

Kinetics of Nano Titanium Dioxide Catalyzed Thermal Decomposition of Ammonium Nitrate and Ammonium Nitrate-Based Composite Solid Propellant

Anuj A. Vargeese,^{*,[a]} Krishnamurthi Muralidharan,^[b] and V. N. Krishnamurthy^[c]

Abstract: This study deals with the influence of nanosized titanium dioxide (TiO₂) catalysts on the decomposition kinetics of ammonium nitrate (AN) and ammonium nitrate-based composite solid propellant. TiO₂ nanocatalyst with an average particle size of 10 nm was synthesized by sol-gel method using titanium alkoxide as precursor. Formation of nanostructured TiO₂ and presence of its anatase and brookite phases was confirmed by powder X-ray diffraction (PXRD) and selected area diffraction (SAED) studies. Nano TiO₂ was further characterized by transmission electron microscopy (TEM), infrared (IR) spectroscopy, and thermogravimetry. The catalytic effect of TiO₂ nanocatalysts on the solid state thermal decomposition reaction of AN and non-aluminized HTPB/AN propellant was evaluated. To ascertain

the effectiveness of the TiO₂ nanocatalyst, the thermal kinetic constants for the catalytic and non-catalytic decomposition of AN and AN propellant samples were computed by using a nonlinear integral isoconversional method. Catalytic influence was evident from the lowering of activation energy for the catalyzed decomposition reactions. Apparently, the nanocatalysts provide Lewis acid and/or active metal sites, facilitating the removal of AN dissociation products NH₃ and HNO₃ and thereby enhance the rate of decomposition. The changes in the critical temperature of thermal explosion of AN and AN propellant samples due to the addition of TiO₂ nanocatalyst were also computed and the possible reasons for the changes are discussed.

Keywords: Nanostructures • Ammonium nitrate • Composite solid propellant • Reaction kinetics • Catalyzed decomposition

1 Introduction

Compared to the conventional ammonium perchlorate (AP)-based solid rocket propellants, combustion products of ammonium nitrate (AN)-based propellants do not contain noxious halides harmful to the atmosphere. However, the poor ignitability, hygroscopic nature, low energetics and the near room temperature polymorphic transitions limit the application of AN in solid rocket propellants [1]. Irrespective of its drawbacks, AN is receiving a reinvigorated interest as a possible substitute for AP. Application of transition metal oxide (TMO) catalysts can surmount the low reactivity and low energetic of AN and the catalyst efficiency of TMOs can be increased by reducing their particle size. Even if a substantial increase in reactivity of the chemical decomposition reactions by nanocatalyst assistance might be anticipated, such catalytic decompositions are often dependent on the material property of the nanocatalysts.

It is widely considered that, catalysts which accelerate the oxidizer decomposition enhance the burning rate of propellant. The catalytic effect of TMO on the thermal decomposition is attributed to many reasons, such as semiconductor properties (degree of *p* or *n* nature), charge transfer process or electron transfer process, etc., but the actual mechanism of activity is still not known to any certainty. The *p* type semiconduction nature of oxides is re-

portedly contributory in enhancing the reactivity [2]. Earlier investigators report a linear dependency between the degree of catalytic activity of TMO on propellants with their redox potentials and the heat of reaction with the electron transfer process [3].

Chemical kinetics deals with the parameterization of the reaction rate as a function of state variables such as temperature, pressure, and concentration [4]. The isoconversional methods of kinetic analysis permit to explore the multistep kinetics of the thermal decomposition reactions and helps in drawing mechanistic conclusions about the

[a] A. A. Vargeese
Department of Chemistry
National Institute of Technology Calicut
Calicut 673601, Kerala, India
*e-mail: dr_anuj@gmail.com

[b] K. Muralidharan
School of Chemistry and Advanced Centre of Research in High Energy Materials
University of Hyderabad
Hyderabad 500 046, India

[c] V. N. Krishnamurthy
38, Janaka, PTP Nagar
Trivandrum 695038, Kerala, India

process and even to determine the thermal stability of material under investigation [5,6].

The inability of AN to sustain stationary burning is known and additives are required to increase the rate and completeness of burning of both pure AN and related compositions. The influence of additives on AN burning/decomposition was studied by many earlier investigators [1,5,7] and it has been reported that derivatives of hexavalent chromium and metal halides are effective combustion catalysts [8]. In the presented study, we have synthesized TiO₂ nanoparticles and the catalytic activity and efficiency of the nanocatalyst on the decomposition of AN and AN propellant samples are evaluated.

