

Nano metal oxide as Catalyst for thermal decomposition of Ammonium perchlorate

Jalpa Vara & P.N.Dave

¹Department of Chemistry, K.S.K.V Kachchh University, Bhuj, Kachchh-370001

²Department of Chemistry, S.P. University, V.V.nagar-388120.

Email: pragneshdave@rediffmail.com, jalpa.vara@gmail.com

Abstract:

Nano metal oxide (NiZnO₂) was synthesis by chemical co-precipitation method. Nano metal oxide was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The Nano-mixed metal oxide use as catalyst for the thermal decomposition of ammonium perchlorate. The study of catalytic activity of Nano metal oxide was on the thermal decomposition of ammonium perchlorate using Thermogravimetric analysis (TGA), Differential Scanning Calorimetric (DSC). Activation energy of high temperature decomposition (HTD) of with Nano metal oxide was calculating using DSC by Kissinger equation. The catalytic activity of Nano metal oxide much sensitive and may be effective to get better the decomposition efficiency of Ammonium Perchlorate.

Keywords

Ammonium perchlorate (AP), XRD, Catalyst, DSC, TGA, Thermal decomposition, Activation energy; Kissinger equation,

1. Introduction

Metal oxide nanoparticles can show only one of its kind physico-chemical properties which are due to their nanometer size and high density of cover or edge surface sites. Nano size oxide particles are fast growing technical importance in classic areas of application [1], such like catalysts, passive electronic components or ceramic materials. Metal oxide nanoparticles are as well used in manufacture of microelectronic circuits, sensors, fuel cells, industrial applications as catalysts and pigments. As additives, they take part in a significant role in the alteration for selective surface of different substrates in the form of coatings [2, 3, and 4].

The chemical reactivity of the surface site of oxide nanoparticles is an extremely vital subject for applications in catalysis [5–7]. A purpose in the up-and-coming field of nanotechnology is to create nanostructures with a very vast surface area [8–10]. In a nano oxide, the ratio of surface atoms to non-surface atoms is generally a lot larger than in a bulk material and surface kind display local geometry opposed from the bulk and strongly affecting chemical reactivity [11].

Composite solid rocket propellants are the main origin of chemical energy in space vehicles and missiles. Ammonium perchlorate (AP) is extensively used as an oxidizer in composite solid propellants [12-16]. It is commonly note that since catalytic activity is mainly a surface occurrence; the size reduction of the catalysts enhances their catalytic activity [17]. The ballistics of a composite propellant can be better by addition a catalyst such as copper oxide (CuO), ferric oxide (Fe₂O₃), nickel oxide (NiO), copper chromite (CuO.Cr₂O₃), etc, which accelerates the rate of decomposition of AP [12-16]. Current studies have shown that without any agglomeration of transition metal oxides nanoparticles can increase the burning rate [18]. The capability of catalytic action increases harshly in nanometer size oxide particles than micro scale oxide particles [19]. The size distribution, morphology and nanostructure of particles are extremely significant uniqueness and do have an effect on the kinetics of decomposition of ammonium perchlorate.

In this article, NiZnO₂ nano metal oxide (NMO) is prepared by a co-precipitation method [20]. The size of the nanoparticles was measured by X-ray diffraction (XRD) and SEM. The catalytic result of NMO on the thermal decomposition of AP was investigating and found to be a superior catalyst for the AP-based composite solid rocket propellants [21]. In the DSC studies at different heating rate, the mechanism of reaction will not be different for the reason that the reaction rate is just dependent on the temperature mechanism and is independent from the heating rate of the sample [22].

2. Material and Method

Without further purification AP (Qualigens) was used. Crystals of AP were ground into fine powder using a pestle and mortar and sieved to 100-200 mesh. Zn (NO₃)₂.6H₂O (Merck), Ni (NO₃)₂.6H₂O (Merck), NaOH (Merck) were used as received.

