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Catalytic effect of commercial nano-CuO and nano-Fe_2O_3 on thermal decomposition of ammonium perchlorate

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Abstract

Size reduction of the catalyst increases the surface area, and hence, the catalytic activity is also increased. The decrease in temperature of decomposition of ammonium perchlorate in the presence of nano-copper oxide and nano-ferric oxide is investigated within the scope of this study. Different mixes of ammonium perchlorate with nano-ferric oxide and nano-copper oxide were prepared. Differential scanning calorimetry test results show that addition of nanometer-sized ferric oxide and copper oxide leads to a significant decrease in higher decomposition temperature of ammonium perchlorate. The most significant decrease in the decomposition temperature was observed in the presence of 3% of nano-copper oxide.

Keywords: Ammonium perchlorate; Thermal decomposition; Catalyst; Nanostructure

Background

At nanoscale, the physicochemical characteristics of materials are considerably various from those found in larger scales and bulk materials [1]. Nanoparticles have many noteworthy properties due to their small size and very large specific surface area [2]. There is a growing interest in the synthesis and use of metal or metal oxide nanoparticles due to their large specific surface area and high activity in most catalytic processes [3,4]. It is noted that nanoparticles are not only effective in the catalytic processes such as gas-solid, gas–liquid–solid or liquid–solid, where the nanoparticles, as the catalyst, are the solid phase, but also effective in the solid-solid catalytic processes [5]. Transition metal oxide nanoparticles exhibit a broad class of materials that have been investigated extensively due to their interesting catalytic properties and wide scope of their potential applications [6]. It has been proven that nanometer-sized metals and metal oxides are effective to improve the decomposition of ammonium perchlorate (AP) [3-5,7-14]. Although the characteristics of AP thermal decomposition can be tailored to some extent by decreasing the particle size of AP, this method is rarely used due to the dangerousness of superfine AP [5,15]. Particle size distribution, morphology, and nanostructure of particles are very important characteristics and affect the kinetics of decomposition of AP [4]. Many researchers have studied the catalytic effects of nanostructures such as nanometer-sized metals and metal oxides on the thermal decomposition of AP and observed their tailoring effect on the thermal decomposition behavior of AP [3-5,7-14]. Table 1 presents a historical background about some important events in the field of the effect of nanostructures on thermal decomposition of AP. In this paper, the catalytic effect of commercial nano-sized ferric oxide and nano-sized copper oxide on the thermal decomposition of AP is investigated.

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Results and discussion

Transmission electron microscopy (TEM) images of nano-CuO and nano-Fe_2O_3 are shown in Figure 1. From this figure, it can be observed that the morphology of these nanoparticles is relatively spherical. Figure 2 shows the X-ray diffraction (XRD) patterns of commercial nano-CuO and nano-Fe_2O_3.

In Figure 2(a), the major peaks located at 2θ values of 20° to 75° correspond to the characteristic diffractions of monoclinic phase CuO [9]. Figure 2(b) can be readily indexed as the rhombohedral crystalline phase [11].

Table 1 Bibliographic history of the effect of nanostructure on thermal decomposition of AP

Author	Year	Significance
Weifan et al. [7]	2006	Nano-sized yttria
Meda et al. [8]	2007	Nano-aluminum
Duan et al. [16]	2007	Nano-sized MgO
Liu et al. [15]	2008	Nanometer-sized $CuFe_2O_4$
Duan et al. [5]	2008	Ni nanoparticles
Hongzhen et al. [3]	2008	Co nanoparticles
Satyawati et al. [4]	2008	Nano-ferric oxide
Wang et al. [9]	2009	CuO nanocrystals
Aijun et al. [10]	2011	Nano-$MnFe_2O_4$
Zhang et al. [11]	2011	Nano α-Fe_2O_3
Zhou et al. [12]	2011	ZnO/AP, Co_3O_4/AP, Fe_2O_3/AP nanocomposites
Chaturvedi and Dave [13]	2011	Nanometals
Alizadeh et al. [14]	2012	Nano-sized CuO, Co_3O_4, and $CuCo_2O_4$

