In-situ and self-distributed: A new understanding on catalyzed thermal decomposition process of ammonium perchlorate over Nd$_2$O$_3$ ☆

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ABSTRACT

Catalyzed thermal decomposition process of ammonium perchlorate (AP) over neodymium oxide (Nd$_2$O$_3$) was investigated. Catalytic performances of nanometer-sized Nd$_2$O$_3$ and micrometer-sized Nd$_2$O$_3$ were evaluated by differential scanning calorimetry (DSC). In contrast to universal concepts, catalysts in different sizes have nearly similar catalytic activities. Based on structural and morphological variation of the catalysts during the reaction, combined with mass spectrum analyses and studies of unmixed style, a new understanding of this catalytic process was proposed. We believed that the newly formed chloride neodymium oxide (NdOCl) was the real catalytic species in the overall thermal decomposition of AP over Nd$_2$O$_3$. Meanwhile, it was the "self-distributed" procedure which occurred within the reaction that also worked for the improvement of overall catalytic activities. This work is of great value in understanding the roles of micrometer-sized catalysts used in heterogeneous reactions, especially the solid–solid reactions which could generate a large quantity of gaseous species.

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1. Introduction

In the last decades or so, ammonium perchlorate (AP) has attracted a great deal of researches and applications in various fields [1,2]. For the reason that perchlorate explosives and propellants are less sensitive to shock and environmental changes than dynamite, AP plays dominant roles in military and aerospace fields [3–5]. High-burning-rate propellants that generate a large quantity of combustion gases in a short time are in demand to enable rockets to fly at faster speeds. Researches indicated that the temperature of AP thermal decomposition has an overwhelming influence on the combustion rate of solid rocket propellant [6–8]. The lower the temperature at which AP begins to decompose by heat, the higher the combustion rate is. The pervasive use of AP has been driven, in part, by the fact that the burning rate can be tailored by the addition of catalysts such as Co$_3$O$_4$ [9,10], MnO$_2$ [11], Cu$_2$O [12], CoO [13], Fe$_2$O$_3$ [14], and CuO [15]. Up to now, numerous works studied the catalytic activities of metal oxides in decomposition of AP by thermal analysis methods and mass spectroscopy (MS) [16–22], but the roles of catalysts and the

catalytic process itself still remain a mystery to a large extent. Although at least two major mechanisms, namely the electron transfer theory and the proton transfer [23–25], have been proposed, it should be noted that one common assumption for current theories is that the structure of the catalyst remains the same during the whole reaction period. Nevertheless our work presented here indicates that the actual catalytic species comes from the initially added catalysts after a particular structural evolution pathway, which has different structural features relative to their precursors.

The oxides of rare earths such as samarium, cerium and neodymium have many important applications, including high-efficiency phosphors and catalysts [26–28]. Particularly, Nd$_2$O$_3$ has gainedconsiderable attentions in the fields of heterogeneous and homogeneous catalysis [29–31]. Survase et al. [32] studied the effect of Nd$_2$O$_3$ on thermal and ballistic properties of AP based composite propellant, and indicated that Nd$_2$O$_3$ appeared to have the potential to offer high-energy propellant required for specific applications demanding dual pressure index regime. Zhao et al. [33] took full advantage of carbon nanotube (CNT) to disperse nano-Nd$_2$O$_3$, which enabled Nd$_2$O$_3$ have an improvement in catalytic performance of AP thermal decomposition to a certain extent. However, the underlying catalytic process of Nd$_2$O$_3$ additives in the thermal decomposition of AP is not clear.

In this work, we initially used differential scanning calorimetry (DSC) and MS techniques to investigate the catalytic performances

of micrometer-sized Nd_2O_3 and nanometer-sized Nd_2O_3 on the thermal decomposition of AP. The emphasis of this paper is focused on the structural and morphological comparative analyses of catalysts prior to and after the thermal decomposition of AP. In order to elaborate the catalytic process further, a control experiment was designed, in which thermal decomposition of AP in the presence of catalysts (nano-Nd_2O_3) in unmixed style was performed. Based upon the results, a new understanding of the thermal decomposition process of AP over Nd_2O_3 was proposed. It appears that the overall catalytic decomposition is an "*in-situ and self-distributed*" catalytic process. Our work is of great help in understanding the roles of catalysts used in heterogeneous solid propellants.

2. Experimental

2.1. Preparation of nano-Nd_2O_3

All chemicals such as hydrogen nitrate (HNO_3) and oxalic acid ($H_2C_2O_4$) used in the preparation of nano-Nd_2O_3 were of analytical grade, and they were used without further purification. Deionized water was used throughout the study. The micrometer-sized Nd_2O_3 used for comparison was purchased from Sinopharm Chemical Reagent Co. Ltd.

