Ammonium perchlorate decomposition in nano-titania

Thermal decomposition of ammonium perchlorate in the presence of commercial nano-titania

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Abstract

Addition of metal and metal oxide nanoparticles (especially transition metal oxides) to ammonium perchlorate improves its thermal decomposition via decreasing the high temperature of decomposition. Two mechanisms including electron-transfer and proton-transfer have been proposed for thermal decomposition of ammonium perchlorate. In this research field, nanometer transition metal oxides have attracted a growing attention. Titanium dioxide exists under three crystalline forms of rutile, anatase, and brookite. All three forms occur naturally but the latter is rather rare and has no commercial interest. Anatase becomes more stable than rutile when the particle size is decreased below 14 nm. In the present study, commercial nano-titania with an average particle size of 10-25 nm was added to ammonium perchlorate. Catalytic effect of the titania nanoparticles on the thermal decomposition of ammonium perchlorate was evaluated. Some samples of ammonium perchlorate consisting of various mass loadings of nano-titania were prepared. Thermogravimetry analysis results indicate that addition of titania nanoparticles to ammonium perchlorate lessens decomposition temperature of ammonium perchlorate. The most decrease in the decomposition temperature was 61 °C and observed in the presence of 3 wt.% of nanometer titanium dioxide.

Keywords: Titania; Ammonium perchlorate; Thermal decomposition; Nanostructure.

1. Introduction

Over the past few years, nanoparticles of many different compounds and combinations have received considerable attention in the scientific and engineering research fields [1]. Nanometer materials exhibit a much larger surface area for a certain mass or volume compared to conventional particles [2]. The oxide nanoparticles are the materials with good electrical, optical, magnetic, and catalytic properties that are different from their bulk counterparts [3]. Reduction in the particle size lessens the transient heat conduction travel through the particle over time, and an increase in the surface-to-volume ratio leads to better dispersion of the particles in the mixture, increasing the reactant sites. Finally, the nanometer particles can have completely different surface chemistry, often better than their micron-sized counterparts [4]. Among these nanostructure oxides, titanium dioxide or titania (TiO_2) nanostructures have emerged as one of the most promising materials because of their potential for gas sensors, especially for humidity and oxygen detection [2, 3, 5], optical devices [3, 5, 6], photocatalysis [2, 3, 6], fabricating capacitors in microelectronic devices due to its unusually high dielectric constant [3, 6], pigments [2, 7], adsorbents [7], and solar cells [5]. A relatively low level of TiO_2 is needed to achieve a white opaque coating which is resistant to discoloration under ultraviolet light. TiO_2 pigment is used in many diverse products, such as paints, coatings, glazes, enamels, plastics, papers, inks, fibers, foods, pharmaceuticals or cosmetics. Pure titanium dioxide is colorless in the massive state, non-toxic, thermally stable, inert versus acids, alkalis and solvents, and insoluble. It exists under three fundamental crystalline phases: rutile which is the most stable and the most abundant form, anatase (octahedrite) and brookite. All three forms occur naturally but the latter is rather rare and has no commercial interest. Anatase becomes more stable than rutile when the particle size is decreased below 14 nm. Generally speaking, the functional properties of nano-TiO_2 are influenced by a large number of factors such as particle size, surface area, synthesis method and conditions, and crystallinity [2].

The presence of nano metals and metal oxides especially transition metal oxides as the nanocatalyst in solid propellant formulations tailors the thermal decomposition of ammonium perchlorate (AP in short). Thermal decomposition improvement of AP as a powerful oxidizer salt has attracted many attentions [1, 4, 8-10]. Decrease amounts of decomposition temperature of AP in the presence of the different nano metal and metal oxides are summarized in Table 1.

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Vargeese [26] showed that significant reduction in activation energy indicates a strong catalytic activity of TiO_2 on the thermal decomposition of AP. Fujimura and Miyake [27] studied the effect of specific surface area of TiO_2 on the thermal decomposition of AP and concluded that the thermal decomposition temperature of AP decreases when the specific surface area of TiO_2 increases.

The catalytic effect of commercial nanometer titanium dioxide on the thermal decomposition of AP is investigated within the scope of this study.

2. Materials and methods

2. 1. Materials

Ammonium perchlorate (monomodal 120 μm) was purchased from Merck. Commercial nano-TiO_2 in anatase form was purchased from Pishgaman Company located in Mashhad, Iran (Figure. 1). Its purity was more than 99%. Chemical composition and physical properties of nano-TiO_2 are given in Tables 2 and 3, respectively.

Table 2 is here

Table 3 is here

2. 2. Methods

2. 2. 1. X-ray diffraction analysis

X-ray diffraction (XRD) patterns of TiO_2 nanoparticles was performed with a Philips PW 1800 powder X-ray diffractometer using CuKα radiation at 40 kV and 30 mA.

2. 2. 2. Transmission Electron Microscopy

Transmission electron microscopy (TEM) image of nano-TiO_2 was prepared on a Philips transmission electron microscope operated at an accelerating voltage of 100 kV.

