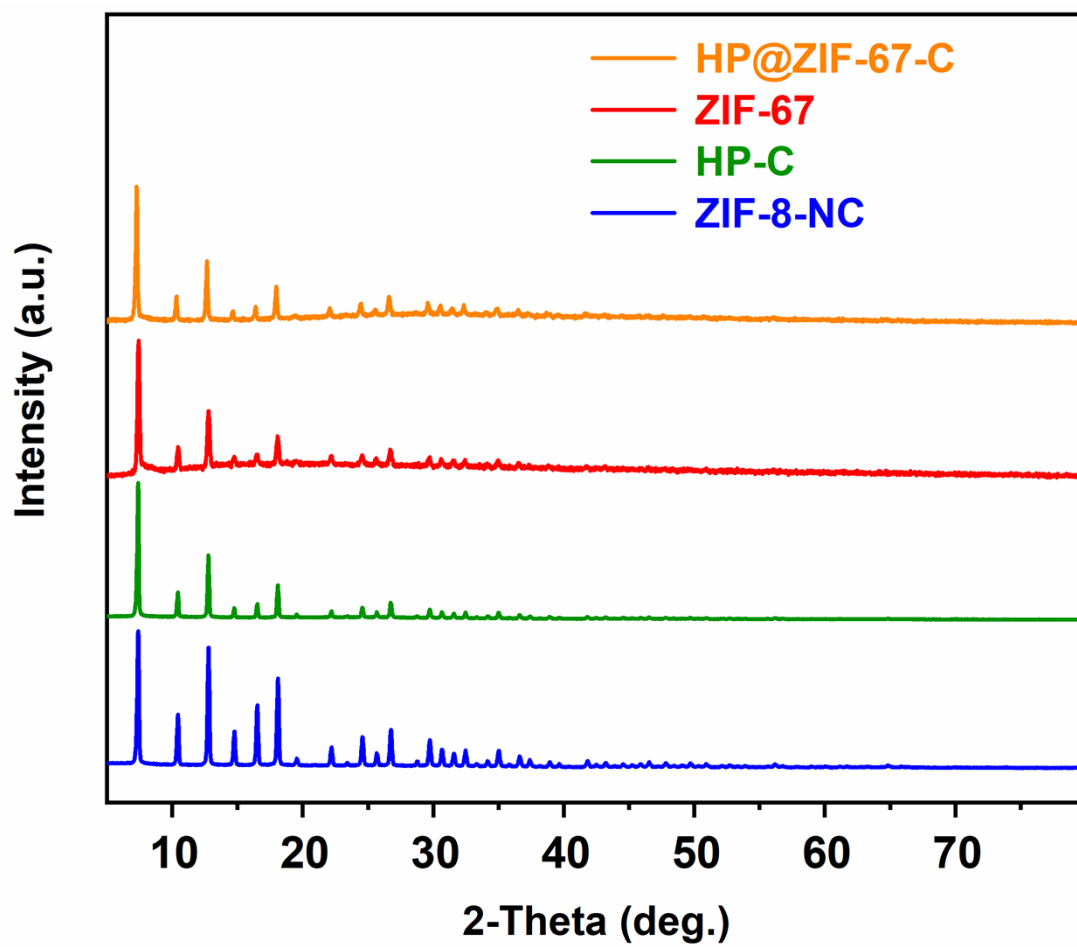**Figure S3**. PXRD patterns of Co-PVP, HN-ZIF-67, and Simulated ZIF-67