Critical temperature of thermal explosion (T_c) is the lowest temperature, below which the thermal explosion of a chemical, of the thermal decomposition type, placed in an atmosphere under isothermal conditions cannot occur. Hence, T_c is a very important parameter for energetic materials. Using nonisothermal DSC curves of the samples, we have estimated the value of T_c for the catalyzed and non-catalyzed samples.

2 Experimental Section

2.1 Materials

The chemicals used for the preparation of TiO₂ nanoparticles, titanium isopropoxide (98%), and isopropyl alcohol (AR) were obtained from Avra Synthesis India Ltd. and SRL Ltd., respectively, and used without further purification.

2.2 Synthesis and Characterization of Nanocatalyst

2.2.1 Synthesis of TiO₂ Nanocatalyst

Nano TiO₂ with uniform size was synthesized by the hydrolysis of titanium isopropoxide solution [9,10]. The detailed procedures of synthesis of TiO₂ nanoparticles were reported in our previous study [6].

2.2.2 Characterization of TiO₂ Nanocatalyst

The high-resolution transmission electron microscopy (HRTEM) study was carried out with a FEI Tecnai G2 F20 S-Twin Transmission Electron Microscope. The samples for transmission electron microscopy (TEM) and HRTEM analysis were obtained by diluting the TiO₂ dispersion with ethanol. A drop of the dilute dispersion solution was placed onto a Formvar covered copper grid and evaporated in air at room temperature.

The powder X-ray diffraction (PXRD) pattern was obtained with a Bruker D8 Advance instrument at room temperature (298 K) and the sample was scanned over a 2θ range of 20–70°. A step size or sampling interval of 0.02° and a scan time of 1 s was used for the characterization. From the obtained PXRD patterns, the interplanar distances

(d) were calculated by Bragg's equation and compared with the JCPDS data.

The Fourier transform infrared spectroscopy (FTIR) spectrum of TiO₂ nanocrystals dispersed in a KBr matrix (pellet) was recorded with a JASCO FTIR-5300.

2.3 Sample Preparation

For the catalytic activity studies on AN, TiO₂ nanocatalyst was mixed with AN in the molar ratio 98:2 by blending on a mechanical stirrer for 12 h. Crushed and sieved particles of AN in the size range of 105–180 μm was used for the experiments. After preparation, the mixture was dried with fused calcium chloride under reduced pressure for 30 min and used for decomposition kinetic analysis and catalytic activity evaluation.

To study the influence of TiO₂ nanocatalyst on AN-based propellants, a non-aluminized (hydroxyl terminated polybutadiene) HTPB/AN propellant was formulated with 80% solid loading. Standard addition procedure was followed for the propellant formulation and prepared 2 g batches through hand mixing. Dibutyl phthalate was used as plasticizer and toluene diisocyanate was used as the curing agent. Two propellant formulations with varying nanocatalyst concentration, 1.6% and 4% by weight of propellant, were prepared and used for the decomposition kinetic analysis and catalytic activity evaluation. To understand the decomposition behavior of non-catalyzed propellant, one such propellant formulation was prepared without any catalyst additive.

2.4 Thermal and Catalytic Decomposition of AN and AN Propellant

Thermal or catalytic decomposition experiments of AN were carried out in a nitrogen atmosphere with a TA instruments SDT Q600 instrument. In all experiments, about 1 mg of sample was loaded in an open 90 μL alumina pan and heated. Nitrogen at a flow rate of 100 mL min^{-1} was used as the purge gas. Following ICTAC recommendations [4], TG measurements were used to compute the thermal kinetic constants from model free method. Nonisothermal TG runs were conducted at heating rates 5, 6 and 7 K min^{-1} and the extent of conversion (α) was computed from the weight loss data using the standard method as described elsewhere [11]. A 0.025 increment in α was used to compute the effective activation energy (E_a) from the nonlinear integral isoconversional method.

2.5 Kinetic Analysis

A model free (isoconversional) nonlinear integral method developed by Vyazovkin [5] was employed for the computation of kinetic parameters and kinetic analysis. The third degree approximation proposed by Senum and Yang [12] was used in the presented study to evaluate the integral in

the Vyazovkin's method. The theoretical background of kinetic analysis is given in the Supporting Information.