Differential scanning calorimetry (DSC) curves for the thermal decomposition of AP in the presence of nano-sized CuO are illustrated in Figure 3. As can be seen in this figure, the thermal decomposition of pure AP occurs in two stages: the endothermic stage and the exothermic stage. By comparing these four curves, the endothermic stage happens at a temperature of about 240°C. This stage is related to crystal phase transition from orthorhombic to cubic. The other two peaks at 314°C and 455°C are the exothermic peaks that are associated with partial decomposition of AP and the formation of some NH_3 and $HClO_4$ via dissociation and sublimation and complete decomposition of AP and the formation of volatile products, respectively. It is obvious that the addition of nano-sized CuO to AP has no deep effect on the crystallographic phase transition temperature of AP, but it has considerable influence on the exothermic decomposition of AP. Two exothermic peaks are converted to a strong peak in the result of added nano-sized CuO, and this indicates the catalytic activity of nano-sized CuO in the thermal decomposition of AP. During the exothermic process, higher thermal decomposition temperatures of AP with nano-CuO contents of 1%, 2%, and 3% are 359°C, 348.9°C, and 347.12°C, respectively. At curves b, c, and d of Figure 3, it can be observed that the peaks become steep in the presence of nano-CuO which indicates that the rate of thermal decomposition of AP also increased.

Figure 4 presents the DSC curves for thermal decomposition of AP in the presence of nano-sized Fe_2O_3. From these curves, it can be found out that the thermal decomposition of AP is catalytically affected by nano-sized Fe_2O_3. The endothermic stage occurring at a temperature of about 240°C is not greatly influenced by nano-ferric oxide. It is clear that the addition of nano-sized Fe_2O_3 to AP has a significant effect on the exothermic temperatures of AP. During the exothermic process, higher thermal decomposition temperature of AP with nano-Fe_2O_3 contents of 1%, 2%, and 3% are 403.57°C, 374.18°C, and 347.87°C, respectively. Rate enhancement of thermal decomposition of AP in the presence of nano-Fe_2O_3 is drawn from steepness modes of the curves b, c, and d.

The results associated with decrease in higher thermal decomposition of AP in the presence of nano-sized CuO and nano-sized Fe_2O_3 are given in Table 2. As it is clear from this table, when nanometer-sized CuO and Fe_2O_3 are added to AP, the higher decomposition of AP is decreased considerably. From this table, it is obvious that the catalytic effect of adding 1% and 2% of nano-sized CuO with an average particle size of 40 nm is greater

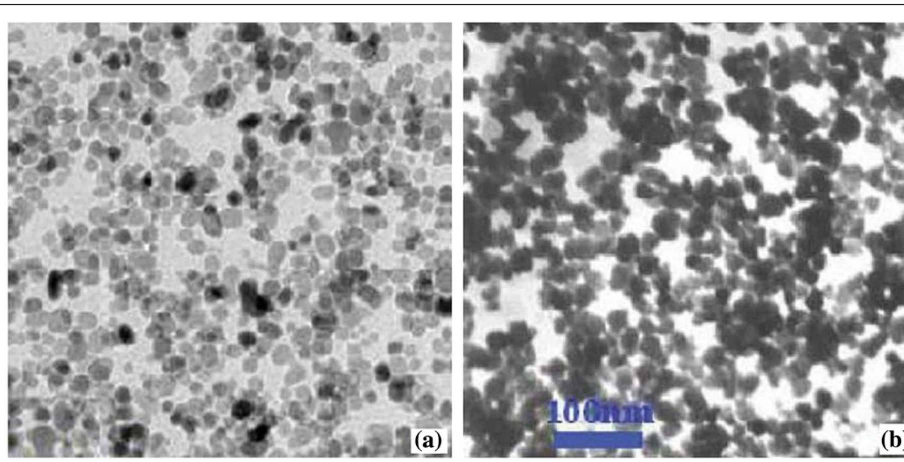

Figure 1 TEM images of (a) nano-CuO and (b) nano-Fe_2O_3.

