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Thermal Decomposition and Kinetic Evaluation of Composite Propellant Material Catalyzed with Nano Magnesium Oxide

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Abstract

Magnesium oxide nano particles have been used to catalyze the composite propellant material based on hydroxy terminated polybutadiene (HTPB) and ammonium perchlorate (AP). Thermal decomposition and the kinetic parameters of catalyzed and non-catalyzed version of the composite solid propellant have been investigated in the present work. X-ray diffraction (XRD) technique and scanning electron microscope (SEM) were used to characterize the MgO nano particles before they were added to the propellant material. The average size of the particles was found to be approximately 20-30 nm. The Arrhenius kinetic parameters of both versions of the propellant were evaluated using Kissinger method. Moreover, three isoconversional methods also have been used for the kinetic analysis of both versions of propellant. These methods include Friedman method, Flynn–Wall–Ozawa method and Kissinger-Akahira-Sunose Method. The comparative analysis of the kinetic parameters as well as the thermal behavior of pure and catalyzed composite solid propellant (CSP) has been done under identical set of reaction conditions. The results indicate that MgO nano particles have an obvious catalytic effect on the thermal decomposition of the composite propellant and consequently, the kinetic parameters also change significantly. The decomposition peak temperature of the propellant decreased nearly 22°C due to the addition of two percent of MgO as a catalyst. The activation energy of the catalyzed propellant however, increased by 28 $kJmol^{-1}$ from 127.1 $kJmol^{-1}$ to 155.4 $kJmol^{-1}$. Both the frequency factor and the rate constant increased in the catalyzed version of the propellant material and confirmed that a noticeable catalytic activity has taken place.

Keywords: Composite propellant, Kinetics, DSC, Arrhenius parameters, MgO nano particles

Introduction

Composite solid propellant (CSP) compositions are generally made up of some inorganic oxidizer such as ammonium perchlorate (AP) and a polymeric binder such as hydroxyl-terminated polybutadiene (HTPB) [1,2]. Ammonium dinitramide (ADN) and Hydrazinium Nitroformate (HNF) are some of the emerging oxidizers in the field of composite propellants. Ammonium perchlorate however is still the most preferred choice because of its well-known advantages that include good oxygen balance, fairly high density and reasonable compatibility with rest of the ingredients. The researchers working in the field of energetic materials have always been keen to investigate the influence of various additives particularly transition metal oxides (TMO) on the thermal cum kinetic behaviour of the AP and AP based composite solid propellants [3-5]. The effect of a small amount of nano magnesium oxide catalyst on the thermal degradation and kinetic parameters of the composite solid propellant has been presented in this work.

The transition metal oxides are frequently used for catalyzing the thermal decomposition of HTPB /AP based CSP and to adjust their burn rates. In this regard, various factors such as the amount of catalyst, the particle size and exposed surface area of the particles have been known to play important role for the alteration of burn rates [6]. Although, conventional catalysts with particle size in the range of micrometers also have the capability to catalyze the decomposition composite propellants, however, nano sized catalysts are generally preferred. The nano particles have more exposed surface area due to which they are expected to significantly enhance the catalytic activity.

Many researchers have investigated the impact of micro and nano sized catalysts on the thermal cum kinetic pattern of ammonium perchlorate and composite propellants. Xuefei et al synthesized ZnO twin cones and used them to catalyze the thermal decomposition of AP [7]. The zinc oxide catalyst in the form of twin cones had a pronounced catalytic effect on ammonium perchlorate and lowered the decomposition temperature prominently. However, the authors have not carried out the kinetic analysis of the catalyzed AP in this work. Prajakta R. et al examined the influence of ferric oxide nano particles on the thermal degradation of the composite solid propellant and found that catalyzed propellant produced a 40 percent higher heat release as compared to the non-catalyzed sample [8]. The authors, interestingly, reported a noteworthy increase in the value of activation energy for catalyzed version as opposed to the common tendency of decrease in the activation energy. Likewise, Duan et al studied the effect of nano MgO on the thermal behaviour of ammonium perchlorate [9]. The authors found that magnesium nano particles strongly catalyzed the thermal decomposition of AP and amount of catalyst also played an important role during the catalytic reaction.

