Tunable catalytic activities of different $\alpha$-Fe$_2$O$_3$ surface areas in ammonium perchlorate thermal decomposition

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Abstract. Different surface areas of $\alpha$-Fe$_2$O$_3$ nanocrystals have been achieved by annealing at different temperatures. Obtained samples were characterized by X-ray diffraction, Brunauer–Emmett–Teller technique, and transmission electron microscopy. The surface areas of $\alpha$-Fe$_2$O$_3$ nanocrystals changed from 136.5 m$^2$/g to 2.1 m$^2$/g with the increase of annealing temperature from 280 °C to 700 °C. $\alpha$-Fe$_2$O$_3$ nanocrystal catalytic activity on the decomposition of ammonium perchlorate (AP) was characterized through thermogravimetric analysis. The decomposition rate of AP with the addition of $\alpha$-Fe$_2$O$_3$ nanocrystals was surface area relative. The 136.5 m$^2$/g $\alpha$-Fe$_2$O$_3$ nanocrystal exhibited the best catalytic activity, which lowered the high-temperature peak temperature of AP by 60.8 °C.

1. Introduction
Hematite ($\alpha$-Fe$_2$O$_3$) has attracted much interest because of its most stable crystallographic phase with an indirect charge transfer band gap of 2.2 eV [1], which is widely used in many catalytic applications including photocatalytic degradation of pentachlorophenol, reduction of H$_2$O$_2$, and soot combustion [2–5]. $\alpha$-Fe$_2$O$_3$ also showed catalytic activity to the thermal decomposition of ammonium perchlorate (AP) [6–10]. AP is one of the most common oxidizing agents used in solid rocket propellants, and the burning properties of solid rocket propellants are highly related to the characteristics of AP. AP burning properties can be tailored by adding catalysts. Catalysts can lower the high-temperature thermal decomposition of AP and increase released heat [11–13]. Xu et al. found that Fe$_2$O$_3$ nanorods and micro-octahedrons exhibited different catalytic performances on the thermal decomposition of AP [7]. Yuan et al. found that graphene significantly improved the catalytic activity of Fe$_2$O$_3$ on the thermal decomposition of AP because of its high specific area [9]. However, all above-mentioned catalytic activities of Fe$_2$O$_3$ on the thermal decomposition of AP are just one particle size or surface area. The controlled synthesis of different surface areas of Fe$_2$O$_3$ is important for understanding the catalytic activity of $\alpha$-Fe$_2$O$_3$ on the thermal decomposition of AP because the catalytic activities of nanocrystals are highly related to particle size or surface area.

In this work, we synthesized $\alpha$-Fe$_2$O$_3$ nanocrystals with controlled surface areas through annealing at different temperatures. The catalytic activities of $\alpha$-Fe$_2$O$_3$ nanocrystals on the thermal decomposition of AP were investigated. Larger $\alpha$-Fe$_2$O$_3$ nanocrystal surface areas showed better catalytic activity on the decomposition temperature of AP.
2. Experimental

Chemical reagents Fe(NO₃)₃·9H₂O and NH₃·H₂O(25%) were used as starting materials. First, Fe(NO₃)₃·9H₂O(0.1 mol) was dissolved in 200 mL water at room temperature, and NH₃·H₂O (25%) was added by drop into the above solution while stirring until the pH of the obtained mixed cloudy solution reached 8. The cloudy solution was aged at room temperature for 24 h to obtain a brown precipitate, which was named as the as-prepared sample. The as-prepared sample was centrifuged and sufficiently washed with distilled water. The different surface areas of α-Fe₂O₃ were obtained through annealing at 280, 350, 400, 450, 550, and 700 °C for 2 h.

Sample structures were examined through powder X-ray diffraction (XRD) with D8 Focus diffractometer with monochromatized Cu Kα radiation (λ=0.15418 nm). Morphologies of the as-obtained products were observed through transmission electron microscopy (TEM) on a JEM 2100 apparatus with an acceleration voltage of 200 kV. The specific surface areas of α-Fe₂O₃ nanocrystals were determined from nitrogen absorption data at liquid nitrogen temperature using the Brunauer–Emmett–Teller (BET) technique on a BEL SORP max surface area using a porosity analyzer. The catalytic activities of α-Fe₂O₃ nanocrystals on the thermal decomposition of AP (180 μm) were studied through thermogravimetric analysis (TG). A STA449C thermal analyzer with open alumina crucibles was used at a heating rate of 20 °C min⁻¹ in a N₂ atmosphere over the temperature range of 30 °C to 500 °C. AP and the α-Fe₂O₃ nanocrystals were mixed at a mass ratio of 98:2 to prepare the target samples for thermal decomposition analyses. A total sample mass of 1.5 mg was used in TG measurements.

