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Effects of Cobalt Salt Precursor Anions on the Crystal Growth of Co-BTC and its Catalytic Performance for Thermal Decomposition of Ammonium Perchlorate

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Abstract

In this work, four cobalt-based metal-organic frameworks (Co-BTC) were synthesized using 1,3,5-benzenetricarboxylic acid (H_3BTC) as the organic ligand and $Co(OAc)_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $CoSO_4 \cdot 7H_2O$ as the metal ion sources via a mild room-temperature stirring method. Structural and morphological characterization showed that the precursor anions significantly affected the nucleation and crystal growth processes, resulting in distinct differences in crystallinity, particle size, and morphology. Among the four samples, Co-BTC-C derived from cobalt acetate exhibited relatively complete crystal morphology and high crystallinity. All Co-BTC samples effectively promoted Ammonium Perchlorate (AP) thermal decomposition. At 4 wt% addition, Co-BTC-C, Co-BTC-Cl, Co-BTC-N, and Co-BTC-S decreased the high-temperature decomposition peak temperature of AP by 105.2, 99.9, 106.5, and 94.5 °C, respectively, while increasing the apparent heat release from 202.7 J·g⁻¹ for pure AP to 723.8, 748.7, 588.5, and 666.5 J·g⁻¹. Considering the structural characteristics, thermal decomposition behavior, and kinetic performance, Co-BTC-C exhibited the best overall catalytic performance. The apparent activation energy of AP decomposition decreased from 312.8 to 219.6 kJ·mol⁻¹ after the addition of 4 wt% Co-BTC-C. Further mechanistic analysis showed that Co-BTC-C was converted into Co_3O_4 before the major decomposition stage of AP, suggesting that the highly dispersed cobalt sites in the MOF precursor and the in situ generated Co_3O_4 may jointly contribute to the enhanced decomposition of AP. These results demonstrate that regulating cobalt salt

precursor anions is an effective strategy for tuning the crystal growth and catalytic performance of Co-BTC.

Key words: Co-BTC, precursor anion, crystal growth, Ammonium perchlorate(AP), catalytic performance

1. Introduction

Composite solid propellants (CSPs) serve as a critical power source for solid rocket motors and aerospace propulsion systems, and their combustion efficiency, energy release rate, and thermal reaction behavior directly influence the burning rate, specific impulse, and operational stability of the propulsion systems. Ammonium perchlorate (AP), owing to its high oxygen content, high gas yield, and suitable thermal stability, has long been the most widely used oxidizer in CSPs, typically accounting for more than 60% by mass^[1-5]. The thermal decomposition process of AP determines the release of oxidizing gases and the subsequent oxidation reaction rate of the fuel, and thus constitutes a key step governing the overall combustion performance of the propellant. However, pure AP suffers from issues such as a relatively high high-temperature decomposition temperature and sluggish reaction kinetics, which are detrimental to rapid and complete energy release of the propellant. Therefore, the development of efficient combustion catalysts that can significantly reduce the decomposition temperature of AP, accelerate the reaction rate, and lower the reaction energy barrier is of great significance for enhancing the overall performance of composite solid propellants^[6-11].

Metals and metal oxides, owing to their ability to promote electron transfer and redox reactions in the process of AP thermal decomposition, have been widely used in catalytic studies on AP thermal decomposition^[12-17]. Among them, cobalt-based oxides, owing to their reversible $\text{Co}^{2+}/\text{Co}^{3+}$ redox behavior and relatively strong oxygen activation ability, can accelerate the AP decomposition process by promoting interfacial electron transfer and reactive oxygen species generation, and thus have received extensive attention in the field of AP thermal decomposition catalysis^[18, 19]. However, traditional metal oxide catalysts are prone to particle agglomeration and grain growth during preparation and high-temperature reactions, resulting in a decrease in effective active surface area and a reduction in the utilization of active sites. Metal-organic frameworks (MOFs), constructed from metal ions or metal clusters and organic ligands through coordination interactions, feature uniform distribution of metal sites, highly tunable structures, and controllable thermal conversion pathways^[18-35], and thus can

serve as an ideal precursor platform for the uniform dispersion and in situ transformation of active metal components. In recent years, the application of Co-based MOFs in the catalysis of AP thermal decomposition has received increasing attention. For example, Feng et al.^[36] constructed a series of ferrocenyl-based metal-organic frameworks, among which Co-FcDA exhibited superior catalytic activity and could significantly reduce the high-temperature decomposition temperature and apparent activation energy of AP, reducing the high-temperature decomposition temperature of AP by 90.0 °C and decreasing the activation energy by 30.5 kJ·mol⁻¹ at a 5 wt% addition amount; Zhang et al.^[46] prepared Co-BTC, and with a catalyst addition of 10 wt%, the decomposition temperature of AP was reduced by 92.3 °C, and the activation energy decreased by 90.67 kJ·mol⁻¹; ZIF-67 and other Co-based MOFs or their derived materials have also been confirmed to possess good catalytic effects^[26, 46]. For MOF materials, their formation process depends not only on the coordination interaction between metal ions and organic ligands, but is also affected by factors such as the coordination ability of precursor anions, the release rate of metal ions, and the solution chemical environment; these factors can further regulate crystal nucleation, growth, and final structural morphology. 1,3,5-Benzenetricarboxylic acid (H₃BTC) possesses a rigid aromatic skeleton and multiple carboxyl coordination sites, and can construct a stable coordination network with metal ions, making it suitable as a ligand system for studying the influence of different metal salt precursors on MOF formation behavior^[37, 38]. However, existing MOF systems mostly rely on hydrothermal or solvothermal conditions, and current related studies mainly focus on the design of MOF structural types and the regulation of derived material composition, while systematic studies on the effects of different metal salt precursors and their anionic environments on the MOF nucleation process, crystal growth behavior, and final catalytic performance are still relatively lacking.

Our research group has previously achieved the room-temperature synthesis of BTC-based HKUST-1 materials and verified the application potential of the BTC coordination system in MOF construction and AP thermal decomposition catalysis^[50]. Based on this, this study further extended the BTC coordination system to Co nodes. Using Co(OAc)₂·4H₂O, CoCl₂·6H₂O, Co(NO₃)₂·6H₂O, and CoSO₄·7H₂O as cobalt sources, a series of Co-BTC materials were prepared by a room-temperature stirring method. The effects of different precursor anions on the structural evolution, crystal morphology, and AP thermal decomposition catalytic performance of Co-BTC were

systematically investigated, and the correlation between “precursor anion—crystal structure—catalytic performance” was established. The results showed that different cobalt salt precursors could significantly regulate the crystal growth behavior of Co-BTC. Among them, Co-BTC-C prepared from cobalt acetate exhibited better structural characteristics and catalytic performance, and could in situ generate highly dispersed Co_3O_4 active species during AP thermal decomposition, thereby effectively promoting the AP thermal decomposition reaction.

2. Experiment

2.1 Materials and Reagents

$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, AR, purchased from Xilong Scientific Co., Ltd.; $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, N,N-dimethylformamide (DMF), triethylamine (TEA), AR, purchased from Sinopharm Chemical Reagent Co., Ltd.; 1,3,5-benzenetricarboxylic acid (H_3BTC), 98%, purchased from Aladdin Reagent (Shanghai) Co., Ltd.

2.2 Preparation of Co-BTC

Water and ethanol were mixed at a volume ratio of 1:1 to prepare a water-ethanol mixed solvent (hereinafter referred to as the mixed solvent). A certain amount of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was weighed, placed in a beaker, and dissolved in the mixed solvent to obtain solution A. A certain amount of H_3BTC was weighed, dissolved in the mixed solvent to obtain solution B. Under magnetic stirring, solution B was added dropwise to solution A at a rate controlled within 5 drops/s. After the addition was complete, 1 mL of TEA was added, and stirring was continued for 24 h. The product was separated by centrifugation, and the filter cake was dried under vacuum at 60 °C. The dried filter cake was ground into a powder in an agate mortar to obtain the Co-BTC product. The specific preparation process is shown in Fig. 1.

A series of different Co-BTC materials were prepared by replacing $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with three other cobalt salts ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$). The molar ratio of cobalt salt to organic ligand was 2.5:1. Every 0.01 mol of cobalt salt was dissolved in 250 mL of the mixed solvent, and every 0.004 mol of organic ligand was dissolved in 50 mL of the mixed solvent. According to the anion type, the four Co-BTC samples were sequentially named Co-BTC-C, Co-BTC-Cl, Co-BTC-N, and Co-BTC-S.

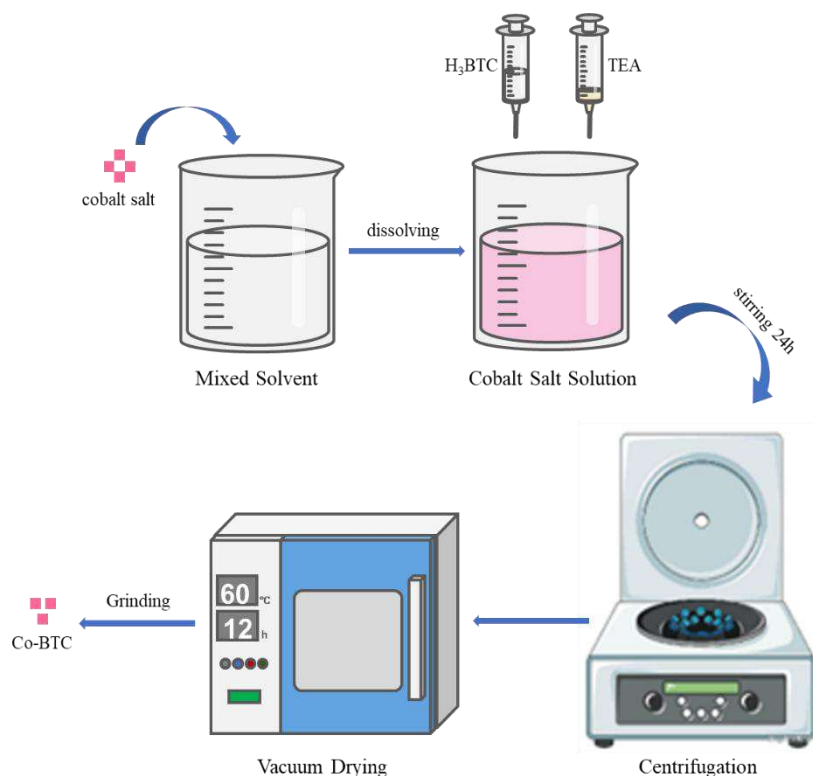


Fig. 1 Flow chart of preparation of Co-BTC

2.3 Preparation of Co-BTC/AP

A certain amount of AP and Co-BTC were weighed at a mass ratio of 96:4 and mixed in an agate mortar. Then, 10 mL of ethyl acetate was added as a dispersant. The mixture was ground until all ethyl acetate had evaporated, and then dried in an electric blast drying oven at 40 °C to obtain Co-BTC/AP, in which Co-BTC accounted for 4%. Blank samples and composite particles with 1%, 2%, 3%, and 5% Co-BTC were prepared using the same method.

2.4 Characterization Methods

Phase characterization was performed using a SmartLab X-ray diffractometer from Rigaku (Japan) with Cu K α radiation as the source, operating at 40 kV and 150 mA, with a step size of 0.01°, a scanning speed of 10°/min, and a scanning range of 5–90°. Structural characterization of the prepared composite particles was carried out using a Tensor37 infrared spectrometer from Bruker Optics (Germany). Morphological characterization was conducted using a Zeiss Gemini Sigma 300 field-emission scanning electron microscope from Carl Zeiss (Germany), and EDS analysis was performed using an Xplore30 energy dispersive spectrometer from Oxford Instruments (UK). Elemental composition and valence states were characterized using an ESCALAB Xi+ X-ray photoelectron spectrometer from Thermo Fisher (USA).

Thermal performance testing of the prepared composite particles was conducted

using a STA449F3 synchronous thermal analyzer from NETZSCH (Germany). Thermogravimetric analysis was performed at heating rates of 5, 10, 15, and 20 °C·min⁻¹. The temperature was programmed to increase from ambient conditions to a final set value of 500 °C.

3. Results and discussion

To systematically investigate the influence of precursor anions on the structural evolution, crystal growth behavior, and catalytic performance of Co-BTC, a series of Co-BTC materials were synthesized using Co(OAc)₂·4H₂O, CoCl₂·6H₂O, Co(NO₃)₂·6H₂O, and CoSO₄·7H₂O as cobalt sources, respectively. The effects of different anion environments on the nucleation and growth processes of Co-BTC were investigated through comprehensive characterization. XRD, FTIR, XPS, and SEM-EDS analyses were subsequently employed to elucidate the differences in crystal structure, chemical composition, morphology, and elemental distribution among the obtained samples, providing insights into the relationship between precursor anions, structural characteristics, and catalytic performance.

3.1 Structural and Morphological Characterization of Co-BTC Derived from Different Cobalt Salts

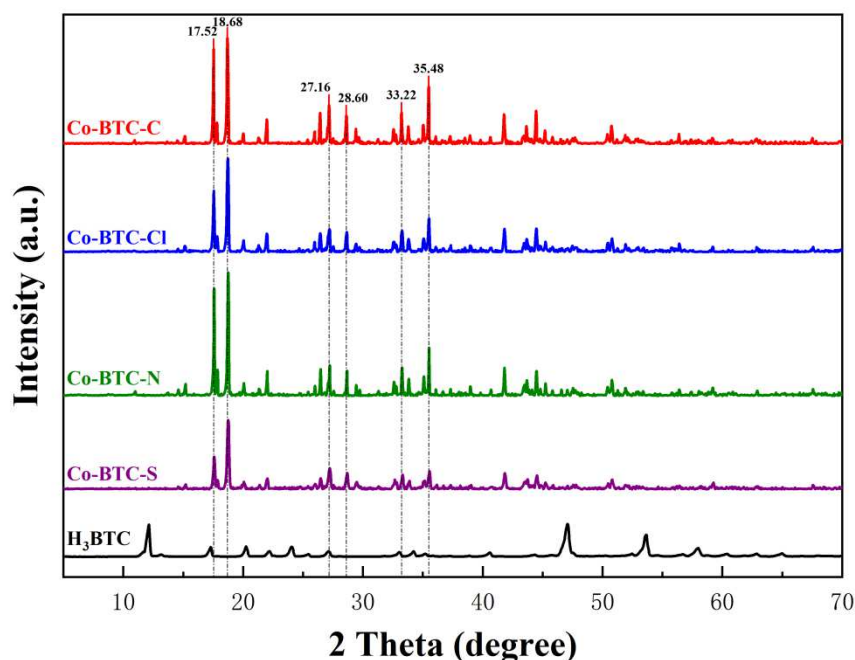


Fig. 2 XRD patterns of Co-BTC-C, Co-BTC-Cl, Co-BTC-N, Co-BTC-S and H₃BTC

The XRD comparison between the raw material H₃BTC and the samples is shown in Fig. 2. In contrast, the characteristic diffraction peaks of H₃BTC before 15° and after 40° completely disappeared in the samples, indicating that the raw material had reacted. All four Co-BTC samples exhibited new major diffraction peaks at 2θ angles of 17.52°,

18.68°, 27.16°, 28.60°, 33.22°, and 35.48°, which are generally consistent with those reported in the literature^[39]. The diffraction peaks showed distinct peak shapes, indicating good crystallinity. Compared with the other samples, Co-BTC-C exhibited the sharpest peaks, suggesting the highest crystallinity, followed in order by Co-BTC-N, Co-BTC-Cl, and Co-BTC-S. Additionally, no obvious characteristic diffraction peaks of cobalt oxide were observed in the samples, indicating that the prepared samples were of high purity.