2.6 Calculation of Critical Temperature of Thermal Explosion (T_c)

We have used a reported method [13] for estimating the value of T_c . The theoretical background of this method is given as Supporting Information. The activation energy value required for the calculations were obtained by taking average of the E_a values computed by the isoconversional method. The onset of decomposition, T_d , at different heating rates were obtained from DSC data collected with a TA instruments SDT Q600 instrument.

Supporting Information (see footnote on the first page of this article): FT-IR and Tg-DT analysis data of TiO_2 nanocatalyst; Tg-DTg curves of AN propellant and AN propellant with nanocatalyst; kinetic analysis data.

3 Results and Discussion

3.1 Characterization of Nanocatalyst

The PXRD pattern of the nano TiO_2 was obtained and is shown in Figure 1. Examination of the PXRD pattern indicates the formation of a mixture of brookite and anatase phase TiO_2 . Reportedly, the sol-gel synthesis of titania using titanium isopropoxide typically produces a mixture of anatase and brookite phase [9]. The presence of brookite phase was evident from the well distinguished peaks corresponding to hkl values 121 and 221. Due to anisotropic peak broadening, the higher intensity peaks were overlapped and could not be resolved. The close by peaks, 100% intensity (101) peak of anatase and the 100% intensity (120) as well as 80% intensity (111) peaks of brookite (JCPDS 21-1272 and 29-1360) were found to be overlapping. Since the higher intensity peaks of anatase (204) and

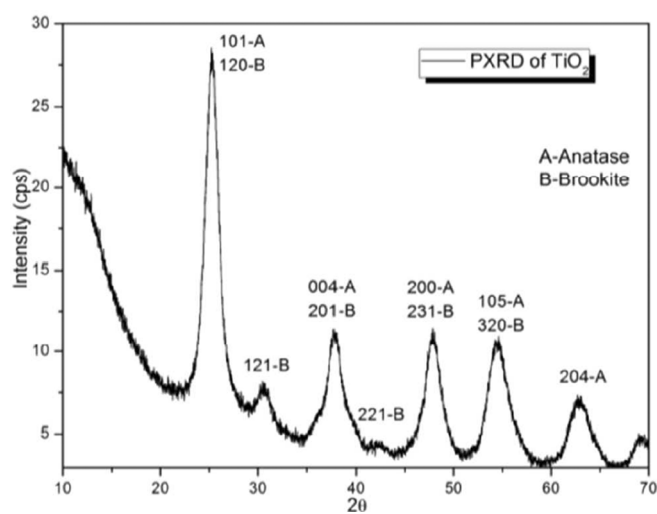


Figure 1. PXRD pattern of the synthesized TiO_2 nanocatalyst.

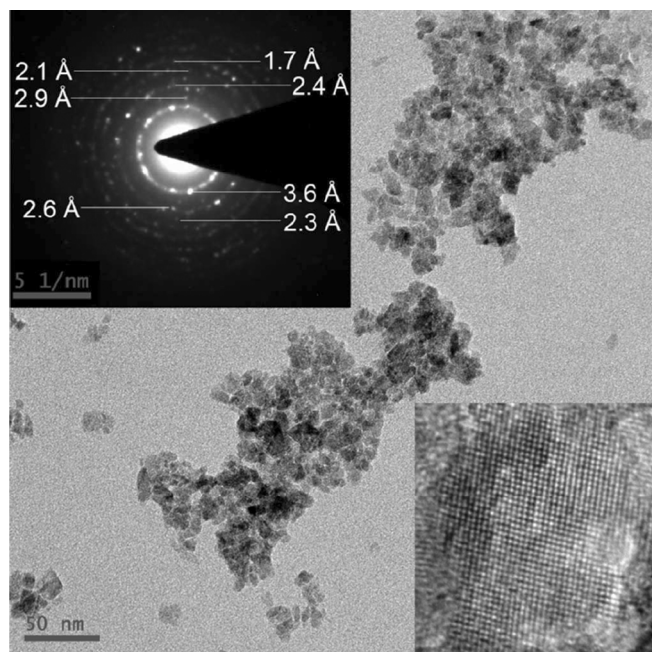


Figure 2. TEM images of nanosized TiO_2 with electron diffraction pattern and HRTEM inset.

brookite (121) could be identified and were well distinguished, the obtained nano TiO_2 was considered as a mixture of anatase and brookite phase.

