Nanochromates $\text{MCr}_2\text{O}_4$ ($\text{M} = \text{Co, Ni, Cu, Zn}$): Preparation, Characterization, and Catalytic Activity on the Thermal Decomposition of Fine AP and CL-20

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ABSTRACT: The chromate nanoparticles such as CoCr$_2$O$_4$, NiCr$_2$O$_4$, CuCr$_2$O$_4$, and ZnCr$_2$O$_4$ were prepared by a modified sol–gel method. The structural and morphological properties of the chromate nanoparticles were characterized by X-ray diffraction (XRD) and a scanning electron microscope (SEM). The catalytic effects of chromates on the thermal decomposition of fine ammonium perchlorate (FAP) and hexanitrohexaazaisowurtzitane (CL-20) were studied by the TG-DTG measurements. Results show that the addition of CoCr$_2$O$_4$, NiCr$_2$O$_4$, CuCr$_2$O$_4$, and ZnCr$_2$O$_4$ nanoparticles makes the activation energies for the thermal decomposition of FAP decrease by 93.9, 94.0, 83.1, and 67.0 kJ·mol$^{-1}$, and the thermal decomposition temperatures decrease by 45.0, 24.9, 57.7, and 38.8 K respectively. On the other hand, a similar trend exists in the case of the thermal decomposition of CL-20. Therefore, the addition of nanochromates shows high catalytic efficiency on the thermal decomposition of both FAP and CL-20 components, which would be beneficial to promote the burning rate of propellants containing FAP and CL-20 components.

INTRODUCTION

As one of the most important propellants, the high burning rate solid rocket propellant has been extensively used in terms of operational rockets, missiles, satellites, and space shuttle launch vehicles. Many efforts have been devoted for developing novel propellants with high burning rate to fulfill the ever-growing and challenging requirements.$^{1-3}$ The burning rate can be tuned by the addition of high energetic materials, combustion catalysts, and even by adjusting the particle size of oxidizers in the solid rocket propellants.$^{4-7}$ In particular, chromate as a transition metal combustion catalyst is capable of increasing the burning rate of solid propellants.$^{8-14}$ Ammonium perchlorate (AP) with the particle size of about 1 $\mu$m, namely, fine AP (FAP), has been widely used as an oxidizer to promote the burning rate of composite propellants.$^{15,16}$ On the other hand, hexanitrohexaazaisowurtzitane (CL-20), a novel high explosive, has aroused great concerns to be used as a high energetic additive to improve the energy of composite propellants.$^{17,18}$

It is well known that the combustion behavior of the composite propellant depends heavily on the thermal decomposition of both AP and CL-20. As thus, tuning the thermal decomposition of above two components by the addition of catalysts suggests great potential strategies to modify the combustion properties of composite propellants. The catalytic effects of transition metal oxides on the thermal decomposition of AP have been well studied,$^{19-24}$ whereas mixed metal oxides were less studied.$^{25}$ On the other hand, the catalytic effects of simple transition metal oxides or mixed metal oxides on the thermal decomposition of CL-20 were seldom reported. Therefore, to the best of our knowledge, the catalytic effects of nanochromates on the thermal decomposition of both FAP and CL-20 have rarely been reported.

In this work, chromate nanoparticles such as CoCr$_2$O$_4$, NiCr$_2$O$_4$, CuCr$_2$O$_4$, and ZnCr$_2$O$_4$ were prepared by a sol–gel method, and their structural and morphological properties were characterized by X-ray diffraction (XRD) and a scanning electron microscope (SEM), respectively. The catalytic effects of chromate nanoparticles on the thermal decomposition of both FAP and CL-20 were studied by the TG-DTG measurements and well discussed.
RESULTS AND DISCUSSION

