

# Nano metal oxide as Potential catalyst for thermal decomposition of Ammonium nitrate

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## Abstract:

Nano metal oxide ( $\text{CuZnO}_2$ ) was successfully prepared by using Chemical co-precipitation process. Nano metal oxide has been characterized by Scanning electron microscopy (SEM) and X-ray diffraction (XRD). The catalytic effect of metal oxide was investigated by the thermal decomposition of ammonium nitrate using Differential Scanning Calorimetric (DSC) and Thermogravimetric analysis (TGA). Activation energy of high temperature decomposition (HTD) with Nano metal oxide was calculated using DSC Kissinger equation. The catalytic activity of Nano-mixed metal oxide is found to be much sensitive and may be efficient to get better the decomposition effectiveness of ammonium nitrate.

## Keywords

Ammonium nitrate (AN); Catalyst; Thermal decomposition; TG; DSC; Activation energy; Kissinger equation; XRD

## 1. Introduction

Ammonium perchlorate (AP) as the main oxidizer is using in most of the solid rocket propellants at present, AP based composite propellants also pass on high thrust at the time of take-off and therefore used in solid boosters of the launch vehicles. Major disadvantage of AP is its chlorinated drain which contains Chlorine oxides ( $\text{ClO}_x$ ), Chlorine (Cl) gas and Hydrochloric acid (HCl) [1]. All these entities are very much corrosive in nature, harmful for the earth environment and for the ozone layer. To defeat these environmental problems, it's required to study utilize of the supposed clean burning composite solid rocket propellants. Consequently, many researchers are going to develop environmentally friendly oxidizers. Ammonium nitrate (AN) has attracted attention many years ago as a potential propellant oxidizer for no HCl presented in production of AN decomposition. However, poor ignitability hygroscopicity, low energy, low burning rate, and polymorphic transitions around room temperature limited AN application in composite solid rocket propellants [2-5].

Metal oxide nanoparticles are also widely used in fuel cells, sensors, production of microelectronic circuits, industrial applications as catalysts and pigments. As adding, they play a significant task in the selective surface change of different substrates in the form of coatings [6, 7, and 8]. Metal oxide nanoparticles can display unique physico-chemical properties because of its nanometer size and high density of cover or edge surface sites.

Some aspects metal oxide nanoparticle can make the chemical activity unique. Nanostructures of the metal oxide composites can accept geometries not observed in the bulk state. In the bulk state could not common oxygen vacancies be present in the nanoparticles increasing its reactivity. A nanoparticle could have an oxygen/ metal ratio larger than for bulk oxides of a given metal [9, 10].

In this article,  $\text{CuZnO}_2$  nano metal oxide (NMO) is prepared by a co-precipitation method [11]. The size of the nanoparticles was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The catalytic affect of NMO on the thermal decomposition of AN was investigated and found to be a good catalyst for the AN-based composite solid rocket propellants [12]. In the DSC experiment at different heating rate, the reaction rate is only dependent on the temperature mechanism and is independent from the heating rate of the sample [13].

## 2. . Material and Method

AN (finar) was used without further purification.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck),  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck), NaOH (Merck) were used.

### 2.1. Synthesis of Nanoparticle

The Nano metal oxide was synthesized by chemical co-precipitation method as reported earlier [20]. Aqueous solution of mixture of 0.1 M metal nitrate of  $\text{M}^{+2}$  and 0.2 M of  $\text{Zn}^{+2}$  nitrate was dissolved in 100 ml distilled water in drop wise adding of 2M NaOH with vigorous stirring. Get precipitation of metal hydroxides at pH 11-12 then washed with distilled water to formulate them free from nitrate ions and dried brown metal hydroxide at

60°C in hot air oven for 5 hours and calcined at 300°C for 5 hours.