2.1. Synthesis of Nano metal oxide

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 M⁺² and 0.2 M of 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 α 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)

Thermal analysis TGA and DSC graph recorded on the Perkin Elmer STA_8000. TGA (Figure 3) of pure AP, and AP with Nano metal oxide, (by mixing in ratio of 99:1) were recorded on the samples (~ 10 mg) in nitrogen atmosphere (200ml/min) at a heating rate 10°C min⁻¹ by platinum crucible with pierced lid.

In the DSC (Figure 3) of AP, and AP with Nano metal oxide, (by mixing in ratio of 99:1) were measurements on the samples (~ 10 mg) using Perkin Elmer (Pyris Diamond) in nitrogen atmosphere (200ml/min) at a heating rate 10°C min⁻¹ by platinum crucible with pierced lid. In this DSC process experiments had completed in 3 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 [24]:

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

On differentiation

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

Where, β 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 (Fig 1) of NiZnO₂ particles has sharp peaks which confirm their crystalline nature

which is consistence with the literatures [25]. The SEM image (Figure 1), the particle size was considered via Scherer's equation [23]. Particle size 35.9 nm was obtained for NiZnO₂; Sizes of these very small particles shows beyond doubt that these prepared Nano metal oxide is in the nano scale range. SEM images of Nano metal oxide are shown in Figure 2.

The thermal analysis TGA thermo-gram for AP

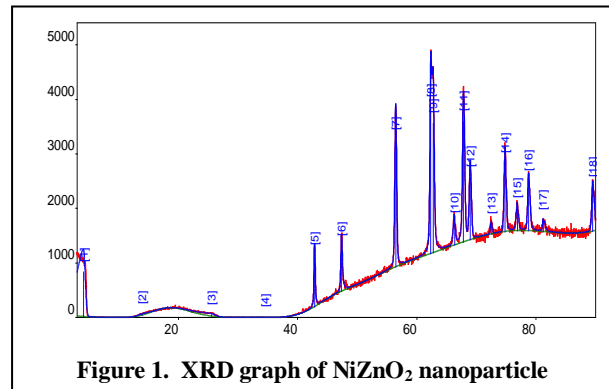


Figure 1. XRD graph of NiZnO₂ nanoparticle

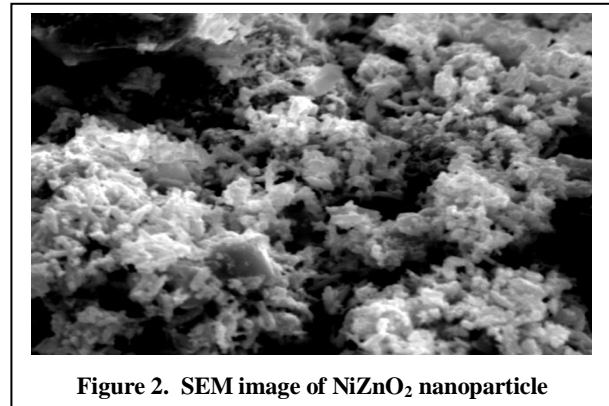


Figure 2. SEM image of NiZnO₂ nanoparticle

(Figure 3) obtains the two steps [26-28]. Heating on AP the first 25% its mass loses at around 310°C, which is low temperature decomposition (LTD). Further than this temperature a plateau is observed and 80% mass loses of AP at around 395°C, that is high temperature decomposition (HTD) (Table 2). It can be seen from TGA thermal graph of AP with Nano metal oxide (Figure 3) that the nano catalysts affect equally LTD and HTD of AP. In thermal analysis of AP+ nano metal oxide mixture is higher percentage mass loss observed in the compare with pure AP. Gasification of AP in presence of nano catalysts in HTD not only begin early, but also complete at lower temperatures.

