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Orginal Research Article

Thermal decomposition of ammonium perchlorate-commercial nano-TiO_2 mixed powder

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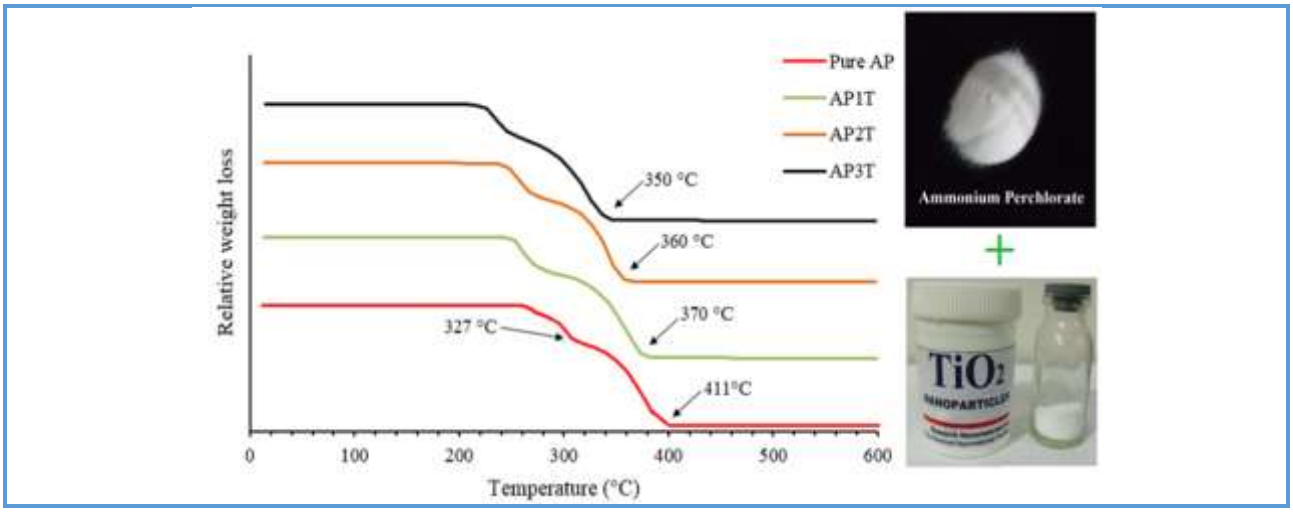
ABSTRACT

Thermal decomposition of ammonium perchlorate was improved via addition of transition metals and metal oxides. This work investigates the thermal decomposition of the ammonium perchlorate under the catalytic effect of the commercial nano-TiO_2 ($nTiO_2$). Characterization of $nTiO_2$ showed that its average particle size ranged from 10 to 25 nm with a relatively spherical morphology. Ammonium perchlorate and $nTiO_2$ mixes were prepared by adding three different $nTiO_2$ mass fractions of 1, 2, and 3 wt% to pure ammonium perchlorate. The results of thermogravimetry analysis revealed that the addition of $nTiO_2$ to pure ammonium perchlorate resulted in a significant decline in its decomposition temperature. The most observed decrease in the decomposition temperature was 61 °C resulted from the addition of 3 wt.% $nTiO_2$.

Graphical Abstract



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Introduction

Over the last 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 a 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. 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].

TiO_2 may have a positive catalytic effect on the improvement of some important chemical reactions such as thermal decomposition of ammonium perchlorate (AP). This idea can be brightened by a glimpse into the catalytic effects of transition metals and metal oxides on the above-mentioned reaction. Since the AP is used for the preparation of energetic materials, investigating its thermal decomposition behavior is of a great importance. Any improvement in the thermal decomposition of AP may lead to an improvement in burning rate of energetic materials. Thus, many researchers have focused on this field of research and concluded that the presence of nano metals and/or metal oxides, especially transition metal oxides, as the nanocatalyst tailors the thermal decomposition of AP [8–10]. The decrease in decomposition temperature of AP in the presence of the different nano metal and metal oxides are presented in Table 1.