## 2.2. Characterization

Characterization of NMO has done using powder XRD and SEM techniques (JEOL; JSM-6510 LV). X-ray diffraction (XRD) measurement were carry out on the NMO by an X-ray diffractometer (Rigaku; miniflex 600) using CuK $\alpha$  radiation ( $\lambda = 1.5418$ ). The diffraction pattern is shown in Figure. 1. Calculate particle size was applying Scherrer's equation [23]. SEM images are shown in the figure 2.

## 2.3. Thermal Analysis (TGA-DSC)

TGA and DSC thermo-gram recorded on the Perkin Elmer STA 8000. TGA (Figure 3, 4) of pure AN, and AN + Nano metal oxide, (by mixing in ratio of 99:1) were recorded on the samples (~ 10 mg) in nitrogen atmosphere (200ml/min) by a heating rate 10 °C min<sup>-1</sup> using platinum crucible with pierced lid.

In the DSC (Figure 3 and 4) of AN, and AN + Nano metal oxide, (by mixing in ratio of 99:1) were recorded on the samples (~ 10 mg) by Perkin Elmer (Pyris Diamond) in nitrogen atmosphere (200ml/min) by a heating rate 10 °C min<sup>-1</sup> with platinum crucible with pierced lid.

In this DSC experiments method had done in three heating rate  $\beta_1=5$ ,  $\beta_2=10$ ,  $\beta_3=15$  degree per minute. In dependent to model free calculation of activation energy done by following Kissinger equation [15]:

$$\frac{d \ln \left[ \frac{\beta}{T_{max}^2} \right]}{d \left[ \frac{1}{T_{max}} \right]} = \frac{(-E)}{R} \quad (1)$$

On differentiation

$$\ln \left[ \frac{\beta}{T_{max}^2} \right] = \frac{-E}{RT} + \text{constant} \quad (2)$$

Where,  $\beta$  heating rate, E activation energy, R gas constant and T specific temperature respectively. A plot graph of  $\ln(\beta / T^2)$  against  $1/T$  yields an estimated straight line with a slope of  $-E/R$ .

## 3. Result and Discussion

The XRD pattern (Figure 1) of CuZnO<sub>2</sub> particles has sharp peaks which confirm their crystalline nature which is consistence with the literatures [16]. The SEM image (Figure.2), calculated the particle size via Scherer's equation [14]. Particle size 18.3 nm was obtained for CuZnO<sub>2</sub>; Sizes of these very small particles shows further than doubt that these

prepared Nano metal oxide is in the nano scale range. SEM images of Nano metal oxide are shown in Figure. 2.