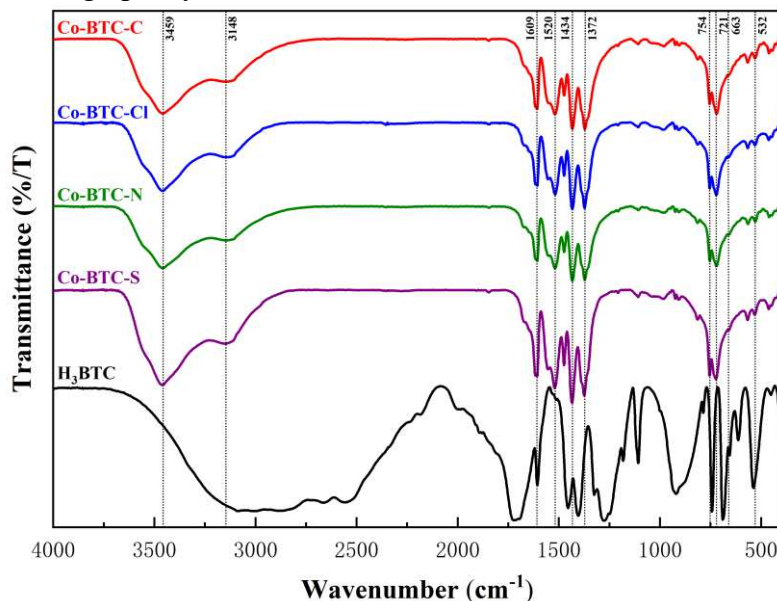


Fig. 3 FTIR patterns of Co-BTC-C, Co-BTC-Cl, Co-BTC-N, Co-BTC-S and H₃BTC

The chemical bonds of the products were characterized by FTIR, as shown in Fig. 3. The characteristic peaks of the carboxyl group in H₃BTC (ν C=O, 538 cm⁻¹; ν C=O, 1721 cm⁻¹; ν OH, 3081 cm⁻¹) disappeared in the products, which is attributed to the coordination reaction between H₃BTC and the metal ions^[40]. The broad absorption peak at 3459 cm⁻¹ corresponds to the O–H stretching vibration of the carboxyl groups in the ligand. The absorption peak at 3148 cm⁻¹ corresponds to the C–H stretching vibration of the benzene ring in the H₃BTC ligand. The strong spectral bands in the regions of 1630–1570 cm⁻¹ and 1440–1370 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of the carboxylate groups, respectively. The three absorption peaks in the fingerprint region at 663 cm⁻¹, 721 cm⁻¹, and 754 cm⁻¹ correspond to the out-of-plane bending vibrations of the C–H bonds on the benzene ring. All the above absorption peaks are characteristic of the H₃BTC ligand in Co-BTC. The peak near 532 cm⁻¹ is likely attributed to the Co–O stretching vibration, indicating that oxygen atoms coordinate with Co, suggesting that Co²⁺ has successfully bound to the organic ligand^[41]. Combined with the XRD results, it can be concluded that Co-BTC was successfully

prepared.

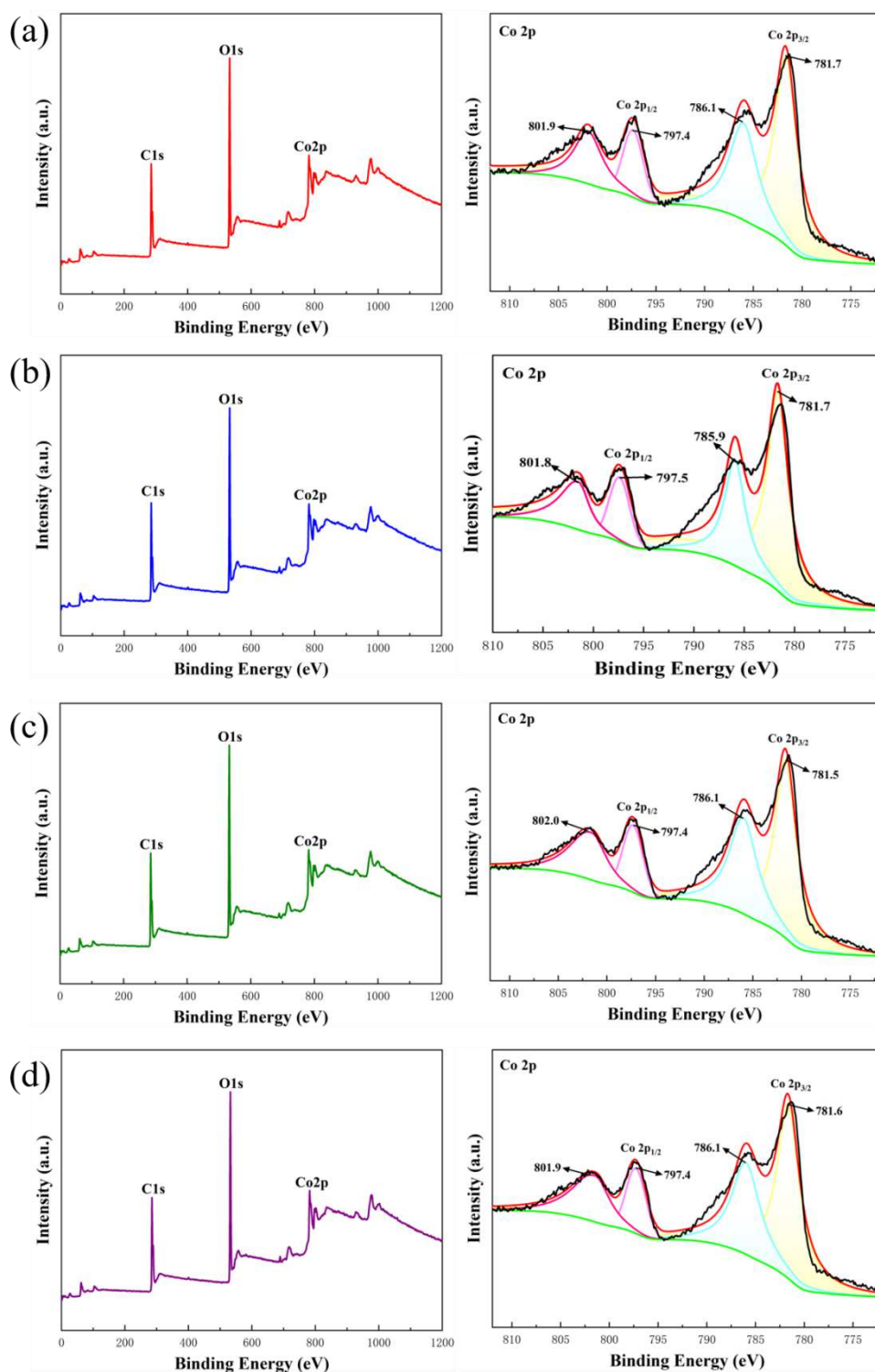


Fig. 4 XPS spectra of (a) Co-BTC-C; (b) Co-BTC-Cl; (c) Co-BTC-N; (d) Co-BTC-S

XPS was employed to analyze the elemental composition and valence states of Co-BTC prepared with different cobalt salts, and the results are shown in Fig. 4. From panels (a), (b), (c), and (d), it can be clearly observed that the materials prepared with different cobalt salts all exhibit characteristic spectral peaks of C 1s, O 1s, and Co 2p.

Meanwhile, the XPS spectra in the Co 2p binding energy region of different Co-BTC samples show no significant difference in the binding energies of Co 2p_{3/2} and Co 2p_{1/2}, indicating that the valence state of cobalt remains essentially unchanged among the materials prepared with different cobalt salts. Taking Co-BTC-C as an example, the binding energies at 781.7 and 797.4 eV correspond to the two main characteristic peaks of Co 2p_{3/2} and Co 2p_{1/2}, respectively, followed by peaks near binding energies of 786.1 and 801.9 eV, corresponding to the positions of two satellite peaks. The energy gaps between the main peaks and the satellite peaks are 4.4 and 4.5 eV. The peak fitting results clearly indicate that cobalt predominantly exists in the divalent form in the product, which is consistent with the literature^[42].

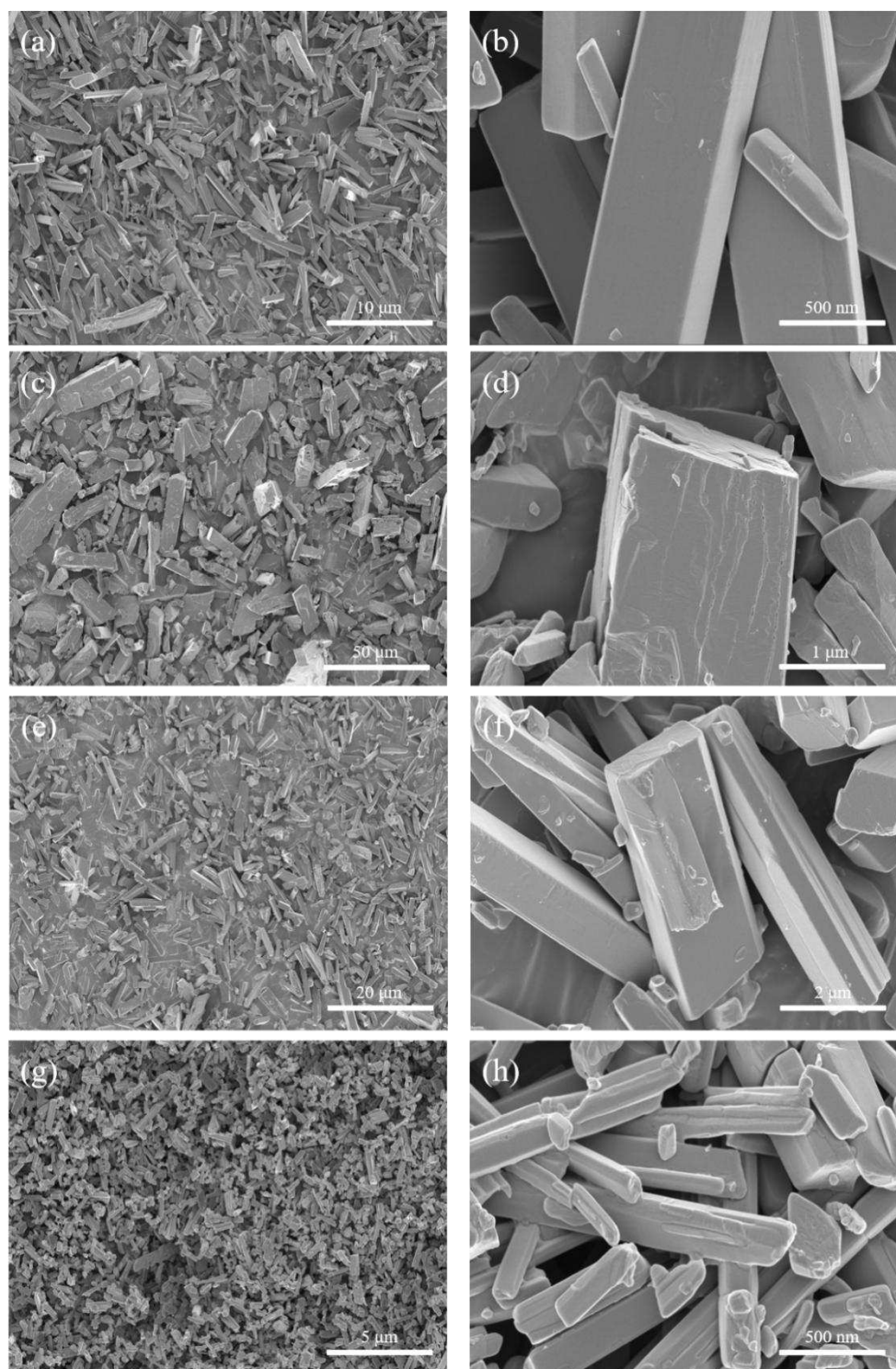


Fig. 5 SEM images of (a)(b) Co-BTC-C; (c)(d) Co-BTC-Cl; (e)(f) Co-BTC-N; (g)(h) Co-BTC-S

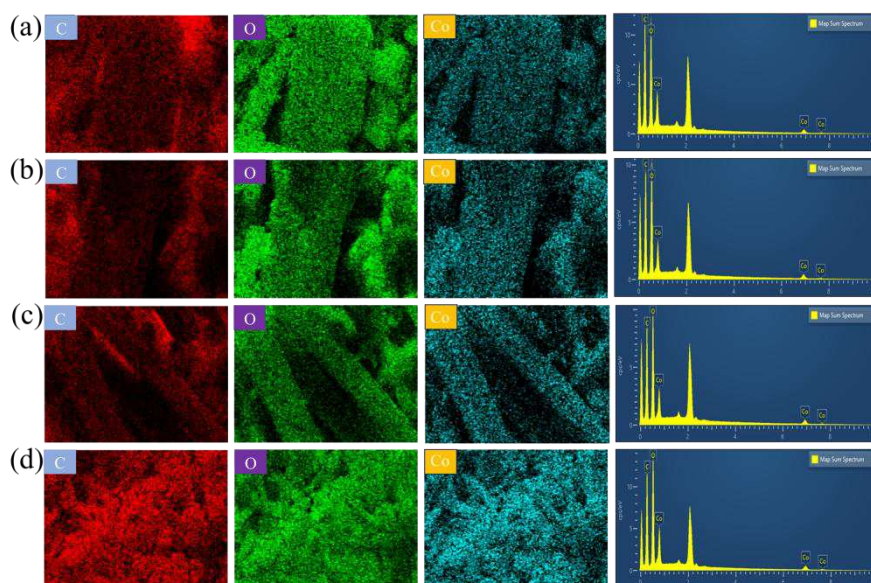


Fig. 6 EDS elemental mapping spectra of (a) Co-BTC-C; (b) Co-BTC-Cl; (c) Co-BTCi-N; (d) Co-BTC-S

Table 1 Semi-quantitative elemental composition (wt%)

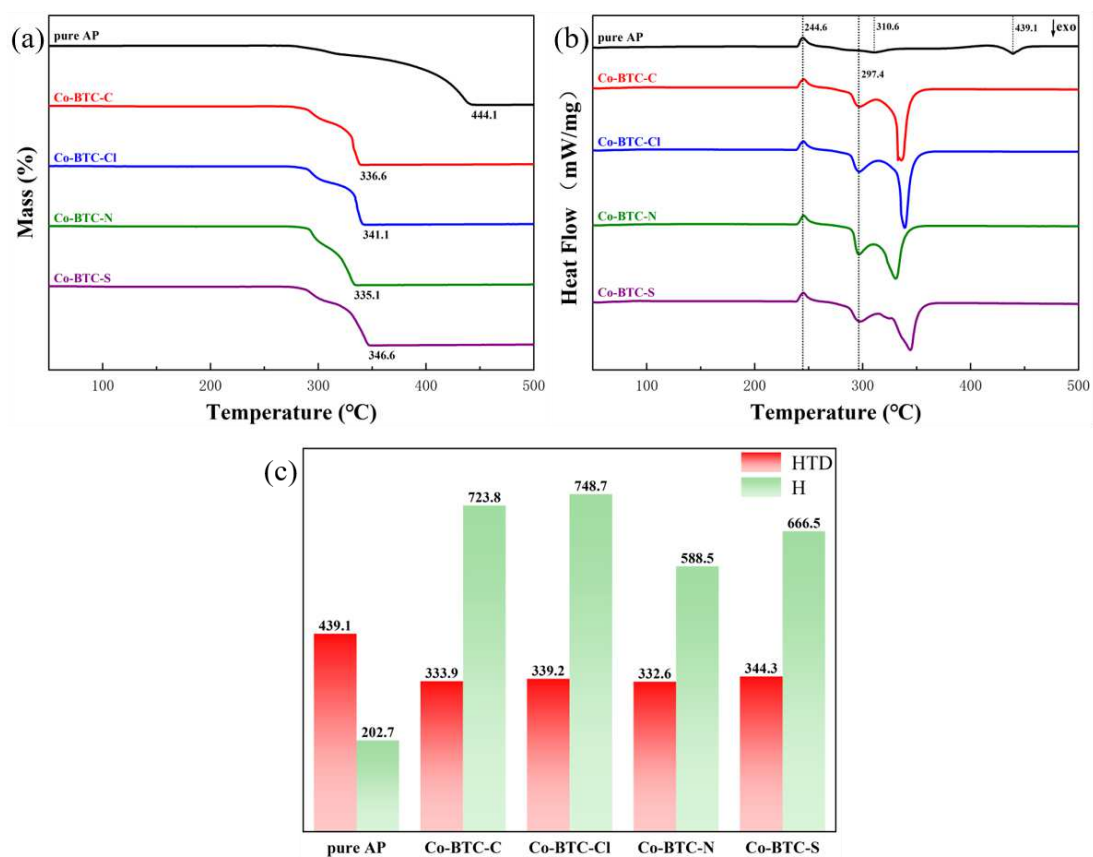
Materials	C (wt%)	O (wt%)	Co (wt%)
Co-BTC-C	43.32	28.46	28.22
Co-BTC-Cl	41.16	27.77	31.07
Co-BTC-N	40.15	27.99	31.85
Co-BTC-S	39.86	29.24	30.90