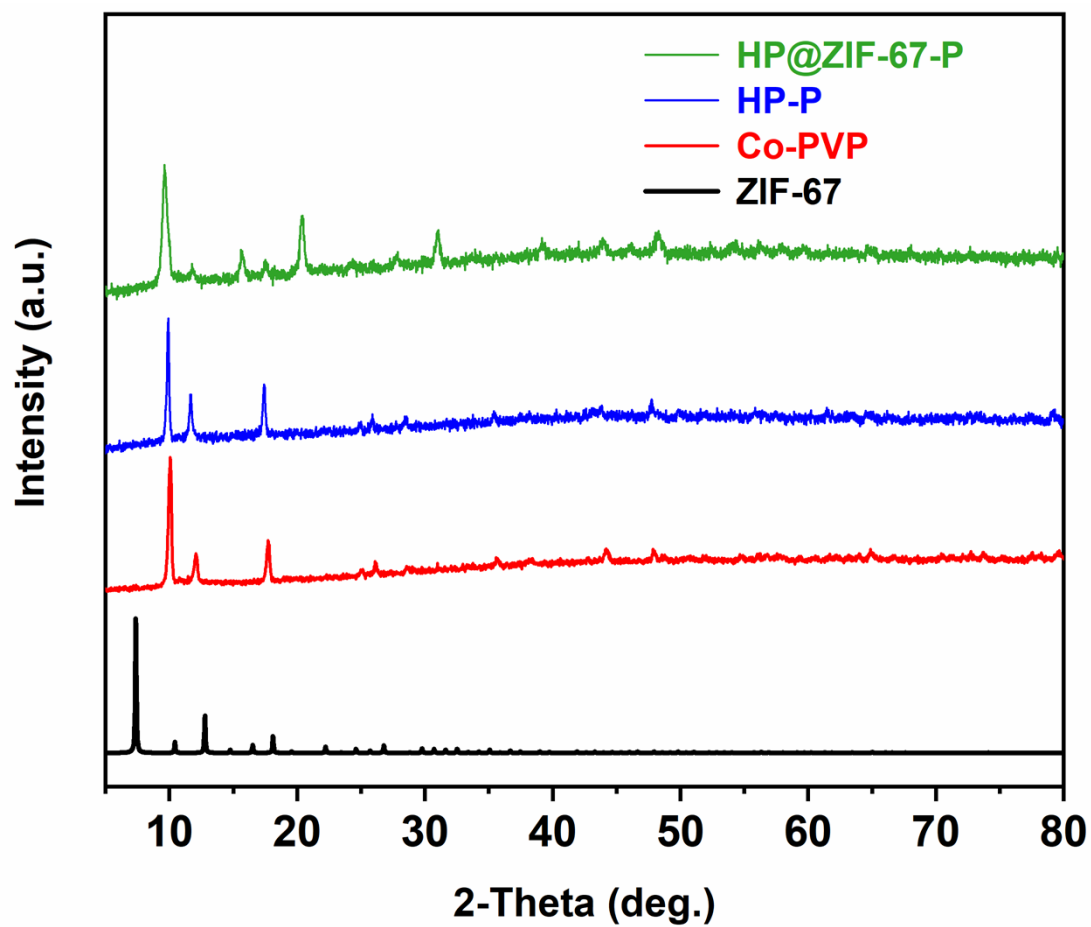**Figure S4**. PXRD patterns of HP@ ZIF-67-C, ZIF-67, HP-C, and ZIF-8-NC.