Table 1. DSC result of the AP and AP + NMO

AP and AP+ Nano metal oxide		
Sample	Peak (Temp °C)	Nature
AP	310	Exo
	395	Exo
AP +NiZnO ₂	306	Exo

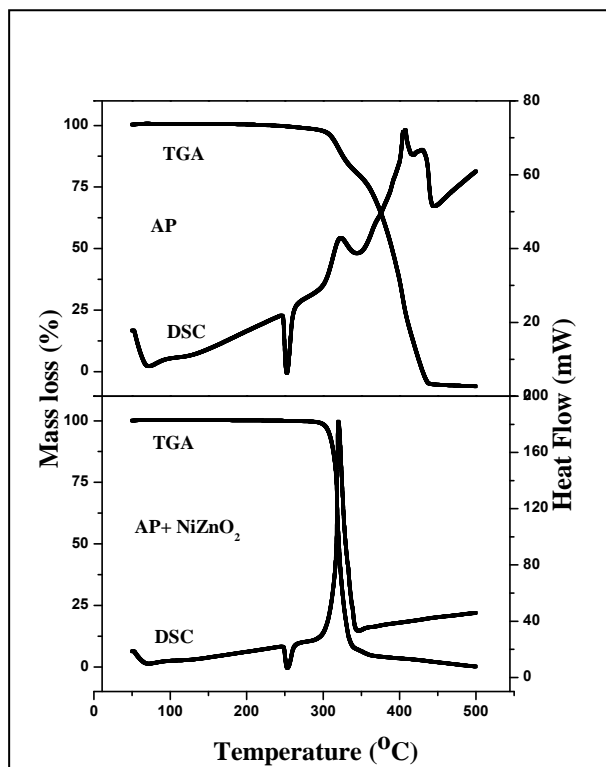


Figure 3. TGA-DSC thermo-gram of AP and AP+NMO

Figure 3 was DSC graph of pure AP shown three major events. The endothermic peak at 244°C for AP corresponds to the transition from orthorhombic to cubic [29]. The thermal decomposition on AP take places in two steps as shown in TGA thermal- gram of AP in the Figure 3, the first exothermic peak corresponds to LTD process and configuration of intermediate product takes place. The second major exothermic peak of AP around higher temperature (395°C) corresponds to HTD process, complete decomposition of the intermediate products into volatile products [27] obtains. The DSC of AP with nano metal oxide observed a clear change in the decomposition pattern (Table 1).

The endothermic peak shows no change in position. In difference, there is small variation in first exothermic peak and large variation in the position of second exothermic peak. HTD process for pure AP was shown on lower temperature for AP with Nano metal oxide indicating the affect of the nano catalyst.

3.1. Kinetics

The activation energy for HTD of pure AP, AP with Nano metal oxide, in continuous heating was calculated by using Kissinger equation. A plot graph of $\ln(\beta/T_{max}^2)$ vs. $1/T$ (Figure 4) yields an estimated straight line with a slope of $-E/R$. Calculated activation energy of pure AP, AP with Nano-oxide on HTD has been given in the Table 2 which noticeably observed the lowering in activation energy for AP in adding or present of Nano metal oxide. Remarkable lowering has been found in presence of nano metal oxide.