The morphologies of Co-BTC prepared with different cobalt salts are presented in Fig. 5. Co-BTC-C crystals (Fig. 5a, b) exhibit complete growth, smooth surfaces, and regular crystal shapes with a length of approximately 5 μm and a width of about 500 nm, showing the highest crystallinity—which is attributed to the weak basicity and moderate coordination ability of Ac^- , which buffers the release rate of Co^{2+} and allows sufficient crystal growth under relatively low supersaturation. In contrast, Co-BTC-Cl crystals (Fig. 5c, d) show irregular particle size distribution, obvious size change and a large number of surface defects, which are caused by the weak coordination ability of Cl^- , which leads to the excessive release of free Co, leading to high nucleation rates but incomplete and uneven growth. Co-BTC-N crystals (Fig. 5e, f) show relatively complete growth, fairly uniform particle sizes, and rectangular cuboid shapes with a length of approximately 10 μm and a width of about 2 μm , exhibiting relatively high crystallinity—this is because NO_3^- , although also a weakly coordinating anion,

influences solution polarity and diffusion coefficients differently from Cl^- , making the growth process relatively more stable. Co-BTC-S crystals (Fig. 5g, h) only shows the trend of forming into a rectangular cube, with obviously incomplete growth and the smallest size (both length and width are about half of that of Co-BTC-C), showing the lowest crystallinity, which is due to the strong coordination ability of SO_4^{2-} , which forms a stable complexes with Co, significantly reducing the concentration of active metal ions and seriously hindering nucleation and growth. It is worth noting that the aforementioned counterions (OAc^- , Cl^- , NO_3^- , and SO_4^{2-}) are not incorporated into the final products as framework components (as evidenced by the absence of lattice shifts in XRD and no detectable characteristic signals in FTIR and XPS spectra). Their adjustment of crystal morphology is entirely due to the kinetic differences in the synthesis process, that is, the crystal size and crystallinity of the products are finally determined by adjusting the effective concentration of active Co in the solution and the evolution path of supersaturation.

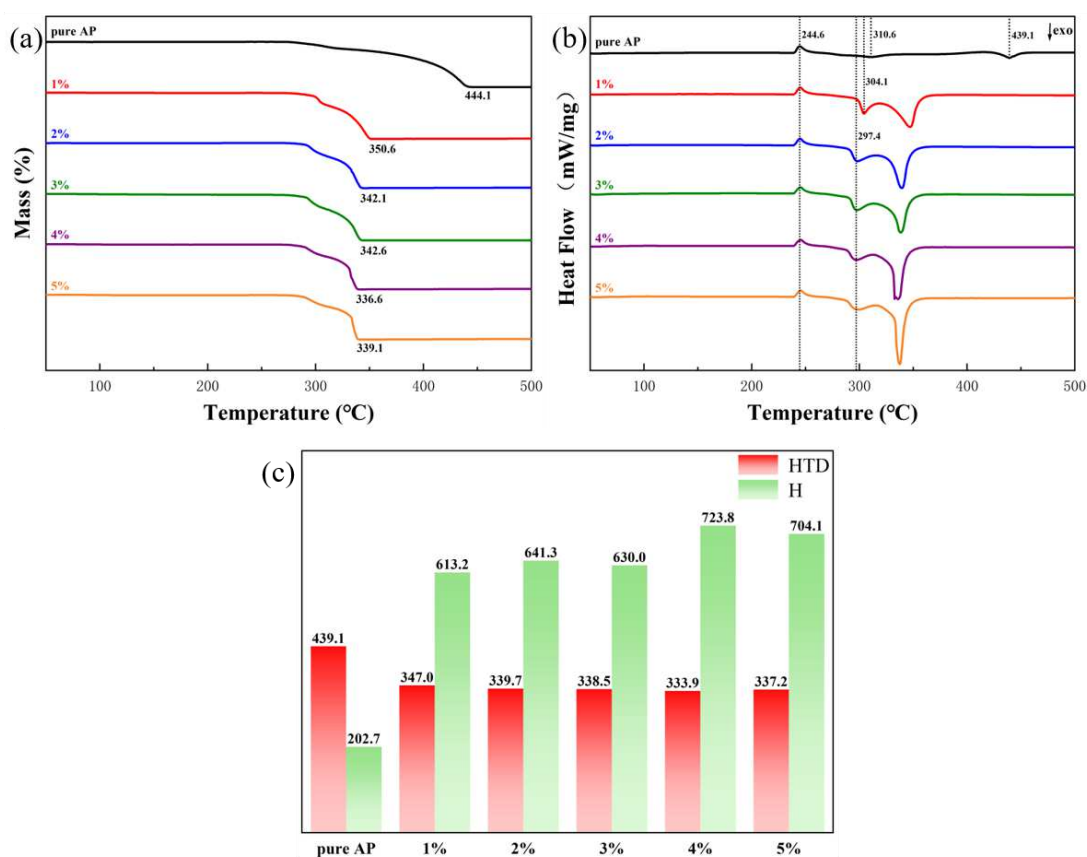
Using energy-dispersive X-ray spectroscopy (EDS) elemental mapping and semi-quantitative analysis, the Co-BTC series materials prepared with 1,3,5-benzenetricarboxylic acid as the ligand and different cobalt salts as metal sources were systematically characterized. As shown in Fig. 6, the C, O, and Co elements in the Co-BTC-C, Co-BTC-Cl, Co-BTC-N, and Co-BTC-S samples are all uniformly distributed, without obvious elemental segregation or phase separation, confirming that different cobalt salt precursors can effectively construct MOF frameworks with homogeneous elemental distribution. Although the theoretical molar amount of Co used in the synthesis was the same, influenced by the anion effect of the precursors and also affected by differences in sample surface states, the semi-quantitative EDS data show that the Co mass fraction in each sample fluctuates within the range of 28.22 – 31.85 wt%. The specific values are listed in Table 1: Co-BTC-C has the lowest Co content (28.22 wt%), Co-BTC-S the highest (31.85 wt%), and Co-BTC-Cl and Co-BTC-N have intermediate values. Meanwhile, the contents of C and O also exhibit corresponding variations with the precursor type.

3.2 Catalytic Performance of Co-BTC toward the Thermal Decomposition of AP



(Note: HTD represents the peak temperature of high-temperature decomposition, and H represents the apparent heat of decomposition)

Fig. 7 (a) TG, (b) DSC curves and (c)HTD and H bar charts of pure AP and Co-BTC/AP



(Note: HTD represents the peak temperature of high-temperature decomposition, and H represents the apparent heat of decomposition)

Fig. 8 (a) TG, (b) DSC curves and (c)HTD versus H bar charts of pure AP and different proportions of Co-BTC-C/AP

To investigate the catalytic effect of Co-BTC prepared with different cobalt salts on the thermal decomposition of AP, TG-DSC characterization was performed on pure AP and Co-BTC/AP at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, and the heat release was calculated. The results are shown in Fig. 7.