In this work, we have investigated the catalytic effect of nano magnesium oxide on the thermal cum kinetic behaviour of the composite propellant containing ammonium perchlorate as an oxidizer and HTPB as a polymeric binder and fuel. SEM and XRD were used to characterize the MgO particles before incorporating in the propellant composition. The main focus in the present work was to calculate the changes in the kinetic parameters of catalyzed and non-catalyzed compositions of the propellant by four different kinetic methods including Kissinger method, Friedman method, Flynn–Wall–Ozawa method and Kissinger-Akahira-Sunose Method.

Energetic materials including propellants, explosives and pyrotechnics are often investigated by using different thermal analysis techniques and methods [10-12]. These techniques require a very minute quantity of the sample during the analysis and therefore considered to be safe for investigation of energetic materials. Differential scanning calorimetry and thermogravimetery are two of the most commonly used thermal analysis techniques for analyzing the thermal decomposition and kinetic parameters of different materials especially energetic composition [13-15].

Methods

Composite solid propellant used in the present work has been synthesized by the national development complex, Pakistan. The composite propellant comprises of 80 percent ammonium perchlorate, 15 percent binder (HTPB) and remaining 5 percent additives. Two different versions of the propellant have been investigated in the present work of which one has been catalyzed with 2 percent of magnesium oxide nano particles. Before mixing with the propellant, the nano particles were characterized with X-ray diffraction (XRD) and the scanning electron microscope (SEM). For the structural analysis, XRD instrument with Cu kα radiations was used. The magnesium oxide sample was scanned from 20° to 80° during the analysis. Magnesium oxide micrographs were taken with JSM- 6490 LA, JEOL scanning electron microscope. Thermal analytical techniques including differential scanning calorimetry (DSC) and thermogravimetery (TG) have been used for the thermal cum kinetic analysis of both the versions of propellant. Thermal analysis instrument by Mettler Toledo model number DSC823e was used for the investigation of propellant samples. The samples were placed in the aluminum crucibles and heated up to 550°C from room temperature to elucidate the entire thermal decomposition process. To maintain an inert atmosphere during the analysis of all the samples, nitrogen gas with a flow rate of approximately 50 ml min^{-1} was used. Multiple heating rate experiments were carried out for both versions of the propellant to carry out the non-isothermal and isoconversional kinetic analysis. Sample heating rates of 10°C min^{-1}, 20°C min^{-1}, 30°C min^{-1} and 40°C min^{-1} were used. Mass of the samples used for experimentation was kept small due to the energetic nature of the composite propellant (1.5 to 2 mg). Heat flow and mass loss data obtained under above mentioned conditions was used for the kinetic evaluation of the propellant by four different methods

Brief Descriptions of the Kinetic Methods

Thermal decomposition of the energetic materials is best described by the kinetic evaluation of the reaction. Thermal cum kinetic analysis of the propellants gives meaningful information regarding their thermal stability and reactivity. The kinetic evaluation of catalyzed and non-catalyzed composite propellant has been carried out by non-isothermal and isoconversional methods. The methods include Kissinger method, Friedman method, Kissinger-Akahira-Sunose method and Flynn–Wall–Ozawa method. Brief explanation of all the four methods is given below.

Kissinger Method

Kissinger method has been derived from the fundamental kinetic equations and therefore it can be used for kinetic evaluation of wide range of materials. In this method, heat flow data at multiple heating rates is used for estimation of the Arrhenius kinetic parameters. Kissinger had suggested different ways in which the kinetic parameters can be estimated from the heat flow data [16].

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{A}{RT}\right) - \frac{E}{R}\cdot\frac{1}{T_p} \text{ for } n = 1 \tag{1}$$

In equation (1), β represents the heating rate at which the experiment was performed, β A is pre-exponential factor or frequency factor, R represents the gas constant, E represents the energy of activation(kJmol^{-1}) and n is the reaction order. When the reaction order is not 1, then the Kissinger relationship takes the following form [17, 18].