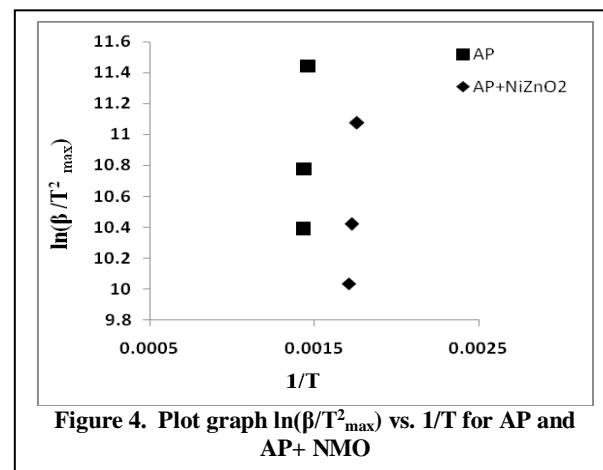


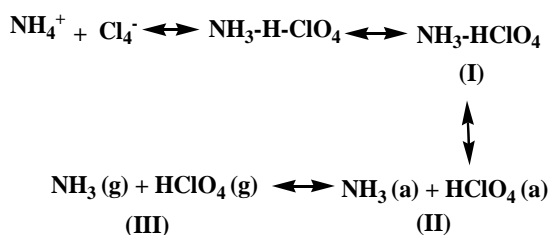
Figure 4. Plot graph $\ln(\beta/T_{max}^2)$ vs. $1/T$ for AP and AP+ NMO

Table 2. Activation energy of HTD of the AP and AP + NMO

Activation energy of AP and AP + NMO	
Sample	Activation energy (E) (kJ/mol)
AP	276.230

AP+NiZnO ₂	168.140
-----------------------	---------

Nano metal oxides used as additives in AP enhances the rate, of N–H bond heterolysis in NH₄⁺ and, O–H bond produce in HClO₄. In the decomposition reactions of energetic materials frequently involve both bond-breaking and bond-forming steps. About 1000 of reactions may be occupied in the decomposition and combustion of AP [21, 29, 30, 31], for the reason that of the four constituents and the full range of oxidation states utilized by nitrogen and chlorine. N–H bond was breaking of then proton transfer from NH₄⁺ to ClO₄⁻ to form an O–H bond leads to the formation of NH₃ and HClO₄ is a primary step in condense phases [32]. At the same time a sequence of reaction occurs to form gaseous NH₃ and HClO₄. N₂O, O₂, Cl₂, H₂O, and little amount of NO are produce. The second decomposition step of AP is gas phase reaction and produce are NO, O₂, Cl₂, and H₂O.



Higher temperature the secondary reactions happen at during complex competitive steps to produce gaseous products. From the beyond declared study we can conclude this Nano metal oxide is enhanced catalytic activity for thermal decomposition of AP, these nano catalysts can be used in the formation of AP-HTPB composite solid rocket propellants for good result.

It is recognized that the Nano metal oxides have large surface area due to their very small size; there are many reactive sites over the surface. Thus during the second exothermic decomposition of AP, NMO can absorb the gaseous reactive molecules on their surface and support the reactions.

Many researches AP combustion mechanism has been investigation in many works and the most important role of the condensed phase reactions at pressures to 10–14MPa is postulate. In the condensed phase more than 70% AP must decompose [33–35]. The remain portion partially dissociates into gaseous perchloric acid and ammonia in the heat transferred reverse from the gas and partially is passed away from the surface to the high-temperature gas region with gases formed and undertakes there decomposition & dissociation. Perchloric acid decomposition reaction and AP primary decomposition are occur in the liquid state [33–35] and support the confirmation for the before stated

assumption on the most important function of chemical processes in thin liquid surface layer on the burning surface of AP [31, 33–35].

4. Conclusion

Nano metal oxide (NiZnO₂) 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 a lot sensitive to oxygen and may be effectual to get better the decomposition effectiveness of AP and AP based propellants.

5. Acknowledgements

The authors are grateful to Department of Chemistry K.S.K.V Kachchh University, Bhuj for laboratory facility and for SEM, XRD, and TGA-DSC analysis.

