



# DSC/TG-MS Study on in Situ Catalytic Thermal Decomposition of Ammonium Perchlorate over $\text{CoC}_2\text{O}_4$

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**Abstract:** In situ catalytic thermal decomposition of ammonium perchlorate (AP) was investigated over  $\text{CoC}_2\text{O}_4$ . The catalytic activity measurements were carried out by DSC and TG-MS. The results show that the new ecological nano-cobalt oxides exhibit better catalytic performance in thermal decomposition of AP. Adding 2% of  $\text{CoC}_2\text{O}_4$  to AP decreases the decomposition temperature by 104 °C and increases the heat of decomposition from 655 J/g to 1469 J/g. Products of thermal decomposition of AP are  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{O}_2$ ,  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$ . The oxidation of adsorbed ammonia by cobalt oxides via the superoxide active centers takes place on the surface of cobalt oxide. The presence of oxygen can accelerate the oxidation thermal decomposition process of AP, with a clear increase in DSC heat release.

**Key words:** cobalt oxalate; in situ catalysis; ammonium perchlorate; thermal decomposition; differential scanning calorimetry/thermogravimetry-mass spectrometry

As it is well known, nanomaterials readily agglomerate due to their small size, large surface area, and high surface activity, which greatly affect their catalytic properties. Moreover, the agglomeration leads to an inhomogeneous dispersion of the nano-catalysts, and the catalysts cannot fully contact with the media, resulting in a decreased catalytic efficiency in reactions. All these problems not only affect the catalytic properties of the nano-catalysts but also increase the practical cost. However, the in situ synthesis of nano-catalysts in a propellant can overcome the problems effectively, which opens a new application prospect for using nano-catalysts in a propellant. The core of the in situ generation technology is to make a homogeneous mixture of a nano-catalyst precursor and oxidant in a conventional way. Then under the effect of external forces, the functional complex decomposes to atom-clusters of metal or metal oxide and further generates a renascent nano-catalyst to catalyze a reaction.

Ammonium perchlorate (AP) is one of the most common oxidants in composite solid propellants, and its thermal decomposition characteristics greatly influence the combustion behavior of propellants. As it has been shown in many studies,

the activation energy, reaction rate, and pyrolysis temperature of the thermal decomposition of AP are related to the properties of solid propellants, especially the combustion rate. The lower the pyrolysis temperature, the shorter the delay time of propellant ignition, and the higher the combustion rate [1,2]. The catalytic applications of some transition metals and their oxides for the thermal decomposition of AP have been widely studied [3–6]. However, the catalytic behavior of cobalt oxalate ( $\text{CoC}_2\text{O}_4$ ) in the thermal decomposition of AP has not been reported. The aim of this work is to investigate the catalytic activities of  $\text{CoC}_2\text{O}_4$  in the thermal decomposition of AP by differential scanning calorimetry (DSC) and thermogravimetry-mass spectrometry (TG-MS).

## 1 Experimental

### 1.1 Catalyst preparation

All reagents were analytical grade and used without further purification.  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and AP were obtained from Shanghai Chemical Factory, China. Oxalic acid was obtained

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from Shanghai Lingfeng Chemical Factory, China.

First, appropriate amounts of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and oxalic acid (molar ratio = 1:1) were added into distilled water. The solution was continuously stirred with a magnet until the pink precipitate formed. Then the products were washed with distilled water and centrifuged. After that, the samples were dried in desiccators at 80 °C for 4 h.

$\text{CoC}_2\text{O}_4$  and AP were mixed in 2:98 mass ratio to prepare the sample for thermal analysis.