TEM images, shown in Figure 2, were used to investigate the particle size, crystallinity and morphology of the synthesized nano TiO_2 . A relatively narrow size distribution of nanoparticles with platelet morphology was revealed by the TEM analysis. Even though a mean particle diameter of 10 nm was observed, small aggregates with diameter 50 nm were also identified. HRTEM images of thin nano TiO_2 revealed lattice fringes that are continuous across the particle. The selected area diffraction (SAED) data was in good agreement with the PXRD observations and confirmed the presence of both anatase and brookite phase. Two characteristic diffraction rings (121 and 221) corresponding to the brookite phase was seen in the SAED pattern.

In the FT-IR spectra (Figure S1 of Supporting Information) of as-prepared nano TiO_2 sample, a broad band related to stretching of hydroxyl (O–H) group due to the presence of surface attached H_2O was observed at around 3360 cm^{-1} . Medium absorption peaks observed at 1618 and 1385 cm^{-1} can be attributed to the in plane bending vibrations of O–H and CO_2 molecules. The known low energy bands at 703 , 589 , and 416 cm^{-1} , due to the stretching vibrations of Ti–O bond in titania [14] were observed with small variations at 685 , 555 , and 450 cm^{-1} . Further, the TGA of nano TiO_2 (Figure S2 of Supporting Information) samples indicated a total weight loss of 12% below 648 K with an approximate weight loss of 4% due to the H_2O removal and 8% due to the organic impurities removal. Since approximately 70%

of the total weight loss occurred before 473 K, the sample was annealed at this temperature for 3 h before evaluating the catalytic efficiency.

3.2 Catalytic Decomposition

It is well accepted that the addition of catalyst lowers the activation energy of the reaction. Activation energy may be correlated to bond energy data and is generally considered as a measure of the energy barrier to a controlling (rate limiting) bond rupture or bond redistribution step. Activation energy can provide reasonable information about the critical energy needed to start the decomposition/reaction of a compound. Since all other parameters are kept similar and assuming that the reaction rate at a constant conversion depends only on the temperature (isoconversional principle), a reduction in the activation energy can be directly related to the catalytic activity of the compound under investigation. The E_a required for the decomposition reaction of AN as well as the AN propellant samples were computed by the isoconversional method [5] as described in the Experimental Section.

3.2.1 Catalytic Decomposition of Ammonium Nitrate

In Figure 3, the E_a values calculated for the catalyzed and noncatalyzed decomposition reaction of AN, plotted against extend of conversion (α) is shown. According to the previous researchers, the overall noncatalyzed decomposition reaction of AN is described by a first-order reaction kinetics. For the noncatalyzed AN decomposition process, recent works including our previous studies, suggest an average activation energy of 90 kJ mol^{-1} and a reaction system following first-order reaction kinetics [6, 15].

In the presented study, we have calculated the average activation energy required for the thermal decomposition of noncatalyzed AN to be 109 kJ mol^{-1} , while 77 kJ mol^{-1}

was obtained for nano TiO_2 catalyzed decomposition. This significant reduction could be identified as catalytic influence of nano TiO_2 on the thermal decomposition reaction of AN. Besides a significant reduction in the E_a values, the plots of E_a against α of catalyzed decomposition indicate a change in the decomposition reaction pathway. Instead of the first-order reaction kinetics, the catalyzed decomposition showed a dependence of E_a on α as the reaction proceeds and in turn multistep reaction kinetics.

3.2.2 Catalytic Decomposition of AN-Based Propellant

Non-aluminized HTPB/AN propellant was formulated with 80% solid loading and its thermal decomposition characteristics in presence of nano TiO_2 catalyst were evaluated. The E_a values of the decomposition reaction of AN propellant samples were computed and plotted against α and are shown in Figure 4. The average activation energy computed for AN propellant yield 73 kJ mol^{-1} , whereas in presence of 1.6% and 4% TiO_2 nanocatalyst the propellant decomposition required an activation energy of 48 and 42 kJ mol^{-1} , respectively. These variations point towards significant catalytic activity by the nanocatalyst.

In the case of AN propellant, both catalyzed and non-catalyzed decompositions showed a dependence of E_a on α , indicating the possibility of a multistep reaction mechanism. It is quite reasonable to assume that propellants undergo a multistep kinetics controlled decomposition due to complex parallel reactions occurring during decomposition.