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{C_o^{n-1}\,.\,A\,.\,R}{E}\right) - \frac{E}{R}\cdot\frac{1}{T_p} \tag{2}$$

$$\text{for } n > o \text{ and } n \neq 1$$

Equation (2) explains how kinetic parameters can be determined with this method. The plot of left hand side of the above equation versus the reciprocal peak temperature gives a nearly straight line. The slope of this line can be used for calculation of the activation energy. When E is known, the frequency factor can be calculated from the following equation [19, 20].

$$A = \left[\beta E \exp\left(\frac{E}{RT_p}\right)\right] / RT_p^2 \tag{3}$$

The rate constant can be easily calculated using Arrhenius relationship given below.

$$k = A \exp(-E/RT_p) \tag{4}$$

The enthalpy of activation can also be calculated once energy of activation is known by using the following relationship.

$$\Delta H^{\neq} = E - RT \tag{5}$$

Flynn Wall Ozawa Method

The isoconversional kinetic methods provide significant and large amount of activation energy data corresponding to certain specific degrees of conversion. The methods are based on basic kinetic equations and therefore can be applied to variety of materials. The isoconversional methods allow model free estimation of the activation energies. Flynn-Wall-Ozawa is an integral isoconversional method named after the scientist who proposed it. This method is based on a basic assumption that temperature dependence of the kinetic equation is that of Arrhenius type and the method has been further simplified by using the Doyle approximation[21]. Final form of the FWO method is presented in equation (6).

$$\ln\beta = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.523 - 1.0518\left(\frac{E}{RT}\right) \tag{6}$$

Where, β represents the heating rate in °C min^{-1}, A is the pre-exponential factor also called frequency factor , α represents the extent or the degree of conversion, E is energy of activation (kJmol^{-1}) and R is the universal constant.

The Plot of $\frac{1}{T}$ versus lnβ for some specified conversion (α) is obtained at multiple heating rates. E is then determined from the slope of the straight line obtained from the FWO graph. The process may be repeated for several times for any degree of conversion and corresponding value of activation energy is calculated.

Friedman Method

Friedman proposed a differentia method which is widely used by scientific community for the isoconversional kinetic analysis of different materials. It is a model free method and may be used to determine numerous activation energy values for different degrees of the conversion [22]. The final equation representing the Friedman kinetic analysis method is presented in equation (7).

$$\ln\left(\beta\frac{d(\alpha)}{dT})\right) = \ln[Af(\alpha)] - \frac{E}{RT} \tag{7}$$

In this equation, β represents the heating rate (°C min^{-1}), α is the extent or degree of conversion, A is the pre-exponential factor or the frequency factor, E represent the energy of activation (kJmol^{-1}) and R is the gas constant.

Plot of the reciprocal temperature against the left hand side of equation (7) gives a straight line whose slope is used to calculate the activation energy corresponding to desired degree of conversion.

Kissinger-Akahira-Sunose Method

This method is modified version of the basic Kissinger method but the main modification is that the temperature for a specific conversion α (T_α) is used instead of peak temperature (T_p) for constructing a plot of reciprocal temperature versus $\ln\left(\frac{\beta}{T_\alpha^2}\right)$. The method makes use of the Coats-Redfern approximation of temperature integral [23]. The final form of the Kissinger-Akahira-Sunose Method is presented in equation (8).

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{A\,.\,R}{E_a\,g(\alpha)}\right) - \frac{E}{RT_\alpha} \tag{8}$$

In the above equation, T_α represents the temperature pertaining to some definite degree of conversion α, β is the heating rate, E is the activation energy (kJ/mol), A is pre-exponential factor and R is the gas constant.

Results and Discussion

Characterization of Nano Particles

Particle size and the morphology of catalyst play an important role in its catalytic behaviour and therefore, a summary of these characteristics has been presented for nano particles of magnesium oxide. Fig. 1(a) shows the SEM micrograph of the M

