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Cu–Co–O nano-catalysts as a burn rate modifier for composite solid propellants

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Abstract

Nano-catalysts containing copper–cobalt oxides (Cu–Co–O) have been synthesized by the citric acid (CA) complexing method. Copper (II) nitrate and Cobalt (II) nitrate were employed in different molar ratios as the starting reactants to prepare three types of nano-catalysts. Well crystalline nano-catalysts were produced after a period of 3 hours by the calcination of CA–Cu–Co–O precursors at 550 °C. The phase morphologies and crystal composition of synthesized nano-catalysts were examined using Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS) and Fourier Transform Infrared Spectroscopy (FTIR) methods. The particle size of nano-catalysts was observed in the range of 90 nm–200 nm. The prepared nano-catalysts were used to formulate propellant samples of various compositions which showed high reactivity toward the combustion of HTPB/AP-based composite solid propellants. The catalytic effects on the decomposition of propellant samples were found to be significant at higher temperatures. The combustion characteristics of composite solid propellants were significantly improved by the incorporation of nano-catalysts. Out of the three catalysts studied in the present work, CuCo-I was found to be the better catalyst in regard to thermal decomposition and burning nature of composite solid propellants. The improved performance of composite solid propellant can be attributed to the high crystallinity, low agglomeration and lowering the decomposition temperature of oxidizer by the addition of CuCo-I nano-catalyst.

Keywords: Metal oxides; Nano-catalysts; Solid propellant; Burn rate; Surface morphology; Thermal analysis

1. Introduction

Transition metal oxides (TMOs) have widely been employed as solid-state catalysts for various energy applications [1,2]. It has been demonstrated that mixed metal oxides (MMOs) are capable of showing better catalytic effects than a single-phase TMO, because of their synergic effects [3,4]. The assessment of bimetallic (Cu–Cr) catalysts has been optimized usefully in the synthesis of some industrial hydrocarbons [5]. The nano-composite of Cu–Cr–O, and nano-alloys of Cu–Ni and Cu–Zn have also been investigated as combustion catalysts in many solid propellants [6–9]. Such catalysts, which were found to alter the burning rate, are always considered as a great interest in modifying the ballistic properties of solid rocket motors.

The MMO nano-catalysts and their synthetic modes have often determined the physical and chemical properties, even with the same starting composition. The crystallinity, inter-dispersion of chemical constituents and specific surface area are the relevant parameters which affect the catalytic performance, which in turn depends primarily on the synthetic methodologies [10]. A considerable effort has been made to find some novel synthetic routes which can give precursor of two or more metals in a single crystalline phase. This has resulted in a well inter-dispersed matrix of MMOs of required specific surface area and particle size. The performance of application materials can be increased or decreased by the inclusion of such catalysts in a fewer percent ratios. The MMOs have great influence on the thermal decomposition behaviors of the oxidizer masses in the solid propellants [11–21]. Recent investigations have shown that MMOs in nano-scales can increase the burning rate effectively. Styborski et al. [14] carried out the burning rate measurements for AP/HTPB composite propellants with iron nanoparticles as additives. They found that the addition of 1% Fe nanoparticles increased the burning rate of propellant by factors of 1.2–1.6. Dave et al. [15] prepared TiO2, ZnO_2, and CrO_2 nanoparticles by quick precipitation method and

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observed an increase in the thermal decomposition of propellants in the presence of transition metal oxide nanoparticles. The size distribution, morphology, and nano-structure of particles are primary characteristics which influence the decomposition kinetics of solid propellants. Li and Cheng have synthesized Cu–Cr–O nano-composites via a citric acid complexing approach and demonstrated that these catalysts are useful in enhancing the catalytic-combustion of AP-HTPB based solid propellants [6]. Dubey et al. [22] prepared nanocomposites of Mn with Co, Ni, and Zn by polyol method, which showed high reactivity toward total combustion of solid propellants. Kawamoto et al. [23] prepared copper chromite from ceramic and co-precipitation methods, which were found to increase the burning rate of HTPB-based solid propellants. Rajeev et al. [24] synthesized Cu–Cr–O composites from thermal decomposition of copper ammonium chromate and observed that the higher burning rates of solid propellants are the consequence of crystal structures, particle sizes, and inter-dispersed metallic phases of the precursors.

