

## Research Article

# Preparation of $\text{CoFe}_2\text{O}_4$ Nanocrystallites by Solvothermal Process and Its Catalytic Activity on the Thermal Decomposition of Ammonium Perchlorate

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Nanometer cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) was synthesized by polyol-medium solvothermal method and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and selected area electron diffraction (SAED). Further, the catalytic activity and kinetic parameters of  $\text{CoFe}_2\text{O}_4$  nanocrystallites on the thermal decomposition behavior of ammonium perchlorate (AP) have been investigated by thermogravimetry and differential scanning calorimetry analysis (TG-DSC). The results imply that the catalytic performance of  $\text{CoFe}_2\text{O}_4$  nanocrystallites is significant and the decrease in the activation energy and the increase in the rate constant for AP further confirm the enhancement in catalytic activity of  $\text{CoFe}_2\text{O}_4$  nanocrystallites. A mechanism based on a proton transfer process has also been proposed for AP in the presence of  $\text{CoFe}_2\text{O}_4$  nanocrystallites.

## 1. Introduction

Ammonium perchlorate (AP) is one of the most common energetic material and oxidizer in composite solid propellants with its content in 60%–80% wt, and the thermal decomposition of AP plays a significant role in the burning behavior of propellants [1–3]. Although the characteristics of AP thermal decomposition can be improved to some extent by reducing the particle size of AP, decreasing the particle size of AP is a dangerous process [4]. Considering the security and the limited loading of AP in propellants, many strategies have intensively investigated the thermal decomposition of AP in the presence of metal oxide modifiers [5–9]. The transition metal oxide and ferrite exert a marked effect on the decomposition of AP [5, 9]. Xu et al. [5] found that the catalytic performance of nanometer-sized  $\alpha\text{-Fe}_2\text{O}_3$  particles was superior to that of micrometer-sized  $\text{Fe}_2\text{O}_3$  particles on the thermal decomposition of AP. For nanometer-sized  $\alpha\text{-Fe}_2\text{O}_3$ , the temperatures shift for high temperature exothermic peak of AP was 48.9°C. Singh et al. [9] have observed an increase in the activity of ternary transition metal ferrite when it is doped with  $\text{Co}^{2+}$  ions. The catalytic efficiency of nanostructural  $\text{M}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  ( $\text{M}=\text{Co}, \text{Cu}, \text{Ni}$ )

on the decomposition of AP increases sharply on using  $\text{Co}^{2+}$  instead of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ; it is a pity that the chemistry of nanostructural  $\text{CoFe}_2\text{O}_4$  is not yet clear. As a cubic spinel-structured ferrite,  $\text{CoFe}_2\text{O}_4$  has been intensively studied due to its unique electric and magnetic properties, which have shown great potential for many important technological applications, extensively in modern electronic technologies, microwave absorbers, catalysts, and biomedical applications [10–15]. However, in the literature works, nanostructural  $\text{CoFe}_2\text{O}_4$  are mainly investigated for their magnetic applications, the catalytic effect of spinel  $\text{CoFe}_2\text{O}_4$  on the thermal decomposition of AP is still overlooked in literatures.

Many strategies have been reported to prepare spinel  $\text{CoFe}_2\text{O}_4$  by various chemistry-based synthetic methods, including coprecipitation [10], colloidal chemical approach [11], microwave-assisted solution method [12], self-flash combustion [13], hydrothermal methods [14], and thermal decomposition of organometallic and coordination compounds [15]. Among these approaches, hydrothermal or solvothermal preparation is very promising for synthesizing promising materials. The main purpose of our present work is to demonstrate a simple and general approach for the fabrication of  $\text{CoFe}_2\text{O}_4$  nanoparticles by a polyol-medium

solvothermal method and to investigate the catalytic activity and active sites of the ferrite catalysts responsible for the enhancement of the decomposition of AP.

## 2. Experiment

**2.1. Chemicals.** Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), sodium acetate (NaAc), ethylene glycol (EG), polyethylene glycol (PEG,  $M_w = 4000 \text{ g} \cdot \text{mol}^{-1}$ ), absolute ethanol, and ammonium perchlorate (AP) were analytical grade and purchased from Shanghai Chemical Company.