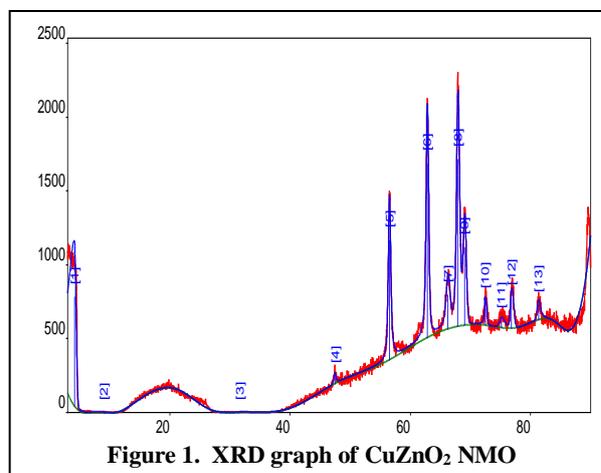


Figure 1. XRD graph of CuZnO<sub>2</sub> NMO

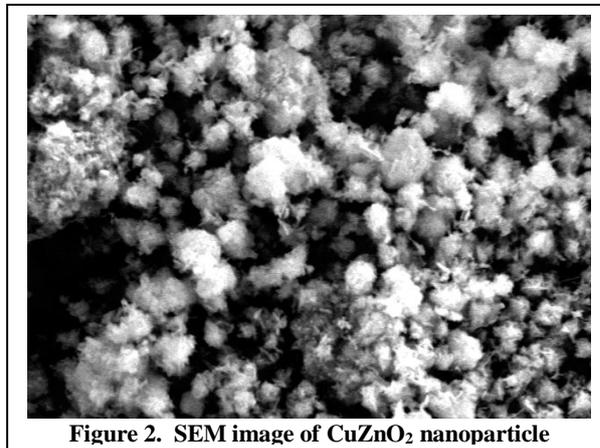


Figure 2. SEM image of CuZnO<sub>2</sub> nanoparticle

Five phase transitions in the Ammonium nitrate temperature range at -16.6 °C to 169 °C. Table 1 summarizes its structure and the phase transition temperatures.

Table 1. Phase transition of AN

Phases	Temperature (°C)	State
-	>168.9(melting point)	Liquid
I	168.9 to124.2	Cubic
II	124.2 to 84.9	Tetragonal
III	84.9 to32.3	$\alpha$ - Rhombic
IV	32.3 to -16.6	Orthorhombic
V	-16.6	Tetragonal

DSC thermograms of AN and AN + CuZnO<sub>2</sub> are shown in figure 3 and 4, as corresponding TGA graph are shown in the figure 3 and 4. Shown from figure 3 that the DSC of AN have four endothermic peaks at 55 °C, 129 °C, 169 °C and 281 °C. First two peaks shows enantiotropic phase changes, 3rd peak is of melting peak and the last peak observed decomposition of AN. Bowen [17] place forwarded

that very dried AN observes no phase transitions at 32 °C (IV→III) and at 84 °C (III→II), however observed only one transition by 50–55 °C and is a metastable state between forms IV and II and so removes form III. TGA of AN observes (figure 3) one step decomposition of AN mass loss of 94.37% in the temperature range of 180–290 °C.