Table 1. Some reported data from the literature on the decline in AP decomposition temperature in the presence of various nano metal or metal oxides

Nanocatalyst	Preparation method	wt.%	Decrease in decomposition temperature (°C)	Ref.
Nano-yttria	Sol-gel	5	114.6	[11]

CuO/AP composite nanoparticles	A novel solvent-nonsolvent method	-	95.83	[12]
Co_2O_3/AP composite nanoparticles	A novel solvent-nonsolvent method	-	137.11	[12]
NiO nanoparticles	Solid-state reaction	2	93	[13]
Ni nanoparticles	Hydrogen plasma method	2-5	92-105	[14]
Nano-sized MgO	Sol-gel	2	75	[15]
Nano-sized α-Fe_2O_3	Electrochemical method	2	59	[16]
Nanometer $CoFe_2O_4$	Polyol-medium solvothermal	2	112.8	[17]
Nano-$MnFe_2O_4$	Co-precipitation phase inversion	3	77.3	[18]
Nano-$MnFe_2O_4$	Low-temperature combustion	3	84.9	[18]
Sphere-like α-Fe_2O_3	$NH_3{\cdot}H_2O$ and NaOH solution to adjust the pH value	-	81	[19]
pod-like α-Fe_2O_3	$NH_3{\cdot}H_2O$ and NaOH solution to adjust the pH value	-	72	[19]
Nanometer CoC_2O_4	Co-precipitation	2	104	[20]
Nano-sized CuO	Sol-gel	-	90.47	[21]
Nano-sized Co_3O_4	Sol-gel	-	92.07	[21]
Nano-sized $CuCo_2O_4$	Sol-gel	-	102.78	[21]
CuO nanocrystals	Simple chemical deposition	2	85	[22]
Nanometer $CuFe_2O_4$	Auto-combustion method	2	105	[23]
Co nanoparticles	Hydrogen plasma	2	145.01	[24]
Cu-Co nanocrystal	Hydrazine reduction in ethylene glycol	1	96	[25]
Cu-Fe		1	89	
Cu-Zn		1	114	

Also, some recent studies have been conducted on the catalytic effect of nano-MnO_2 [26], nano-M_xO_y (M=Mn, Fe) [27], Co_3O_4 nanowires [28], CuO/Al_2O_3 composite [29], flower-like $ZnO@Fe_2O_3$ nanstructures [30], and hierarchical flower-like Co_3O_4 [31] on the thermal decomposition of AP. All these studies reported more than 100 °C decrease in the pyrolysis temperature of AP. *Vargeese* [32] indicated that TiO_2 has a strong catalytic effect on the thermal decomposition of AP. *Fujimura* and *Miyake* [33] investigated the influence of specific surface area of TiO_2 on the thermal decomposition of AP. They expressed that as the specific surface area of TiO_2 increases, thermal decomposition temperature of AP diminishes. Within the scope of this study, the catalytic effect of commercial $nTiO_2$ on the thermal decomposition of AP is probed.

Experimental

Materials and methods

Ammonium perchlorate (AP) was purchased from Merck. It was monomodal with the particle size of 120 μm. Commercial $nTiO_2$ was purchased from Pishgaman Company, Mashhad, Iran. It was in anatase form and its purity was more than 99%. Tables 2 and 3 show the chemical analysis of the impurities and physical properties of $nTiO_2$, respectively.

Table 2. Chemical impurities of $nTiO_2$

Element	Mg	Nb	Al	S	Si	Ca
Amount (ppm)	≤67	≤82	≤19	≤128	≤116	≤75

Table 3. Physical properties of $nTiO_2$

Bulk density (g/cm^3)	Actual density (g/cm^3)	Average particle size (nm)	Specific surface area (m^2/g)
0.24	3.90	10-25	200-240

Sample preparation

The AP/$nTiO_2$ mixtures were prepared with various mass loadings of $nTiO_2$ namely 1, 2, and 3 wt.% for the evaluation of the thermal decomposition of AP. The mixtures were labeled as AP1T (AP+1% $nTiO_2$), AP2T (AP+2% $nTiO_2$), and AP3T (AP+3% $nTiO_2$). The samples were manually homogenized before any thermal decomposition experiments.