The nano-Nd_2O_3 was prepared starting from the micrometer-sized Nd_2O_3. In a typical synthesis route, 0.5 g micro-Nd_2O_3 was dissolved in dilute hydrogen nitrate, and then diluted to a pink solution of 1 mol/L. A certain amount of PEG400 was added into the solution as a surfactant. Thereafter, the mixture was transferred into a round bottom flask, and maintained at 40 °C in a water bath under continuous stirring. As appropriate amounts of 0.03 mol/L $H_2C_2O_4$ solution was added dropwise, a kind of pale purple sediment was formed. After the reaction was completed, the precipitated powders were collected by centrifugation, and washed alternately with deionized water and ethanol several times. The precursors were dried in an oven at 60 °C for 10 h prior to be calcined in a muffle furnace at 800 °C for 2 h. The calcined products were subsequently collected for further analyses.

2.2. Catalytic mechanism studies of Nd_2O_3 in thermal decomposition of AP

In this work, AP was obtained from Shanghai Chemical Factory and was ground into fine powder by a ball grinder. In order to investigate the catalytic activity of Nd_2O_3 in thermal decomposition of AP, nanometer-sized Nd_2O_3 and micrometer-sized Nd_2O_3 were used as catalysts. Catalysts and the finely powdered AP were mixed in a mass ratio of 2:98. Then the mixtures were ground in an agate mortar for 30 min to prepare the samples for DSC and MS analyses.

In contrast to the common standpoint in the previous studies on the thermal decomposition of AP, a new point of view, which is the structural and morphological studies of Nd_2O_3 prior to and after the thermal decomposition of AP, was used to investigate the real catalytic process. In order to easily capture this process, the catalytic thermal decomposition reaction in a large amount was carried out in a crucible. At first, micro-Nd_2O_3 and nano-Nd_2O_3 were mixed well with the finely powdered AP in a weight ratio of 10:90 in an agate mortar for 20 min, respectively. Then the mixture was put in the crucible with several thermal stable glass slides prior to be reached at 360 °C in a muffle furnace for 5–10 min. In the overall reaction, thermally stable glass slides were used to cool down and collect the solid compounds in real time for the structural and morphological analyses.

It describes that the contact between catalysts and reactants in a solid phase reaction to the principle knowledge is a critical factor for the catalytic performance. To investigate the influence of the dispersion of catalysts between reactants, unmixed style of the nano-Nd_2O_3 and fine AP was designed. Nano-Nd_2O_3 and AP were merely put together. One side was the nano-Nd_2O_3 and the other side was AP.

2.3. Characterization

Crystalline structures of Nd_2O_3 and solid products were identified by a powder X-ray diffractometer (XRD, Bruker D8 Advance, operated at 36 kV, 20 mA), employing Cu $K\alpha 1$ radiation ($\lambda = 0.15406$ nm). The sample was scanned from 10° to 60° (2θ) with a scanning rate of 5°/min. The average crystalline size of as-synthesized nano-Nd_2O_3 was estimated according to the Scherrer's equation and further confirmed by its transmission electron microscopy (TEM, JEOL JEM2100, worked at 200 kV) results. The particle size of micrometer-sized Nd_2O_3 was also characterized by TEM. Morphologies of the solid products were recorded on a JEOL S4800 field emission scanning electron microscope (FESEM).

Thermal decomposition characteristics of the samples were determined with a simultaneous thermal analyzer (Mettler Toledo, model TGA/SDTA 851e) coupled on line with quadrupole mass spectrometry (Pfeiffer Vacuum, model Thermostar GSD301T3). The mass spectrometer was operated with an electron impact ionizer with energy 70 eV, and the mass scan speed was 1 amu s^{-1}. The connection between the thermobalance and the mass spectrometer was made by means of a stainless steel capillary, which was maintained at 150 °C. DSC experiments of the samples (the quantum: 1.30 mg) were performed on a Mettler Toledo DSC823E in the temperature range of 50–500 °C.

All the thermal decomposition processes were studied in the flowing argon gas atmosphere (purity, 99.99%; flowing rate, 30 ml/min; atmospheric pressure) at the heating rate of 10 °C/min when the sample quantum was about 1.30 mg with Al_2O_3 crucible as reference.

3. Result and discussion

3.1. Microstructure characterization

Fig. 1 shows the TEM micrographs of nano-Nd_2O_3 and micro-Nd_2O_3. From Fig. 1a, the nano-Nd_2O_3 obtained after the precursors are calcined at 800 °C for 2 h is thin flake in shape and essentially consists of different sizes varying from 50 nm to 100 nm. In addition, these flakes are stacked together and the size of the aggregates is found to be in the range of 200–250 nm. By contrast, it is revealed from Fig. 1b that the as-purchased micro-Nd_2O_3 are micron scale particles in the range of 10–12 μm. Fig. S1 shows XRD pattern of the as-synthesized nano-Nd_2O_3. All of these diffraction peaks in Fig. S1 are quite consistent with those of the standard JCPDS Card no. 65-6729 for the pure and hexagonal Nd_2O_3. According to the Scherrer's formula $D = 0.89\lambda/(\beta\cos\theta)$, [34] where D represents the average particle size, β stands for the full width at half-height of the peaks, λ is the X-ray wavelength, and θ is the Bragg's angle of the peak, the mean particle size of the as-synthesized nano-Nd_2O_3 was thus calculated at about 78 nm. Owing to the reunion of nanoparticles, the resulting particles of nano-Nd_2O_3 are bigger than the mean grain size calculated by the Scherrer's formula.