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RESEARCH PAPER

DSC/TG-MS Study on in Situ Catalytic Thermal Decomposition of Ammonium Perchlorate over CoC₂O₄

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Abstract: In situ catalytic thermal decomposition of ammonium perchlorate (AP) was investigated over CoC₂O₄. 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 CoC₂O₄ 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 H₂O, NH₃, O₂, HCl, Cl₂, NO, N₂O, and NO₂. 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 (CoC₂O₄) in the thermal decomposition of AP has not been reported. The aim of this work is to investigate the catalytic activities of CoC₂O₄ 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. Co(NO₃)₂·6H₂O 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.

CoC_2O_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 Al_2O_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 N_2 atmosphere over the range 20–500 °C with Al_2O_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 CoC_2O_4 are shown in Fig. 1(b). There are noticeable changes in the decomposition pattern. The thermal decomposition of AP catalyzed by CoC_2O_4 contains only one step corresponding to 99% weight loss.

The DSC curves for pure AP and AP in the presence of CoC_2O_4 are also shown in Fig. 1. The endothermic peak at 245 °C is due to a crystallographic transition. The CoC_2O_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.

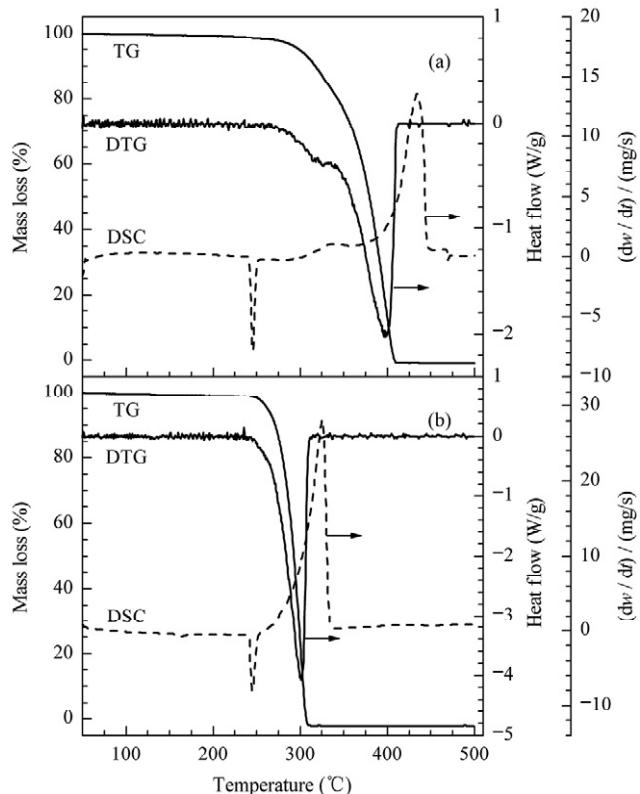


Fig. 1. TG, DTG, and DSC curves of pure ammonium perchlorate (AP) (a) and AP+2% CoC_2O_4 (b).

The DSC curve of AP in the presence of CoC_2O_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 CoC_2O_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 CoC_2O_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 H_2O^+ , 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 NH_3 , H_2O , and a small amount of N_2O and O_2 . During the high-temperature stage of AP decomposition, HCl , H_2O , N_2O , NH_3 , Cl_2 , NO , O_2 , NO_2 , and a small amount of ClO_2 are formed.

