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# A novel hydrolysis method to synthesize chromium hydroxide nanoparticles and its catalytic effect in the thermal decomposition of ammonium perchlorate

## Ping Li<sup>a,b</sup>, Zhen Zhou<sup>a</sup>, Hongbin Xu<sup>a,b,\*</sup>, Yi Zhang<sup>a,b</sup>

<sup>a</sup> Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China
<sup>b</sup> National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Chinese Academy of Science, Beijing 100190, PR China

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## ABSTRACT

A procedure for the preparation of spherical  $Cr(OH)_3$  nanoparticles was developed based on the aging of chromium nitrate aqueous solutions in the presence of sodium fluoride, urea, and polyvinylpyrrolidone. Using scanning electron microscopy, transmission electron microscopy, and energy dispersive spectroscopy, the morphological characteristics of  $Cr(OH)_3$  were controlled by altering the molar ratio of fluoride ion to chromium ion, as well as the initial pH and chromium ion concentration. The prepared nanosized  $Cr(OH)_3$  decreased the temperature required to decompose ammonium perchlorate from 450 °C to about 250 °C as the catalyst. The possible catalytic mechanism of the thermal decomposition of ammonium perchlorate was also discussed.

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#### 1. Introduction

Chromium hydroxide  $(Cr(OH)_3)$  nanoparticles have found potential technological applications, i.e., in nitrogen fertilizer, and petrochemical engineering catalysis, as a pigment, or as a model system in colloid science [1–3].

 $Cr(OH)_3$ nanoparticles traditionally synthesized are by hydrolysis of very diluted Cr<sup>3+</sup> aqueous solutions  $(2 \times 10^{-4} - 1 \times 10^{-3} \text{ mol dm}^{-3})$  in the presence of SO<sub>4</sub><sup>2-</sup> at moderate temperatures (60–90 °C) for long durations (18 h to several days) [4,5]. Strengthening methods are also adopted to synthesize monodispersed Cr(OH)<sub>3</sub> particles such as forced hydrolysis and microwave dielectric heating. For example, Ocaña prepared nanosized Cr(OH)<sub>3</sub> spherical particles by forced hydrolyzing aqueous solution of  $Cr(NO_3)_3$  and  $Na_2SO_4$  in the presence of urea and polyvinyl pyrrolidone K-30 (PVP) [6]. Gómez et al. synthesized Cr(OH)<sub>3</sub> sub-micro- and nanoparticles by microwave dielectric heating both chrome alum (KCr(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O) solutions and solutions of  $Cr(NO_3)_3 - K_2SO_4$  with different initial  $[Cr^{3+}]/[SO_4^{2-}]$ ratios, at the boiling temperature [7]. The role of  $SO_4^{2-}$  has been proved to be crucial in the formation of Cr(OH)<sub>3</sub> nanoparticles because the  $SO_4^{2-}$ , acting as a counter ion, forms complexes such as  $[Cr_2(OH)_2SO_4]^{2+}$  and  $Cr(OH)SO_4$  and others that are believed to constitute units of precursor complexes [8,9].

Ammonium perchlorate (AP) is the most common oxidizer used in composite solid propellants. The characteristics of its thermal decomposition influence the combustion of these propellants. A specific feature of the thermal decomposition of AP is its extreme sensitivity to metal oxide additives, which accelerate the lowtemperature thermal decomposition of AP [10]. The best metal oxide catalyst is CuCr<sub>2</sub>O<sub>4</sub>, which decreases thermal decomposition temperature of AP from about 450 °C to 273 °C [11].

The thermal decomposition of AP initially produces  $NH_3$  and  $HClO_4$  as intermediates which are catalyzed by metal oxides to further decompose to  $NH_3$ ,  $H_2O$ ,  $N_2O$ , NO,  $N_2$ ,  $Cl_2$ , and so on [12]. Some p-type metal oxides, such as CuO and NiO which catalyze AP thermal decomposition at 275.8 °C and 357 °C, respectively, have been shown to be efficient catalysts of the thermal decomposition of AP. In addition, recent investigations have shown that nanosized particles of metal oxides can increase the burning rate of AP. The efficiency of this catalytic process increases dramatically when nanosized oxide particles are used rather than microscale and bulk particles [13].