3. Results and discussion

Figure 1 shows the XRD pattern of the as-prepared sample and samples annealed at 280, 350, and 700 °C. Figure 1 shows the as-prepared sample in an amorphous phase. All peaks of the annealing samples matched well with the standard data of the hexagonal-phase of α-Fe₂O₃ (JCPDS file, No. 33-0664). No peaks were attributed to the other phases of α-Fe₂O₃, indicating the high purity of the as-prepared products. An increase of annealing temperature corresponded with narrower peaks. Sample particle sizes increased and surface area decreased with an increase of annealing temperature. The morphology of the as-prepared products was observed through TEM. Figure 2 shows the TEM image of a sample prepared at 280 °C. α-Fe₂O₃ nanocrystals consisted of irregular spherical particles.
Calculating particle size through TEM was difficult because the morphology of α-Fe₂O₃ was stacked together; therefore, we addressed the particle size effect of α-Fe₂O₃ using the BET technique. The surface areas of all annealing samples are shown in Table 1. Samples annealed at 280 °C possessed the largest surface area of 136.5 m²/g. The surface areas of the samples systematically decreased as annealing temperature increased. The surface area became only 2.1 m²/g when annealing temperature reached 700 °C.

When used as catalytic additives, α-Fe₂O₃ nanocrystals accelerate the thermal decomposition of AP. Figure 3 shows the TG of pure AP and of AP mixed with α-Fe₂O₃ nanocrystals at annealing temperatures 280, 450, and 700 °C. The decomposition of pure AP is generally centered at temperatures ranging from 329 °C to 434 °C. The addition of α-Fe₂O₃ nanocrystals accelerates the decomposition of AP. Larger sample surface areas led to a higher catalytic activity to AP. As shown in Table 1 and Figure 3, an increase of surface area from 2.1 m²/g to 136.5 m²/g corresponded with a decreased ending decomposition temperature of AP from 421.1 °C to 382.1 °C.

Table 1 Surface areas of α-Fe₂O₃, ending decomposition temperature of AP, HTD peak temperature of AP, lowering HTD peak temperature of AP with addition of α-Fe₂O₃ with different annealing temperature.

| Annealing Temperature (°C) | Surface area (m²/g) | Ending decomposition temperature of AP (°C) | HTD peak temperature of AP (°C) | Lowering HTD peak temperature (°C) |
|---------------------------|---------------------|---------------------------------------------|---------------------------------|-----------------------------------|
| 280                       | 136.5               | 382.1                                       | 379.8                           | 60.8                              |
| 350                       | 47.0                | 387.9                                       | 386.4                           | 54.2                              |
| 400                       | 39.5                | 394.4                                       | 392.1                           | 48.5                              |
| 450                       | 22.1                | 398.1                                       | 397.4                           | 43.2                              |
| 550                       | 9.5                 | 408.9                                       | 407.3                           | 33.3                              |
| 700                       | 2.1                 | 421.1                                       | 417.5                           | 23.1                              |
Figure 4 shows the differential thermal analysis (DTA) curves of pure AP and mixtures of AP with \( \alpha \)-Fe\(_2\)O\(_3\) nanocrystals at annealing temperatures 280, 450, and 700 °C. Three obvious thermal steps were observed in the thermal decomposition of pure AP as previously reported [14–15]. The first endothermic peak is associated with the phase transition from orthorhombic to cubic AP at 250.6 °C. The second exothermic peak observed at 357.9 °C is ascribed to the low-temperature decomposition (LTD) of AP, and the third exothermic peak observed at 440.6 °C is the high-temperature thermal decomposition (HTD) of pure AP. The phase transition temperature of AP remained unchanged with the addition of \( \alpha \)-Fe\(_2\)O\(_3\) nanocrystals at different annealing temperatures. With the addition of \( \alpha \)-Fe\(_2\)O\(_3\) nanocrystals at 280 °C, only one exothermic peak was observed, which is attributed to the high-temperature decomposition of AP. AP also showed two exothermic peaks as pure AP with the addition of \( \alpha \)-Fe\(_2\)O\(_3\) nanocrystals with smaller surface areas. HTD peak temperature systematically decreased as surface area increased, as shown in Figure 4 and Table 1, which is consistent with CuO and NiO nanocrystals [16–17]. The sample with a surface area of 136.5 m\(^2\)/g showed the highest catalytic activity to the thermal decomposition of AP, which lowered HTD peak temperature by 60.8 °C.