As it can be seen from the Figure 4, the E_a values gave consistent/realistic values only when the α values were between 0.05 and 0.80. Hence, for comparison the apparent activation energy only in this range was presented in Figure 4. The reason for apparent activation energy resulting in inconsistent values above $\alpha=0.8$, can be traced to the mass loss behavior (in the range of 673–773 K) of the propellant. For better understating, the differential ther-

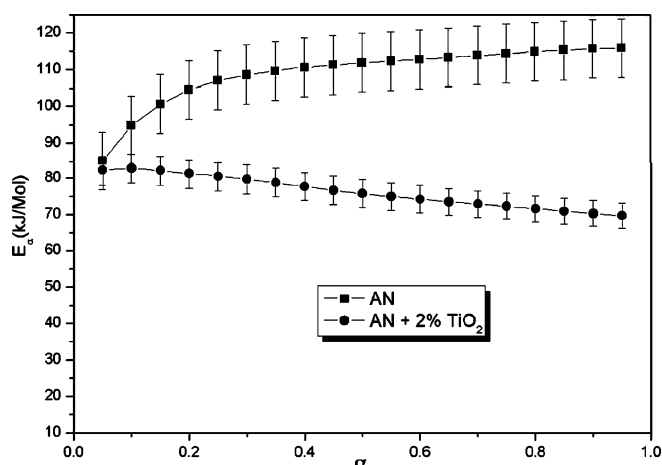


Figure 3. Variation of E_a with respect to reaction progress for AN and AN with nanocatalyst.

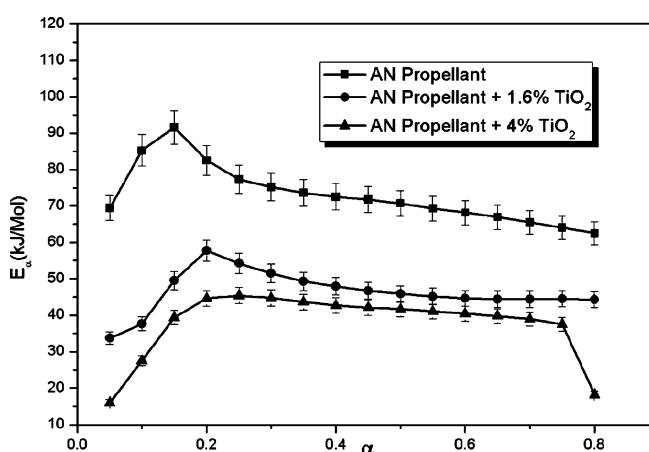
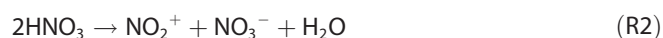


Figure 4. Variation of E_a with respect to reaction progress for AN propellant and AN propellant with nanocatalyst.

mogravimetry (DTG)-temperature curves (Figure S3 of Supporting Information) were examined. The DTG curve shows a major decomposition in the 373–523 K which reaches a peak mass loss of 3 % per degree Kelvin at 473 K and this peak major accounts for the oxidizer decomposition. However, another minor mass loss is observed in the range of 673–773 K with peak mass loss of 0.25 % per degree Kelvin. The rate of decomposition is significantly low in this region and isoconversional principle is not specifically obeyed, which lead to inconsistent α values. This decomposition, probably the removal of carbonaceous materials consequently caused the inconsistent E_{α} values above $\alpha=0.8$.

3.3 Mechanism of Catalytic Decomposition

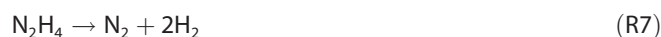
Even though the literature reports a variety of decomposition pathways that AN can undergo [1], it is widely accepted that the thermal decomposition is initiated by the vaporization of melted AN accompanied by an endothermic proton transfer reaction R1 [1,16]. The combustion behavior of AN mixtures with different additives, fuels, and energetic materials were intensely studied by earlier investigators [8]. The thermal decomposition mechanism of AN is highly dependent on temperature, and only the dissociative sublimation, which occurs around 473 K is endothermic in nature [1]. Since all other reported decomposition pathways are exothermic in nature, and the DSC curve indicated an endothermic decomposition, the possibility of reaction shown in R1 seems apparent in the present context. However, many secondary reactions occur rapidly in the gas phase between the dissociation products, NH_3 and HNO_3 . In the non-catalyzed AN decomposition, the HNO_3 further dissociates to form NO_2^+ , NO_3^- , and H_2O (R2). The NH_3 formed according to R1 is subsequently oxidized by the NO_2^+ through the reaction shown in R3, leading to an overall decomposition reaction given by R4 [5,8,16]. It is also suggested by different studies that the H_2O and NH_3 formed during the decomposition reaction presumably prevents the sustained burning of pure AN [8,16].