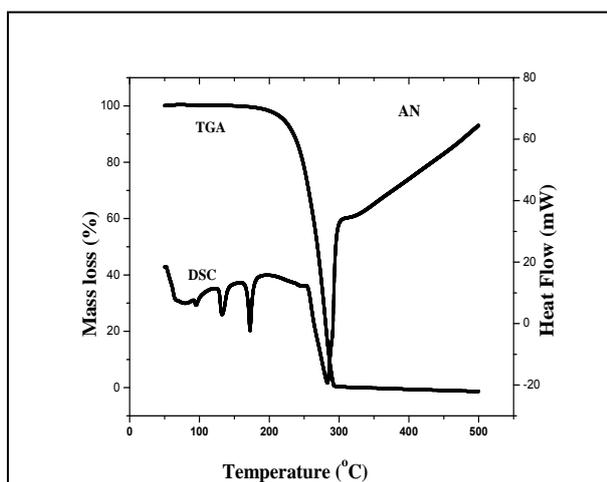


Figure 3. TGA-DSC graph of Pure AN

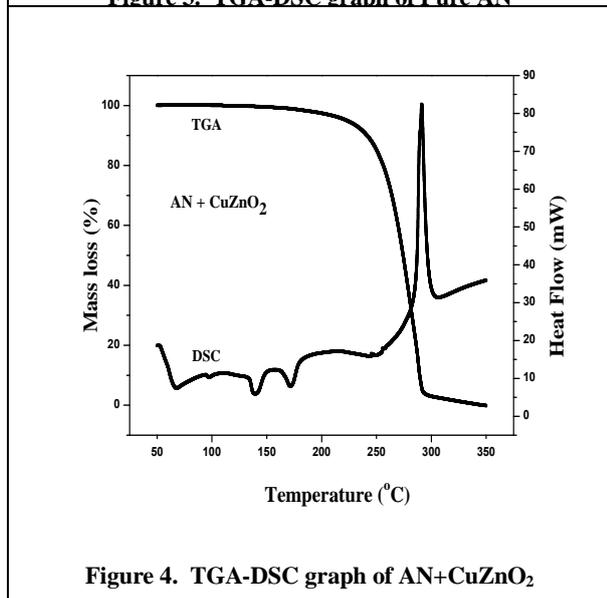


Figure 4. TGA-DSC graph of AN+CuZnO<sub>2</sub>

DSC graph of AN+CuZnO<sub>2</sub> in Figure 4, the first phase transition and decomposition peaks were shown at 88 °C and at 260 °C in presence of CuZnO<sub>2</sub>. It showed that CuZnO<sub>2</sub> is an improved phase additive and decomposition catalyst for AN. Second phase transition and melting peaks are almost the same for AN and AN with nano metal oxide samples. One exothermic peak is shown in the temperature range of 275–325 °C, just after decomposition in presence of catalyst. This sharp peak is possibly because of fast oxidation reaction among the NH<sub>3</sub> and decomposition products of

HNO<sub>3</sub>. NO<sub>2</sub> reacts with NH<sub>3</sub> to form N<sub>2</sub>O and H<sub>2</sub>O. This reaction take placed instantly in presence of catalyst and therefore one exothermic peak was observed immediately following decomposition according to literature data [18].

In figure 4 TGA thermo-gram observe two steps decomposition for samples. First major decomposition observed in the temperature range of 200–300 °C. In between 200 and 300 °C, AN breaks into NH<sub>3</sub> and HNO<sub>3</sub>, and further HNO<sub>3</sub> further breaks into N<sub>2</sub>, NO<sub>2</sub> and H<sub>2</sub>O. The DSC and TGA result for AN and AN with nano metal oxide are given in Tables 1 and 2, respectively.

Table 2. DSC data of AN and AN with NMO

AN and AN+ Nano metal oxide		
Sample	Peak (Temp °C)	Nature
AN	169	Endo
	281	Endo
AN +CuZnO <sub>2</sub>	162	Endo
	260	Endo

### 3.1. Kinetics

In shows figure 5 the activation energy for HTD of pure AN, AN with Nano-Metal oxide, in continuous heating was calculated by Kissinger equation. A plot graph of  $\ln(\beta/T^2_{max})$  vs.  $1/T$  yields an estimated straight line with a slope of  $-E/R$ . Calculated activation energy of pure AN, AN-Nano-metal oxide at HTD has been observed in the Table 3 which without a doubt the lowering in activation energy for AN in being there of Nano metal oxide. Remarkable lowering has been found in presence of nano metal oxide.

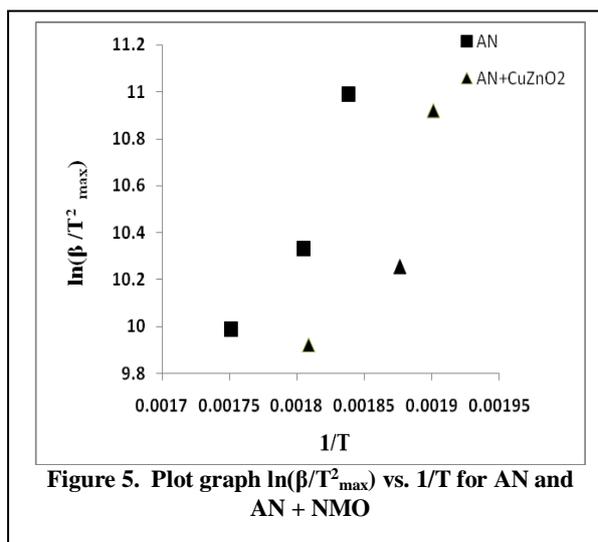


Figure 5. Plot graph  $\ln(\beta/T^2_{max})$  vs.  $1/T$  for AN and AN + NMO

A lot of researchers have been proposed thermal decomposition mechanism. Oxley suggested a widely accepted mechanism. Oxley [19, 20] observed so as to the decomposition mechanism of