Analysis of the TG-DSC curves of pure AP in Fig. 7 (a) and (b) reveals that the thermal decomposition of pure AP can be divided into three stages. The first stage is the crystal transition of AP, corresponding to the endothermic peak at $244.6\text{ }^{\circ}\text{C}$ in the DSC curve, during which no significant mass loss of AP occurs. The second stage is the low-temperature decomposition (LTD) of AP, corresponding to the exothermic peak at $310.6\text{ }^{\circ}\text{C}$ in the DSC curve, during which AP loses about one quarter of its mass. The third stage is the high-temperature decomposition (HTD) of AP, corresponding to the exothermic peak at $439.1\text{ }^{\circ}\text{C}$ in the DSC curve, during which AP is completely converted into gaseous products with no residue. The TG curve shows that the mass of AP no longer decreases after $444.1\text{ }^{\circ}\text{C}$, indicating that AP has completely decomposed.

Comparing the TG-DSC curves in Fig. 7 (a) and (b) after adding 4 wt% of Co-

BTC-C, Co-BTC-Cl, Co-BTC-N, and Co-BTC-S catalysts, respectively, it can be found that the completion temperature of AP decomposition advances to 336.6 °C, 341.1 °C, 335.1 °C, and 346.6 °C, respectively, which are 107.5 °C, 103 °C, 109 °C, and 97.5 °C lower than that of pure AP. The crystal transition temperature of AP does not change significantly, while the low-temperature decomposition peak temperature shifts forward by 13.2 °C to 297.4 °C in all cases. Analysis of Fig. 7 (c) shows that after adding Co-BTC catalysts, the HTD of AP decreases to 333.9 °C, 339.2 °C, 332.6 °C, and 344.3 °C, respectively, which are 105.2 °C, 99.9 °C, 106.5 °C, and 94.5 °C lower than that of pure AP. Meanwhile, the heat release increases from 202.7 J·g⁻¹ for pure AP to 723.8 J·g⁻¹, 748.7 J·g⁻¹, 588.5 J·g⁻¹, and 666.5 J·g⁻¹, respectively. Furthermore, from Fig. 7 (b), it can be seen that the high-temperature decomposition peaks of Co-BTC-C/AP and Co-BTC-Cl/AP are sharper, indicating that their high-temperature decomposition reactions are more intense and better meet practical requirements. Considering all the above, Co-BTC-C is the best catalyst among these four catalysts.

To investigate the effect of catalyst addition amount on the catalytic performance toward AP, Co-BTC-C was selected and a series of Co-BTC-C/AP composite particles with catalyst addition amounts of 1%, 2%, 3%, and 5% were prepared using the same method. The obtained samples were characterized by TG-DSC under the same test conditions as those for the 4% Co-BTC-C/AP composite particles. The test results are shown in Fig. 8.

From the decomposition completion temperature of AP in Fig. 8 (a), it can be seen that when the catalyst addition amount is 4%, the decomposition completion temperature is 336.6 °C, which is significantly lower than those at other addition amounts: 350.6 °C, 342.1 °C, 342.6 °C, and 339.1 °C. It can be seen from Fig. 8 (b) that regardless of the catalyst addition amount, the crystal transition temperature of AP does not change. When the addition amount is 1%, the LTD of AP decreases to 304.1 °C, while at other addition amounts it remains at 297.4 °C. From Fig. 8 (c), it is evident that as the catalyst addition amount increases from 1% to 4%, the HTD of AP gradually decreases to 347.0 °C, 339.7 °C, 338.5 °C, and 333.9 °C, respectively. However, when the addition amount increases to 5%, the HTD of AP rises to 337.2 °C. Moreover, at a catalyst addition amount of 4%, the heat release of AP reaches a maximum value of 723.8 J·g⁻¹, which is significantly higher than those at other addition amounts: 613.2 J·g⁻¹, 641.3 J·g⁻¹, 630.0 J·g⁻¹, and 704.1 J·g⁻¹. Therefore, when the addition amount of Co-BTC-C reaches 4%, its catalytic performance has already reached a

saturation state.

To further investigate the catalytic effect of Co-BTC, the kinetic parameters of thermal decomposition were calculated. The DSC curves of pure AP and 4% Co-BTC-C/AP composite at heating rates of 5–20 °C·min⁻¹ are shown in Fig. 9. As the heating rate increases, the peak temperature of HTD shifts to higher temperatures. Curve fitting using the Kissinger equation (Eq. (3-1)) and the Flynn–Wall–Ozawa equation (Eq. (3-2)) was respectively performed to calculate the activation energies^[43, 44].

$$\ln\left[\frac{\beta}{T^2}\right] = \ln\left[\frac{RA}{E}\right] - \frac{E}{RT} \quad (3-1)$$

$$\ln[\beta] = -1.052 \frac{RA}{E} - \frac{E}{RT} \quad (3-2)$$

In Equation 3-1 and 3-2, β is the heating rate in thermal analysis, in K/min; A is the pre-exponential factor in the Arrhenius equation, with the same dimension as the reaction rate constant k; E is the activation energy of the reaction, in J·mol⁻¹; R is the gas constant, 8.314 J·(mol·K)⁻¹; T is the peak temperature in the DSC curve, in K. Based on the high-temperature decomposition peak temperatures (T) obtained from the DSC curves, linear fitting of $\ln(\beta/T^2)$ and $\ln\beta$ against $1000/T$ was performed, yielding slopes k. The activation energies were then calculated as $E_a = -Rk$ (for the Kissinger method) and $E_a = -Rk/1.052$ (for the Flynn–Wall–Ozawa method), with the units in kJ·mol⁻¹. The fitting results are shown in Fig. 10.

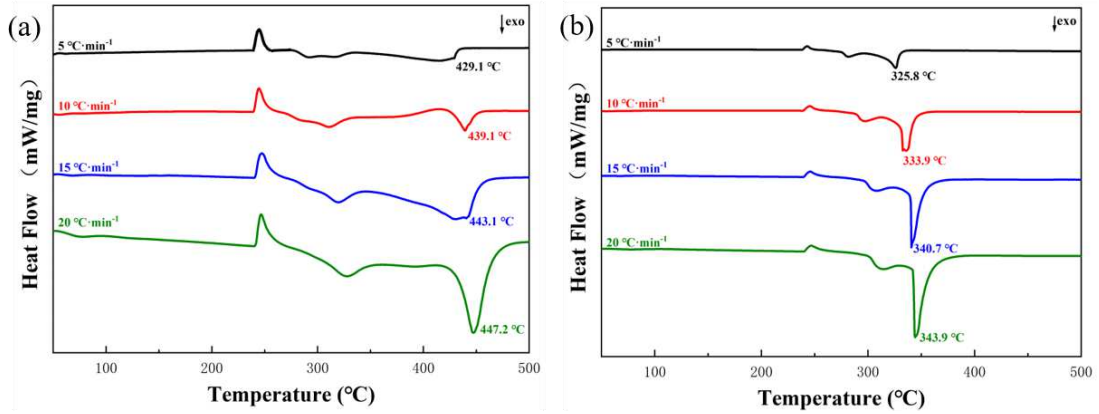


Fig. 9 DSC curves of (a) pure AP and (b) 4% Co-BTC-C/AP at different heating rates