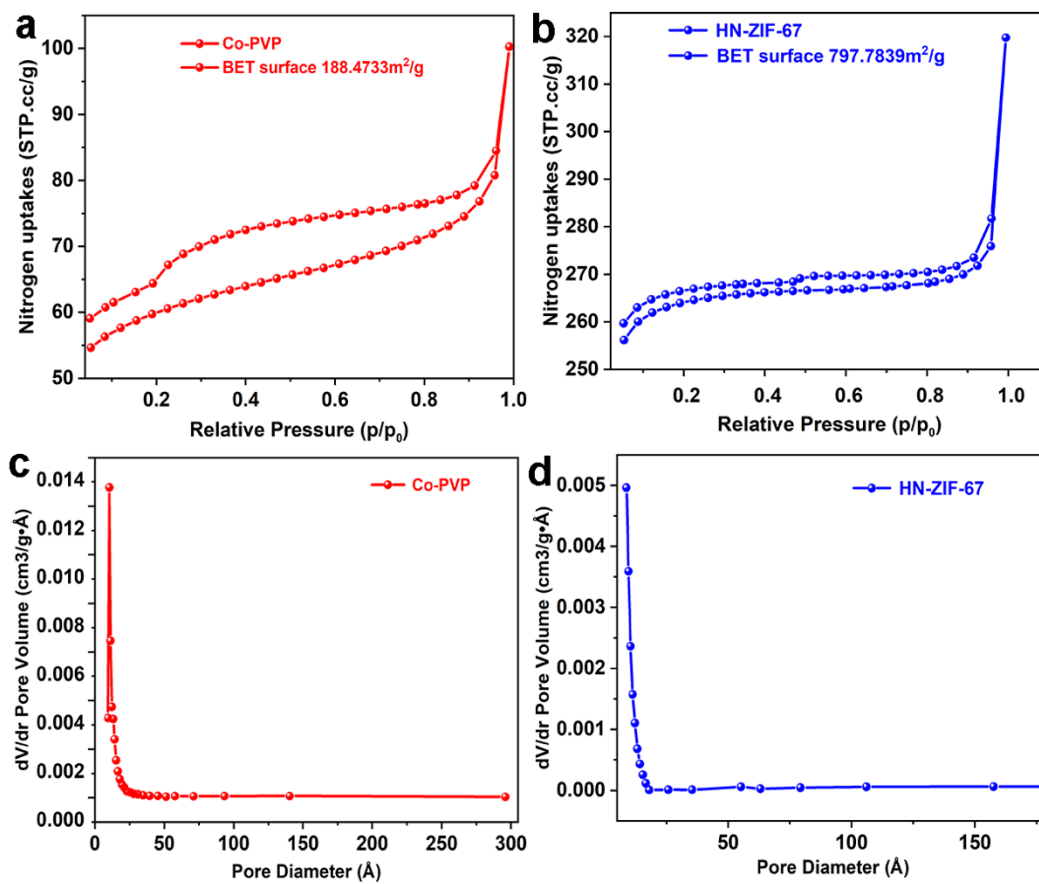**Figure S5**. PXRD patterns of HP@ ZIF-67-P, ZIF-67, HP-P, and Co-PVP.

