Mesoporous carbon-encapsulated Co single atoms synthesized via NH4Cl-templated ZnCo －ZIF pyrolysis for efficient ammonium perchlorate catalysis

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1. Experiment

1.1 Synthesis of ZnCo-ZIF and ZnCo-ZIF-NH4Cl (ZnCo-ZIF-N)

Dissolve 4 mmol of $Zn(NO_3)_2·6H_2O$ and 4 mmol of $Co(NO_3)_2·6H_2O$ in 80 mL of methanol, respectively. Slowly add 80 mmol of 2-methylimidazole in methanol solution (80 mL) to the previous solution while stirring, and stir continuously at 500 rpm for 24 hours. Centrifuge several times with methanol and dry overnight in a vacuum drying oven at 60 ℃.

There is no need to change the synthesis method and reaction raw material input for ZnCo-ZIF, only 40 mg NH_4Cl needs to be added to the corresponding metal ion solution, and the ZIF material introduced with NH_4Cl is called ZnCo-ZIF -N.

Zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$), cobaltous nitrate hexahydrate ($Co(NO_3)_2·6H_2O$), 2-methylimidazole, methanol and ammonium chloride (NH_4Cl)

were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were not further purified.

1.2 Synthesis of Zn-ZIF (ZIF-8) and Zn-ZIF-NH_4Cl (ZIF-8-N)

Pristine ZIF-8 was prepared in a similar manner to ZnCo-ZIF except that 4 mmol $Zn(NO_3)_2 \cdot 6H_2O$ and 4 mmol $Co(NO_3)_2 \cdot 6H_2O$ were replaced by 8 mmol $Zn(NO_3)_2 \cdot 6H_2O$.

The synthesis of ZIF-8-N does not require any changes in the synthesis method or the input of reaction raw materials. Simply add 40 mg of NH_4Cl to the corresponding metal ion solution. The ZIF material with the introduction of NH_4Cl is called ZIF-8-N.

1.3 Synthesis of Co-SA/Meso-C, Co-SA-C and Meso-C

The previously synthesized ZnCo-ZIF-N was heated to 300 ℃ in an inert atmosphere at a heating rate of 5 ℃ min^{-1}, and then heated to 400 ℃ at a heating rate of 1 ℃ min^{-1} for the decomposition and slow diffusion of NH_4Cl. In order to obtain Co-SA/Meso-C, the temperature was raised to 950 ℃ before insulation to ensure complete removal of Zn. Wait for natural cooling to obtain Co-SA/Meso-C.

The synthesis method of Co-SA-C is the same as that of Co-SA/Meso-C, except that ZnCo-ZIF-N is replaced by ZnCo-ZIF. The synthesis method of Meso-C and the input of reaction raw materials do not need to be changed, only ZnCo-ZIF-N needs to be replaced by ZIF-8-N.

1.4 Preparation of AP/Catalyst composite materials

Preparation of AP/catalyst composite materials by solvent non solvent method. Firstly, mix the synthesized catalyst and AP in a mass ratio of 5:95, then add DMF until

a saturated solution of AP is formed. Disperse the above suspension by ultrasound to form an AP solution with uniformly dispersed catalyst. Then add non solvent ethyl acetate until the AP particles are completely crystallized. After centrifugation, freeze dry the solid powder and then evenly disperse it in a mortar until the color of the mixture is uniform.

2. Characterization

Use Cu-kα Ray (λ=0.15418 nm), for the range (2θ: 10-80 ° and scanning rate of 10 °·min^{-1}) was tested by X-ray diffraction (XRD, RIGAKU miniflex 600) to obtain the crystal structure of the material. Field emission scanning electron microscopy (FESEM) (Uitra 55, Cari Zeiss, Germany) was used to explore the micro morphology and structure formation mechanism. Escalab250xi XPS was used to measure the element distribution and valence change on the surface of catalyst; Thermogravimetric analyzer (STA-2500, Netzsch) and Q20 Differential scanning calorimeter were used to detect the thermal stability and catalytic behavior of the prepared catalyst in a certain temperature range and heating rate. The structure and decomposition products of AP/catalyst was characterized by TG-IR. ICP characterization: The metal loading of Zn and Co in the catalyst Co-SA/Meso-C was measured by inductively coupled plasma optical emission spectroscopy (Agilent 5800 ICP-OES). The 300kV Cs Constrained Transmission Electron Microscope is used to test the atomic scale structure of materials, with instrument model JEM-ARM300F2 (GRAND ARM2).