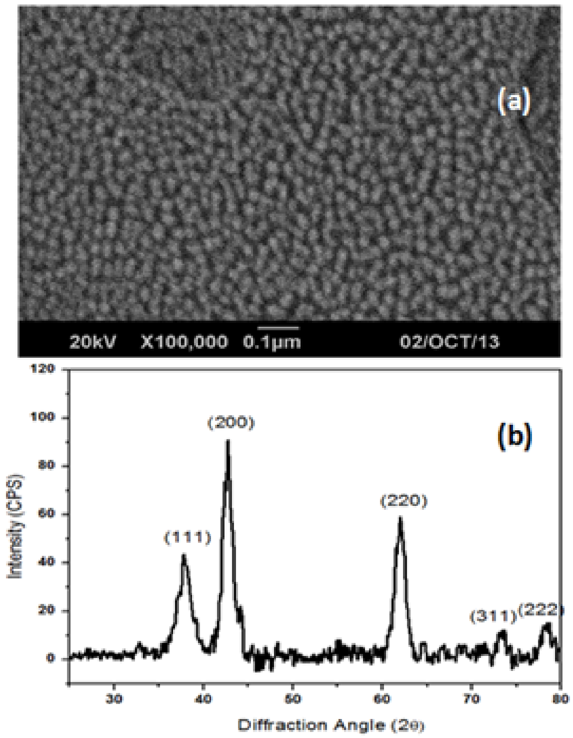


Fig. 1: (a) SEM micrograph of MgO nano particles and (b) XRD spectra of cMgO nano particles

The particles are seen to be well dispersed and exhibit regularity in their morphology. The particles are not perfectly spherical rather they seem to be elliptical in shape. The measurements from the SEM micrograph show that average diameter of the magnesium oxide particles is between 20 to 30 nm (measured for the elongated side). On the other hand, the average diameter was found to be nearly 15 to 20 nm for the shorter side. The size of MgO particles is therefore well within the range of nano meters and considered to be very suitable for its use as a catalyst.

XRD spectra of the MgO nano particles have been presented in fig. 1(b). There are five main diffraction peaks in the spectra which are located at a peak position of 37.9°, 42.6°, 62.2°, 73.3°, 78.4°. The diffraction data agrees well with the reference pattern No 01-074-1225 and the above mentioned peaks represent magnesium oxide (MgO). The Miller Indices corresponding to all the have been marked in the figure. The diffraction peaks are not very sharp showing that the particles are not very crystalline and have a small particle size. Scherer formula has been used to calculate the crystallite size of the nano particles and the average crystallite size has been found to be nearly 9nm.

Thermal Analysis of Composite Propellant

Thermal analysis of composite propellant has been carried out in the temperature range of 50°C-550°Cto investigate the thermal decomposition process and to evaluate the kinetic parameters. The DSC curves at multiple heating rates are presented in Fig. 2.

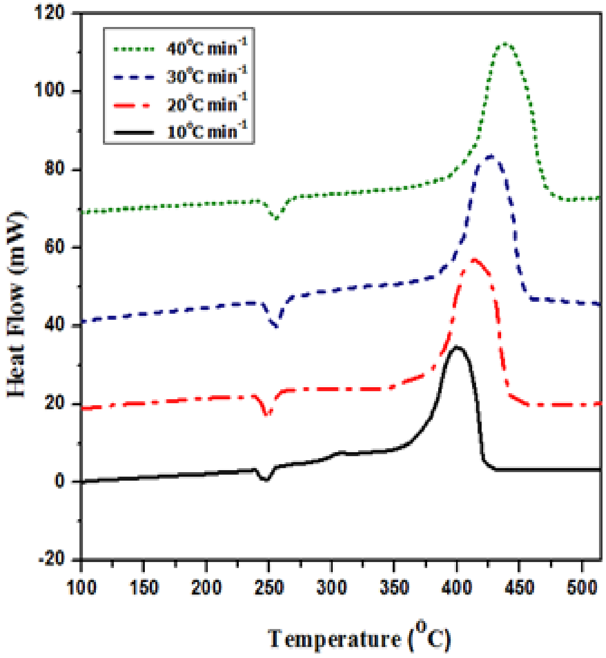


Fig. 2: DSC curves of composite propellant at multiple heating rates

Two prominent peaks can be seen from the figure in each curve. The first peak which is endothermic in nature represents a solid state phase transformation of the AP present in the propellant. This phase transformation changes the crystal structure of ammonium per chlorate from orthorhombic to cubic [24]. The peak appears close to a temperature of 250°C and is not seen to be effected much by the increasing heating rates. The next peak is exothermic in the nature and corresponds to the decomposition of the composite propellant. This peak shifts to higher temperatures with the increase in the heating rates. The peak appears at a temperature of 398.8°C at the heating rate is 10°C min^{-1} and shifts to a temperature of 437.9°C at a heating rtae of 40°C min^{-1}. The details of the peak temperatures of composite propellant at different heating rates are presented in Table 1. Ideally speaking, the peak temperature should not change with the change in the heaing rate but the experimental results confirm that the heating rate effects the decompositions peak temperatures. At higher heating rates, the sample is exposed to the same heating range for less time and therefore thermal lag phenomina comes into play. Many researchers working in the field of energetic materials have reported the similar trend for the multiple heating rate experiments [25, 26] .