Figure S6. The N_2 adsorption isotherm and pore distribution curves of Co-PVP and HN-ZIF-67
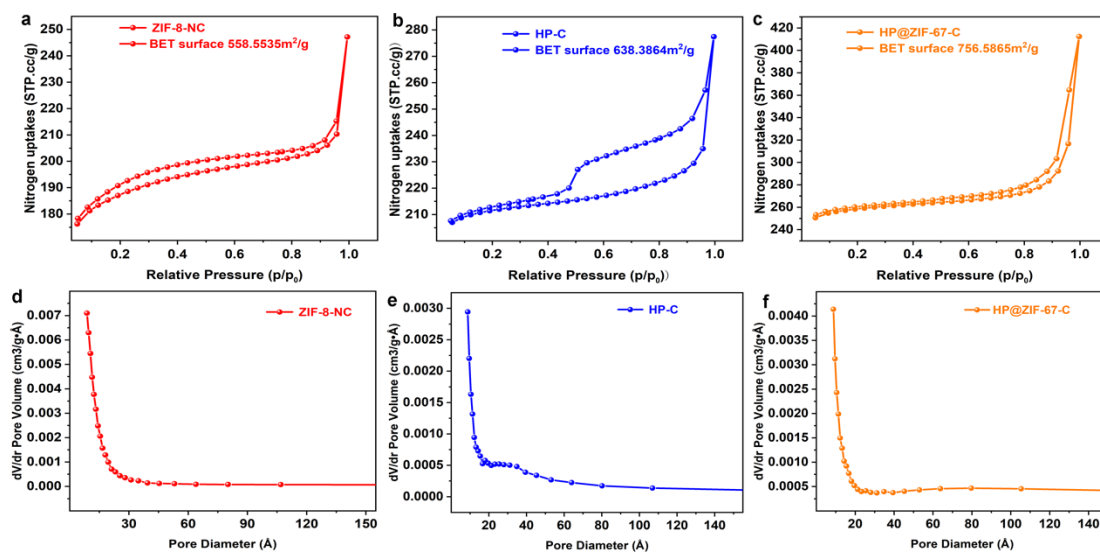
Figure S7. The N_2 adsorption isotherm