## 1.2 Catalyst characterization

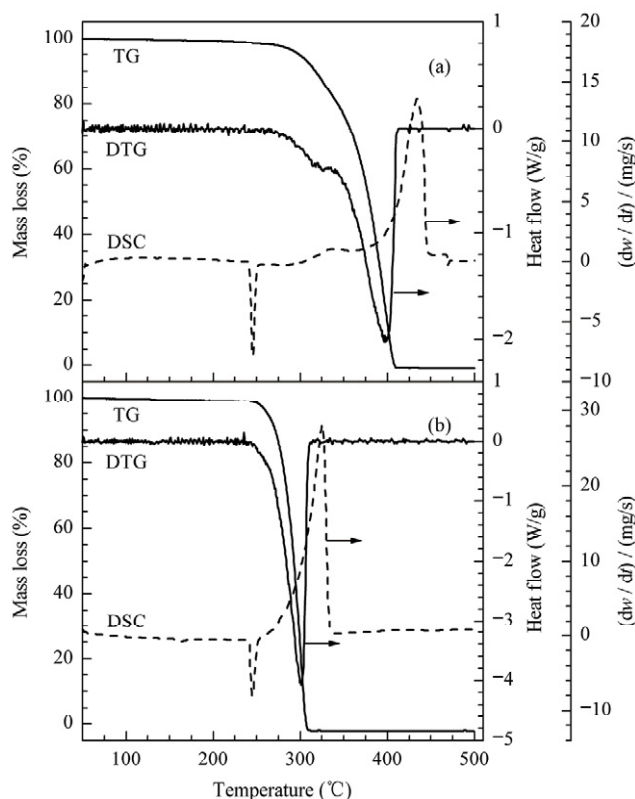
Thermal decomposition characteristics of the sample were determined with a thermal gravimetric analyzer (Mettler Toledo, model TGA/SDTA 851E) coupled with an online quadrupole mass spectrometer (Pfeiffer Vacuum, model ThermoStar GSD 301 T3), operated under flowing argon (purity = 99.99%, 50 ml/min flow rate, atmospheric pressure) with a heating rate of 10 °C/min. The sample size was about 1.00 mg with  $\text{Al}_2\text{O}_3$  used as reference. The connection between the thermobalance and the mass spectrometer was done by means of a stainless steel capillary, which was maintained at 150 °C. The mass spectrometer was operated with an electron impact ionizer with energy 70 eV. A Mettler Toledo DSC823E instrument was used at a heating rate of 20 °C/min in  $\text{N}_2$  atmosphere over the range 20–500 °C with  $\text{Al}_2\text{O}_3$  as reference.

## 2 Results and discussion

### 2.1 TG-DTG and DSC analysis of the thermal decomposition of AP

The results of the DTG and TG experiments are shown in Fig. 1. As it is shown in Fig. 1(a), the thermal decomposition of pure AP exhibits two weight loss steps. The 20% weight loss at low temperature (< 350 °C) is attributed to the partial decomposition of AP. The 80% weight loss at high temperature (> 350 °C) is caused by the complete decomposition of the intermediate to volatile products. The DTG and TG curves for the thermal decomposition of AP in the presence of  $\text{CoC}_2\text{O}_4$  are shown in Fig. 1(b). There are noticeable changes in the decomposition pattern. The thermal decomposition of AP catalyzed by  $\text{CoC}_2\text{O}_4$  contains only one step corresponding to 99% weight loss.

The DSC curves for pure AP and AP in the presence of  $\text{CoC}_2\text{O}_4$  are also shown in Fig. 1. The endothermic peak at 245 °C is due to a crystallographic transition. The  $\text{CoC}_2\text{O}_4$  additive has no effects on the crystallographic transition temperature. The exothermic peak at 330 °C in Fig. 1(a) is attributed to the low-temperature stage of AP decomposition, and the exothermic peak at about 434 °C is the second step of AP decomposition, corresponding to the two weight loss steps.