**2.2. Preparation of  $\text{CoFe}_2\text{O}_4$  Nanoparticles.** The synthesis of  $\text{CoFe}_2\text{O}_4$  nanoparticles was carried out by a polyol-medium solvothermal method according to [16] with some modification. For example, the initial concentration of part reactants and the reaction temperature were changed. Typically,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.675 g, 2.5 mmol) and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.3 g, 1.25 mmol), 3.6 g NaAc and 1 g PEG were dissolved into 40 mL ethylene glycol with constant stirring for 30 min to form into a stable solution. Then the solution was sealed in a Teflon-lined stainless steel autoclave (50 mL capacity) and maintained at  $250^\circ\text{C}$  for 12 h. After cooling to room temperature naturally, the products were obtained and separated by a magnet, washed with distilled water and absolute ethanol twice to remove excess electrolytes.

**2.3. Characterization and the Investigation of Catalytic Activity.** X-ray powder diffraction (XRD) patterns were recorded using a Bruker D8-Super Speed X-ray diffractometer with high-intensity  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The transmission electron microscopy (TEM) micrographs and selected area electron diffraction (SAED) were taken with a Philips Tecnai 12 transmission electron microscope with an accelerating voltage of 120 kV.

The  $\text{CoFe}_2\text{O}_4$  nanoparticles were blended with AP in different contents to prepare the samples for thermal decomposition experiments. The thermal decomposition process of the samples was characterized by thermogravimetry and differential scanning calorimetry analysis (TG-DSC) by using a thermal analyzer (TA instrument SDT-Q600) under flowing  $\text{N}_2$  atmosphere (purity 99.99%, flowing rate  $100 \text{ mL} \cdot \text{min}^{-1}$ ).

## 3. Results and Discussion

**3.1. Characterization of Samples.** The crystalline structure of  $\text{CoFe}_2\text{O}_4$  was characterized by XRD. As shown in Figure 1, the discernible peaks can be indexed to (220), (311), (400), (422), (511), and (440) planes of a cubic structure  $\text{CoFe}_2\text{O}_4$ , which are characteristics for  $\text{CoFe}_2\text{O}_4$  in cubic spinel-type structure and match well with the standard data of  $\text{CoFe}_2\text{O}_4$  (JCPDS no. 79-1744). The XRD pattern indicates the synthesized nanomaterials consist of pure phases. By using Scherrer's equation [17], it could be ascertained that the broadened diffractive peaks of  $\text{CoFe}_2\text{O}_4$  indicate that the crystalline size of  $\text{CoFe}_2\text{O}_4$  particles is 24 nm.

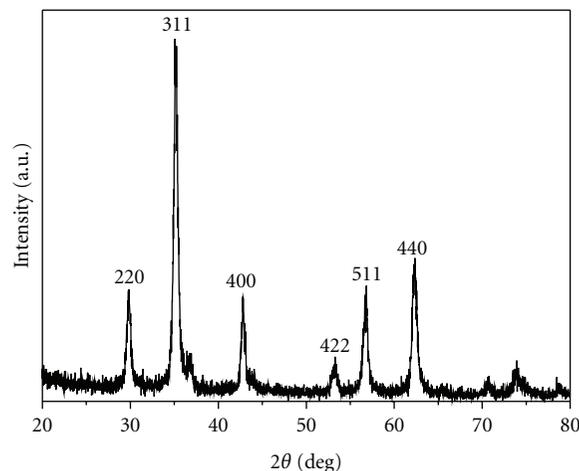


FIGURE 1: XRD pattern of  $\text{CoFe}_2\text{O}_4$  nanoparticles.

The morphology and microstructure of the  $\text{CoFe}_2\text{O}_4$  nanoparticles were further examined with TEM and SAED. Figures 2(a) and 2(b) show the typical TEM images of  $\text{CoFe}_2\text{O}_4$  nanoparticles at low and high magnifications, respectively. It can be seen that the size of  $\text{CoFe}_2\text{O}_4$  nanoparticles is in the range of 20–30 nm. In our case, the nonaqueous solution of ethylene glycol could slow the aggregating rate of  $\text{CoFe}_2\text{O}_4$  nanocrystals due to greater viscosity, providing enough time for  $\text{CoFe}_2\text{O}_4$  nanocrystals to rotate to the low-energy configuration interface. At the same time, the weak capping agent PEG might act as a stabilizer to further prevent fast growth of  $\text{CoFe}_2\text{O}_4$  crystallite [18, 19]. As shown in the inset of Figure 2(b), the SAED pattern shows well-defined rings and spots characteristic of the nanocrystalline materials, and the diffraction rings correspond to (2 2 0), (3 1 1), (4 0 0), (4 2 2), and (5 1 1) [20], respectively, which is accorded with the XRD data.