and pore distribution curves of ZIF-8-NC, HP-C, and HP@ZIF-67-C
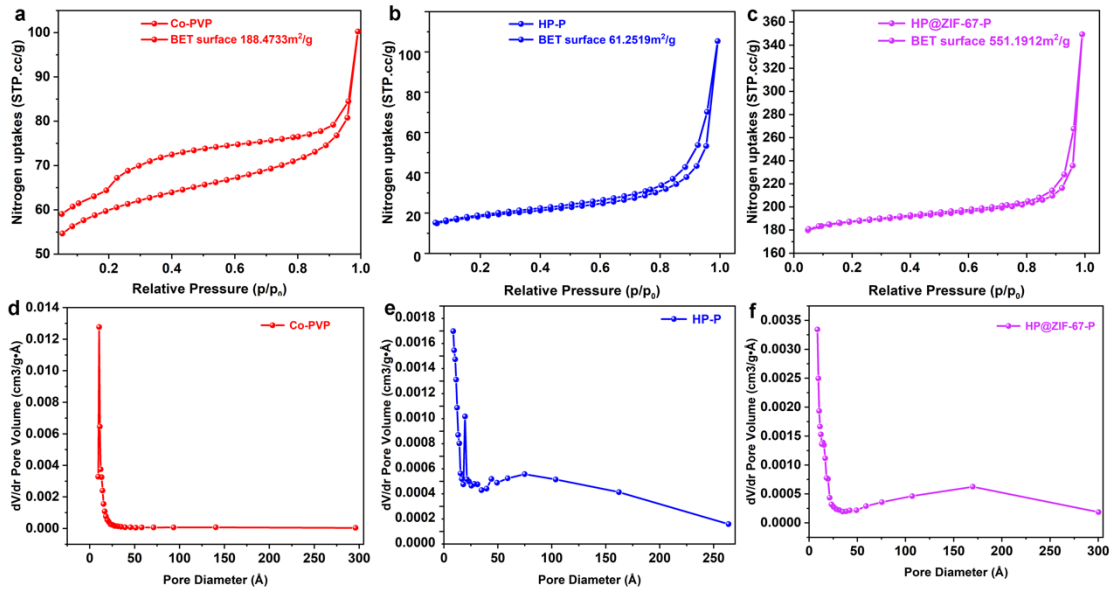
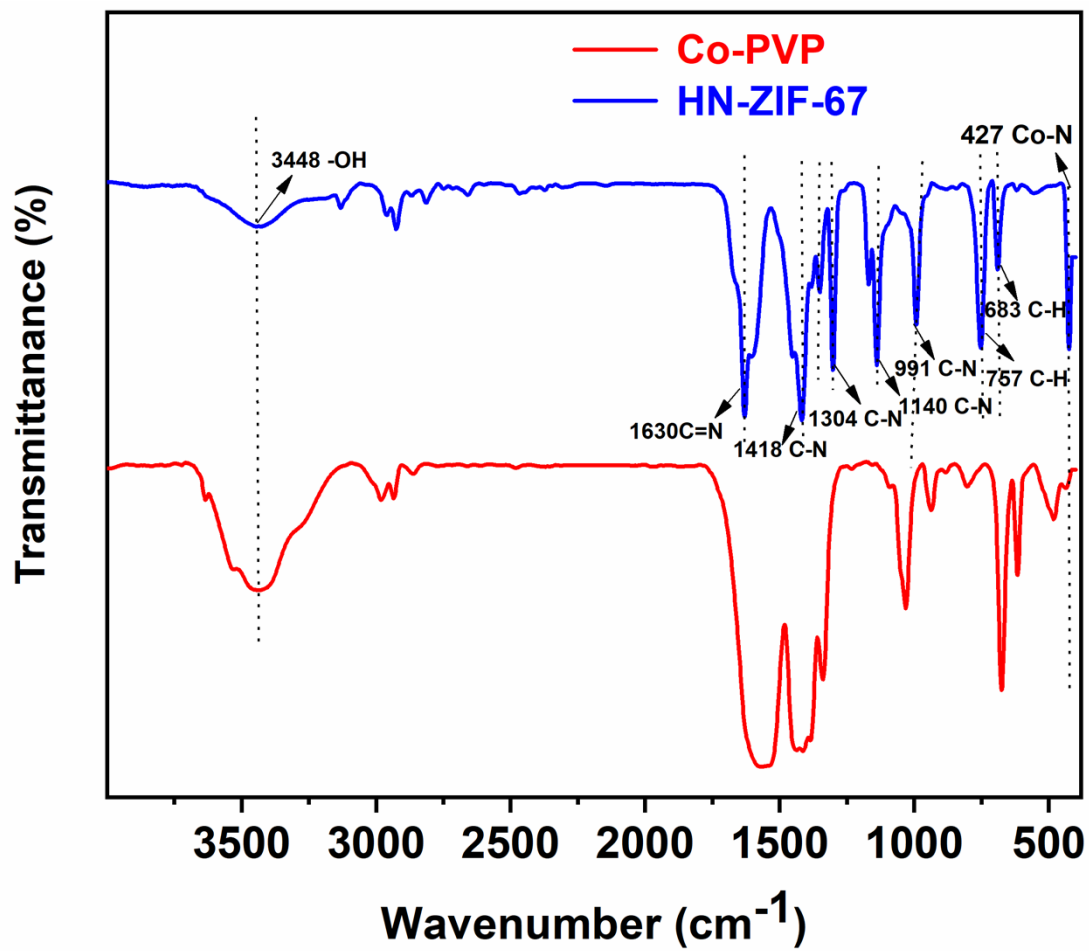**Figure S8**. The N$_2$ adsorption isotherm and pore distribution curves of Co-PVP, HP-P, and HP@ZIF-67-P.
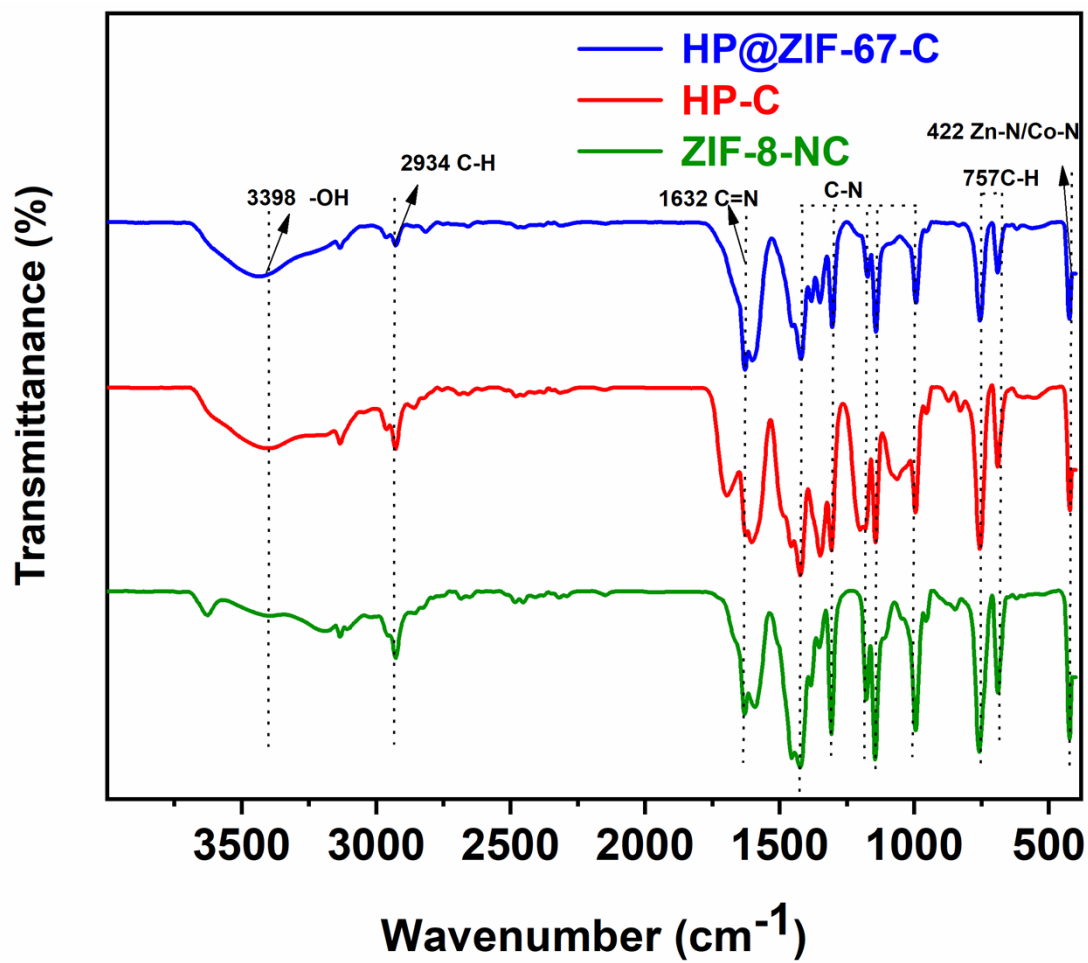
Figure S9. The FTIR of Co-PVP and HN-ZIF-67.

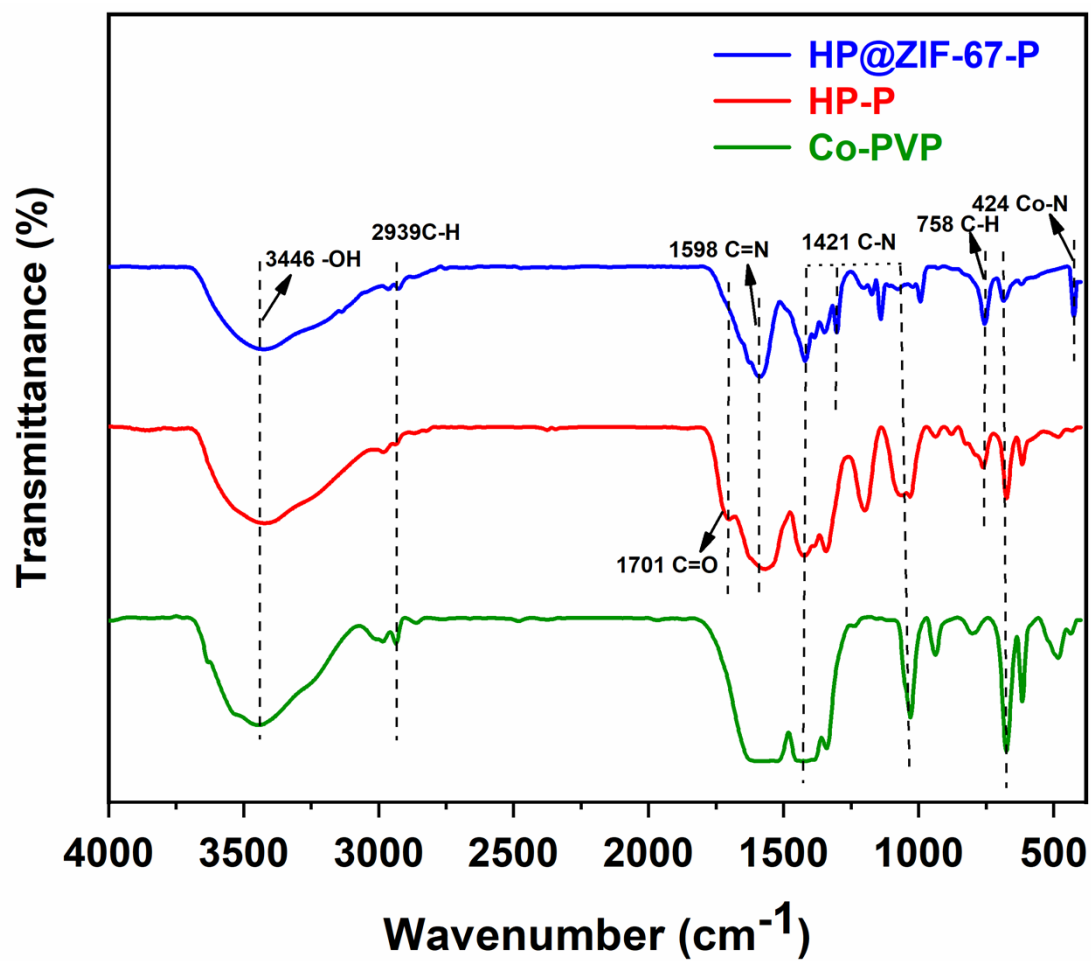**Figure S10**. The FTIR of HP@ZIF-67-C, HP-C, and ZIF-8-NC.
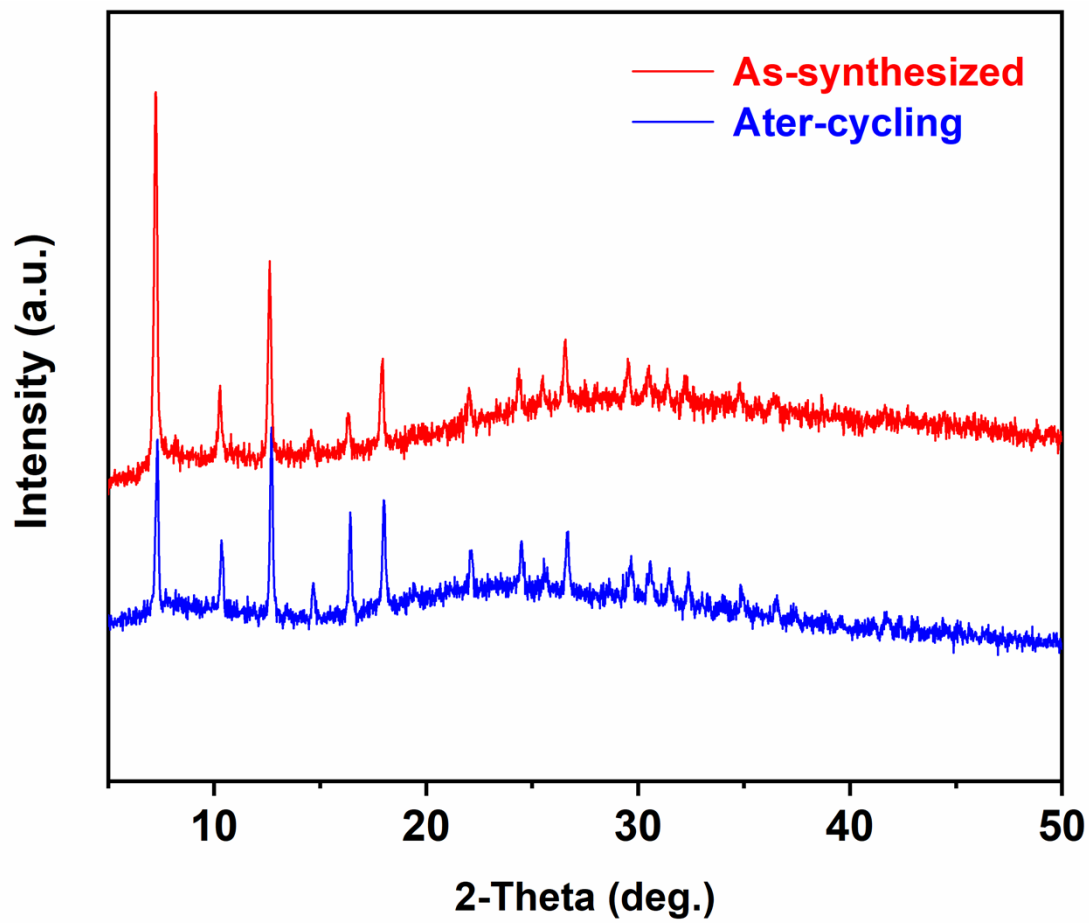
Figure S11. The FTIR of HP@ZIF-67-P, HP-P, and Co-PVP.