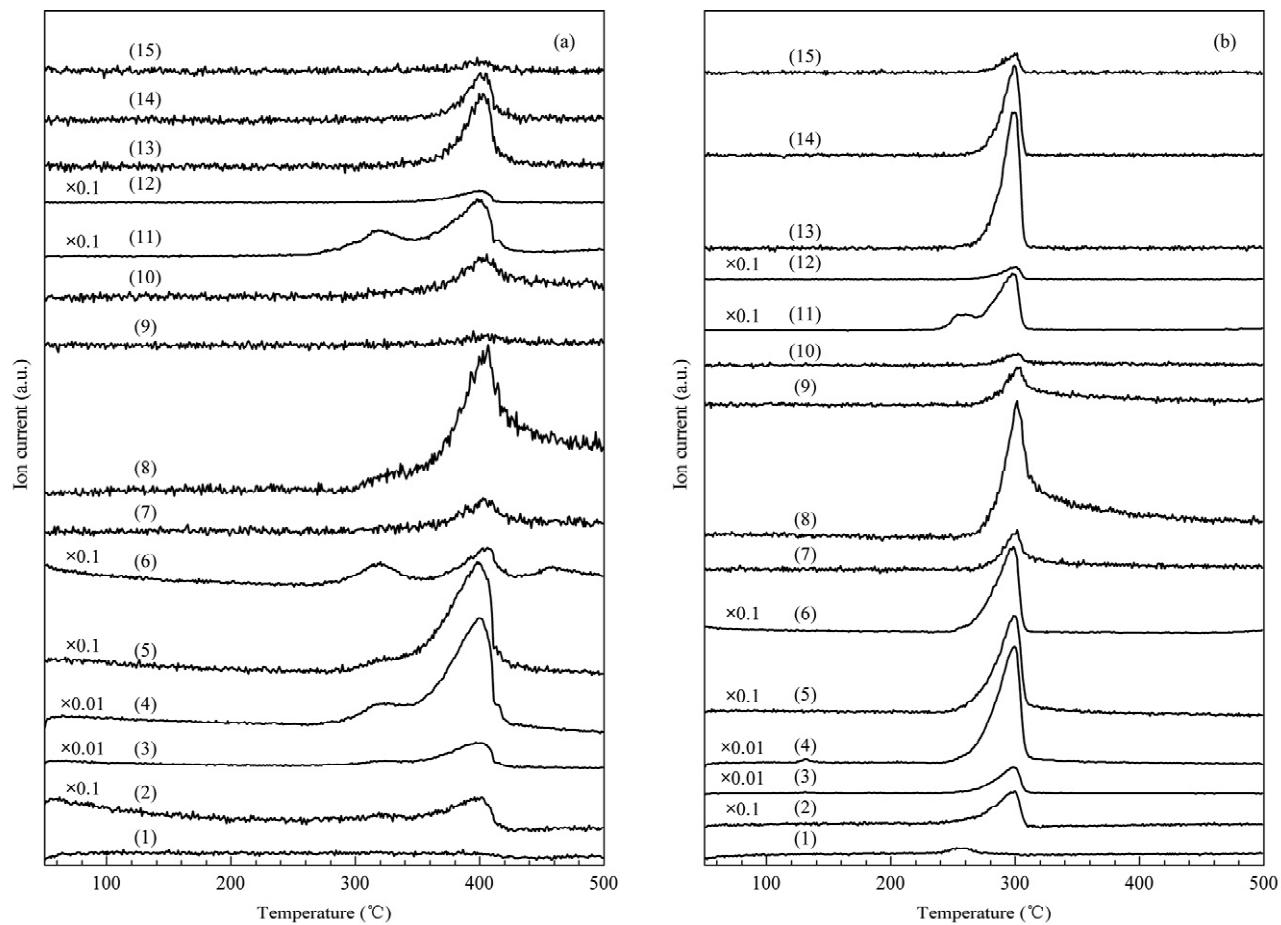


Fig. 2. Comparison of ion intensity curves during the thermal decomposition of pure AP (a) and AP + 2% CoC₂O₄ (b). (1) C⁺; (2) NH₃⁺, O⁺; (3) H₂O⁺; (4) NH₂⁺; (5) NO⁺; (6) O₂⁺; (7) H³⁵Cl⁺; (8) H³⁵Cl⁺; (9) H³⁷Cl⁺; (10) ³⁷Cl⁺; (11) N₂O⁺, CO₂⁺; (12) NO₂⁺; (13) ³⁵Cl₂⁺; (14) ^{35,37}Cl₂⁺; (15) ³⁷Cl₂⁺.

