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Bi-metallic nanocomposites of Mn with very high catalytic activity for burning rate enhancement of composite solid propellants

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ABSTRACT

Bimetallic nanocomposites of Mn with Co, Ni and Zn were successfully synthesized by polyol method. Particles of the nanocomposites varied in shape from spherical to cubic having an average size of the order of 9–18 nm. The nanocomposites showed very high activity as burning rate catalysts for composite solid propellants (CSPs) containing hydroxyl terminates polybutadiene (HTPB) as binder and ammonium perchlorate (AP) as oxidizer. MnCo was the best catalyst among the three nanocomposites as it enhanced the burning rate of the CSP to more than three fold. Catalytic activity of the nanocomposites for thermal decomposition of AP and CSPs was investigated by simultaneous thermogravimetric analysis–differential scanning calorimetry (TGA–DSC) and ignition delay measurements. MnCo was found to be the best catalyst in terms of lowering decomposition temperature of both AP and CSPs. Kinetics of catalyzed thermal decomposition of AP was also studied using isoconversional method from isothermal TGA data.

1. Introduction

Solid propellants are the first generation rocket propellants that are in vogue since 13th century [1]. Alternative rocket fuels such as liquids and hybrids have replaced solid propellants in many applications recently, due to their better efficiency and controllability [2]. However, CSPs are still being used at least partially for propelling rockets. They are also widely being used to propel missiles due to their high storage stability and reliable ignition properties [3]. Though, CSPs are in vogue for a long time and their performance have been well optimized, there is still scope to improve their performance, especially their burning rates can be modified. This is important as internal ballistics of rocket propellants are inherently related to their burning rates [4]. Enhancement in burning rates can help in enhancing the thrust generated. Enhancement in thrust, even to a small extent can boost the performance of the rockets and missiles in terms of either or both of payload and trajectory. This fact is the main driver for research on the development of better additives to boost the burning rates of CSPs. Additionally, there are known processing issues associated with the presently used transition metal oxides (TMOs) [5]. Moreover, the effectiveness of TMOs as burning rate catalysts is concentration dependent [6]. As with most of the heterogeneous catalysts, the catalytic activity of TMOs is related to particle size also. With the advancement of nanotechnology, there is increased research activity in the search for nanomaterial catalysts as burning rate enhancers for CSPs [7,8]. The renewed interest in the development of nanomaterial catalyst for the burning rate enhancement of CSPs is not just limited to TMOs and mixed metal oxides. There is also considerable interest recently to use nanoparticles of metals, alloys or metal nanocomposites [9–12].

Here we report a comparative study on the activities of three bimetallic nanocomposites of Mn with Co, Ni and Zn as burning rate catalysts for CSPs. We have also thoroughly evaluated the catalytic activity of the nanocomposites on the thermal decomposition of CSPs and AP. MnCo nanocomposite was found to be the best catalyst for the thermal decomposition of AP and CSPs over MnNi and MnZn nanocomposites.

2. Experimental

2.1. Materials

AP was obtained from CECRI, Karaikudi; acetates of Mn, Co, Ni and Zn (SD-fine 99%), propylene glycol (SD-fine 99%), NaOH (Merck 98%), methanol, HTPB of VSSC, Thiruvanthapuram, IPDI (Isophoron diisocynate) of Merck and DOA (dioctyl adipate) of Merck were used without further purification.

2.2. Synthesis of nanocomposites

The metal nanocomposites were prepared by slightly modifying a reported procedure for the synthesis of Cu and Ni nanoparticles [12]. In the modified procedure, a mixture of metal acetates (0.1 M

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each) was dissolved in 50 mL propylene glycol in 1:1 molar ratio, followed by the addition of 0.6 M NaOH. The solution was refluxed in a round bottom flask at 70 °C for up to 2 h. The precipitates were filtered, washed several times with methanol and dried in vacuum oven at room temperature.

2.3. Characterizations of nanocomposites

Crystallinity of the nanocomposites was analyzed using powder X-ray diffraction (Bruker AXD8 advance) with CuKα (λ = 1.5418 Å) radiation. The morphology and structure of the nanocomposites was characterized by transmission electron microscopy (TEM) imaging. Crystallinity of the nanocomposites was analyzed by selected area electron diffraction (SAED) also.

2.4. Preparation of CSPs and burning rate measurements

CSPs were prepared by dry mixing of sieved AP (100–200 mesh) with and without nanocomposites (1 wt.%. of AP) and HTPB [13]. Ground powder of AP was first sieved through a sieve having mesh size 100 and then with another sieve having mesh size 200 to obtain a unimodal particle size distribution. The solid materials were mixed with HTPB in the ratio of 3:1 at 70 °C for 1 h followed by the addition of a curing agent (IPDI) in equivalent ratio to HTPB along with a plasticizer (DOA, 30% wt./wt. to HTPB). The propellants prepared were casted into aluminum plates having dimensions 1 cm × 3 cm × 10 cm. The samples were cured in an incubator at 70 °C for 9 days. The burning rate of cured CSPs was measured in the same way as reported earlier [14]. Typically, the propellant strands were inhibited by applying PVC tape to check side burning. The vertically held strands were ignited electrically from the top with the help of a nichrome wire. The time required for burning of a certain length of the strand was recorded by a stop watch.