3. Catalytic AP thermal decomposition performance test

Heat the mixture from room temperature to 500 ℃ in 20 mL·min^{-1} nitrogen

atmosphere at a scanning speed of 10 ℃ min^{-1}, and conduct thermal analysis test with STA-2500 synchronous thermal analyzer and Mettler TGA/DSC3+ differential scanning calorimetry. The gas phase pyrolysis products (wave number range 4000-400 cm^{-1}) during AP/ catalyst heating (30-500 ℃) were monitored by TG-IR test.

4. TG-GC-MS test

The detection process of TG-GC-MS involves injecting the gas and carrier gas (He) generated at different times (temperatures) during the heat treatment of the TG end sample into the SRA (IST-16) gas storage tank (can store up to 16 gases with different reaction times), and then injecting the above gases into the GC-MS (Trace1600 and ISQ7610) combination cell at a certain heating rate for detection and analysis, in order to obtain the content comparison and molecular weight information of the decomposition products of the sample. This function can obtain specific information and relative content of gases generated at a specific temperature point. And combined with the test results of TG-IR, calculate the relative content of NH_3 oxidation products generated during the decomposition process. It is worth noting that due to the existence of certain systematic errors, this method is only used to compare the differences between the catalysts mentioned in this study, and its absolute value does not have reference value. The heating program for TG is the same as above, while the heating program for GC is from room temperature to 200 °C, with a heating rate of 5 °C min^{-1}.

5. Theoretical calculations

Referring to relevant research and optimizing it, the $Dmol^3$ program was used to calculate the target material unit cell through density functional theory. The Perdew

Burke Ernzerhof (PBE) functional of the generalized gradient approximation (GGA's) was used to describe electron exchange correlation energy. The convergence accuracy of the self-consistent field is 1.0×10^{-5} Hatree, the multipole expansion is Hexadecapole, and DIIS (size=10) and smearing (smearing=0.005 Hatree) are used to accelerate convergence. The k-point is 2×2×2, and the truncation radius is 4.1 Å.

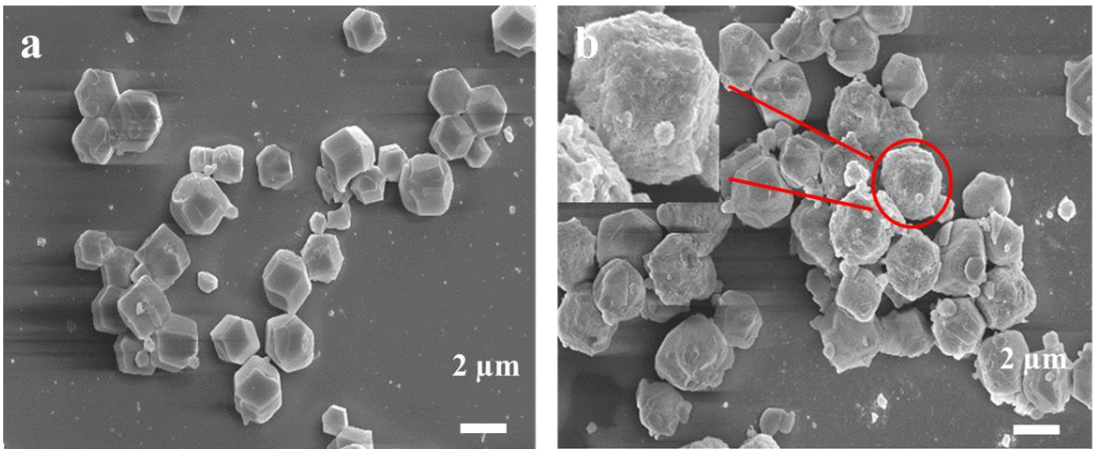

Figure S1 (a) SEM test results of ZnCo-ZIF-350 ℃ and (b) ZnCo-ZIF-N-350 ℃.