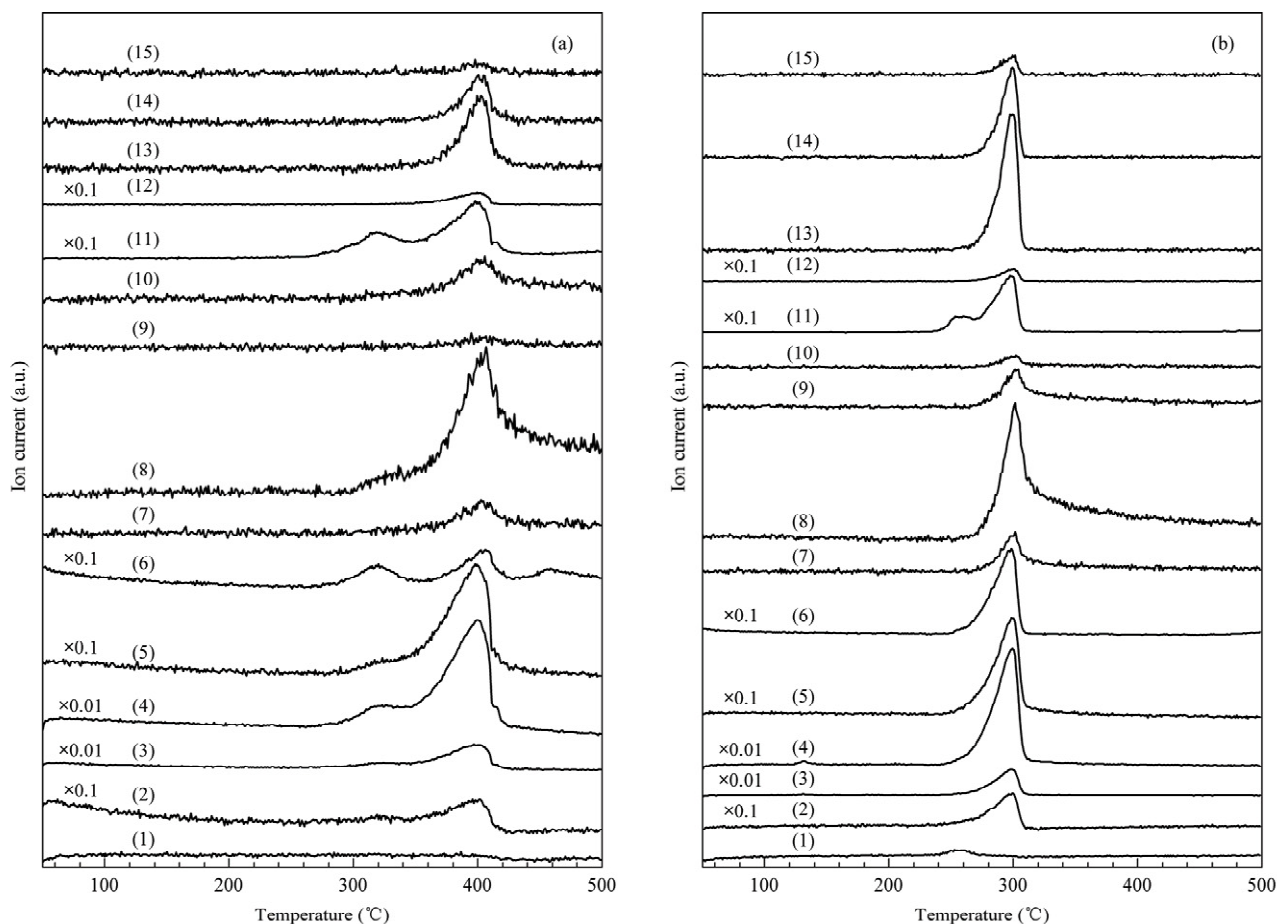
**Fig. 1.** TG, DTG, and DSC curves of pure ammonium perchlorate (AP) (a) and AP+2%  $\text{CoC}_2\text{O}_4$  (b).

The DSC curve of AP in the presence of  $\text{CoC}_2\text{O}_4$  shows significant changes in the decomposition pattern. The first exothermic peak occurring at 325 °C changed into a sharp one associated with the one-step weight loss. The second exothermic is absent. AP is completely decomposed at lower temperature in shorter time. The heat of decomposition increases from 655 J/g to 1469 J/g. The experiment results indicate that  $\text{CoC}_2\text{O}_4$  is an effective catalyst.

### 2.2 TG-MS analysis of the thermal decomposition of AP

Fig. 2(a) and (b) show the gaseous products during the thermal decomposition of pure AP and AP in the presence of  $\text{CoC}_2\text{O}_4$ . Table 1 lists the maximum mass spectrometric ion intensity values ( $I_{m/z}$ ).  $I_{m/z}$  values are normalized to the ion current of  $\text{H}_2\text{O}^+$ ,  $I_{18}$ , which is most intense among the evolved products. The following gaseous products of AP decomposition in nitrogen are identified on the basis of these relative  $I_{m/z}$  values.

Fig. 2(a) shows the ion intensity curves during the thermal decomposition of pure AP. As shown in Fig. 2(a) the decomposition of pure AP proceeds in two steps. At low temperature, the products of thermal decomposition of pure AP are  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and a small amount of  $\text{N}_2\text{O}$  and  $\text{O}_2$ . During the high-temperature stage of AP decomposition,  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{Cl}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{NO}_2$ , and a small amount of  $\text{ClO}_2$  are formed.



**Fig. 2.** Comparison of ion intensity curves during the thermal decomposition of pure AP (a) and AP + 2%  $\text{CoC}_2\text{O}_4$  (b). (1)  $\text{C}^+$ ; (2)  $\text{NH}_2^+$ ,  $\text{O}^+$ ; (3)  $\text{H}_2\text{O}^+$ ; (4)  $\text{NH}_3^+$ ; (5)  $\text{NO}^+$ ; (6)  $\text{O}_2^+$ ; (7)  $\text{H}^{35}\text{Cl}^+$ ; (8)  $^{35}\text{Cl}^+$ ; (9)  $\text{H}^{37}\text{Cl}^+$ ; (10)  $^{37}\text{Cl}^+$ ; (11)  $\text{N}_2\text{O}^+$ ,  $\text{CO}_2^+$ ; (12)  $\text{NO}_2^+$ ; (13)  $^{35}\text{Cl}_2^+$ ; (14)  $^{35,37}\text{Cl}_2^+$ ; (15)  $^{37}\text{Cl}_2^+$ .