Figure S12. PXRD patterns of as-synthesized HN-ZIF-67and after cycling HN-ZIF-67.

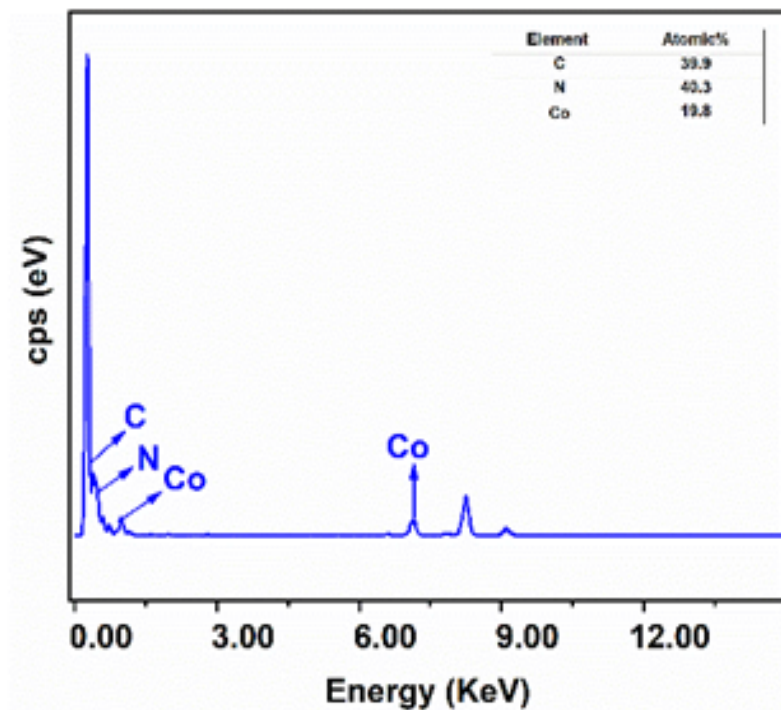| Element	Atomic%
C	39.9
N	40.3
Co	19.8

Figure S13. ICP-AES element analysis results for the HN-ZIF-67 catalyst.

S5. Turnover frequency Calculation

Loading capacity：19.8%

Catalyst amount：10 mg

Substrate amount：0.195 mmol

Catalysis time：20 minutes

Conversion percent：99%

TOF=N/(M*Time)

N: Total conversion of substrate in 20 min

M: The amount of cobalt contained on the catalyst surface

M= (10/1000) *0.198/58.9=3.36*10^{-5}

N= (0.195/1000) *0.99=1.93*10⁻⁴

TOF=N/(M*Time) = 1.93*10⁻⁴/ (3.36*10⁻⁵*20) =0.2872min⁻¹=17.232 h⁻¹