According to the literature, the most reactive catalyst for the decomposition of  $HClO_4$  is  $Cr_2O_3$  [14].  $Cr_2O_3$  also serves as an excellent catalyst for the decomposition of NH<sub>3</sub> by catalyzing the oxidation of NH<sub>3</sub> to form N<sub>2</sub> and H<sub>2</sub>O at 240 °C [15]. However,  $Cr_2O_3$  is proved to be a less efficient catalyst of the thermal decomposition of AP [16] due to its n-type semiconducting structure which is believed to accept an electron from the perchlorate ion hardly.

In this work, a novel hydrolytic method, using  $F^-$  instead of  $SO_4^{2-}$ , was developed to prepare nanosized  $Cr(OH)_3$ . The spherical

<sup>\*</sup> Corresponding author. Tel.: +86 10 8254 4808; fax: +86 10 8254 4808. *E-mail address:* lipinggnipil@home.ipe.ac.cn (H. Xu).

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Table 1

Precipitates	$Cr(NO_3)_3(M)$	F <sup>-</sup> /Cr <sup>3+</sup> mole ratio	Initial pH	$PVP(g dm^{-3})$	Urea (M)	Composition	Morphological Characteristics	
							Shape	Mean size
S1	0.005	0	5.0	20	0.02	Cr, O	Aggregated	-
S2	0.005	5	5.0	20	0.02	Cr, O	Spherical	50 nm
S3	0.005	20	5.0	20	0.02	Cr, O	Spherical	500 nm
S4	0.005	50	5.0	20	0.02	Na, Cr, F, O	Cubic-like	>2 µm
S5	0.005	5	3.0	20	0.02	Na, Cr, F	Spherical	>2 µm
S6	0.02	5	5.0	20	0.02	Cr, O	Spherical	500 nm
S7	0.02	5	1.0	20	0.02	Na, Cr, F	Spherical	10 µm
S8	0.005	5	1.0	20	0.02	Na, Cr, F	Spherical	>2 µm
S9	0.005	5	5.0	-	0.02	Cr, 0	Aggregated	-
S10	0.005	5	5.0	20	-	Cr, O	Spherical	500 nm

Composition and morphological characteristics of the prepared precipitates by aging for different initial pH, solutions containing variable amounts of NaF, Cr(NO<sub>3</sub>)<sub>3</sub>, urea, and PVP.

Cr(OH)<sub>3</sub> nanoparticles were synthesized by altering the molar ratio of  $F^{-}/Cr^{3+}$ , initial pH, and  $Cr^{3+}$  concentration. The catalytic effect of the prepared Cr(OH)<sub>3</sub> nanoparticles on the thermal decomposition of AP was studied in detail.

### 2. Experimental

All chemicals were analytical grade reagents and used as received without further purification. Cr(NO<sub>3</sub>)<sub>3</sub>, NaF, urea and PVP were dissolved in distilled water to prepare an aqueous solution. In a typical synthesis, 100 mL deionized water, 20 mL 0.2 M Cr(NO<sub>3</sub>)<sub>3</sub>, 20 mL 0.8 M urea, 20 mL 200 g dm<sup>-3</sup> PVP, 40 mL 0.5 M NaF aqueous solution were added to a Pyrex test tubes (250 cm<sup>3</sup>) which were tightly sealed with Teflon caps and placed in a preheated oven at 100 °C for 24 h. 0.1 M HNO<sub>3</sub> was used to adjust initial pH. After aging, the dispersions were cooled naturally and then centrifuged at 7000 rpm. The precipitates were washed several times with buffer solution (pH 10.14), filtered and freeze-dried at -50 °C for 24 h. The concentration of reagents and initial pH in the starting solutions was systematically varied to analyze morphological characteristics (shape and size) and the F<sup>-</sup>-dependence of the particles with regard to the particle size.

In order to study catalytic effect of the prepared precipitates on the thermal decomposition of AP, different amounts of the precipitates were mixed with saturated aqueous solution of AP; and then freeze-dried in 10 Pa at -50 °C for 24 h. The obtained samples were sintered in argon atmosphere in a pipe furnace with 10°C min<sup>-1</sup> from atmospheric temperature to 500 °C.