**3.2. Catalytic Effect.** The TG and DSC curves of pure AP and AP with different blend ratios of  $\text{CoFe}_2\text{O}_4$  spinel are shown in Figure 3. The DSC curve for heat decomposition of pure AP (Figure 3) shows three stages, while the TG curve exhibits only two. The endothermic peak at  $243.7^\circ\text{C}$  is due to a crystallographic transition, which is accompanied by zero weight loss. The first exothermic peak at  $326.2^\circ\text{C}$ , accompanied by a weight loss of 20.3%, can be attributed to the partial decomposition of AP and formation of some intermediates and sublimation. The second exothermic peak at about  $433.2^\circ\text{C}$  is associated with a 76.6% weight loss, which is caused by the complete decomposition of the intermediate to volatile products [21].

The TG and DSC curves for decomposition of AP in the presence of  $\text{CoFe}_2\text{O}_4$  nanocrystallites with different blend ratio showed a noticeable change in the decomposition pattern. The catalytic effect of  $\text{CoFe}_2\text{O}_4$  is significant not only on the high-temperature decomposition (HTD) process but also on the low-temperature decomposition (LTD) process, and especially during the HTD process not only begins early, but also completes with only one-step weight loss at lower

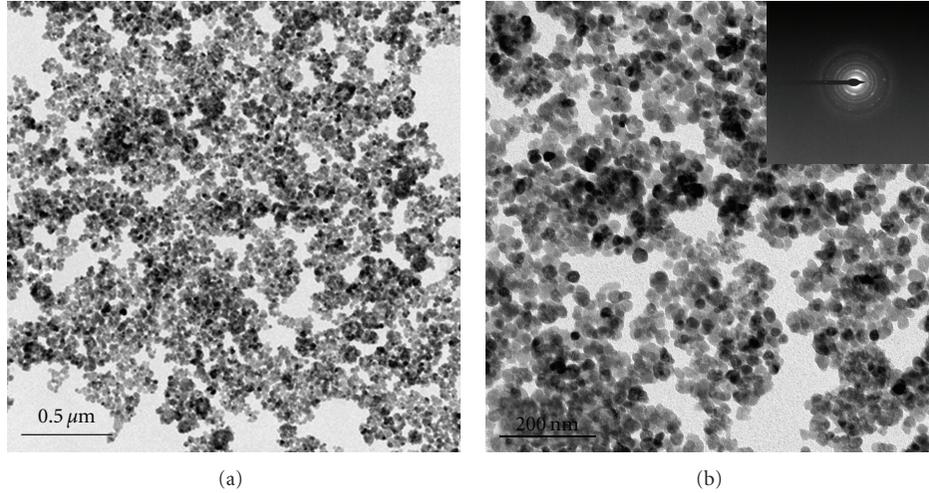


FIGURE 2: TEM micrographs at low (a) and high (b) magnification of  $\text{CoFe}_2\text{O}_4$  nanoparticles. The inset shows the corresponding SAED pattern of  $\text{CoFe}_2\text{O}_4$  nanocrystallites.

TABLE 1: Kinetic parameters of pure AP and as catalyzed by 5% content of  $\text{CoFe}_2\text{O}_4$  nanocrystallites at HTD process.

Compositions	Heating Rate/ $^{\circ}\text{C}\cdot\text{min}^{-1}$	Peak $T_p$ /K	$\Delta H/\text{J}\cdot\text{g}^{-1}$	$E_a/\text{KJ}\cdot\text{mol}^{-1}$	$Z/\text{min}^{-1}$	$k/\text{s}^{-1}$
Pure AP	20	706.3	517.1	178.1	$2.3 \times 10^{11}$	0.015
AP + 5% $\text{CoFe}_2\text{O}_4$	20	570.5	923.5	106.5	$2.9 \times 10^9$	0.514

temperature. From the obtained DSC curves of catalyzed AP, it can be seen that the endothermic peak shows only small changes in position while the first exothermic peak disappears. In contrast, the second exothermic peak changes into a sharp exothermic one. Its position depends strongly on the content of the catalyst, and the catalytic activity is found to be increased with increasing the amount of the catalysts.