2. 2. 3. Thermogravimetry analysis

The thermal decomposition processes of the samples were characterized by thermogravimetry analysis (TGA) using Dupont 2000 instrument at a heating rate of 10 °C/min until temperature of 600 °C.

2. 2. 4. Sample preparation

The AP was mixed with various mass loadings of TiO_2 nanoparticles namely 1, 2, and 3 wt.% to prepare the samples for thermal decomposition study. Theses samples were labeled as AP1T (AP+1% nano-TiO_2), AP2T (AP+2% nano-TiO_2), and AP3T (AP+3% nano-TiO_2). Before thermal decomposition experiments using TGA technique, the samples were homogenized.

3. Results and discussion

3. 1. Characterization of nanostructure

The TEM analysis was performed to confirm the actual size of the particles and the distribution of the crystallites. It is clear from the micrograph that the average size of the particles is located in range of 10-25 nm. TEM image of TiO_2 nanoparticles is shown in Figure 2. Clear spherical structure can be seen from this figure. Figure 3 shows the X-ray diffractogram of the commercial nano-TiO_2. It can be obviously seen that that diffraction peaks appear in the pattern associated with the anatase phase with proper crystalline nature. A very strong anatase peak is observed at 2ÆŸ of 25. 25°, assigned to (101) plane. Other anatase peaks are observed at 2ÆŸ of 37. 7° (004), 47. 7° (200), 53. 54° (105), and 62. 32° (204).

3. 2. Catalytic activity of nano-titania

Figure 4 shows the TGA curve for the thermal decomposition of pure AP. As can be seen in figure 4, the first exothermic peak is appeared in temperature of 327 °C that accompanied by a weight loss of 18 wt.%. This peak can be related to the partial decomposition of AP and the formation of some NH_3 and $HClO_4$ via dissociation and sublimation. The second exothermic peak is occurred in temperature of 411 °C. The weight loss in this stage is about 92 wt.% that is corresponding to complete decomposition of transition products to volatile products. Figure 5 presents the TGA curves associated with thermal decomposition of AP in the presence of 1, 2, and 3 wt.% of TiO_2 nanoparticles. From this figure, it is clear that the partial decomposition of AP in the presence of 1, 2, and 3 wt.% of TiO_2 nanoparticles is happened in a temperature much lower than 327 °C. Also, complete decomposition of AP in the presence of 1, 2, and 3 wt.% of TiO_2 nanoparticles is occurred in temperatures of 370, 360, and 350 °C, respectively that accompanied by decrease of 41, 51, and 61°C, respectively. It is obvious that addition of nano-sized TiO_2 to AP has deep effect on the exothermic decomposition of AP. According to these results, it can be concluded that the catalytic effect of nano-sized TiO_2 is observed mainly on high-temperature decomposition process and not on the initial stages of decomposition.

3. 3. Mechanism of thermal decomposition of AP

Based on the recent studies, two main mechanisms have been suggested for thermal decomposition of AP [11, 16, 17, 21]:

First mechanism: electron transfer from perchlorate ion to ammonium ion which is as follows:

$ClO_4^- + NH_3^+ \rightarrow ClO_4^0 + NH_4^0$

$NH_4^0 \rightarrow NH_3 + H$

$ClO_4^0 + ClO_4^- = ClO_4^- + ClO_4^0$

$HClO_4 + H \rightarrow H_2O + ClO_3$

Second mechanism: proton transfer from ammonium ion to perchlorate ion which is as follows:

$NH_4ClO_4(s) \rightarrow NH_4^+ + ClO_4^- \rightarrow NH_3(s) + HClO_4(s) \rightarrow NH_3(g) + HClO_4(g)$

For first mechanism, it is proposed that the rate-determining stage is electron transfer and inasmuch as the p-type semiconductors have positive holes, they can accept the released electron from perchlorate ion. Thus, these catalysts accelerate the electron transfer.

$e^-_{oxide} + ClO_4^- \rightarrow O_{oxide} + ClO_3^- \rightarrow 1/2O_2 + ClO_3^- + e^-_{oxide}$

in which e^-_{oxide} is a positive hole in the valence band of the oxide and O_{oxide} is an abstracted oxygen atom from oxide. It is clear that this mechanism includes two steps: 1) oxidation of ammonia and 2) dissociation of ClO_4^- species into ClO_3^- and O_2.

In first step, metal oxides exhibit high catalytic activity in ammonia oxidation and in second step metal oxides accept the released electron from ammonia oxidation that may promote the dissociation of ClO_4^- into ClO_3^- and O_2 .

For second mechanism, steps (I)-(III) have been proposed. In step (I), the ammonium and perchlorate ions are paired. Step (II) is started with proton transfer from NH_4^+ cation to ClO_4^- anion and the molecular complex is formed that then is decomposed into NH_3 and $HClO_4$ in step (III). The molecules of NH_3 and $HClO_4$ react in adsorbed layer on the perchlorate surface or they are desorbed and sublimed that is accompanied by interactions in gas phase.