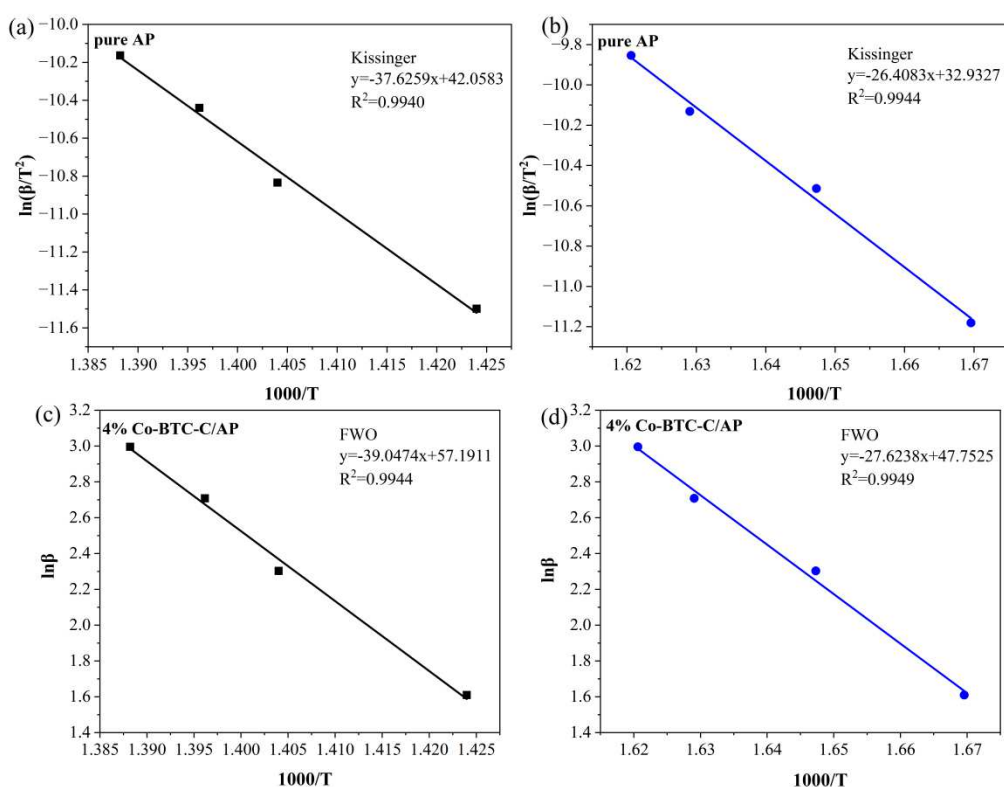


Fig. 10 the fitted equations of HTD at different rates by different methods Kissinger and FWO

As can be seen from Fig. 9, with increasing heating rate, the HTD of AP and 4% Co-BTC-C/AP gradually increases. This may be attributed to the fact that, as the heating rate increases, the internal heat transfer rate of the AP sample becomes lower than the programmed temperature increase rate. Consequently, the decomposition rate cannot keep up, which is known as the "temperature lag phenomenon"^[45]. From the fitting curves in Fig. 10, the apparent activation energies (E_a) of thermal decomposition for pure AP and 4% Co-BTC-C/AP are calculated to be $312.8 \text{ kJ}\cdot\text{mol}^{-1}$ and $219.6 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. The activation energy of AP thermal decomposition decreases significantly by $93.2 \text{ kJ}\cdot\text{mol}^{-1}$ after adding the catalyst. The activation energies calculated by the Flynn–Wall–Ozawa (FWO) method were $308.59 \text{ kJ}\cdot\text{mol}^{-1}$ and $218.31 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, which are close to those obtained by the Kissinger method. A lower activation energy indicates higher catalytic activity of the catalyst, demonstrating that the catalyst effectively promotes the thermal decomposition of AP.

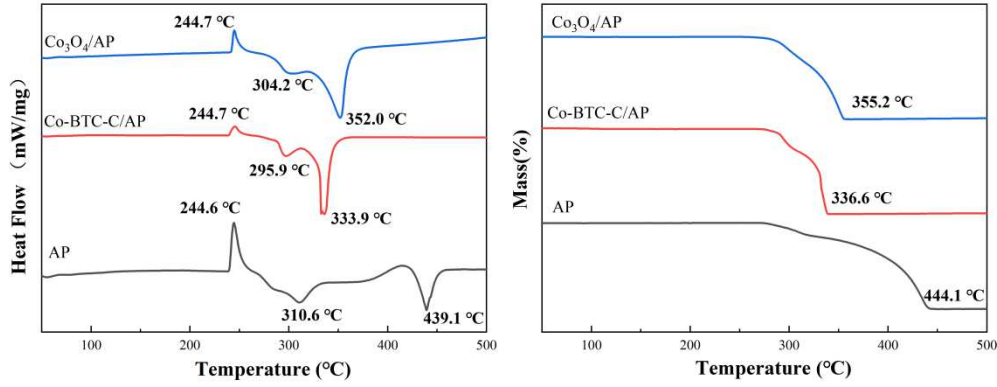


Fig. 11 TG-DSC curves of $\text{Co}_3\text{O}_4/\text{AP}$, Co-BTC-C/AP , pure AP

To verify the catalytic advantage of the Co-BTC-C MOF in the thermal decomposition of AP, we compared it with pure oxide Co_3O_4 (the catalyst addition amount was 4% of the AP mass for both), and the results are shown in Fig. 11. For pure AP, the high-temperature decomposition peak temperature is 439.1°C , and the total heat release is 202.7 J/g . Upon the addition of Co_3O_4 , the high-temperature decomposition peak temperature decreased to 352.0°C , while the heat release increased to 710.8 J/g . In contrast, the Co-BTC-C MOF significantly reduced the peak decomposition temperature of AP to 333.9°C , and increased the heat release to 723.8 J/g , and the process of thermal weight loss significantly moved to a lower temperature range. These results confirm that Co_3O_4 has a clear catalytic promoting effect on the thermal redox decomposition process of AP. However, the superior catalytic activity of Co-BTC-C cannot be simply attributed to the cobalt oxide active species generated in the system. Its high performance originates from the highly dispersed cobalt metal active sites derived from the MOF precursor, as well as the synergistic catalytic effect established between the carbon-based framework and the metal sites. This combination of multiple advantages endows it with superior catalytic ability for AP thermal decomposition over single Co_3O_4 metal oxide.

Table 2 Comparison of catalytic effects of different catalysts on the thermal decomposition of ammonium perchlorate

Materials	Mass (wt%)	HTD (AP) ($^\circ\text{C}$)	Reduction of HTD ($^\circ\text{C}$)	Ea(AP) ($\text{kJ}\cdot\text{mol}^{-1}$)	Reduction of Ea ($\text{kJ}\cdot\text{mol}^{-1}$)	References
Co-BTC	10.0	417.5	92.3	215.9	90.7	[46]
Co-MOF	5.0	388.0	82.2	178.82	11.8	[47]
ZIF-67	5.0	409.7	87.8	-	-	[48]
Co_3O_4	2.0	424.5	98.2	200.9	20.3	[49]

Cu-BTC-C	2.0	437.3	110.8	192.8	66.9	[50]
Co-BTC-C	4.0	439.1	105.2	312.8	93.2	This work

To further evaluate the catalytic performance of Co-BTC-C toward the thermal decomposition of AP, its catalytic effect was compared with representative catalysts reported in previous studies, as summarized in Table 2. It should be noted that because of differences among studies in the source and particle size of AP raw materials and in the testing and kinetic analysis conditions, the apparent activation energy of pure AP fluctuates to some extent in different systems. Therefore, the data in the table are mainly used to compare the relative effects of different catalysts on the thermal decomposition temperature of AP and their ability to reduce the activation energy. The results indicate that catalysts such as Co-BTC, Co-MOF, ZIF-67, and Co_3O_4 can effectively promote AP thermal decomposition. Among them, Co-BTC-C reduced the high-temperature decomposition temperature of AP by 105.2 °C and the activation energy by 93.2 $\text{kJ}\cdot\text{mol}^{-1}$ at a relatively low addition amount (4 wt%), demonstrating an excellent catalytic promoting effect. Compared with some Co-based MOF catalysts that require higher addition amounts, Co-BTC-C shows higher catalytic efficiency.

3.3 Decomposition mechanism study

Unlike conventional catalysts, MOFs undergo reactions such as decomposition and combustion during heating. To further investigate the reaction of Co-BTC-C during the heating process, Co-BTC-C was heated to different temperatures using a muffle furnace, and the residual samples were collected for XRD analysis. The results are shown in Fig. 12.