As reported earlier, solid and liquid phase gasification of AN occur at 443 K [15]. Also, the leading role of AN thermal gasification and subsequent gas phase reactions on the combustion of AN composite propellants is rightly pointed out by different investigators [17,18]. The gaseous products undergo exothermic redox reactions near the surface which governs gasification of AN and pyrolysis of the binder [17]. The burning catalysts could influence the burn-

ing characteristics of AN propellants mainly through heterogeneous catalysis of redox gas phase reactions [17]. Hence in presence of the nanocatalyst, the evolved gases might have undergone further reactions on the catalyst surfaces, consequently lowering the activation energy of the process.

In an earlier theoretical investigation [19], it was reported that the TiO_2 surfaces with different structures have quite different reactivities. Compared to anatase, brookite has slightly shorter interatomic distances and the structural building blocks are arranged in a different way. These differences significantly change the reactivity towards adsorption of various molecules, and most importantly, generate highly active sites at the junction between the different structural units [19]. The titanium atoms remaining after dehydroxylation are incompletely coordinated (and behave as Lewis acid centers) and can therefore fix either a water molecule or an ammonia molecule [20]. In fact, there are many studies which report the ammonia adsorption on the TiO_2 surface [21]. Furthermore, it is reported that the adsorbed ammonia undergoes an endothermic dissociation reaction on the nanocatalyst surface and give rise to N_2 through the decomposition of hydrazine produced by the dimerization of NH_2 species (R5–R7) [5,22,23]. Also, it is quite likely that the highly reactive acidic HNO_3 will undergo surface reactions and breakdown into smaller species.



3.4 Critical Temperature of Thermal Explosion (T_c)

One of the most important parameters for the thermal stability of high energy materials is the T_c under a given set of conditions. Especially, the thermal stability of AN is known to be significantly influenced by additives. The estimated values of T_c for the catalyzed and non-catalyzed AN samples are given in Table 1. In the tables, T_i is the onset temperatures obtained at different heating rates (β) and the T_{i0} is the onset temperature corresponding to $\beta=0$ calculated by the method referred in the Experimental Section.

Table 1. Calculated results of T_c for AN samples.

Sample	T_i^a [K]	T_{i0} [K]	E_{α} [kJ mol^{-1}]	T_c [K]
AN	446	438.7	90	458
	451			
	456			
AN TP2	434	431.2	76	453
	436			
	438			

a) Heating rates $\beta=2.5, 5$, and 10 K min^{-1} .

Table 2. Calculated results of T_c for AN propellant.

Sample	$T_i^{a)}$ [K]	T_{i0} [K]	E_a [kJ mol ⁻¹]	T_c [K]
AN propellant	449	434.1	72.9	458
	452			
	455			
AN propellant with 1.6 % TiO ₂	448	418.1	46.3	455
	451			
	453			
AN propellant with 4 % TiO ₂	442	407.1	42.3	446
	446			
	449			

a) Heating rates $\beta = 5, 6, \text{ and } 7 \text{ K min}^{-1}$.

Calculated T_c of AN can be used to evaluate the risk of spontaneous explosion and as evidently seen from the data (Table 1) the addition of nanocatalyst has reduced the T_c indicating a lesser stability. The T_c for the catalyzed and non-catalyzed AN propellant samples were also calculated and tabulated in Table 2. As is evident from the tabulated data, the T_c decreases with addition of nanocatalyst to both AN and AN propellant.

4 Conclusions

The catalytic effect of the synthesized TiO₂ nanoparticles on the solid state thermal decomposition reaction of AN and AN-based propellant was evaluated. The activation energy required for the decomposition reactions, computed by a nonlinear integral isoconversional method illustrates a substantial lowering, suggesting the catalytic activity. Irrespective of catalyst addition, AN propellant samples indicated a dependence of activation energy on the extent of conversion, pointing towards a multi step reaction mechanism. Presumably, the TiO₂ nanocatalyst assist the removal of AN dissociation products NH₃ and HNO₃ by providing Lewis acid and/or active metal sites and thereby enhances the reactivity and the decomposition rate. The findings suggest the application of TiO₂ nanocatalyst in the catalytic decomposition reactions of solid propellants, eventually leading to the application as burn-rate catalyst for environmentally benign solid propellant systems. Though, the catalytic effect was clearly evident, thermal analysis in combination with evolved gas analysis would be very helpful to reveal the discussed reaction pathways.

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