Materials Chemistry and Physics 181 (2016) 12–20

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Fabrication of ammonium perchlorate/copper-chromium oxides core-shell nanocomposites for catalytic thermal decomposition of ammonium perchlorate

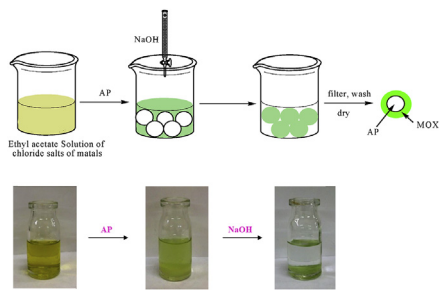
Abbas Eslami [a, *], Nafise Modanlou Juibari [a], Seyed Ghorban Hosseini [b]

[a] Department of Inorganic Chemistry, Faculty of Chemistry, University of Mazandaran, P.O.Box 47416-95447, Babolsar, Iran
[b] Department of Chemistry, Malek Ashtar University of Technology, P.O. Box 16765-3454, Tehran, Iran

HIGHLIGHTS

- The Cu-Cr-O nanoparticles were synthesized by chemical liquid deposition method.
- Then, the AP/Cu-Cr-O core-shell nanocomposites were prepared.
- The core-shell samples showed high catalytic activity for AP decomposition.
- Thermal decomposition of samples occurs at lower temperature range.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 January 2015
Received in revised form
6 May 2016
Accepted 29 May 2016
Available online 28 June 2016

Keywords:
Composite materials
Nanostructures
Differential scanning calorimetry (DSC)
Electron microscopy
Precipitation

ABSTRACT

The ammonium perchlorate/Cu(II)-Cr(III)-oxides(AP/Cu-Cr-O) core-shell nanocomposites were in-situ prepared by deposition of copper and chromium oxides on suspended ammonium perchlorate particles in ethyl acetate as solvent. The results of differential scanning calorimetery (DSC) and thermal gravimetric analysis (TGA) experiments showed that the nanocomposites have excellent catalytic effect on the thermal decomposition of AP, so that the released heat increases up to about 3-fold over initial values, changing from 450 J/g for pure AP to 1510 J/g for most appropriate mixture. For better comparison, single metal oxide/AP core-shell nanocomposite have also been prepared and the results showed that they have less catalytic effect respect to mixed metal oxides system. Scanning electron microscopy (SEM) results revealed homogenous deposition of nanoparticles on the surface of AP and fabrication of core-shell structures. The kinetic parameters of thermal decomposition of both pure AP and AP/Cu-Cr-O samples have been calculated by Kissinger method and the results showed that the values of pre-exponential factor and activation energy are higher for AP/Cu-Cr-O nanocomposite. The better catalytic effect of Cu-Cr-O nanocomposites is probably attributed to the synergistic effect between Cu^{2+} and Cr^{3+} in the nanocomposites, smaller particle size and more crystal defect.

1. Introduction

Metal oxides are an attractive class of inorganic materials for a variety of applications ranging from catalysis and medicine to cosmetic, plastic, rubber, and as the co-assistant components in

* Corresponding author.
E-mail addresses: eslami@umz.ac.ir, eslami_a@yahoo.co.uk (A. Eslami).

http://dx.doi.org/10.1016/j.matchemphys.2016.05.064
0254-0584/

some electric materials [1]. The good catalytic activity of transition metal oxides was ascribed to the existence of several readily interconvertible oxidation states. Nanoparticles of metal oxides are also extensively applied in several industries such as catalysts, ceramics and pigments [2,3]. Furthermore, they have significant influence on the surface modification of various substrates [4,5]. One of the important applications of metal oxides is their good catalytic activity in thermal decomposition of solid propellants [2,3,6–10].

Ammonium perchlorate (AP) is one of the main oxidizing agents that has been used in various propellants [11–13]. The thermal decomposition of pure AP occurs through three sequential processes. Initially, an endothermic process takes place at around 250 °C which is assigned to the solid state phase transition from the orthorhombic phase to the cubic one. Then, a partial decomposition occurs exothermically at the temperatures around 300–330 °C which leads to formation of an intermediate product. Finally, the last event, which is also an exothermic process and happens at the temperatures higher than 350 °C, is attributed to the complete decomposition of the intermediate product into volatile products. This thermal behavior of AP particles is known to have significant effect on the combustion behavior of the AP-based propellant [14,15]. A specific characteristic of the thermal decomposition of AP is its high sensitivity to the presence of various additives. AP-additive mixtures are either a homogeneous composite or a heterogeneous mixture, which can either promote or obstruct AP decomposition [16]. This is a crucial feature of AP-based mixtures for propellant applications [17–20].

In the past decades, core–shell nanostructures, which preserve the properties of both cores and shells, have attracted much attention due to their tunable surface properties, which can enhance their magnetic, electronic, and catalytic properties [21]. Combining several nanomaterials into a nanoparticles shell is a beneficial route to fabricate composite materials with desirable physical and chemical properties [22]. Metal oxides have high surface activity which would be expected to be suitable for catalytic applications, but their tendency to agglomeration limits their utilization [23,24].