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

<i>m/z</i>	Assignment	Pure AP		AP+2%CoC ₂ O ₄	
		Temperature ranges of single and double peaks (°C)	Relative values of ion current	Temperature ranges of single and double peaks (°C)	Relative values of ion current
16	NH ₃ ⁺ , O ⁺	290–350, 350–440	4.30, 4.88	250–320	4.13
17	NH ₂ ⁺ , OH ⁺	290–350, 350–440	18.03, 24.64	250–320	23.85
18	H ₂ O ⁺	280–350, 350–440	69.08, 100	250–330	100
30	NO ⁺	310–440	8.23	250–340	7.82
32	O ₂ ⁺	280–350, 350–430, 430–500	1.98, 2.51, 1.83	250–310	5.08
35	H ³⁵ Cl ⁺	350–440	0.29	260–360	0.33
36	H ³⁵ Cl ⁺	350–440	0.20	270–400	0.18
37	H ³⁷ Cl ⁺	350–440	0.74	260–360	0.89
38	H ³⁷ Cl ⁺	350–440	0.33	270–400	0.33
44	N ₂ O ⁺	270–350, 350–440	1.21, 2.37	220–270, 270–310	1.04, 3.19
46	NO ₂ ⁺	350–440	0.62	250–320	0.74
67	ClO ₂ ⁺	350–440	0.42	—	—
70	³⁵ Cl ₂ ⁺	350–440	0.33	260–310	0.83
72	^{35,37} Cl ₂ ⁺	350–440	0.21	260–310	0.58
74	³⁷ 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 CoC₂O₄. As shown in Fig. 2(b), AP is completely decomposed at lower

temperature in shorter time. The products of thermal decomposition are HCl, H₂O, N₂O, NH₃, Cl₂, NO, O₂, and NO₂. However, ClO₂ 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 CoC_2O_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 NH_4^+ to ClO_4^- becomes mobile, and then NH_3 and 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 ClO_3 , ClO , O_2 , and H_2O . NH_3 is oxidized by the decomposition products. N_2O is the only product of oxidation as can be seen in Fig. 2(a). NH_4NO_3 is formed during the decomposition and oxidation of AP [9], and it is the possible precursor of N_2O and water. The active sites will be covered by NH_3 and H_2O at low temperature, which leads to the stopping of chemical reaction.

At high temperature ($> 350^\circ\text{C}$), the main gas products of the thermal decomposition of AP are HCl , H_2O , N_2O , NH_3 , Cl_2 , NO , O_2 , and 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 NH_3 and the deliquescence of AP, chemical reactions between the thermal decomposition products HClO_4 and NH_3 occur both on the surface of AP and in the gas phase above the surface with rising temperature. When the amount of HClO_4 and its degradation products increases, the oxidation of NH_3 also increases, and the exothermic decomposition reaction has the dominant advantages. It can be seen from the mass spectrogram that nitrogen oxides (NO_2 , NO , N_2O) are substantially produced, and the heat output significantly increases. Cl_2 reacts with H_2O and converts to 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 CoC_2O_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), C^+ ions are generated at about 253°C , which proves that the gaseous product is CO_2 while $m/z = 44$ is detected at 253°C . This also indicates that CoC_2O_4 decomposes to nano-cobalt oxide at about 253°C under the protection of N_2 . Fig. 1(b) is the DTG curve of AP decomposition catalyzed by CoC_2O_4 . It is shown that AP begins to lose weight at about 255°C , while the weight loss of pure AP begins around 320°C . It seems that the presence of CoC_2O_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 renascent 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 CoC_2O_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 unstable. 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 J/g to 1469 J/g. Compared with Co_2O_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 NH_3 and O_2 on the surface of cobalt oxide. The mechanism of catalytic action is based on the presence of superoxide ions (O_2^-) on the surface of cobalt oxide [15,16]. When the partial pressure of O_2 increases, the formation of O_2^- -covered sites on cobalt oxide is increased, and the presence of oxygen can accelerate the oxidation of NH_3 . Fig. 2 ($m/z = 30, 44$, and 46) and Table 1 show that the mass spectrometric ion intensities of nitrogen oxides (NO , N_2O , and NO_2) are bigger than those during the thermal decomposition of pure AP. The oxidation of NH_3 is an exothermic reaction. It increases the exothermic heat of the thermal decomposition process.

3 Conclusions

CoC_2O_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 CoC_2O_4 in AP decreases the high temperature peak of AP decomposition by 104°C and increases the exothermic heat of decomposition from 655 J/g to 1469 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 CoC_2O_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 O_2 can accelerate the oxidation thermal decomposition process of AP, with a clear increase of DSC heat release.

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