6. References

1. Feldmann, C. and Jungk, H.-O., "Polyol-mediated preparation of nanoscale oxide particles", *Angew. Chem. Int. Ed.* 40, 19 January 2001, pp. 359–362.
2. O'Regan, B. and Gratzel, M., "A low-cost, high-efficiency solar cell based on dye sensitized colloidal TiO₂ films", *Nature* 353, 24 October 1991, pp. 737–740.
3. Hagfeldt A. and Gratzel, M., "Light-induced redox reactions in nanocrystalline systems", *Chem. Rev.* 95, 1 January 1995, pp. 49–68.
4. Ertl, G., Knozinger, H. and Weitkamp, J. (eds.), "Handbook of Heterogeneous Catalysis", Wiley-VHC, Weinheim, 1997.
5. Noguera, C. *Physics and Chemistry at Oxide Surfaces*, Cambridge University Press, Cambridge, UK 1996, pp. 1–223.
6. Kung, H. H., "Transition Metal Oxides, Surface Chemistry and Catalysis", Elsevier, Amsterdam 1989, pp. 1336.
7. Henrich, V. E., Cox, P. A., "The Surface Science of Metal Oxides", Cambridge University Press, Cambridge, UK 1994, pp. 1482.
8. Trudeau, M. L., Ying, J. Y., "Nanocrystalline Materials in Catalysis and Electrocatalysis: Structure Tailoring and Surface Reactivity", *Nanostruct. Mater.* 7, 1996, pp. 245–258.
9. Edelstein, A. S., Cammarata, R. C., "Nanomaterials: Synthesis, Properties and Application", Institute of Physics Publishing, London 1998, pp. 1–283.
10. Dohnalek, Z., Kimmel, G. A., McCready, D. E., Young, J. S., Dohnalkova, A., Smith, R. S., Kay, B. D., "Structural and Chemical Characterization of Aligned Crystalline Nanoporous MgO Films Grown