The morphological characteristics, quantitative analysis, and microstructure of precipitates were investigated by field-emission scanning electron microscopy (SEM), using a FEI 200/INCA Oxford (USA/UK), energy dispersive spectroscopy (EDX) and transmission electron microscopy (TEM) on a JEOL JEM 2010 instrument subjected to an acceleration voltage of 200 kV. Phases of



Fig. 1. SEM and TEM micrograph of precipitates S2, S3, and S4; SAED pattern of precipitate S2; EDX mapping of precipitates S2 and S4 (Cu and Au were attributed to Cu TEM grid in the TEM detection and high vacuum gold jetting in the SEM measurement, respectively).



Fig. 2. XRD patterns and Raman spectra of precipitates S2, S3, S4.

precipitates and samples were characterized by powder X-ray diffraction (XRD). Differential thermal analysis (TGA) and differential scanning calorimetry (DSC) of precipitates and samples were performed in argon atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Raman spectra of the precipitates were obtained with a laser Raman apparatus with the 514.5 nm line of an Ar<sup>+</sup> laser as the excitation source. The elemental composition of the precipitate was carried on an Optima 5300DVPerkin-Elmer inductively coupled plasma (ICP-AES).

## 3. Results and discussion

Table 1 summarizes the effects of the  $F^-/Cr^{3+}$  molar ratio, initial pH, urea, PVP, and Cr(NO<sub>3</sub>)<sub>3</sub> concentrations, on the morphological characteristics and composition of the particles precipitated via hydrolysis route. Low Cr(NO<sub>3</sub>)<sub>3</sub> concentration, suitable  $F^-/Cr^{3+}$  molar ratio, and high initial pH are beneficial to preparing nanosized particles. Through the aging of solutions with the  $F^-/Cr^{3+}$  molar ratio at 5, the Cr(NO<sub>3</sub>)<sub>3</sub> concentration maintained at 0.005 M, and the initial pH (5.0) constant, nanoparticles with a spherical 50 nm were synthesized (S2). The morphological characteristics of the particles were as follows: spherical, 500 nm and cubic-like, 2  $\mu$ m, under the condition of the  $F^-/Cr^{3+}$  molar ratio of 20 (S3) and 50 (S4). The spherical particle size growth resulted from the initial pH decreased from 5.0 to 1.0 and the Cr(NO<sub>3</sub>)<sub>3</sub> concentrations



**Fig. 3.** (a) TG and DSC curves of precipitate S2. (b and c) XRD pattern and Raman spectra of sample calcined by precipitate S2 at 360 °C.

increased from 0.005 M to 0.2 M, implying that size of the particles was sensitive to the reaction conditions. It should be noted that the solutions without NaF or PVP addition yielded aggregated particles (S1 and S9) whereas for without urea addition spherical particles with 500 nm (S10) were obtained. PVP as capping agent and urea as release precipitation agent, have been used to prepare a lot of nanomaterials such as  $Fe_2O_3$  microcages and  $BaCO_3$  nanoparticles [17,18].

The composition of precipitates synthesized in this work was confirmed by EDX, as can be seen in the attached EDX of Fig. 1.



**Fig. 4.** Morphological evolution of precipitates with different F<sup>-</sup>/Cr<sup>3+</sup> molecular ratios: (a) S1; (b) Cr(NO<sub>3</sub>)<sub>3</sub> = 0.005 M, NaF = 0.01 M (F<sup>-</sup>/Cr<sup>3+</sup> molecular ratio = 2); (c) enlarged photograph of (b); (d) S2.

The nanoparticles (S2) were consisted of Cr and O, which were obtained by the  $F^-/Cr^{3+}$  molar ratio of 5 and the initial pH of 5. The microparticles (S5, S7, and S8) were consisted of Na, Cr and F which were determined by the lower initial pH ( $\leq$ 3). The microparticles (S4) were found to possess higher content of F and Na, as well as the presence of O, Cr, which resulted from higher content of  $F^-/Cr^{3+}$  molar ratio (50). Besides, Cu and Au also could be found in the EDX mappings of Fig. 1S2 and S4, which were attributed to Cu TEM grid in the TEM detection and high vacuum gold jetting in the SEM measurement, respectively. Not any Cu or Au which was sensitive to catalytic ability was added in the precipitate preparation.