XRD Analysis. The chemical compositions of chromate nanoparticles were studied by X-ray diffraction (XRD). As shown in Figure 1, all the main XRD peaks were indexed for the planes accordingly, and those diffraction peaks of these chromate nanoparticles were well consistent with those standard JCPDS cards of CoCr$_2$O$_4$ (no. 22-1084),$^{26,27}$ NiCr$_2$O$_4$ (no. 89-6615),$^{28}$ CuCr$_2$O$_4$ (no. 34-0424),$^{29,30}$ and ZnCr$_2$O$_4$ (no. 22-1107),$^{31,32}$ respectively. For example, the diffraction peaks at 2$\theta$ angles from Figure 1d appeared 30.41°.
35.75°, 37.44°, 43.49°, 53.91°, 57.35°, and 62.95° could be assigned for scattering from the (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) planes, respectively, which were well matched with the XRD patterns of the spinel crystal lattice of ZnCr2O4 (no. 22-1107).31,32 Notably, the diffraction peaks of the samples were so distinct that good crystallinity and high purity of objective samples were facilely prepared. Moreover, after comparison with corresponding XRD patterns and reference spectra, XRD studies confirmed the absence of reactant oxides of Co2O3 (no. 73-1701), NiO (no. 73-1519), CuO (no. 48-1548), and ZnO (no. 36-1541), respectively.33–35 Besides, all the calcined production displayed prominent peaks and an increased peak width in XRD patterns suggesting that the chromate nanoparticles fabricated by the sol–gel approach possessed rather small crystallite sizes. Furthermore, the crystallite sizes of these nanochromates were calculated from their corresponding XRD peak broadening of the most intense diffraction peak (3 1 1) using the Scherrer formula, \( D = \frac{K\lambda}{β \cos(θ)} \), and the average crystallite sizes of CoCr2O4, NiCr2O4, CuCr2O4, and ZnCr2O4 nanoparticles were determined as 22.0, 23.4, 23.4, and 22.7 nm, respectively.

**SEM Analysis.** The morphologies of chromates were observed by SEM, as shown in Figure 2. The SEM image of CoCr2O4 displays a uniform distribution of spherical particles with particle size in the ranges of 20–50 nm after calcination. Both NiCr2O4 and CuCr2O4 show cubic morphologies with particle sizes ranging from 20 to 60 nm. The larger sizes shown in SEM than those calculated by the Scherrer equation are due to the agglomeration of nanoparticles. ZnCr2O4 nanoparticles show an irregular particle shape and much more agglomeration than other chromate.

**Optimization of Experimental Conditions.** To synthesize the CuCr2O4 nanoparticles in high purity, we studied the effects of several factors such as the ratio of the raw materials, pH values, as well as the calcined temperatures used in the synthesis of CuCr2O4. Table 1 shows the constitution of products by varying the Cu/Cr mole ratios. Notably, to obtain the pure CuCr2O4, the mole ratio of Cu(NO3)2 and Cr(NO3)3 has to be fixed at 0.5.

| Table 1. Influence of Cu/Cr Mole Ratio on the Constitution of Product |
|---|
| \( n(Cu)/n(Cr)/R \) | \( R < 0.5 \) | \( R = 0.5 \) | \( 0.5 < R < 1 \) | \( R = 1 \) |
| constitution | CuCrO4 | CuCr2O4 | CuCr3O4 | CuCrO2 |

Also, the pH value in the sol–gel process plays a crucial role on the constitution of products. To study the effects of the pH value, the mole ratio of raw materials was maintained constant at 0.5, and the calcined temperature was set at 820 °C. The citric acid was used as the complexing agent. Table 2 shows the purity of copper chromate products as a function of pH value. It is found that the purity of the product increases with the increase in the pH value and reaches 100% at the pH values of 10–11. Then, the purity of the product decreases to 80% when increasing the pH values to 11–12. It is believed that the citric acid combines with the copper and chromium metal ions in different ratios at different pH values, which leads to the generation of CuO and Cr2O3 in calcination.

To investigate the effects of calcined temperature on the particle size of CuCr2O4, the mole ratio of Cu(NO3)2 and Cr(NO3)3 was set at 0.5, and the pH value was adjusted in the range of 10–11. The citric acid was used as a complexing agent. Table 3 shows the particle size of chromate nanoparticles obtained at different calcination temperatures. It is found that the particle size of chromates decreases with the increase in the calcined temperature, and the minimum particle size of about 23 nm was achieved at 820 °C. Based on the above studies, the optimal experimental condition for the preparation of all chromate nanoparticles can be determined, and the results are listed in Table 7.

**Effect of Chromates on Thermal Decomposition of FAP and CL-20.** The DTG curve of FAP shows a single thermal decomposition peak at 634.5 K without the appearance of crystal transformation, as shown in Figure 3a. It is due to the adsorption of a large amount of NH3 and HClO4 gases on the surface of FAP particles. On the other hand, Figure 3b shows that CL-20 decomposes at 520.5 K. The TG-DTG curves for FAP and CL-20 containing chromate catalysts are shown in Figures 4 and 5, respectively. As shown in Table 4, the addition of chromate nanoparticles leads to a significant decrease in the decomposition temperature of FAP. In particular, the addition of CuCr2O4 leads to the largest decrease in the decomposition temperature of AP by 57.7 °C, suggesting that CuCr2O4 has a remarkably higher catalytic efficiency than that of the other chromates. It is known that most of the transition metal oxides enable both catalytic decomposition of the perchlorate ion and oxidation of ammonia. The high catalytic efficiencies of chromate nanoparticles on the decomposition of AP lie in their large surface area, numerous Lewis acid sites, as well as the synergetic effects of the M2+ and Cr3+, the large number of surface atoms enable formation of coordinate bonds between chromates and the nitro groups (–NO2), resulting in weakening/breaking of the N–N bond. Increasing the temperature leads to a fast formation of –NO2 in liquid CL-20, which results in a self-catalysis of CL-20.