2.5. Thermal analysis of AP and CSPs with and without nanocomposites

Non-isothermal TGA studies of CSPs with and without nanocomposites (wt ~ 20 mg) were undertaken in static air at the heating rate of 10 °C min^{-1} using an indigenously fabricated TG apparatus [15]. A round bottom gold crucible was used as the sample holder. Isothermal TGA of AP with and without nanocomposites (wt ~ 20 mg) was undertaken in static air using the aforementioned TG apparatus in the temperature range (300–340 °C). Non-isothermal TGA–DSC thermal curves of AP with and without nanocomposites (by mixing in ratio of 99:1, 97:3 and 95:5 by weight) were recorded on the samples (~2 mg) using STA F1 Jupiter from Netsczh under nitrogen atmosphere (flow rate 60 mL min^{-1}). Heating rate was 10 °C min^{-1} and the samples were taken in an alumina pan with alumina lid with a pin hole at the middle.

2.6. Kinetic analysis of isothermal TG data

Kinetic analysis of thermal decomposition of solids is usually based on a single-step kinetic equation (1)

$$\frac{da}{dt} = k(T)f(\alpha) \tag{1}$$

where t is the time, T is the temperature, α is the extent of conversion ($0 < \alpha < 1$), k(T) the rate constant, and $f(\alpha)$ is the reaction model, which describes the dependence of the reaction rate on the extent of reactions [16]. The value of α is experimentally derived from the global mass loss in TGA data. The reaction model may take various forms. The temperature dependence of k(T) can be satisfactorily described by the Arrhenius equation. On substitution of Arrhenius equation into Eq. (1) yields

$$\frac{da}{dt} = A\exp(-E/RT)\cdot f(\alpha) \tag{2}$$

where A is pre exponential factor, E activation energy and R the gas constant.

2.6.1. Conventional model fitting method

Rearrangement and integration of Eq. (1) for isothermal conditions gives

$$g_j(\alpha) = k_j(T)t \tag{3}$$

where $g(\alpha) = {}_0\int^{\alpha}[f(\alpha)]^{-1}\, d\alpha$ is the integrated form of the reaction model. The subscript j has been introduced to emphasize that substituting a particular reaction model in Eq. (3) results in evaluating the corresponding rate constant, which is determined from the slope of a plot of $g_j(\alpha)$ verses t. For each reaction model selected, the rate constants are evaluated at several temperatures T_i and Arrhenius parameters are determined using the Arrhenius Eq. (4) in its logarithmic form

$$\ln k_j(T_i) = \ln A_j - \frac{E_j}{RT_i} \tag{4}$$

2.6.2. Model-free isoconversional method

We have evaluated the kinetic parameters from isothermal TGA data using a model free isoconversional method developed by Vyazovkin [17]. This method allows the activation energy to be evaluated without making any assumptions about the reaction model. Additionally, the method evaluates the effective activation energy as a function of the extent of conversion which allows one to explore multistep kinetics.

The basic assumption of the isoconversional method is that the reaction model as defined in Eq. (1) is not dependent on temperature or heating rate. Under isothermal conditions, on combining Eqs. (3) and (4) we get,

$$-\ln t_{\alpha,i} = \ln[A_\alpha/g(\alpha)] - \frac{E_\alpha}{RT_i} \tag{5}$$

where E_α is evaluated from the slope of the plot of $-\ln t_{\alpha,i}$ against $T_i{}^{-1}$. Thus, E_α at various α_i for AP with and without nanocomposites have been evaluated.

2.7. Ignition delay (D_i) measurements

To understand the thermal response of AP and CSPs with and without nanocomposites at very fast heating rates, the D_i measurements were undertaken by tube furnace (TF) technique using 20 mg of each sample [18]. The accuracy of the temperature measurement of TF was ±1 °C. The sample was taken in an ignition tube (5 cm length × 0.4 cm diameter) and the time interval between the insertion of the ignition tube into the TF and the moment of appearance of a flame noted with the help of a stop watch with accuracy of 0.1 s gave the value of D_i. The ignition tube clamped in a bent wire was inserted manually into the furnace up to a fix depth (14 cm) just above the probe of the temperature indicator cum controller. The time for insertion of the ignition tube was also kept constant. Each run was repeated three times, and mean D_i values are reported.

3. Results and discussion

The polyol solutions of the mixture of metal salts had typical color and the change in color on heating the solutions gave a preliminary indication of the progress of reaction. The observed color change for each solution was as follows: