Thermal decomposition of ammonium perchlorate in the presence of functionalized MWCNTs as nanocatalysts

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INTRODUCTION AND ABSTRACT

In this study, the effect of multi-walled carbon nanotubes (MWCNTs) as a catalyst on the thermal decomposition behavior of ammonium perchlorate (AP) has been investigated using Differential Scanning Calorimetry (DSC). The MWCNTs were used with the average approximate diameter of nanotubes varies from 20 to 30 nm and their lengths from 5 to 10 µm. Characterization of MWCNTs was performed by Thermo-Gravimetric-Differential Scanning Calorimetry (TG-DSC), Fourier Transform Infrared Spectroscopy (FT-IR), Raman Spectroscopy, X-ray Diffraction Spectroscopy (XRD), Transmission Electron Microscopy (TEM), and Field Emission Scanning Electron Microscopy (FE-SEM). The prepared catalysts were mixed with AP and the products were analyzed by DSC to determine the decomposition temperature of AP. The results showed that using 3 wt.-% nano- MWCNTs catalysts lowered the decomposition temperature of AP by 83.5 °C. The total enthalpy, for this case, was 1308.71 J g -1.

NTRODUCTION

AP is the most common oxidant in composite solid propellants, and its thermal decomposition characteristics directly influence the combustion behavior of the solid propellant[1]. By decreasing the particle size of AP, it can improve the combustion behavior of the solid propellant, but this method is restricted and in the case of superfine AP, it is so dangerous[2]. Recently, many researchers investigated different catalysts on AP thermal decomposition to improve the combustion behavior of solid propellants[3, 4]. Ammonium perchlorate, as the important high-energy ingredient of solid propellants in the military field, occupies a large proportion in the formula. The thermal decomposition of AP can directly affect the burning velocity and energy features of propellants. Therefore, an extensive study on the thermal decomposition of AP was carried out by researchers[5]. Results show that a small amount of catalyst can reduce the thermal decomposition temperature of AP, increase apparent decomposition heat of AP, to improve the burning velocity and efficiency of propellant. [6]

However, since MWCNTs is an allotropic form of carbon, and its diameter is in the nanometer range with a large surface area, it can be considered to be a good catalyst. Therefore, in this study, the catalytic effect of MWCNTs as catalysts on AP decomposition has been investigated using differential scanning calorimetry as a function of catalyst concentration.

MARERIALS AND METHOD

The used reagents include Multi-walled carbon nanotubes (MWNTs) with 90-95 % (National Iranian Oil Company), Methyl isobutyl ketone, from India Co LOBA Chemie, and ammonium perchlorate (AP 150 µm). All used chemicals in the experiments were of analytical purity.

The raw MWCNTs need to be purified before preparing the AP/MWCNT nanostructure. MWCNTs were calcined at 350 °C for 2 h to remove amorphous carbon. The calcined MWCNTs (1 g) were dispersed in 100 mL HNO3 at the concentration of 7.0 mole / L and via ultrasonic processing for 15 min, then refluxing at 120 °C for 10 h with stirring. The products were rinsed with deionized water until the solution was neutral and finally dried under the oven at 60 °C. Then, the modified nanosized MWCNTs were mixed physically with 3 wt% AP and were analyzed by TG-DSC.

RESULTS

Click Figure 1 shows the FT-IR spectra of the unmodified and modified MWCNTs. The FT-IR spectra of carboxylation carbon nanotubes (MWNT-COOH) group peak can be seen at 1713 cm-1 and a hydroxyl group peak at 3384 cm-1[1]. to add text

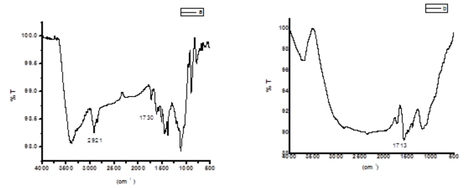

Figure 1: FT-IR spectra of carbon nanotubes: (a) unmodified carbon nanotubes; (b) modified carbon nanotubes

Figure 2 shows the Raman spectra of impure MWCNTs and acid-treated MWCNTs. The D band is attributed to defects in the disorder-induced modes (or sp3-hybridized carbons). The D band at 1358 cm-1 and G band at 1592 cm-1 characterized by Raman spectroscopy spectra, showed ID/IG area 0.85 and 0.89, respectively[2].

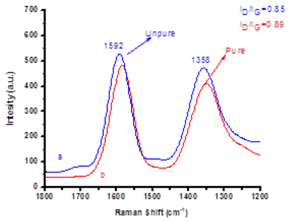

Figure 2: Raman spectra of (a) impure-MWCNTs and (b) acid-treated MWCNTs.

Figure 3 shows the XRD patterns of MWCNTs after functionalization. The diffraction peaks of MWCNTs at 2θ=26.48° and 43.78° can be attributed to the plane of (002) and (100) of graphite, respectively[2].

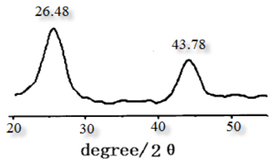

Figure 3: XRD patterns of the MWCNTs after functionalization.

Figure 4 shows the surface morphology of MWCNTs using a Field Emission Scanning Electron Microscopy (FE-SEM). As the Figures show there is no major destruction and macroscopic impurities in the MWCNTs form and structure. Usually, the surface of MWCNTs is impure and it needs to be certain of its purity after functionalizing.

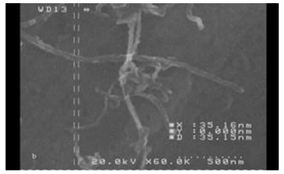

Figure 4: FE-SEM image of MWCNTs after functionalization.

Figure show the DSC and TG-DSC curves of pure AP and a physical mixture of AP and 3 wt.-% functionalized MWCNTs at the rate of increase in temperature of 10 0C min-1. The endothermic DSC peak at 2470C in pure AP is due to the crystallographic transition from orthorhombic to cubic form [3].The first low-temperature exothermic peak (LTD) at 3090C is attributed to the partial decomposition of AP while the second and main high temperature exothermic (HTD) at 4370C corresponds to complete decomposition of intermediate products into volatile products[3].

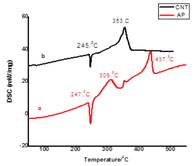

Figure 6: DSC patterns of different samples: (a) pure AP, (b) sample of MWCNTs and AP mixture.

CONCLUSIONS

The following results were obtained.

The purification and functionalization of raw MWCNTs were prepared by the concentration of 7.0 mole / L nitric acid. The nature of carboxylation and hydroxyl group peaks for carbon nanotubes in the final product, characterized by FT-IR, showed at 1713 cm-1 and 3384 cm-1. The D band at 1358 cm-1 and G band at 1592 cm-1 characterized by Raman spectroscopy spectra, showed ID/IG area 0.85 and 0.89, respectively. The diffraction peaks of MWCNTs at 2θ=26.48° and 43.78° can be attributed to the plane of (002) and (100) of graphite, respectively The results showed that using 3 wt.-% nano- MWCNTs catalysts lowered the decomposition temperature of AP by 83.5 °C. The total enthalpy, for this case, was 1308.71 J g -1.

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