The thermal decomposition kinetics was further explored to study the effect of chromates on the activation energy of thermal decomposition of FAP and CL-20, respectively. To obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the exothermic decomposition reaction for the nanochromates, multiple heating methods (Kissinger’s method36 and Ozawa’s method37) were employed as follows: Kissinger’s equation:

| Table 2. Influence of pH on the Purity of Products |
|---|
| pH | 7–8 | 8–9 | 9–10 | 10–11 | 11–12 |
| purity (%) | 50 | 55 | 70 | 100 | 80 |

| Table 3. Influence of Calcination Temperature on the Particle Size |
|---|
| calcination temperature (°C) | 450 | 540 | 620 | 680 | 760 | 820 | 900 |
| particle size (nm) | 80.2 | 65.8 | 40.5 | 43.2 | 32.8 | 23.4 | 25.1 |
where $T_p$ is the peak temperature (K), $\beta$ is the linear heating rate (K min$^{-1}$), $E$ is the apparent activation energy (kJ mol$^{-1}$), $A$ is the pre-exponential constant (s$^{-1}$), $R$ is the gas constant (J mol$^{-1}$ K$^{-1}$), and $C$ is a constant.

The calculated results of the apparent activation energy ($E_a$) and the apparent pre-exponential factor ($A$) were tabulated in Table 6. The $E_a$ values of nano-CoCr$_2$O$_4$/FAP, nano-NiCr$_2$O$_4$/FAP, nano-CuCr$_2$O$_4$/FAP, and nano-ZnCr$_2$O$_4$/FAP were determined by the Kissinger method as 129.5, 129.2, 140.4, and 157.0 kJ·mol$^{-1}$, respectively, of which were reduced by 95.8, 96.1, 84.9, and 68.3 kJ·mol$^{-1}$, respectively, compared with that of FAP (225.3 kJ·mol$^{-1}$). The results determined by the Ozawa method were inconsistent with those of the Kissinger method. The same trend was found in the case of CL-20. Therefore, the addition of chromate nanoparticles can reduce the activation energy in the thermal decomposition of both FAP and CL-20, suggesting that chromates allow to...

Figure 3. TG-DTG curves of (a) FAP and (b) CL-20.

Figure 4. TG-DTG curves of nanochromates: (a) nano-CoCr$_2$O$_4$/FAP, (b) nano-NiCr$_2$O$_4$/FAP, (c) nano-CuCr$_2$O$_4$/FAP, and (d) nano-ZnCr$_2$O$_4$/FAP.
increase the burning rate of propellants containing FAP and CL-20 components.

**CONCLUSIONS**

The chromate nanoparticles such as CoCr$_2$O$_4$, NiCr$_2$O$_4$, CuCr$_2$O$_4$, and ZnCr$_2$O$_4$ were prepared by a sol–gel method, and their compositional and morphological properties were studied by XRD and SEM measurements. Moreover, their catalytic effects on the thermal decomposition of FAP and CL-20 were studied by using TG-DTG analysis. Specifically, the addition of CoCr$_2$O$_4$, NiCr$_2$O$_4$, CuCr$_2$O$_4$, and ZnCr$_2$O$_4$ nanoparticles induced an obvious decrease in the activation energy for the thermal decomposition of FAP and CL-20 as well as the corresponding thermal decomposition temperatures of FAP and CL-20. Therefore, those reported nanochromates could be applied as efficient catalysts for the thermal decomposition of both FAP and CL-20 components.