Selected area electron diffraction (SAED) of the S2 is also provided in Fig. 1. It was shown that the isolated  $Cr(OH)_3$  nanoparticle was a totally disordered structure. Besides, chemical composition of the S2 was investigated by ICP-AES, Cr content of the nanosized  $Cr(OH)_3$  was about 46%, close to 50.48% of theoretical value; not other metal such as Cu, Ni, and Au, was detected.

Fig. 2a shows XRD patterns of the S2  $(F^-/Cr^{3+}$  molecular ratio of 5) and the S4  $(F^-/Cr^{3+}$  molecular ratio of 50) obtained by aging 0.005 M Cr(NO<sub>3</sub>)<sub>3</sub> at the initial pH of 5.0. The S2 showed amorphous phase, which coincided with chromium hydroxide (Cr(OH)<sub>3</sub>) [19]. Compared to the S2, peaks of the S4 could be clearly indexed as a cryolite phase, which was consistent with the reported data, for Na<sub>3</sub>CrF<sub>6</sub> (JCPDS 27-0675). It can be concluded that the  $F^-/Cr^{3+}$ molecular ratio increase results in not only particle size growth but also phase transition. The Raman spectra of these precipitates are shown in Fig. 2b. One band at  $293 \,\mathrm{cm}^{-1}$  of the S4 was observed and characteristic of Na<sub>3</sub>CrF<sub>6</sub> which could be inferred from XRD pattern. One band each at  $534 \,\mathrm{cm}^{-1}$  of the S2,  $540 \,\mathrm{cm}^{-1}$  of the S3, and  $540 \,\mathrm{cm}^{-1}$  of the S4 was observed. The Raman band in the  $530-550 \,\mathrm{cm}^{-1}$  was of  $E_g$  symmetry in the octahedral crystal field of chromium compounds [20]. This type of band shifted toward higher wavenumbers which indicated reduction of interatomic distance, increase in the interaction force between adjacent atoms, and implied that the higher F<sup>-</sup>/Cr<sup>3+</sup> molecular ratio contributed to better crystallinity as a result of chemical bond formation within the synthesized particles.

DSC and TG analysis of the S2 are shown in Fig. 3a. The obtained DSC curve revealed a weak endothermic peak at about 100 °C associated with a weight loss of 17% that was attributed to the release of absorbed water. The endothermic peak (252 °C) and its associated weight loss detected between 250 and 300 °C (11.7%) could be ascribed to removal of crystal water. The endothermic peak (330 °C) observed on the TG curve corresponded to crystalline  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> manifesting the crystallization of the initially amorphous Cr(OH)<sub>3</sub> that the crystallization process normally occurred at least at 450 °C [21]. The TG and DSC curves showed that the S2 had the lower crystalline formation temperature, which could be attributed to the nanometer range of Cr(OH)<sub>3</sub> particles.

Fig. 3b and c shows the XRD pattern and Raman spectra of calcination product of the S2 at 360 °C. The diffraction peaks of the XRD pattern were consistent with JCPDS-01-084-1616 of the  $Cr_2O_3$ with bad crystallization. Bands of the Raman spectra at 300 cm<sup>-1</sup>,



**Fig. 5.** DSC curves of thermal decomposition of AP as it is catalyzed by different amounts of  $Cr_2O_3$  and  $Cr(OH)_3$ . A1: pure AP; A2: AP mixed with 2% P1 (commercial  $Cr_2O_3$  prepared by thermal decomposition of  $CrO_3$ ); A3: AP mixed with 2% P2 (commercial  $Cr_2O_3$  prepared by reducing  $Na_2CrO_7$  with  $(NH_4)_2SO_4$ ); A4: AP mixed with 5% nanosized  $Cr_2O_3$ ; A5: AP mixed with 30% sub-micro- $Cr(OH)_3$  (S3); A6: AP mixed with 30% nanosized  $Cr(OH)_3$  (S2).