We studied the effects of \( \alpha \)-Fe\(_2\)O\(_3\) nanocrystal content on the thermal decomposition of AP because additive content is also a main factor that influences the decomposition of AP [14]. Figure 5 shows the DTA curves of pure AP and its mixtures with different amounts of \( \alpha \)-Fe\(_2\)O\(_3\) at annealing temperature 280 °C. Figure 5 shows that the HTD peak temperature of AP significantly decreased with an increase of additive content, which is consistent with \( \gamma \)-MnO\(_2\) [18]. The HTD peak temperature of AP decreased gradually from 405.8 °C to 350.4 °C with the additive content increased from 1% to 10%. An additive content of 10% could lower the HTD peak temperature by 90.2 °C.

![Figure 4](image1.png)
![Figure 5](image2.png)
According to previous reports, LTD of AP is the decomposition of the following: 
\[ \text{NH}_4\text{ClO}_4 \rightarrow \text{NH}_4^++\text{ClO}_4^- \rightarrow \text{NH}_3(\text{g})+\text{HClO}_4(\text{g}) \]. HTD of AP is associated with the reaction of gas-phase products of AP, such as Cl\text{2}, O\text{2}, NO, and N\text{2}O [10]. Our experimental results showed that adding \(\alpha\)-Fe\text{2}O\text{3} nanocrystals could accelerate thermal decomposition. According to traditional electron theory, the addition of \(\alpha\)-Fe\text{2}O\text{3} nanocrystals could offer accelerated electrons to speed up the decomposition process [19]. The presence of a partially filled third orbit in Fe\text{3}+ provides assistance in the electron transfer process, and the positive hole can accept electrons from AP ions and accelerate thermal decomposition [10]. Larger \(\alpha\)-Fe\text{2}O\text{3} surface area could show higher catalytic activity to the thermal decomposition of AP (Figure 4) given that larger surface areas have more active sites. Combined with Reference [20], the catalytic process can be depicted by the following equations:

\[ \text{NH}_4\text{ClO}_4 \rightarrow \text{NH}_4^++\text{ClO}_4^- \]  
(1)

\[ \text{NH}_4^++\text{ClO}_4^- \rightarrow \text{ClO}_4^+\text{NH}_4 \]  
(2)

\[ \text{Fe}_3^++\text{ClO}_4^- \rightarrow \text{Fe}_2^++\text{ClO}_4^- \]  
(3)

\[ \text{Fe}_2^++\text{NH}_4^+ \rightarrow \text{Fe}_3^++\text{NH}_4^- \]  
(4)

4. Conclusions

In this work, the surface areas of \(\alpha\)-Fe\text{2}O\text{3} nanocrystals were obtained through calcination method. Adding \(\alpha\)-Fe\text{2}O\text{3} nanocrystals can result in a decrease in the decomposition of AP. The catalytic activity of \(\alpha\)-Fe\text{2}O\text{3} nanocrystals on the decomposition of AP is surface area relative. The \(\alpha\)-Fe\text{2}O\text{3} nanocrystal with the largest surface area showed the best catalytic activity by decreasing the high-temperature peak temperature of AP by 60.8 °C.

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References

[1] Tang B, Wang G L, Zhuo L H, Ge J C and Cui L J 2006 Facile route to \(\alpha\)-FeOOH and \(\alpha\)-Fe\text{2}O\text{3} nanorods and magnetic property of nanorods *Inorg. Chem.* **45** 5196-200

[2] Xie J, Zhou Z, Lian Y W, Hao Y J, Li P and Wei Y 2015 Synthesis of \(\alpha\)-Fe\text{2}O\text{3}/ZnO composites for photocatalytic degradation of pentachlorophenol under UV–vis light irradiation *Ceram. Int.*** **41** 2622-5

[3] Harraz F A, Ismail A A, Al-Sayari S A and Al-Hajry A 2015 Novel \(\alpha\)-Fe\text{2}O\text{3}/polypyrrole nanocomposite with enhanced photocatalytic performance *J. Photochem. Photobiol. A*** **299** 18-24