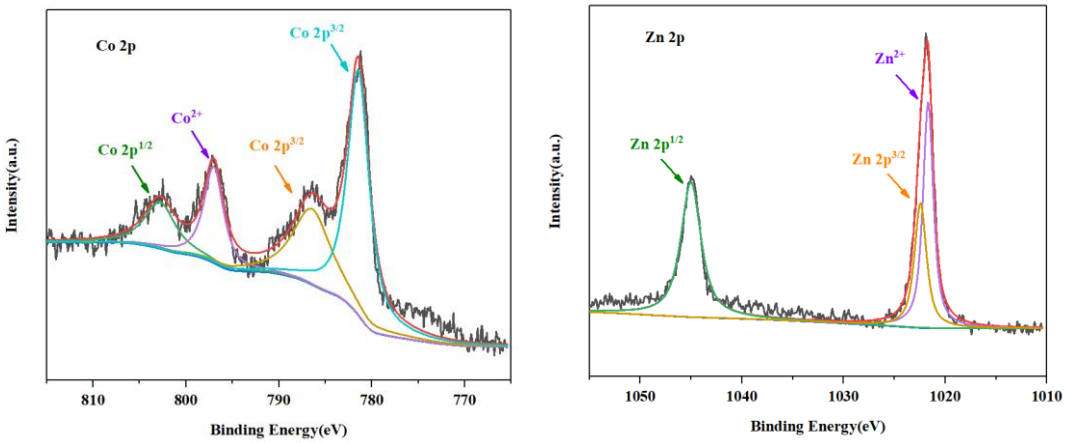

Figure S2 XPS test results of ZnCo ZIF-N.

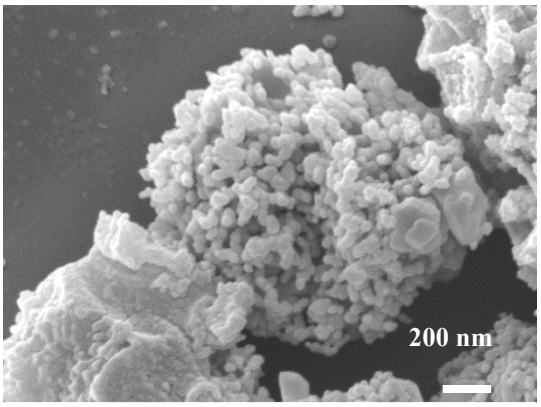

Figure S3 SEM test results of ZnCo-ZIF-N under fast heating rate.

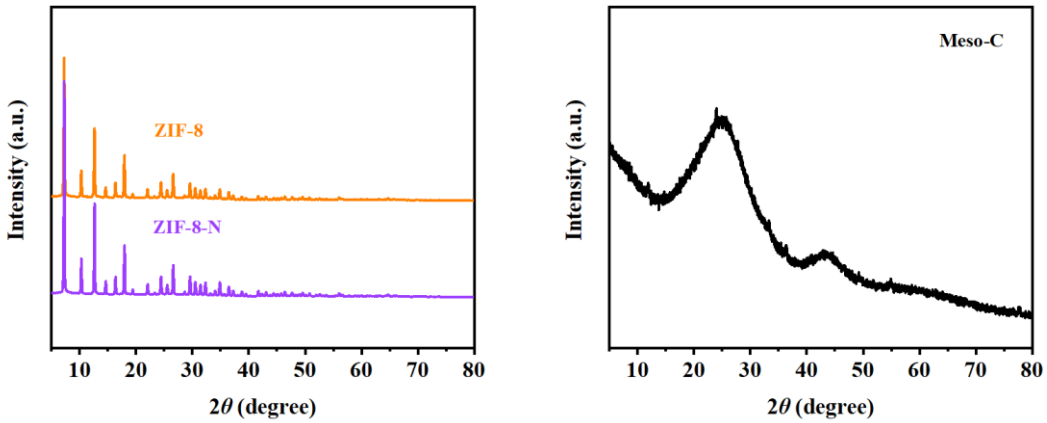

Figure S4 XRD results of Zn-ZIF (ZIF-8) and Zn-ZIF-N (ZIF-8-N) and Meso-C (pyrolyzed ZIF-8-N).