 $343 \text{ cm}^{-1}$ ,  $542 \text{ cm}^{-1}$ ,  $600 \text{ cm}^{-1}$ , and  $1359 \text{ cm}^{-1}$  were characteristic of  $Cr_2O_3$  [22]. Compared to the bands of  $Cr_2O_3$  reported by literature, a low-frequency shift of  $5-10 \text{ cm}^{-1}$  was observed, such red shift effect was due to the greater interatomic distance or nanoeffect disappearance.

Fig. 4 shows the morphology evolution of the prepared nanoparticles with different  $F^-/Cr^{3+}$  molecular ratios. Without the addition of  $F^-$  ion, hydroxylation process of chromium ion occurred, polymerization of the precipitated precursors resulted in coagulation (Fig. 4a). By controlling the  $F^-/Cr^{3+}$  molecular ratio in the range of 2–10, spherical particles with size between 40 and 80 nm could be obtained (Fig. 4b and d). Complex ions of chromium fluoride, such as  $CrF_2^+$ ,  $CrF^{2+}$ , and  $CrF_3^0$  [23,24], were formed and became dominating; these complex ions of chromium fluoride contributed to the separation of coagulated material and obtaining of nanoparticles. Every particle that was approximately 50 nm in size consisted of several subunits that were approximately 5–10 nm in size, as shown in Fig. 4c. The  $F^-$  ion is believed to have a tailoring effect, different from the  $SO_4^{2-}$  ion that induces the formation of units of precursor complexes reported in the literature [8].

When used as catalytic additives, metal oxides mainly accelerate or decelerate the low-temperature thermal decomposition of AP. Cr<sub>2</sub>O<sub>3</sub> has little catalytic effect on the AP thermal decomposition, due to its n-type semiconducting structure, compared to other metal oxides such as CuCr<sub>2</sub>O<sub>4</sub>, MnO<sub>2</sub>, and NiO. The DSC curves for pure AP, AP with addition of Cr<sub>2</sub>O<sub>3</sub> and nanosized Cr<sub>2</sub>O<sub>3</sub>, and AP with addition of sub-micro-Cr(OH)<sub>3</sub> particle (S3) and nanosized Cr(OH)<sub>3</sub> particles (S2) are shown in Fig. 5. The DSC curve of the thermal decomposition of pure AP(A1) included one endothermic peak at 245 °C (i.e., the crystallographic transition temperature) and one exothermic peak at approximately 450 °C. The endothermic DSC peak at 245 °C was also accompanied by zero weight loss. This represents the transition from orthorhombic to cubic AP [25]. The heat of decomposition of pure AP was  $546 \text{ Jg}^{-1}$ . The thermal decomposition temperature of AP decreased from 450 to 429°C, with addition of 2% commercial Cr<sub>2</sub>O<sub>3</sub> P1 or P2 which was prepared by thermal decomposition of CrO<sub>3</sub> or by reducing Na<sub>2</sub>CrO<sub>7</sub> with  $(NH_4)_2SO_4$  (A2 or A3); the exothermic peaks at 339 °C and 309 °C were attributed to the partial decomposition of AP and formation of some intermediates namely NH<sub>3</sub> and HClO<sub>4</sub> by dissociation and sublimation [26] which were identical with those reported in



**Fig. 6.** DSC and TG curves of thermal decomposition of AP as it is catalyzed by different amounts of nanosized Cr(OH)<sub>3</sub>. B1, B2, B3, B4, B6, and B7: AP mixed with 1%, 5%, 10%, 20%, 50%, or 100% nanosized Cr(OH)<sub>3</sub>, respectively.

literature [10]. With adding 5% commercial nanosized  $Cr_2O_3$ , the thermal decomposition temperature of AP decreased from 450 to 410 °C. It is difficult to further decrease the thermal decomposition temperature of AP with addition of higher concentration commercial or nanosized  $Cr_2O_3$ . However, when the AP was mixed with the 30% prepared sub-micro- $Cr(OH)_3$  (S3) and the 30% prepared nanosized  $Cr(OH)_3$  (S2), the thermal decomposition temperature of AP decreased from 450 to 318 °C (A5) and 288 °C (A6), respectively, indicating that the prepared  $Cr(OH)_3$  catalyzed thermal decomposition of AP effectively.