Characterization techniques

X-ray diffractogram of the $nTiO_2$ was recorded using a powder X-ray diffractometer (Philips PW 1800) with Cu-Kα radiation at 40 kV and 30 mA. The morphology of $nTiO_2$ particles was disclosed using SIGMA VP-500 FESEM microscope (ZEISS) at 15 kV. A thermogravimetry analyzer (Dupont 2000) was employed to study the thermal decomposition of the as-prepared mixtures at a heating rate of 10 °C/min from room temperature until 600 °C.

Results and Discussion

Characterization of $nTiO_2$

Figure 1 depicts the X-ray diffractogram of the commercial $nTiO_2$. It can clearly be seen that diffraction peaks in the pattern are associated with the anatase phase with an appropriate crystalline nature. A very intense anatase peak is observed at 2θ of 25.25°, assigned to (101) plane. Other anatase peaks appeared at 2θ of 37.7° (004), 47.7° (200), 53.54° (105), and 62.32° (204).

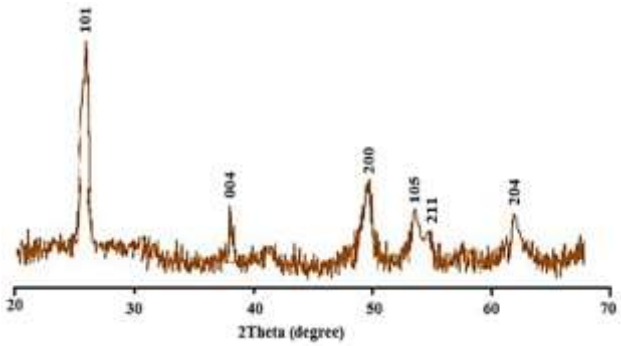

Figure 1. XRD pattern of $nTiO_2$

The field emission scanning electron microscopy (FESEM) micrographs were obtained to reveal the morphology of the particles. The obtained FESEM images are displayed in Figure 2. It is obvious from the micrographs that the $nTiO_2$ particles are agglomerations of relatively spherical particles.