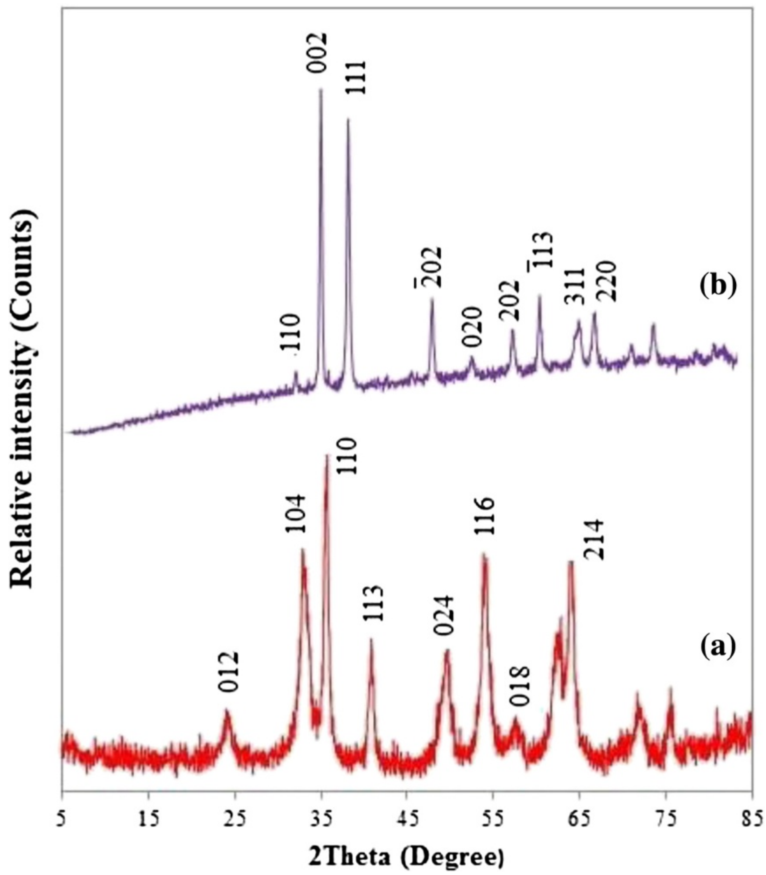

Figure 2 XRD patterns of (a) nano-Fe_2O_3 and (b) nano-CuO.

than that of the nano-sized Fe_2O_3 with an average particle size of 20 nm.

In Table 3, the results of the catalytic effect of as-synthesized nano-CuO and nano-Fe_2O_3 in some recent studies are given. As can be seen from this table, the catalytic effect of as-synthesized nano-CuO is higher than that of the as-synthesized Fe_2O_3. A similar comparison associated with commercial nano-sized CuO and nano-sized Fe_2O_3 is also concluded from this study.

Conclusions

The results of differential scanning calorimetry illustrate that nanometer-sized copper oxide and ferric oxide have a significant catalytic effect on the thermal decomposition of ammonium perchlorate. The presence of these nano-sized metal oxides reduces significantly the higher decomposition temperature of ammonium perchlorate. With increase of content of nanometer-sized metal oxide, the decrease in higher decomposition temperature of ammonium perchlorate becomes greater. Also, the catalytic effect of nano-sized copper oxide with larger particle size is more sizable than that of the nano-sized ferric oxide.

Methods

Materials

Ammonium perchlorate (monomodal 120 μm) was purchased from Merck (Darmstadt, Germany). Commercial nano-CuO and nano-Fe_2O_3 were purchased from Pishgaman Company located in Mashhad, Iran. Physical properties of nano-CuO and nano-Fe_2O_3 such as bulk density, actual density, specific surface area, and average particle size are given in Table 4. The Chemical compositions of these two nano-sized metal oxides are given in Tables 5 and 6.

Methods

X-ray diffraction analysis

XRD patterns of nano-CuO and nano-Fe_2O_3 was performed with a Philips (Amsterdam, The Netherlands) PW 1800 powder X-ray diffractometer using CuKα radiation at 40 kV and 30 mA.

Transmission electron microscopy

TEM images of nanoparticles were prepared on a Philips (Amsterdam, The Netherlands) transmission electron microscope operated at an accelerating voltage of 100 kV.