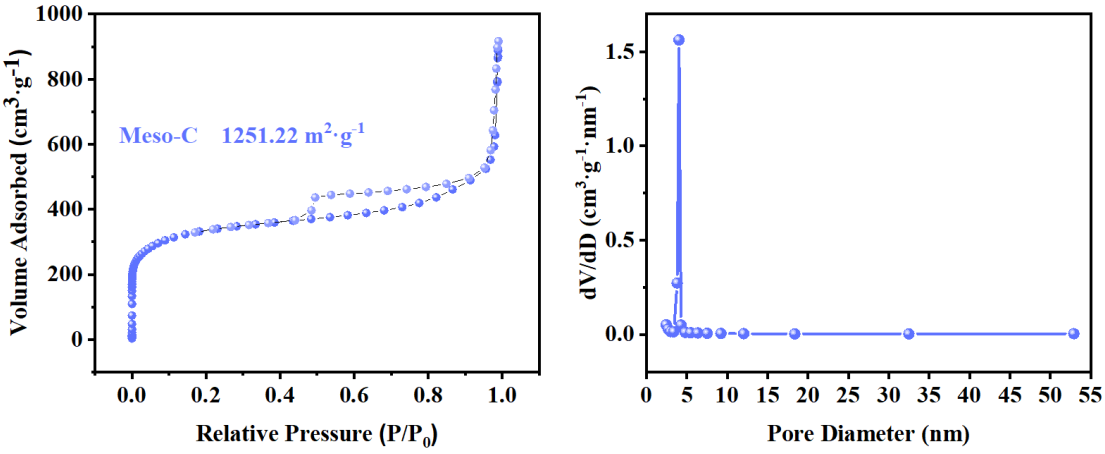

Figure S5 BET results of Meso-C.

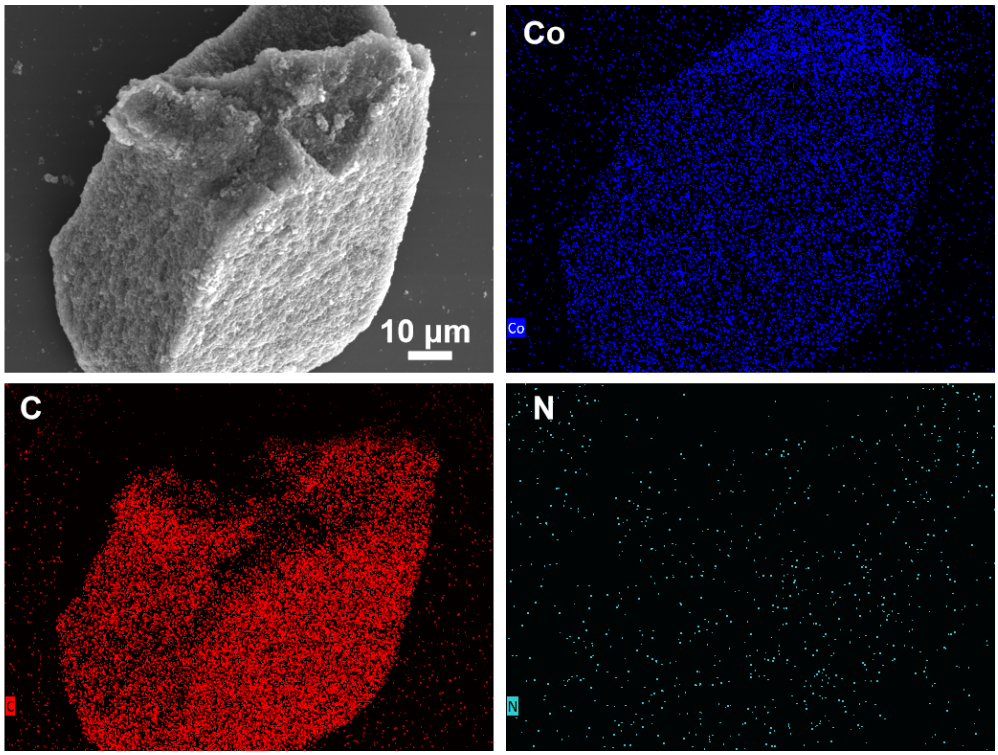

Figure S6 The EDS mapping of the Co-SA-C (unetched).