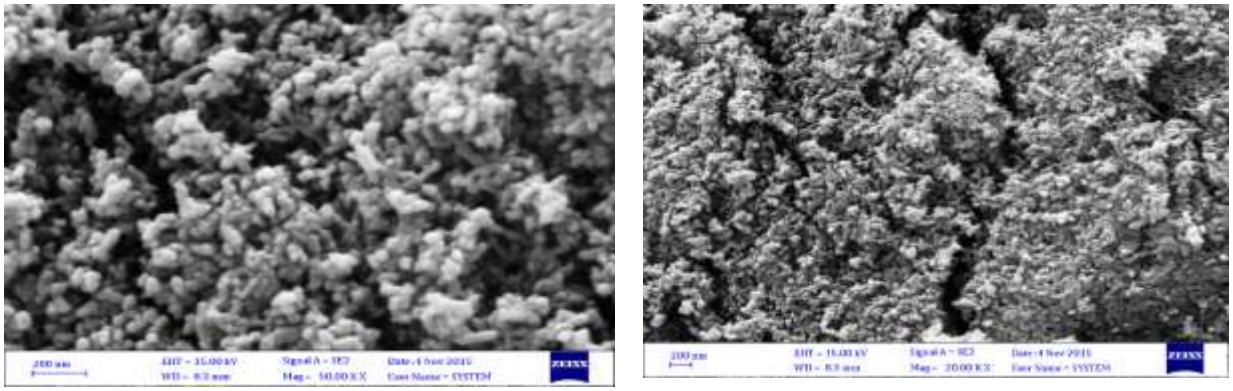

Figure 2. FESEM images of $nTiO_2$

Effect of $nTiO_2$

Figure 3 indicates the TGA results of the pure AP and AP/$nTiO_2$ mixtures. As can be observed in the curve related to pure AP, the first exothermic peak appeared at 327 °C that accompanied by a weight loss of around 18%. This peak is associated with the partial decomposition of AP and the formation of some amounts of NH_3 and $HClO_4$ via dissociation and sublimation. The second exothermic peak took place at 411 °C, corresponding to a weight loss of about 92%. In this stage, transition products are completely decomposed to volatile products.

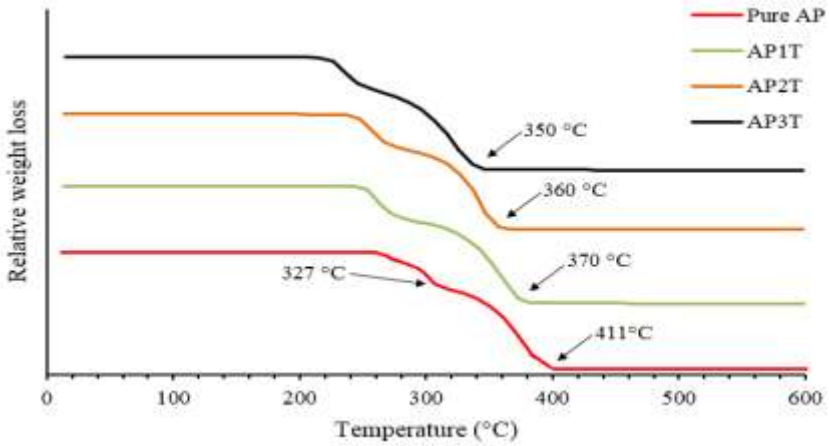

Figure 3. TGA curves of pure AP and AP/$nTiO_2$ mixtures

According to the TGA curves of AP/$nTiO_2$ mixtures, it is clear that the partial decomposition of AP in the presence of 1, 2, and 3 wt.% of $nTiO_2$ happened at a temperature much lower than 327 °C. Also, complete decomposition of AP in the presence of 1, 2, and 3 wt.% of $nTiO_2$ occurred at temperatures of 370, 360, and 350 °C, respectively. These temperatures are accompanied by a decline of 41, 51, and 61 °C, respectively. It is obvious that addition of $nTiO_2$ to pure AP has a deep effect on its exothermic decomposition. According to these results, it can be concluded that the catalytic effect of $nTiO_2$ is observed mainly on high-temperature decomposition stage and not on the initial stages of decomposition.

Despite the very good catalytic activity of the nanomaterials listed in Table 1 and also some

recent results, the $nTiO_2$ has advantages such as lower price, availability and ease of synthesis, making this inorganic oxide more attractive for real applications.

Mechanism of thermal decomposition of AP

Two main mechanisms have been suggested for thermal decomposition of the AP [11, 16, 17, 21]:

The first mechanism is based on hypothesis of electron transfer from perchlorate ion to ammonium ion which is as follows:

$$ClO_4^- + NH_3^+ \longrightarrow ClO_4^0 + NH_4^0 \quad (1)$$

The high electron transfer capacity and the large specific surface area of $nTiO_2$ play a significant role in the acceleration of the thermal decomposition of AP. The occurrence of reaction (1) can be explained as follows:Titanium has the electronic configuration of $[Ar]3d^24s^2$. Experiments have demonstrated that Ti can form +2, +3 and +4 oxidation states, so it can lose 2, 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 $3d^04s^0$ electronic configuration. These orbitals have not been filled with electrons and therefore provide an appropriate space for electron transfer in AP thermal decomposition process and play the role of a bridge (reactions (2)-(5)).