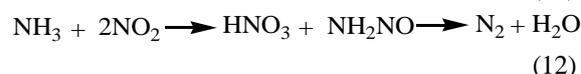
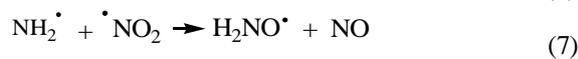
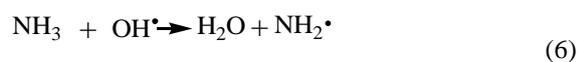
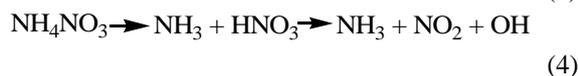
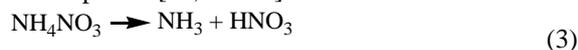
AN followed two pathways: an ionic reaction and a radical reaction. The ionic reaction occurred on low temperature and has comparatively low rate.

**Table 3. Activation energy of HTD (via Kissinger equation) of the AP and AP with NMO**

Activation energy of AN and AN with Nano-ferrites	
Sample	Activation energy (E) (kJ/mol)
AN	91.753
AN+CuZnO <sub>2</sub>	79.180

The radical reaction occurred at high temperature. AN melted at 169°C and began to decompose immediately it melted. Reaction (3) was commonly believed as the thermal decomposition initiating reaction, which was an endothermic proton transfer. However, Izato and Miyake found that the molten AN was first dissociated to NH<sup>+</sup> and NO<sub>3</sub><sup>-</sup>. The NO<sub>3</sub><sup>-</sup> in molten AN was more stable than the HNO<sub>3</sub> [21]. While the molten AN was heated from 470 K to 500 K, exothermic decomposition reaction (3) occurred [22] Reaction (4) was additional ordinary and was the basis of commercial production of N<sub>2</sub>O.

But, the activation energy of the homolysis of HNO<sub>3</sub> was extremely high on regarding 190 kJ/mol; it was the rate controlling step. Therefore, at high temperature, the ionic mechanism of AN decomposition was overtaken by radical reactions, [23] with homolysis of HNO<sub>3</sub> being the rate-controlling step as shown in reaction (5). The reference also create the energy barrier was lowest in different reaction pathways [24]. Then amidogen radical (NH<sub>2</sub>·) was reacted as showed in reactions (6) and (7). But Cagnina et al. [25] thought NH: was produced as showed in reaction (8). It was additional reacted as showed in reactions (9 to 11). Hence, we thought NO<sub>2</sub>· was easy to be formed at high temperature. When heated beyond 500 K, reaction (4) was the leading decomposition pathway. On the basis of reaction (12), the following mechanism has been reported [19, 26–29].



When NH<sub>3</sub> was absorbed on the nanoparticle surface, the reaction carried out by the formation of CuZnO<sub>2</sub> and NH<sub>3</sub> and amine (NH<sub>2</sub>). The mechanism of AN thermal decomposition was suggested. At low temperature (<200°C), most likely mechanism was that NH<sub>2</sub> was oxidized by HNO<sub>3</sub> or NO<sub>3</sub><sup>-</sup> to form N<sub>2</sub>O, especially HNO<sub>3</sub>. In the process, CuZnO<sub>2</sub> played a key role. CuZnO<sub>2</sub> absorbed NH<sub>3</sub> to form NH<sub>2</sub>. This process supported AN disassociation reaction to form large amount of HNO<sub>3</sub>. Because we all know, acid catalyzed AN thermal decomposition [26]. Thus, CuZnO<sub>2</sub> can catalyze AN thermal decomposition notably. The fundamental reason was that HNO<sub>3</sub> catalyzed AN thermal decomposition at low temperature.

## 4. Conclusion

Nano metal oxide (CuZnO<sub>2</sub>) was synthesized through chemical co-precipitation method and characterized by X-ray diffraction (XRD) and Scanning electron microscope (SEM). This Nano metal oxide shows good catalytic effect on the thermal decomposition of AP using TGA, DSC investigation. The catalytic activity of nano metal oxide is greatly sensitive to oxygen and possibly effective to get better the decomposition effectiveness of AN and AN based propellants.

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## 6. References

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