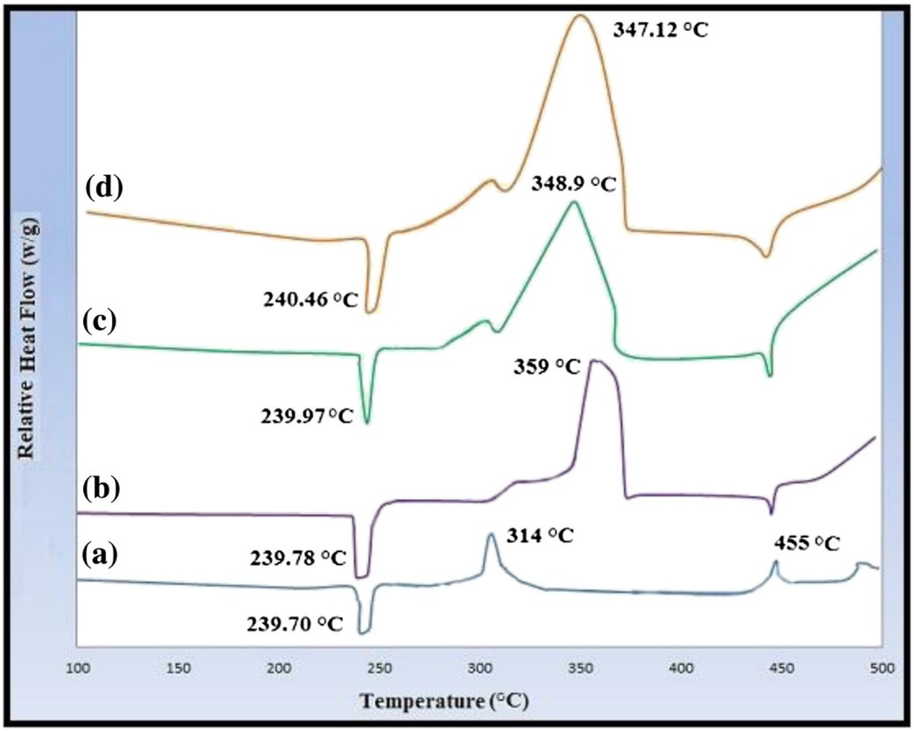

Figure 3 DSC curves related to (a) pure AP, (b) AP1C, (c) AP2C, and (d) AP3C.

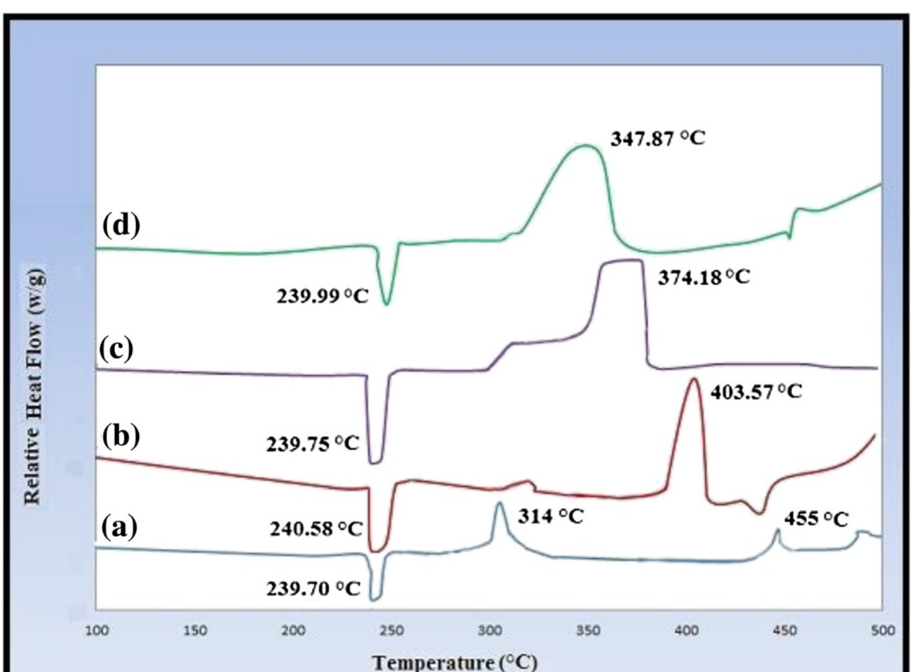

Figure 4 DSC curves related to (a) pure AP) (b) AP1F, (c) AP2F, and (d) AP3F.