In the present study, MMO nano-catalysts containing Cu–Co–O have been synthesized by citric acid complexing method. Three types of MMO nano-catalysts, namely CuCo-I, CuCo-II and CuCo-III, were prepared, by varying the molar ratios of the starting reactants. Characterization of precursors, as well as crystallized MMO nano-catalysts, was carried out using SEM, EDS, FTIR and thermal techniques. Efforts have been made to analyze the particle sizes, inter-dispersed metallic phases and structural features of all three nano-catalysts. The catalytic performance of all the nano-catalysts was studied in HTPB-AP based solid propellants. Burning rate measurements were carried out at atmospheric conditions.

2. Experimental sections

2.1. Materials and methods

Copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) and cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) of AR grade, procured from Central Drug House India Pvt. Ltd., New Delhi, were used without further purification. The citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$) and benzoic acid of AR grade, obtained from Merck Millipore (India) Pvt. Ltd., were used as complexing agent and standard sample for calibration of bomb calorimeter respectively. Ammonium perchlorate (AP) was used as an oxidizer in the present study, which was obtained from Tamilnadu Chlorates, Madurai. Hydroxyl-Terminated Poly Butadiene (HTPB) was used as a fuel-binder, which was obtained from VSSC, Trivandrum. Bis (2-ethylhexyl) adipate (BEHA) and Isophorone Di-Isocyanate (IPDI) were procured from Fluka Analytical, Germany, which were used as the plasticizer and curing agent respectively for solid propellant formulations.

The physical characteristics of nano-catalysts were analyzed using FTIR technique. The crystal phases and particle characterization of nano-catalysts and solid-state propellants were studied with the help of SEM. In a typical procedure, the beam of high energy electrons is focused on the solid specimen. The electrons react with the sample and emit signals of various energies. Of all the signals emitted, the secondary electron detector in conjunction with energy dispersive spectroscopy (EDS) was used to examine the elemental composition as well as molecular orders of metal oxides. The samples were coated with platinum to make them electrically conductive. The beams were operated at 25 keV to characterize the surfaces of nano-catalysts. The TGA/DTA analyzer, in the temperature range of ambient to 400 °C and at a heating rate of 10 °C/min, was used to examine the decomposition behavior of solid propellants with and without nano-catalysts. Bomb calorimeter was used to measure the heat of combustion of solid propellants of various compositions. The bomb calorimeter was used in isothermal conditions.

Table 1
Molar concentration and product yield of prepared nano-catalysts.

Catalyst	Copper nitrate/ ($mol{\cdot}dm^{-3}$)	Cobalt nitrate/ ($mol{\cdot}dm^{-3}$)	Citric acid/ ($mol{\cdot}dm^{-3}$)	Molar ratio/ (Cu/Co)	Product yield/ (%)
CuCo-I	0.00248	0.00247	0.0149	1.0	20.0
CuCo-II	0.00248	0.00494	0.0149	0.5	25.0
CuCo-III	0.00496	0.00247	0.0149	2.0	32.0

2.2. Preparation of nano-catalysts

By varying the molar concentrations of Cu/Co nitrates as presented in Table 1, three types of nano-catalysts were synthesized. During the synthesis process, the $Cu(NO_3)_2{\cdot}3H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were dissolved separately in 25 mL of doubly distilled water (DDW). The solution mixtures were added together in a porcelain evaporator dish (100 mL) and stirred adequately to make a homogenous nitrate solution. Citric acid ($C_6H_8O_7{\cdot}H_2O$) was then added to the nitrate solution mixture and stirred vigorously for a period of 10 min. The final solution mixture was heated at 105 °C for 4 hours so that the water content is evaporated, producing a viscous gel. Fig. 1(a) shows a representative gel of CA–(Cu–Co–O) precursor. The gel was then dried at 165 °C for 2 hours to obtain foamy textures as shown in Fig. 1(b). It was then calcined at 550 °C for 3 hours, which produced black powder of MMOs. A representative scheme for synthesis of nano-catalysts is shown in Eq. (1). The stoichiometry of nano-catalysts may varied as: $x = 2, 3, 4$, $y = 2, 4$ and $z = 3, 4, 6$.

$$Cu(NO_3)_2 \cdot 3H_2O + Co(NO_3)_2 \cdot 6H_2O + C_6H_8O_7 \cdot H_2O \rightarrow Cu_xCo_yO_z \quad (1)$$

This was again grinded properly and stored for characterization and its application as a catalyst for the combustion of solid rocket propellants.

2.3. Preparation of solid composite propellants

HTPB and AP were used as a fuel-binder and solid oxidizer for the formulation of solid propellants. The loading percentage of AP was kept fixed at 70% by weight in the entire set of experiments. Two particle sizes of AP were used in the present study, i.e. 250 μm and 44 μm, which were employed in the ratio