The core-shell nanocomposites, which can be synthesized by templating with organic or inorganic cores, often show appropriate dispersion and resistance properties and very strong interactions at the interface of the core-shell that can be beneficial for catalytic purposes [25–29]. Although many investigations have been carried out on the catalytic improvement of thermal decomposition of AP particles by various additives such as metals [30,31], metal oxides [32–35], inorganic materials, and metal salts [36,37], those with core-shell structures have rarely been performed [38]. In addition to binary metal oxides, mixed metal oxides (MMO) have also been used as additive for the improvement of thermal decomposition of ammonium perchlorate. The catalytic activity of MMO systems in AP decomposition has usually been attributed to the higher surface area of nanoparticles, the existence of crystal defects in nanostructures, and the synergistic effects of the catalyst and substrate in the nanocomposites [39]. However, to the best of our knowledge, there is no report of the preparation of mixed metal oxides AP/(MMO) core-shell nanocomposites, which may have significant influence on the heat of decomposition, kinetic parameters, and thermal decomposition temperatures of AP. Therefore, it is of interest to develop a facile method to prepare AP/(MMO) core-shell nanocomposites.

In this study, AP powders were successfully coated with MMO to form the core-shell nanostructures by a feasible deposition method at room temperature. One of the most important characteristic of the preparation is the in-situ growth of MMO particles and homogeneous precipitation on the surface of the AP powders. The obtained nanocomposites showed excellent self-catalytic effects for the thermal decomposition of AP in lowering the decomposition temperature and increasing the released heat. The coating state and thermal characteristics of desired samples have been investigated by means of differential scanning calorimetery (DSC), thermogravimetery analysis (TGA), X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), and energy dispersion X-ray spectrometer (EDS).

2. Experimental

2.1. Materials and physical techniques

Copper chloride ($CuCl_2 \cdot 6H_2O$), chromium chloride ($CrCl_3 \cdot 6H_2O$), ethyl acetate ($CH_3COOC_2H_5$) and sodium hydroxide (NaOH) were all purchased from Merck and AP (98%) was obtained from Fluka and used as received without further purification.

Scanning electron microscopy (SEM) (Oxford LEO 1445), equipped with energy dispersion X-ray spectrometer (EDS) and operated at an acceleration voltage of 10.0 KV, was used to investigate the morphologies of core-shell nanocomposites. The crystal phase structures of the products were analyzed by X'Pert Pro MPD (PANalytical) X- Ray using Cu Kα radiation(λ = 1.54 Å) in the 2θ range from 20° to 80°. The DSC curves were obtained by DuPont differential scanning calorimeter model DSC 910S, in the temperature range of 50–600 °C using an aluminum crucible at different heating rates (5, 10, 15 and 20 °C/min), under air atmosphere with the flow rate of 50 ml/min. The approximate mass of samples was 3.5 mg in all runs. Thermogravimetery (TG) experiments were carried out using a Stanton Redcroft, STA-780 series with an aluminum crucible, applying at heating rate of 10 °C/min in a temperature range of 50–600 °C, under air atmosphere.

2.2. Procedures of the preparation

A key point in the synthesis of AP/MMO core-shell nanocomposites is the selection of a suitable solvent for metal salts which can act as non-solvent for AP. Our examination revealed that ethyl acetate is the most appropriate solvent for this purpose. Typical procedure includes three main steps which are shown in Fig. 1.

In the first step, calculated amounts of $CuCl_2 \cdot 2H_2O$ and $CrCl_3 \cdot 6H_2O$ salts were successively dissolved in 15 mL ethyl acetate. Then, 0.5 g AP powder, which acts as template, was added to the solution and vigorously stirred to make AP powders well distributed in the solution. Subsequently, a desired volume of NaOH solution (0.05 M or 0.5 M) was added dropwise to the mixture which leads to reaction of the metal ions with NaOH and precipitation of nanocomposites in the solution. In accordance with the principle of heterogeneous nucleation, the MMO nanocrystals would be nucleated and then flourished on the surface of AP and establishing the nanocomposites with core–shell structure [38]. Then the products were filtered and dried at 80 °C to obtain the nanocomposites. The core-shell samples with different mass ratios (or shell thickness) were prepared according to the conditions given in Table 1 (AP2-6). The investigated parameters are concentration of metal salts, ratio of coating agent to AP mass, volume and concentration of sodium hydroxide (NaOH). Based on the thermal analysis data, kinetic parameters for thermal decomposition processes of pure and completely coated AP particles have been estimated.

In order to investigate the structure of the shell, an experiment without addition of AP has been performed. In a typical experiment and similar to above-mentioned one, 0.01 g $CrCl_3$ and 0.02 g $CuCl_2$ were completely dissolved in 15 mL ethyl acetate and then 1 mL 0.05 M sodium hydroxide added to this solution. The suspension