Figure 4 shows the decomposition of AP in the presence of 5 wt. %  $\text{CoFe}_2\text{O}_4$  nanocrystallites at different heating rates. A shift is observed from the TG and DSC curves in the HTD process with increasing heating rate from 5 to  $20^{\circ}\text{C}\cdot\text{min}^{-1}$ . Table 1 gives the kinetic parameters for high-temperature decomposition process of AP in the presence of 5 wt. %  $\text{CoFe}_2\text{O}_4$  nanocrystallites at different heating rates. Apparent activation energy  $E_a$  and pre-exponential factor  $A$  of the thermal decomposition are calculated according to Kissinger method [22]

$$\ln \frac{\beta}{T_r^2} = \ln \frac{R \cdot Z}{E_a} - \frac{E_a}{R} \cdot \frac{1}{T_r}, \quad (1)$$

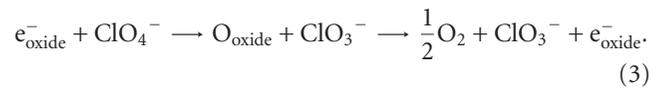
where  $\beta$  is heating rate,  $T_r$  is absolute temperature,  $E_a$  is activation energy,  $R$  is gas constant, and  $Z$  the pre-exponential factor.

Then through Arrhenius equation to calculate the reactive rate constant  $K$  of thermal decomposition reaction,

$$K = Z \cdot \exp\left(-\frac{E_a}{T \cdot R}\right). \quad (2)$$

From Table 1, it was observed that the  $E_a$  of AP in the presence of 5 wt. % for HTD was much lower than

pure AP. This lowering in  $E_a$  is in agreement with the generally observed trend of lowering of  $E_a$  for a reaction whose rate is increased by a catalyst. This has been further confirmed by observing higher rate constant values in the catalyzed AP. Moreover, the apparent decomposition heat  $\Delta H$  reading out from the DSC curves increased from 517.1 to  $923.5 \text{ J}\cdot\text{g}^{-1}$ , which clearly indicates an enhanced catalytic activity of AP in the presence of  $\text{CoFe}_2\text{O}_4$  nanocrystallites. Concerning the catalytic mechanism of transition metal oxides on the thermal decomposition of AP, Freeman and Anderson [23] and Survase et al. [24] and Patil et al. [25] proposed an electron transfer mechanism, in which the oxides could provide a bridge in an electron-transfer process (3) as follows:



However, the AP is a typical dielectric, and according to the primary stage of process of thermal decomposition of AP reported by earlier researchers [26], the primary products detected in these experiments were  $\text{NH}_3$  and  $\text{HClO}_4$ . Hence, the process cannot be explained by electron transfer at low temperature of thermal decomposition. This allowed assuming that the primary stage of process of thermal decomposition of AP is proton transfer [27]. Step (I) corresponds to the pair of ions in AP lattice. Step (II) involves the decomposition or sublimation step that starts with proton transfer from the cation  $\text{NH}_4^+$  to the anion  $\text{ClO}_4^-$ , then the molecular complex is formed and decomposes into  $\text{NH}_3$  and  $\text{HClO}_4$  in Step (III). The molecules of  $\text{NH}_3$  and



## 4. Conclusions

The TG-DSC study reveals that the  $\text{CoFe}_2\text{O}_4$  nanocrystallites synthesized successfully by polyol-medium solvothermal method have pronounced catalytic effect on the thermal decomposition of AP and the catalytic activity is found to be enhanced with the increase of content of  $\text{CoFe}_2\text{O}_4$  nanocrystallites. The kinetic parameters such as the decrease in activation energy and increase in rate constant further confirmed the enhancement in the catalytic activity of AP. Based on the proton transfer process, a mechanism has been proposed for the thermal decomposition of AP in the presence of  $\text{CoFe}_2\text{O}_4$  nanocrystallites.

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