[4] Wang M Y, Shen T, Wang M, Zhang D E, Tong Z W and Chen J 2014 One-pot synthesis of \(\alpha\)-Fe\text{2}O\text{3} nanoparticles-decorated reduced graphene oxide for efficient nonenzymatic H\text{2}O\text{2} biosensor *Sens. Actuators B*** **190** 645-50

[5] Stelmachowski P, Kopacz A, Legutko P, Indyka P, Wojtasik M, Ziemiański L, Żak G, Sojka Z and Kotarba A 2015 The role of crystallite size of iron oxide catalyst for soot combustion *Catal. Today*** **257** 111-6

[6] Hosseini S G, Ahmadi R, Ghavi A and Kashi A 2015 Synthesis and characterization of \(\alpha\)-Fe\text{2}O\text{3} mesoporous using SBA-15 silica as template and investigation of its catalytic activity for thermal decomposition of ammonium perchlorate particles *Powder Technol.*** **278** 316-22
[7] Xu H, Wang X B and Zhang L Z 2008 Selective preparation of nanorods and micro-octahedrons of Fe₂O₃ and their catalytic performances for thermal decomposition of ammonium perchlorate Powder Technol. 185 176-80
[8] Songa L M, Zhang S J, Chen B, Gea J J and Jia X C 2010 A hydrothermal method for preparation of α-Fe₂O₃ nanotubes and their catalytic performance for thermal decomposition of ammonium perchlorate Colloid Surf. A: Physicochem. Eng. 360 1-5
[9] Yuan Y, Jiang W, Wang Y J, Shen P, Li F S, Li P Y, Zhao F Q and Gao H X 2014 Hydrothermal preparation of Fe₂O₃/graphene nanocomposite and its enhanced catalytic activity on the thermal decomposition of ammonium perchlorate Appl. Surf. Sci. 303 354-9
[10] Zhang Y F, Liu X H, Nie J R, Yu L, Zhong Y L and Huang C 2011 Improve the catalytic activity of α-Fe₂O₃ particles in decomposition of ammonium perchlorate by coating amorphous carbon on their surface J. Solid State Chem. 184 387-90
[11] Zhang Y F, Wang N N, Huang Y T, Wu W B, Huang C and Meng C G 2014 Fabrication and catalytic activity of ultra-longV₂O₅ nanowires on the thermal decomposition of ammonium perchlorate Ceram. Int. 40 11393-8
[12] Zou M, Wang X, Jiang X H and Lu L 2014 In-situ and self-distributed: A new understanding on catalyzed thermal decomposition process of ammonium perchlorate over Nd₂O₃ J. Solid State Chem. 213 235-41
[13] Zhang W J, Li P, Xu H B, Sun R D, Qing P H and Zhang Y 2014 Thermal decomposition of ammonium perchlorate in the presence of Al(OH)₃·Cr(OH)₃ nanoparticles J. Hazard. Mater. 268 273-80
[14] Chaturvedi S and Dave P N 2013 A review on the use of nanometals as catalysts for the thermal decomposition of ammonium perchlorate J. Saudi. Chem. Soc. 17 135-49
[15] Dubey R, Chawlab M, Siril P F and Singh G 2013 Bi-metallic nanocomposites of Mn with very high catalytic activity for burning rate enhancement of composite solid propellants Thermochim. Acta 572 30-8
[16] Chen L J, Li G S, Qi P and Li L P 2008 Thermal decomposition of ammonium perchlorate activated via addition of NiO nanocrystals J. Therm. Anal. Calorim. 92 765-9
[17] Chen L J, Li G S, Qi P and Li L P 2008 CuO nanocrystals in thermal decomposition of ammonium perchlorate: Stabilization, structural characterization and catalytic activities J. Therm. Anal. Calorim. 91 581-7
[18] Chen L J and Zhu D Y 2015 Effects of different phases of MnO₂ nanorods on the catalytic thermal decomposition of ammonium perchlorate Ceram. Int. 41 7054-8
[19] Li N, Geng Z F, Cao M H, Ren L, Zhao X Y, Liu B, Tian Y and Hu C W 2013 Well-dispersed ultrafine Mn₃O₄ nanoparticles on graphene as a promising catalyst for the thermal decomposition of ammonium perchlorate Carbon 54 124-32
[20] Liu T, Wang L S, Yang P and Hu B Y 2008 Preparation of nanometer CuFe₂O₃ by auto-combustion and its catalytic activity on the thermal decomposition of ammonium perchlorate Mater. Lett. 62 4056-8