- via Reactive Ballistic Deposition", *J. Phys. Chem. B* 2002, 106, pp. 3526.
11. Lucas, E., Decker, S., Khaleel, A. Seitz, A., Futzl, S., Ponce, A., Li, W., Klabunde, C. K. J., "Nanocrystalline Metal Oxides as Unique Chemical Reagents/Sorbents", *Chem.-Eur. J.* 5 June 2001, 7, pp. 2505.
 12. Shen, S. M., Chen, S. I. and Wu, B. B., "The thermal decomposition of ammonium perchlorate (AP). Containing a burning rate modifier," *Thermochim Acta*, 1993, 223, pp.135-43.
 13. Said, A. A., "Thermal decomposition of ammonium metavanadate doped with iron, cobalt or nickel hydroxides", *Thermal Analysis*, 1991, 37, pp. 959-62.
 14. Nema, A. K., Jain, S.; Sharma, S. K., Nema, S.K. and Verma, S. K., "Mechanistic aspect of thermal decomposition and burn rate of binder and oxidizer of AP/HTPB composite propellants comprising HYASIS-CAT", *Int. J. Plastics Tech.*, 8, 2004, pp.344-54.
 15. Gao, J., Guan, F. and Zhao, Y., "Preparation of ultrafine nickel powder and its catalytic dehydrogenation activity", *Mat. Chem. Phys.*, 2001, 71, pp. 215-19.
 16. Chaturvedi, S., Dave, P. N., "Review: Nano Metal Oxide: Potential Catalyst on Thermal Decomposition of Ammonium Perchlorate". *J. of Exp. Nanosci.* 15, 2011 pp.1-27.
 17. Singh, G., Kapoor, I. P. S., Dubey, S. Siril, P. F., "Preparation, Characterization and Catalytic Activity of Transition Metal Oxide", *Nanocrystals, J. Sci. Con. Proc.* 2008, 1, 7.
 18. Simonenko, V.N.; Zarko, V.E.; Kiskin, A.B. and Sedoi, V.S. In 32nd International Annual Conference of ICT, 2001.
 19. Telkar, M.M., Rode, C.V., Choudhary, R.V., Joshi, S. S. and Nalawade, A.M. "Shape controlled preparation and catalytic activity of metal nanoparticles for hydrogenation of 2-butyne-1, 4-diol and styrene oxide". *J. Appl. Cata., A*, 2004, 273, 11-19.
 20. Yang, J., Li, J., Lu, H., Yang, X., Wang, N., Tong, X., "Synthesis and Characterization of Regular Hexagonal NiCo₂O₄ Nanosheets", *Key Eng. Mater.* 2027, 2007, pp.336-338.
 21. Chaturvedi S., Dave P. N., "A Review on the Use of Nanometals as Catalysts for the Thermal Decomposition of Ammonium Perchlorate", *J. Saudi Chem. Soc.* 17, 2013, pp.135-149.
 22. Wang H. R., Ye Y. F., Min G-H., Chen Y., Teng X-Y., "Crystallization kinetics of an amorphous Zr-Cu-Ni alloy calculation of the activation energy", *J. Alloys and Comp.* 353, 2003, 200-206.
 23. Birks, L. S. and Friedman, H., "Particle size determination from X-Ray line broadening", *J. Appl. Phys.*, vol. 17, no. 8, 1946, pp. 687-692.
 24. Lu, K., Wei, W. D., and Wang, J. T., "Grain growth kinetics and interfacial energies in nanocrystalline Ni-P alloys", *J. Appl. Phys.*, vol. 69, 1991, pp. 7345-7347.
 25. Chaturvedi S., Dave P. N., Nikul N., Patel N. N., "Nano-alloys: Potential catalyst for thermal decomposition of Ammonium Perchlorate", *Synth. Reactivity Inorg. Metal-Organic, and Nano-Metal Chem.* 42, 2014, 258-262.
 26. Jacobs, P. W. M. and Pearson, G. S., "Mechanism of the decomposition of ammonium perchlorate", *Combust. Flame*, vol. 13, no. 4, 1969, pp. 419-425.
 27. Rosser, W. A., Inami, S. H., "Thermal decomposition of ammonium perchlorate", *Combust. Flame* 12, 1968, pp. 427-435.
 28. Kishore, K. and Sridhara, K., "Solid Propellant Chemistry: Condensed Phase Behavior of Ammonium Perchlorate Based Solid Propellants", New Delhi, India: DESIDOC, 1999
 29. Zhi, J. and Feng-Qi, Z., "Study on effects of nanometer metal powder on thermal decomposition of HMX", *J. Propul. Tech.*, vol. 23, 2002, pp. 258-261.
 30. Boldyrev, V. V., "Thermal decomposition of ammonium perchlorate", *Thermochim. Acta*, vol. 443, no. 1, 2006, pp. 1-36.
 31. Singh, G. and Pandey, D. K., "Studies on energetic compound: Part 24 – Hexaminemetal perchlorate as high energetic burning rate catalysts", *J. Energ. Mater.* vol. 20, 2002, pp. 223-244.
 32. Manelis, G. B., "Thermal Decomposition and Combustion of Explosives and Propellants", Boca Raton, FL: CRC Press, 2003. ISBN 10: 0415299845; ISBN 13: 9780415299848.
 33. Sinditskii, V. P., Egorshv, V. Yu., Serushkin, V. V., Levshenkov, A. I., Berezin, M. V., Filatov, S. A., and Smirnov, S. P., "Evaluation of decomposition kinetics of energetic materials in the combustion wave", *Thermochim. Acta*, vol. 496, no. 1, 2009, pp. 1-12.
 34. Sinditskii, V. P., Egorshv, V. Y., Serushkin, V. V., Levshenkov, A. I., Berezin, M. V., and Filatov, S. A., "Combustion of energetic materials governed by reactions in the condensed phase", *Int. J. Energetic Mater. Chem. Propul.*, vol. 9, no. 2, 2010, pp. 147-192.
 35. Sinditskii, V. P., Egorshv, V. Yu., Serushkin, V. V., Levshenkov, A. I., and Filatov, S. A., "Combustion of energetic materials controlled by condensed-phase reactions", *Combust. Explos. Shock Waves*, vol. 48, no. 1, 2012, pp. 81-99.