As shown in Fig. 12, at 200 °C, the XRD pattern of Co-BTC-C exhibits no obvious diffraction peaks, indicating that most of its crystal structure has collapsed. This is because the ligand of Co-BTC-C undergoes carbonization and combustion during heating, leading to the destruction of the original crystal structure and the disappearance of the diffraction peaks of Co-BTC-C. When the temperature reaches 300 °C, new diffraction peaks clearly appear in the sample at 18.98°, 31.26°, 36.82°, 38.64°, 44.78°, 55.62°, 59.32°, and 65.20°, corresponding to the (111), (220), (311), (222), (400), (422), (511), and (440) crystal planes of Co_3O_4 (PDF #97-006-9366), indicating that Co-BTC-C has been completely converted to Co_3O_4 . This is because the cobalt ions in Co-BTC-C form Co_3O_4 in situ with the oxygen from the ligand, thus giving rise to the diffraction peaks of Co_3O_4 . Meanwhile, as the temperature increases, all the relevant XRD diffraction peaks of Co_3O_4 gradually become sharper, and the full width at half

maximum gradually narrows, indicating that the crystal structure of Co_3O_4 becomes more complete and its particle size gradually increases. From the XRD patterns of the Co-BTC-C samples after heating, it can be seen that Co-BTC-C undergoes a decomposition reaction between 200 °C and 300 °C and is completely transformed into Co_3O_4 . Moreover, with increasing temperature, the particle size gradually increases, the crystal structure gradually improves, and the crystallinity becomes higher.

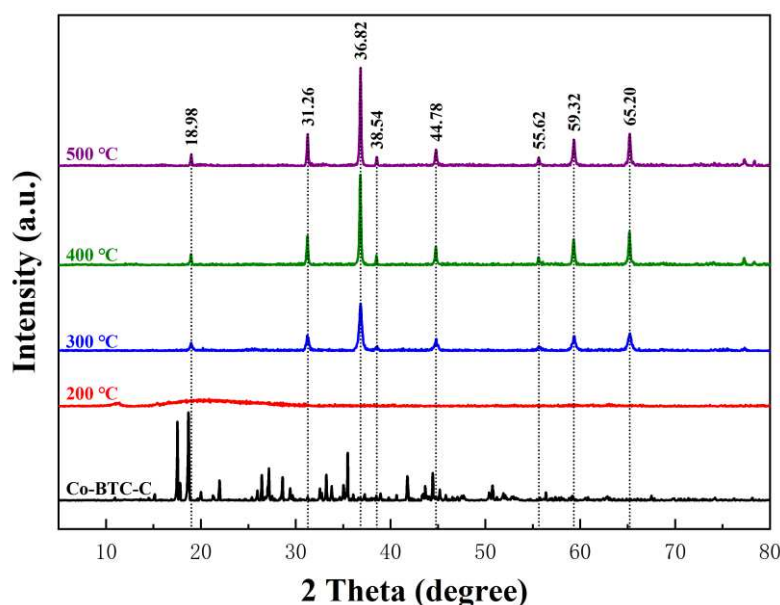


Fig. 12 XRD patterns of Co-BTC-C heated to different temperature

According to the electron transfer mechanism^[51-54], during the low-temperature decomposition stage, a small portion of AP begins to decompose to generate NH_4^+ and ClO_4^- . Meanwhile, the generated NH_3 adsorbs onto the surface of undecomposed AP until it is completely covered, terminating the decomposition of AP. During the high-temperature decomposition stage, NH_3 on the AP surface desorbs and is continuously oxidized under the action of active oxygen until it is completely converted into nitrogen oxides and H_2O . The specific process of AP thermal decomposition is as follows: the electron e^- transfers from ClO_4^- to NH_4^+ , generating ClO_4 and NH_4 . NH_4 further decomposes into NH_3 and active H. Under the action of active H, ClO_4 is first converted into HClO_4 , and then into ClO_3 and H_2O . ClO_3 further decomposes into ClO and O , and reacts with NH_3 to release heat^[55].

Based on the TG-DSC characterization, the decomposition temperature of Co-BTC is lower than the low-temperature decomposition temperature of AP. Therefore, before the thermal decomposition of AP occurs, Co-BTC has already decomposed to form Co_3O_4 . As a MOF, Co-BTC possesses highly dispersed metal active sites, and the Co_3O_4 generated at a relatively low temperature has a small particle size, thus exhibiting

high catalytic activity. During the catalytic process, a $\text{Co}^{2+}/\text{Co}^{3+}$ redox cycle takes place: the reducing species $\text{NH}_3/\text{NH}_4^+$ reduces Co^{3+} to Co^{2+} , while the reactive oxygen species $\text{O}_2/\text{O}_2^-/\text{O}^-$ oxidizes Co^{2+} back to Co^{3+} . This redox cycling accelerates interfacial electron transfer, thereby promoting the cleavage of the Cl-O bond. The reaction first generates key intermediates such as HClO_4 , NH_3 , ClO_3^- , ClO_2 , and ClO ; subsequently, NH_3 is further oxidized and ultimately converted into gaseous products including NO_x , N_2 , H_2O , and HCl . (see Fig. 13).

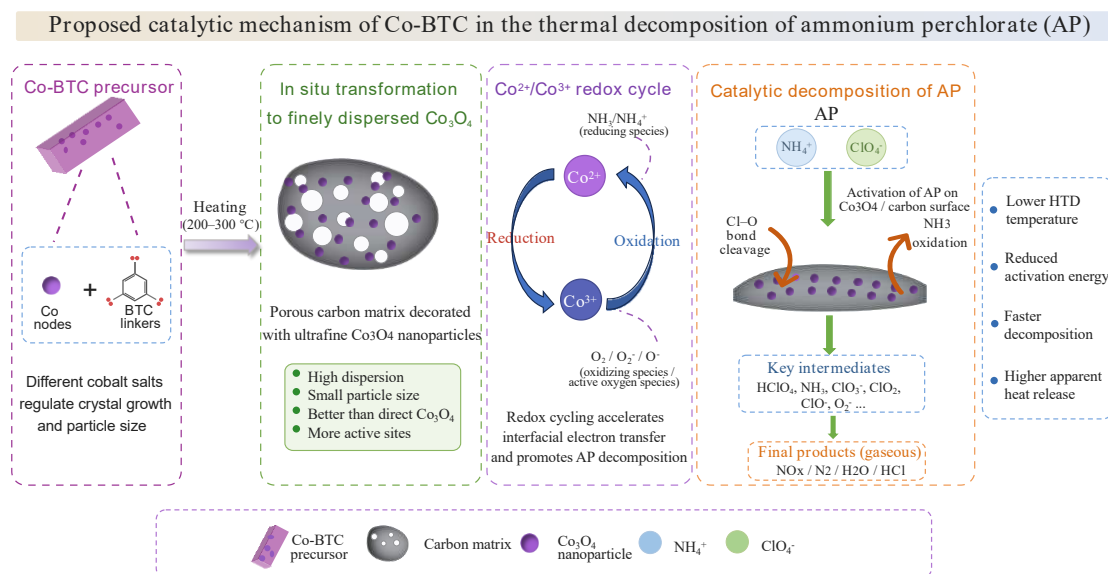


Fig. 13 Mechanism diagram of the thermal decomposition process of AP catalyzed by Co-BTC

4. Conclusions

Using a room-temperature stirring method, four types of Co-BTC with a rectangular cuboid morphology but different particle sizes and crystallinities were successfully synthesized, indicating that under the same reaction conditions, the type of cobalt salt directly and significantly affects the crystal growth rate and particle size of Co-BTC. All four Co-BTC catalysts exhibited good catalytic activity toward the thermal decomposition of AP, among which 4 wt% Co-BTC-C showed the most outstanding performance, reducing the HTD of AP by 105.2 °C, increasing the heat release by 2.6 times, and decreasing the reaction activation energy by 93.2 $\text{kJ}\cdot\text{mol}^{-1}$. Mechanistic analysis further revealed that Co-BTC-C underwent framework decomposition and formed Co_3O_4 in the range of 200–300 °C, prior to the major decomposition stage of AP. Therefore, the highly dispersed cobalt sites in the MOF precursor and the in situ generated Co_3O_4 may jointly contribute to the enhanced thermal decomposition of AP. Overall, this work establishes a correlation among precursor anions, Co-BTC crystal growth, and AP thermal decomposition performance, providing a useful basis for regulating the structure and catalytic properties of Co-based

MOFs through precursor selection.

Statements and Declarations

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