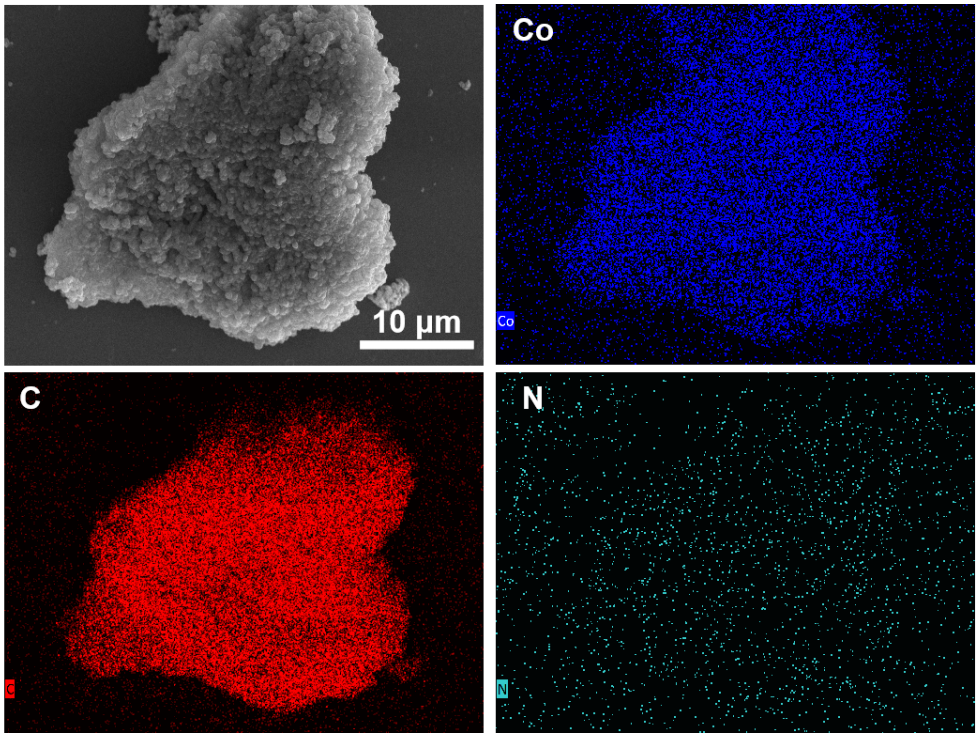

Figure S7 The EDS mapping of the Co-SA/Meso-C.

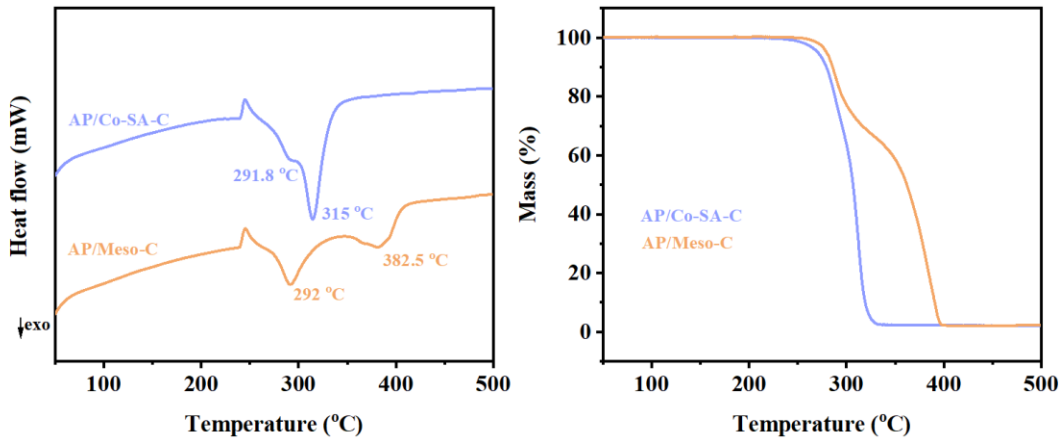

Figure S8 Thermal analysis test results of AP/catalyst (Meso-C and Co-SA-C with 5 wt%).