The decomposition and associated kinetics of composite propellant are essentially dependent on its ingredients especially the oxidizer and the binder i.e. ammonium perchlorate and HTPB in this case. The HTPB binder provides a matrix to hold different ingredients of the propellant and also acts as a fuel to facilitate the combustion. The TG curve of the composite solid propellant has been presented in Fig. 3. The mass loss of the composite propellant starts near a temperature of 240°C. The mass loss is initially slow and represents the decomposition of the plasticizer present in the propellant. There is rapid loss in the mass of the sample beyond 330°C indicating the simultaneous decomposition of the HTPB binder and AP present in the propellant due to strong binding between them. During this stage of the mass loss, it is difficult to determine the exact contribution of the each component of the composite propellant; however, the major mass loss is primarily due to AP with a simultaneous decomposition of the binder. It is also confirmed by the TG curve that the decomposition shifts to higher temperatures when the heating rates are increased.

Table 1: Kinetic data obtained by Kissinger Method for non-catalyzed and catalyzed composite propellant

	Heating Rate (°C min^{-1})	Peak Temperature (°K)	E_a (kJ mol^{-1})	A (sec^{-1})	k (sec^{-1})	$?H^{\neq}$ (kJ mol^{-1})
Non-catalyzed	10	671.8	127+7%	44.6 x 10^6	5.66 x10^{-3}	121.4
	20	687.5		49.4 x 10^6	10.7 x10^{-3}	
	30	700.1		47.9 x 10^6	15.6 x10^{-3}	
	40	710.9		44.4 x 10^6	20.1 x10^{-3}	
Catalyzed	10	650.1	155.4±2%	22.5 x 10^9	7.37 x 10^{-3}	149.8
	20	664.5		23.1 x 10^9	14.1 x 10^{-3}	
	30	673.6		23 x 10^9	20.5 x 10^{-3}	
	40	680.9		22.3 x 10^9	26.8 x 10^{-3}	

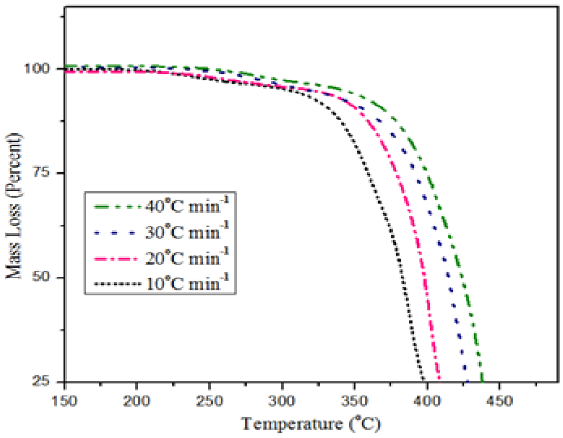


Fig. 3: The TG curves of the composite solid propellant at multiple heating rates

The propellant sample in this case is made up of 80 percent ammonium per chlorate, therefore, it was expected that the thermal behaviour of the composite propellant will be similar to AP. However, comparison of the thermal behaviour of composite propellant with AP showed some variation. We had observed in our earlier published work on the thermal behaviour of different oxidizers that AP decomposition showed two main exothermic peaks related to low and high temperature decomposition steps of AP as opposed to a single exothermic peak representing the decomposition of CSP in this case [27]. This is thought to be due to the strong binding of the AP particles in the polymeric matrix of HTPB which also acts as a fuel and simultaneous decomposition of the HTPB and AP takes place.