**Table 1** Assignments and intensity maxima of the mass spectroscopic ions during the thermal decomposition of AP

$m/z$	Assignment	Pure AP		$\text{AP} + 2\% \text{CoC}_2\text{O}_4$	
		Temperature ranges of single and double peaks ( $^{\circ}\text{C}$ )	Relative values of ion current	Temperature ranges of single and double peaks ( $^{\circ}\text{C}$ )	Relative values of ion current
16	$\text{NH}_2^+$ , $\text{O}^+$	290–350, 350–440	4.30, 4.88	250–320	4.13
17	$\text{NH}_3^+$ , $\text{OH}^+$	290–350, 350–440	18.03, 24.64	250–320	23.85
18	$\text{H}_2\text{O}^+$	280–350, 350–440	69.08, 100	250–330	100
30	$\text{NO}^+$	310–440	8.23	250–340	7.82
32	$\text{O}_2^+$	280–350, 350–430, 430–500	1.98, 2.51, 1.83	250–310	5.08
35	$^{35}\text{Cl}^+$	350–440	0.29	260–360	0.33
36	$\text{H}^{35}\text{Cl}^+$	350–440	0.20	270–400	0.18
37	$^{37}\text{Cl}^+$	350–440	0.74	260–360	0.89
38	$\text{H}^{37}\text{Cl}^+$	350–440	0.33	270–400	0.33
44	$\text{N}_2\text{O}^+$	270–350, 350–440	1.21, 2.37	220–270, 270–310	1.04, 3.19
46	$\text{NO}_2^+$	350–440	0.62	250–320	0.74
67	$\text{ClO}_2^+$	350–440	0.42	—	—
70	$^{35}\text{Cl}_2^+$	350–440	0.33	260–310	0.83
72	$^{35,37}\text{Cl}_2^+$	350–440	0.21	260–310	0.58
74	$^{37}\text{Cl}_2^+$	350–440	0.21	260–310	0.21

Fig. 2(b) shows the ion intensity curves during the thermal decomposition of pure AP in the presence of  $\text{CoC}_2\text{O}_4$ . As shown in Fig. 2(b), AP is completely decomposed at lower

temperature in shorter time. The products of thermal decomposition are  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{Cl}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{NO}_2$ . However,  $\text{ClO}_2$  is not detected. Compared with the decompo-

sition of pure AP, it can be seen that the products are formed in one step during the thermal decomposition of AP in the presence of  $\text{CoC}_2\text{O}_4$ .

### 2.3 Mechanism of thermal decomposition of AP

The thermal decomposition of AP is a complex process, which contains hundreds of chain reactions. At low temperature, the thermal decomposition of AP is a gaseous and solid multiphase reaction. At first, a proton passing from  $\text{NH}_4^+$  to  $\text{ClO}_4^-$  becomes mobile, and then  $\text{NH}_3$  and  $\text{HClO}_4$  are formed. There are two competitive processes, decomposition and sublimation [7,8]. Chloric acid decomposes more rapidly because it is less stable. Its decomposition products include  $\text{ClO}_3$ ,  $\text{ClO}$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$ .  $\text{NH}_3$  is oxidized by the decomposition products.  $\text{N}_2\text{O}$  is the only product of oxidation as can be seen in Fig. 2(a).  $\text{NH}_4\text{NO}_3$  is formed during the decomposition and oxidation of AP [9], and it is the possible precursor of  $\text{N}_2\text{O}$  and water. The active sites will be covered by  $\text{NH}_3$  and  $\text{H}_2\text{O}$  at low temperature, which leads to the stopping of chemical reaction.

At high temperature ( $> 350\text{ }^\circ\text{C}$ ), the main gas products of the thermal decomposition of AP are  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{Cl}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{NO}_2$ . It starts with the same elementary proton transfer step from the ammonium ion to the perchlorate ion. The difference is that the process starts not in a subsurface site but on the surface [10–12].

Because of the desorption of  $\text{NH}_3$  and the deliquescence of AP, chemical reactions between the thermal decomposition products  $\text{HClO}_4$  and  $\text{NH}_3$  occur both on the surface of AP and in the gas phase above the surface with rising temperature. When the amount of  $\text{HClO}_4$  and its degradation products increases, the oxidation of  $\text{NH}_3$  also increases, and the exothermic decomposition reaction has the dominant advantages. It can be seen from the mass spectrogram that nitrogen oxides ( $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ) are substantially produced, and the heat output significantly increases.  $\text{Cl}_2$  reacts with  $\text{H}_2\text{O}$  and converts to  $\text{HCl}$  in the high-temperature decomposition range.