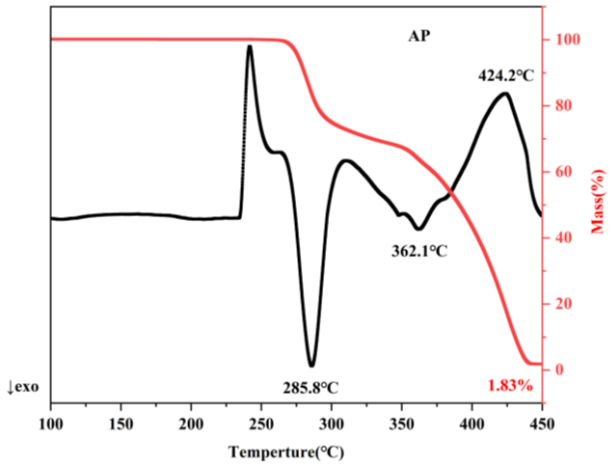

Figure S9 The thermal decomposition behavior of AP

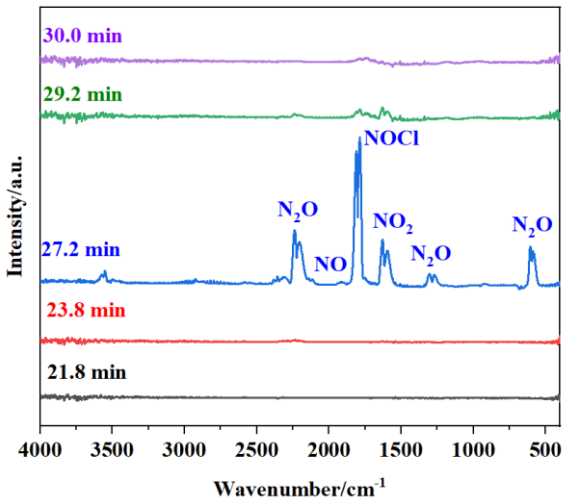

Figure S10 IR spectra in TG-IR of AP/Co-SA/Meso-C at different heat treatment times (temperature).

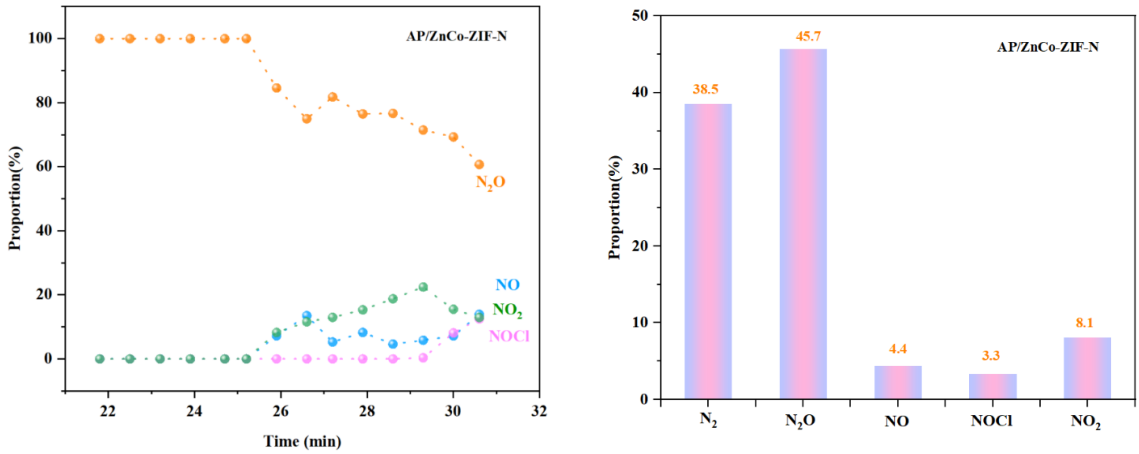

Figure S11 TG-IR and TG-GC-MS test results and gas production analysis of AP/ZnCo-ZIF-N.