Table 4. Thermal Decomposition Data of Nanochromates/FAP Mixtures

| Sample                | $T_d$ (K) | $\Delta T$ (K) |
|-----------------------|-----------|-----------------|
| nano-CoCr$_2$O$_4$/FAP| 589.5     | 45.0            |
| nano-NiCr$_2$O$_4$/FAP| 609.6     | 24.9            |
| nano-CuCr$_2$O$_4$/FAP| 576.8     | 57.7            |
| nano-ZnCr$_2$O$_4$/FAP| 595.7     | 38.8            |

Table 5. Thermal Decomposition Data of Nanochromates/CL-20 Mixtures

| Sample                | $T_d$ (K) | $\Delta T$ (K) |
|-----------------------|-----------|-----------------|
| nano-CoCr$_2$O$_4$/CL-20 | 515.5     | 5.0             |
| nano-NiCr$_2$O$_4$/CL-20 | 514.8     | 5.7             |
| nano-CuCr$_2$O$_4$/CL-20 | 513.7     | 6.8             |
| nano-ZnCr$_2$O$_4$/CL-20 | 513.8     | 6.7             |

Table 6. Thermal Decomposition Kinetic Parameters of Nanochromates/FAP and Nanochromates/CL-20

| Sample                | $E_k$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r_k$ | $E_O$ (kJ mol$^{-1}$) | $r_O$ | $E_{\text{Average}}$ (kJ mol$^{-1}$) |
|-----------------------|-----------------------|-------------------|-------|------------------------|-------|--------------------------------------|
| FAP                   | 225.3                 | 16.6              | 0.9948 | 224.3                 | 0.9962 | 224.8                                |
| nano-CoCr$_2$O$_4$/FAP| 129.5                 | 9.71              | 0.9606 | 132.2                 | 0.9655 | 130.9                                |
| nano-NiCr$_2$O$_4$/FAP| 129.2                 | 8.98              | 0.9736 | 132.4                 | 0.9771 | 130.8                                |
| nano-CuCr$_2$O$_4$/FAP| 140.4                 | 10.2              | 0.9999 | 142.9                 | 0.9999 | 141.7                                |
| nano-ZnCr$_2$O$_4$/FAP| 157.0                 | 11.9              | 0.9999 | 158.6                 | 0.9999 | 157.8                                |
| CL-20                 | 257.7                 | 24.1              | 0.9906 | 253.3                 | 0.9912 | 255.5                                |
| nano-CoCr$_2$O$_4$/CL-20 | 200.4               | 18.5              | 0.9768 | 198.7                 | 0.9785 | 199.6                                |
| nano-NiCr$_2$O$_4$/CL-20 | 234.5               | 22.1              | 0.9843 | 231.1                 | 0.9859 | 232.8                                |
| nano-CuCr$_2$O$_4$/CL-20 | 231.9               | 21.9              | 0.9999 | 228.7                 | 0.9999 | 230.3                                |
| nano-ZnCr$_2$O$_4$/CL-20 | 254.9               | 24.2              | 0.9817 | 250.6                 | 0.9828 | 252.8                                |
would benefit the promotion of the burning rate of propellants containing FAP and CL-20 components.

**EXPERIMENTAL SECTION**

**Materials.** Ammonia aqueous solution at a concentration of 25 wt % and other raw materials such as chromic nitrate, citric acid, cupric nitrate, cobalt nitrate, nickel nitrate, and zinc nitrate with the purities higher than 98% were all purchased from J&K Chemical Technology.

**Instruments and Analysis.** An X-ray diffractometer (XRD, ARL XTRA) was used to analyze the crystallization of chromate nanoparticles. The size, shape, and structures of chromate were studied using a scanning electron microscope (SEM, JSM-588).

**Preparation of Nanochromates.** For the synthesis of CoCr$_2$O$_4$ nanoparticles, 2.9 g of (0.01 mol) Co(NO$_3$)$_2$ and 1.35 g of (0.007 mol) Cr(NO$_3$)$_3$ and 3.85 g of (0.02 mol) citric acid as surfactants were dissolved in 100 mL of deionized water as solution A. Weights of 8.0 g of (0.03 mol) chromic nitrate with the purities higher than 98% were all purchased from J&K Chemical Technology. Weights of 8.0 g of (0.03 mol) chromic nitrate with the purities higher than 98% were all purchased from J&K Chemical Technology.

**Catalytic Experiments.** Differential thermal gravity (DTG) analysis was conducted to measure the mass loss of FAP and CL-20 as functions of temperature under the catalytic effect of chromate nanoparticles using a TA instrument Q-200. Prior to performing thermal decomposition, each chromate additive was uniformly mixed with FAP and CL-20, respectively. The measurements were carried out at the heating rates of 5, 10, and 20 K min$^{-1}$ at ambient pressure in N$_2$ atmosphere (sample mass was 0.5–1.5 mg).

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**Notes**

The authors declare no competing financial interest.

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