$NH_4^+ ClO_4^- \leftrightarrow NH_3\text{-H-}ClO_4 \leftrightarrow NH_3\text{-}HClO_4 \leftrightarrow NH_3(a)+HClO_4(a)$

(I) (II) (III) â†• â†•

$NH_3(g)+HClO_4(g)$

At low temperature (<350 °C), the surface reaction is performed more rapidly than the sublimation in gas phase and by-products such as O_2 , N_2O, Cl_2 , NO, and H_2O are formed.

Based on proton transfer, during high-temperature decomposition, the nanoparticles adsorb the reactive molecules on their surface and catalyze the reaction. The existence of more holes in p-type semiconductor catalysts is responsible for the increasing of the AP decomposition.

In this study, the mechanism of thermal decomposition of AP in the presence of the TiO_2 nanoparticles can be explained as follows:

Titanium has the electronic configuration of $[Ar]3d^2 4s^2$. Experiments have demonstrated that it can form both +3 and +4 oxidation state, so it can lose 3 or 4 electrons to form cations. The +4 state is the most common and stable, because it is able to form an octet. The +3 state is less stable (more reactive) because it leaves a single d electron in the valence orbital.

Ti^{4+} cation in TiO_2 structure has s and d-type orbitals with $3d^0 4s^0$ electronic configuration. These orbitals have not been filled with electrons and provide a useful space for electron transfer in AP thermal decomposition and play the role of a bridge. By accepting transferred electrons resulted from ClO_4 degradation, ClO_4 degradation is promoted. On the other hand, TiO_2 nanoparticles have high specific surface area and large amount of surface active sites that increase adsorption of reactive molecules in gas phase to the surface and promote the redox reactions between them.

4. Conclusions

The results of thermogravimetry analysis show that the nanometer titanium dioxide has significant catalytic effect on the thermal decomposition of ammonium perchlorate. The presence of nano-sized titanium dioxide improves significantly the thermal decomposition of ammonium perchlorate. With increase of content of nanometer titanium dioxide, the decrease in decomposition temperature of ammonium perchlorate becomes greater.

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Figure legends

Figure 1. Commercial nano-TiO_2 used in this study

Figure 2. TEM image of TiO_2 nanoparticles

Figure 3. XRD patterns of TiO_2 nanoparticles

Figure 4. TGA curve related to pure AP

Figure 5. TGA curves related to (a) AP1T, (b) AP2T, and (c) AP3T

Table 1. Reported data from the literature on the decrease in AP decomposition temperature in the presence of different nano metal and metal oxides.

Nanocatalyst	Preparation method	Amount (wt.%)	Decrease in decomposition temperature (°C)
Nano-yttria	Sol-gel	5	114. 6
CuO/AP composite	A novel solvent-nonsolvent	–	95. 83

nanoparticles	method		
Co_2O_3/AP composite nanoparticles	A novel solvent-nonsolvent method	–	137. 11
NiO nanoparticles	Solid-state reaction	2	93
Ni nanoparticles	Hydrogen plasma method	2-5	92-105
Nano-sized MgO	Sol-gel	2	75
Nano-sized α-Fe_2O_3	Electrochemical method	2	59
Nanometer $CoFe_2O_4$	Polyol-medium solvothermal	2	112. 8
Nano-$MnFe_2O_4$	Co-precipitation phase inversion	3	77. 3
Nano-MnFe2O4	Low-temperature combustion	3	84. 9
Sphere-like α-Fe_2O_3	$NH_3 \cdot H_2O$ and NaOH solution to adjust the pH value	–	81
pod-like α-Fe_2O_3	$NH_3 \cdot H_2O$ and NaOH solution to adjust the pH	–	72

	value		
Nanometer CoC_2O_4	Co-precipitation	2	104
Nano-sized CuO	Sol-gel	–	90. 47
Nano-sized Co_3O_4	Sol-gel	–	92. 07
Nano-sized $CuCo_2O_4$	Sol-gel	–	102. 78
CuO nanocrystals	Simple chemical deposition	2	85
Nanometer $CuFe_2O_4$	Auto-combustion method	2	105
Co nanoparticles	Hydrogen plasma	2	145. 01
Cu-Co nanocrystal	Hydrazine reduction in ethylene glycol	1	96
Cu-Fe	1	89	
Cu-Zn	1	114	

Table 2. Chemical composition of nano-TiO_2

Element	Mg	Nb	Al	S	Si	Ca

Amount (ppm)	<= 67	<= 82	<= 19	<= 128	<= 116	<= 75

Table 3. Physical properties of nano-TiO_2

Bulk density (g/cm^3)	Actual density (g/cm^3)	Average particle size (nm)	Specific surface area (m^2/g)
0. 24	3. 90	10 to 25	200 to 240

1