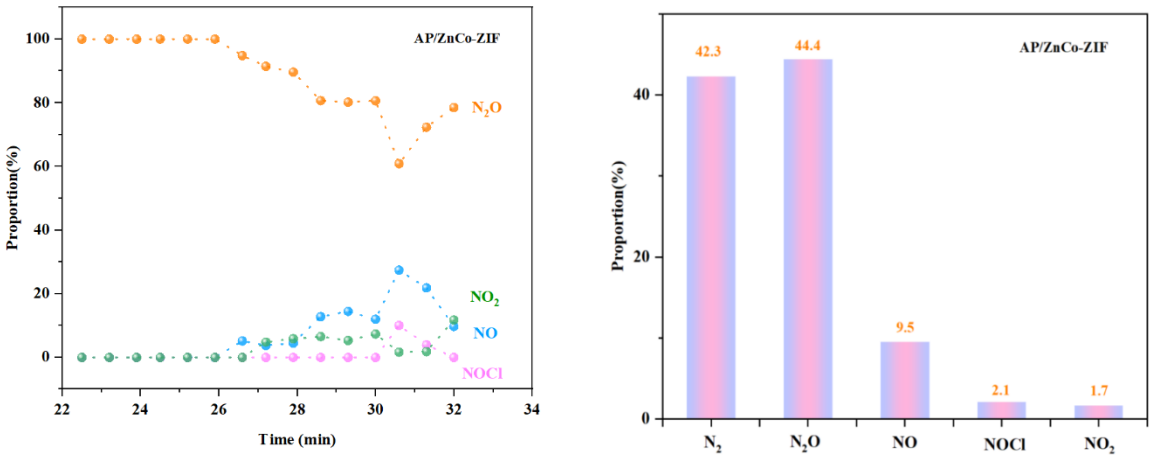

Figure S12 TG-IR and TG-GC-MS test results and gas production analysis of AP/ZnCo-ZIF.