Table 2 Decreased values of higher decomposition temperature of AP

	AP + nano-sized Fe_2O_3			AP + nano-sized CuO		
	3%	2%	1%	3%	2%	1%
Decrease in higher decomposition temperature (°C)	107.13	80.82	51.43	107.88	106.1	96

Table 3 Catalytic activity results of as-synthesized nano-sized CuO and nano-sized Fe_2O_3

Sample	Average particle size (nm)	Decrease in higher decomposition temperature of AP (°C)	Reference
AP + nano-CuO (chrysalis-like)	-	85	[9]
AP + nano-CuO	16.5	90.47	[14]
AP + nano-Fe_2O_3	30	57	[4]
AP + nano-Fe_2O_3 (sphere-like)	25	81	[11]
AP + nano-Fe_2O_3 (pod-like)	-	72	[11]

Table 4 Physical properties of nano-CuO and nano-Fe_2O_3

Nano-metal oxide	Bulk density (g/cm^3)	Actual density (g/cm^3)	Specific surface area (m^2/g)	Average particle size (nm)
Nano-CuO	0.79	6.40	20	40
Nano-Fe_2O_3	1.20	5.24	40 to 60	20

Table 5 Chemical composition of nano-CuO

Element	Mn	Pb	Fe	Mg	P	K	Ca	Sr	Zn	Co	Cd	Ba
Amount (ppm)	3.5	90	87	75	300	300	400	2.3	195	6.4	2.5	0.75

Table 6 Chemical composition of nano-Fe_2O_3

Element	Mn	Na	Al	S	SiO_2	P	Cr	Ca
Amount (ppm)	0.095	0.0005	0.0002	0.12	0.134	0.016	0.037	0.024

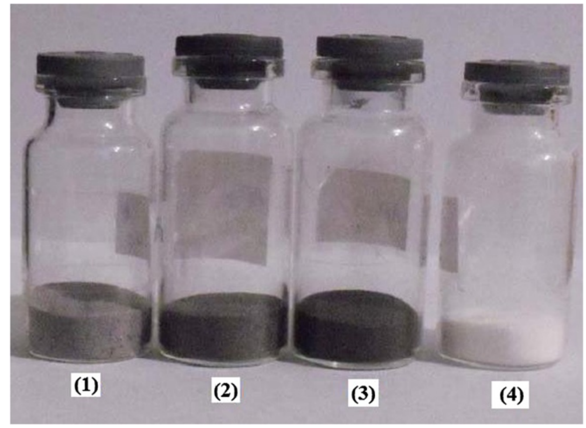

Figure 5 AP1C (1), AP2C (2), AP3C (3), and pure AP (4).

Differential scanning calorimetry

The thermal decomposition processes of the samples were characterized by DSC using Dupont (Wilmington, DE, USA) 2000 instrument at a heating rate of 10°C/min.

Sample preparation

The CuO nanoparticles were blent with AP in different contents of 1, 2, and 3 wt.% to prepare the samples for thermal decomposition experiments. These samples were labeled as AP1C (AP + 1% nano-CuO), AP2C (AP + 2% nano-CuO), and AP3C (AP + 3% nano-CuO). Also, in a similar way, the Fe_2O_3 nanoparticles were mixed with AP, and the samples were labeled as AP1F (AP + 1% nano-Fe_2O_3), AP2F (AP + 2% nano-Fe_2O_3), and AP3F (AP + 3% nano-Fe_2O_3). Before the thermal decomposition experiments using DSC technique, the samples were homogenized. Figures 5 and 6 show the samples used in this study.

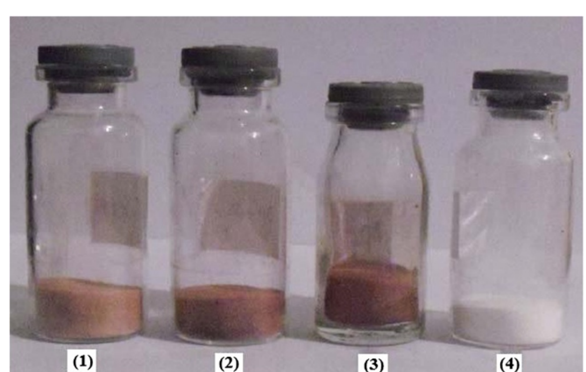

Figure 6 AP1F (1), AP2F (2), AP3F (3), and pure AP (4).

Competing interests
The author has no competing interests.

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MM is a student in M.Sc. of Chemical Engineering in Iran University of Science and Technology (IUST).

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