Fig. 2(b) shows the ion intensity changes at different temperatures during the thermal decomposition of AP catalyzed by  $\text{CoC}_2\text{O}_4$ . Compared with thermal decomposition of pure AP, the gaseous products are mainly produced in the first decomposition step, while  $m/z = 44$  involves two-step generation. As it can be seen from Fig. 2(b) curve (1),  $\text{C}^+$  ions are generated at about  $253\text{ }^\circ\text{C}$ , which proves that the gaseous product is  $\text{CO}_2^+$  while  $m/z = 44$  is detected at  $253\text{ }^\circ\text{C}$ . This also indicates that  $\text{CoC}_2\text{O}_4$  decomposes to nano-cobalt oxide at about  $253\text{ }^\circ\text{C}$  under the protection of  $\text{N}_2$ . Fig. 1(b) is the DTG curve of AP decomposition catalyzed by  $\text{CoC}_2\text{O}_4$ . It is shown that AP begins to lose weight at about  $255\text{ }^\circ\text{C}$ , while the weight loss of pure AP begins around  $320\text{ }^\circ\text{C}$ . It seems that the presence of  $\text{CoC}_2\text{O}_4$  can evidently lower the decomposition temperature of AP, which can be explained by the in situ generation technol-

ogy. In this procedure the nano-cobalt oxide is produced directly in the catalytic medium, and thus the renescent nano-catalyst has a higher catalytic activity and a larger surface area and can participate in the catalytic reaction immediately. Thus it can exert its maximum effectiveness.

The cobalt oxide generated from  $\text{CoC}_2\text{O}_4$  decomposition plays an intense catalytic role in the thermal decomposition of AP. Transition metal oxides playing such a role may be owed to their multi-valence character, which can accelerate the rate of charge transfer in an oxidation-reduction reaction [13]. Moreover, during the catalytic process, the transition metal oxide transforms into a metal perchloride intermediate, which is thermodynamically instable. As a result, the initial activation energy of AP is reduced, which in turn lowers the decomposition temperature and then speeds up the thermal decomposition of AP.

The decomposition heat increases from  $655\text{ J/g}$  to  $1469\text{ J/g}$ . Compared with  $\text{Co}_2\text{O}_3$  nanocrystals catalyzing the thermal decomposition of AP, the heat of decomposition is increased and the decomposition temperature is decreased [14]. The larger area and more active reaction centers of the new ecological nano-catalyst are beneficial for the adsorption of  $\text{NH}_3$  and  $\text{O}_2$  on the surface of cobalt oxide. The mechanism of catalytic action is based on the presence of superoxide ions ( $\text{O}_2^-$ ) on the surface of cobalt oxide [15,16]. When the partial pressure of  $\text{O}_2$  increases, the formation of  $\text{O}_2^-$ -covered sites on cobalt oxide is increased, and the presence of oxygen can accelerate the oxidation of  $\text{NH}_3$ . Fig. 2 ( $m/z = 30, 44$ , and  $46$ ) and Table 1 show that the mass spectrometric ion intensities of nitrogen oxides ( $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$ ) are bigger than those during the thermal decomposition of pure AP. The oxidation of  $\text{NH}_3$  is an exothermic reaction. It increases the exothermic heat of the thermal decomposition process.

### 3 Conclusions

$\text{CoC}_2\text{O}_4$  shows an intensive catalytic effect on the thermal decomposition of AP. It can raise the decomposition speed of AP, increase the exothermic heat, and lower the decomposition temperature. Adding 2% of  $\text{CoC}_2\text{O}_4$  in AP decreases the high temperature peak of AP decomposition by  $104\text{ }^\circ\text{C}$  and increases the exothermic heat of decomposition from  $655\text{ J/g}$  to  $1469\text{ J/g}$ . It can be foreseen that the transition metal oxalate will be an attractive catalyst used in the AP-based propellant. In situ catalytic thermal decomposition of AP has been investigated over  $\text{CoC}_2\text{O}_4$ . The results show that the new ecological nano-cobalt oxides exhibit better catalytic performance in the thermal decomposition of AP. The oxidation of adsorbed ammonia by cobalt oxides via the superoxide active centers takes place on the surface of cobalt oxide. The presence of  $\text{O}_2$  can accelerate the oxidation thermal decomposition process of AP, with a clear increase of DSC heat release.

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