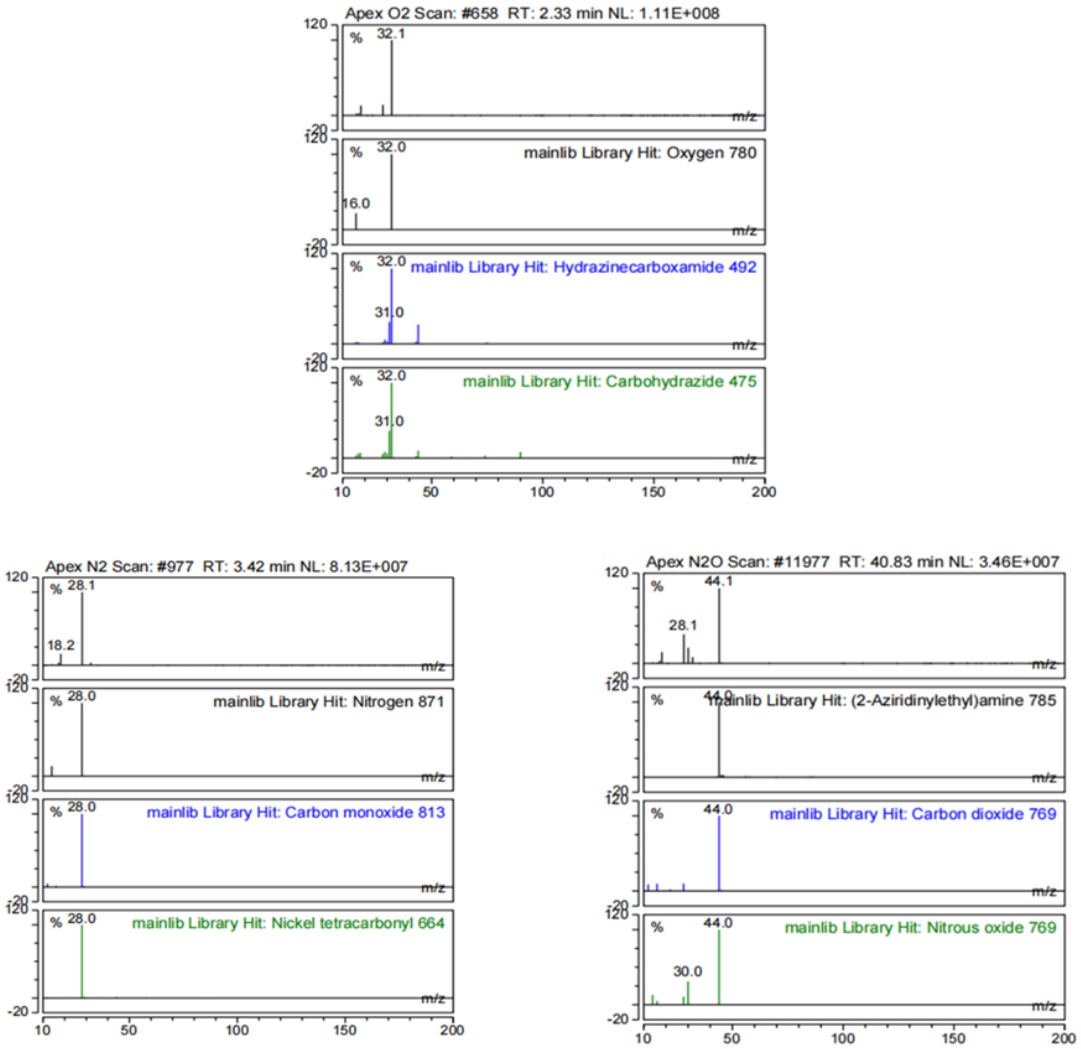

Figure S13 TG-GC-MS test results of AP/Co-SA/Meso-C (taken from one of the results).

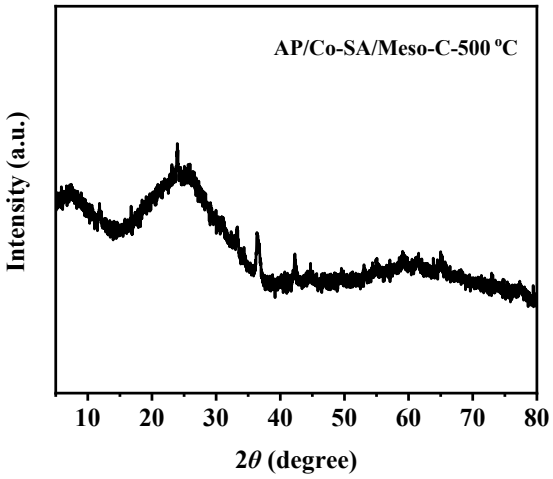

Figure S14 XRD results of AP/Co-SA/Meso-C-500 ℃.

Table S1. ICP results of Co and Zn in the catalyst Co-SA/Meso-C

Element	Co	Zn
Concentration	250354.73 ppm	6.06 ppm
Proportion	25.0354%	0.0006%

Table S2 Mechanism function of solid decomposition behavior

Function serial number	Integral formula
1	α^2
2	$\alpha + \ (1-\alpha)\ \ln(1-\alpha)$
3	$(1-\frac{2}{3}\alpha) - (1-\alpha)^{\frac{2}{3}}$
4-5	$[1-(1-\alpha)^{\frac{1}{3}}]^n$ (n=2, $\frac{1}{2}$)
6	$[1-(1-\alpha)^{\frac{1}{2}}]^{\frac{1}{2}}$
7	$[(1+\alpha)^{\frac{1}{3}}-1]^2$
8	$[\left(\frac{1}{1+\alpha}\right)^{\frac{1}{3}}-1]^2$
9	$-\ln\ (1-\alpha)$
10-16	$[-\ln(1-a)]^n \quad n=(\frac{2}{3},\frac{1}{2},\frac{1}{3},4,\frac{1}{4},2,3)$
17-22	$1-(1-\alpha)^n \quad n=(\frac{1}{2},3,2,4,\frac{1}{3},\frac{1}{4})$
23-27	$\alpha^n \quad (n=1,\frac{3}{2},\frac{1}{2},\frac{1}{3},\frac{1}{4})$
28	$\frac{1}{1-\alpha}$
29	$\frac{1}{1-\alpha}-1$
30	$(1-\alpha)^{-\frac{1}{2}}$