$$Ti^{4+}+ClO_4^-\rightarrow Ti^{3+}+ClO_4^0 \quad (2)$$

$$Ti^{3+}+ClO_4^-\rightarrow Ti^{2+}+ClO_4^0 \quad (3)$$

$$Ti^{3+}+NH_4^+\rightarrow Ti^{4+}+NH_4^0 \quad (4)$$

$$Ti^{2+}+NH_4^+\rightarrow Ti^{3+}+NH_4^0 \quad (5)$$

By accepting electrons transferred from ClO_4 degradation, ClO_4 degradation is promoted. On the other hand, commercial $nTiO_2$ has a large specific surface area and large amount of active sites. These sites increase adsorption of the reactive molecules in gas phase to the surface and promote the redox reactions between them. Figure 4 illustrates a schema of the above-mentioned mechanism.

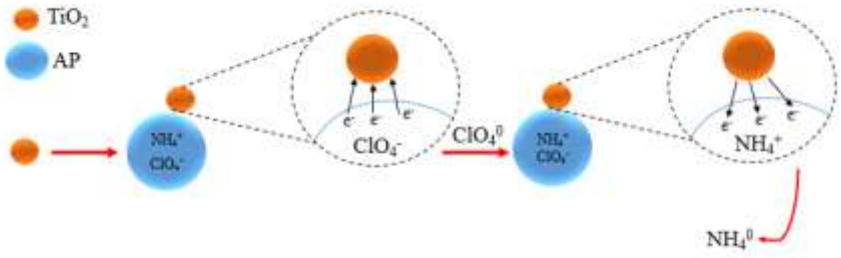

Figure 4. A schema of electron transfer mechanism by TiO_2

The second mechanism relies on proton transfer from ammonium ion to perchlorate ion which is as follows:

$$NH_4ClO_4(s)\rightarrow NH_4^+ + ClO_4^-\rightarrow NH_3(s) + HClO_4(s)\rightarrow NH_3(g) + HClO_4(g) \quad (6)$$

For the first mechanism, it is proposed that the rate-determining step 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.

$$e^-_{oxide}+ClO_4^-\rightarrow O_{oxide}+ClO_3^-\rightarrow 1/2O_2+ClO_3^-+e^-_{oxide} \quad (7)$$

where 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 exhibited high catalytic activity in ammonia oxidation and in second step metal oxides accepted the released electron from ammonia oxidation that may promote the dissociation of ClO_4^- into ClO_3^- and O_2.For the second mechanism, steps (I)-(III) were proposed. In step (I), the ammonium and perchlorate ions were paired. Step (II) starts with proton transfer from NH_4^+ cation to ClO_4^- anion and thus a molecular complex was formed. The formed complex was finally decomposed into NH_3 and $HClO_4$ in step (III). The molecules of NH_3 and $HClO_4$ either reacted on the perchlorate surface or they are desorbed and sublimed that is accompanied by interactions in gas phase.

$$NH_4^+ClO_4^- \text{ (Step I)} \leftrightarrow NH_3\text{-}H\text{-}ClO_4 \text{ (Step II)} \leftrightarrow NH_3\text{-}HClO_4 \text{ (Step III)} \leftrightarrow NH_3(ads.)+HClO_4(ads.) \text{ or } NH_3(g)+HClO_4(g) \quad (8)$$

At low temperature (<350 °C), the surface reaction was performed more rapidly compared with the sublimation in gas phase.

Based on the 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.

Conclusions

Thermal decomposition of the ammonium perchlorate was investigated in the presence of the nano-TiO_2. For this purpose, three different ammonium perchlorate/nano-TiO_2 mixtures were prepared by adding various mass fractions of nano-TiO_2 to pure ammonium perchlorate. The thermal decomposition experiments were then performed using thermogravimetry analysis. The results indicated that the nano-TiO_2 had a significant catalytic effect on the thermal decomposition of ammonium perchlorate. By increasing the nano-TiO_2 mass fraction, a greater decline in decomposition temperature of ammonium perchlorate, especially at the second exothermic stage was achieved. An electron transfer mechanism was proposed, as well.

Orcid

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