The decomposition pattern of AP with the nanosized  $Cr(OH)_3$ addition shows noticeable changes. The DSC curves of the thermal decomposition of AP catalyzed by different amounts of the nanosized  $Cr(OH)_3$  are shown in Fig. 6a. Addition of 5%, 10%, 20%, 50%, or 100% nanosized  $Cr(OH)_3$  lowered the thermal decomposition temperature of AP by 32 °C, 118 °C, 152 °C, or 200 °C, respectively. As the amount of nanosized  $Cr(OH)_3$  increased, the two exothermic peaks that were attributed to the partial decomposition of AP and formation of some intermediates gradually shifted toward lower temperatures. Especially, the two exothermic peaks were overlapped at about 250 °C with the 100%  $Cr(OH)_3$  addition in the thermal decomposition of AP, which was close to the crystallographic transition temperature.

Higher content of nanosized Cr(OH)<sub>3</sub> addition is also beneficial for accelerating thermal decomposition rate of AP. Fig. 6b shows TG



Fig. 7. Mass spectral analysis of the sample A6.

curves of B1, B3, B6, and B7, each curve exhibited similar weight loss step, corresponding to the exothermic peaks of the DSC curve. The thermal decomposition rate of AP with 100%  $Cr(OH)_3$  addition was the fastest, AP with 10% or 50%  $Cr(OH)_3$  addition was slower, pure AP was the slowest.

The thermal decomposition of pure AP produces NH<sub>3</sub>, H<sub>2</sub>O, N<sub>2</sub>O, NO, N<sub>2</sub>, Cl<sub>2</sub>, and so on [12]. Fig. 7 shows the mass intensities of molecules that are produced from the thermal decomposition of A6 to determine the products of the AP thermal decomposition. NH<sub>3</sub>, H<sub>2</sub>O, N<sub>2</sub>O, NO, N<sub>2</sub>, and Cl<sub>2</sub> molecules were identified as products of the A6 thermal decomposition. It could be found that the NH<sub>3</sub> was firstly oxidized to form N<sub>2</sub>O:

$$2NH_3 + 2O_2 \to N_2O + 3H_2O \tag{1}$$

NO,  $Cl_2$  and  $H_2O$  were then formed simultaneously:

 $4NH_3 + 5O_2 \to 4NO + 6H_2O$  (2)

$$2\text{HClO}_4 \to \text{H}_2\text{O} + \text{Cl}_2 + (7/2)\text{O}_2 \tag{3}$$

Combined with the decomposition products of pure AP and the AP catalyzed by the nanosized  $Cr(OH)_3$ , it could be presumed that the oxidization of NH<sub>3</sub> is the rate-limiting step. The catalyzed oxidation of NH<sub>3</sub> could be accelerated via the nanosized  $Cr(OH)_3$ , forming the three reaction products: N<sub>2</sub>, N<sub>2</sub>O, and NO [27], resulting in decrease of thermal decomposition temperature of AP.

#### 4. Conclusions

A novel method to synthesize  $Cr(OH)_3$  nanoparticles and its catalytic effect of AP was studied, leading to the following conclusions:

- (1) Spherical Cr(OH)<sub>3</sub> nanoparticles could be obtained by aging at 100 °C aqueous solutions of Cr(NO<sub>3</sub>)<sub>3</sub> (0.005 M) in the presence of NaF (F<sup>-</sup>/Cr<sup>3+</sup> molar ratio=5), urea (0.2 M) and PVP (20 g dm<sup>-3</sup>) with initial pH of 5. The chromium fluoride complex ions such as CrF<sup>2+</sup>, CrF<sub>2</sub><sup>+</sup>, and CrF<sub>3</sub><sup>0</sup> which formed with F<sup>-</sup> and Cr<sup>3+</sup>, tailored the aggregation to form the Cr(OH)<sub>3</sub> nanoparticles.
- (2) The prepared Cr(OH)<sub>3</sub> nanoparticles were found to decrease the thermal decomposition temperature of AP from 450 °C to 250 °C, demonstrating that its catalytic effects were determined by the size of the nanoparticles.

(3) Catalytic mechanism of thermal decomposition of AP showed that the Cr(OH)<sub>3</sub> nanoparticles were beneficial to catalyzed oxidation of NH<sub>3</sub> so that thermal decomposition of AP was accelerated.

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