Thermal Analysis of Catalyzed Composite Propellant

Thermal analysis of the composite propellant catalyzed with magnesium oxide nano particle has also been carried out in the temperature range of 50°C-550°C. The DSC curves for catalyzed composite propellant at multiple heating rates are presented in Fig. 4. The curve for the catalyzed propellant also shows two main peaks similar to non-catalyzed version of the propellant. First peak related to phase transformation of AP did not change much and appeared nearly at the same temperature close to 250°C. The second peak however has changed a lot in terms of its position and shape. The peak appears at a temperature of 377.1°C at a heating rate of 10°C min-1. This means that the decomposition temperature of the catalyzed composite propellant has lowered by approximately 22°C due to addition of MgO nano particles. Moreover, the decomposition peaks in the catalyzed propellant are relatively sharp as compared to the ones for non-catalyzed propellant. The decomposition peaks in this case also shift to higher temperatures when the heating rates are increased. The peak temperatures for the catalyzed version of propellant are 377.1°C, 391.5°C, 400.6°C and 407.9°C respectively for heating rates of 10_{o}C min^{-1}, 20_{o}C min^{-1}, 30°C min^{-1} and 40°C min^{-1}.

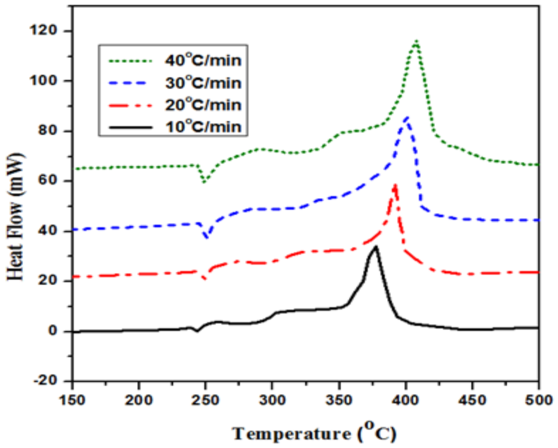


Fig. 4: The DSC curves for catalyzed composite propellant at multiple heating rates

The TG curves for the catalyzed propellant are shown in Fig. 5 at different heating rates. The mass loss is initially slow in this case as well and represents the decomposition of the plasticizer present in the propellant. There is rapid loss in the mass of the sample beyond 300°C indicating the simultaneous decomposition of the HTPB binder and AP present in the propellant due to strong binding between them. The TG curve also confirms lowering of the decomposition temperature in the catalyzed version of propellant. The effect of heating rate is similar to the one seen for non-catalyzed sample of composite propellant.

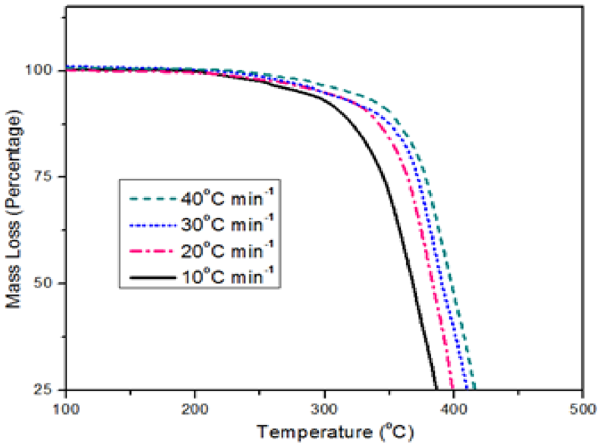


Fig. 5: The TG curves for the catalyzed propellant at multiple heating rates

Kinetic Evaluation of Composite Propellant

Four different methods have been used to estimate the kinetic parameters of composite solid propellant. The guidelines provided by international committee of thermal analysis and calorimetry (ICTAC) have been followed for the conduct of experiments for kinetic evaluation [28]. The Kissinger graph for non-catalyzed composite propellant is presented in figure 6. The activation energy of the composite solid propellant calculated using Kissinger method is 127.1kJ mol^{-1}. The activation energy of HTPB/AP based propellant in our case is quite close to the reported values in the published literature. Rocco et al investigated the thermal decomposition of composite propellant containing AP and HTPB [29]. The authors found that the activation energy of composite propellant came out to be 126.2 kJmol^{-1} by the Kissinger method and134.5 kJmol^{-1} by the Ozawa method. The activation energy of composite propellant was further used to calculate the pre-exponential factor, reaction rate constant and the enthalpy of activation and the kinetic data is summarized in table 1. It is seen from the table 1 that the pre exponential factor shows slight variation with respect to the change in the decomposition peak temperature. Average value of the pre exponential factor in this case has been found to be 46.5 x10^{6} s^{-1}. The rate constant of the non- catalyzed propellant is 5.66 x 10^{-3} for peak temperature corresponding to a heating rate of 10°C min^{-1} and its value increases as the peak temperature increases.

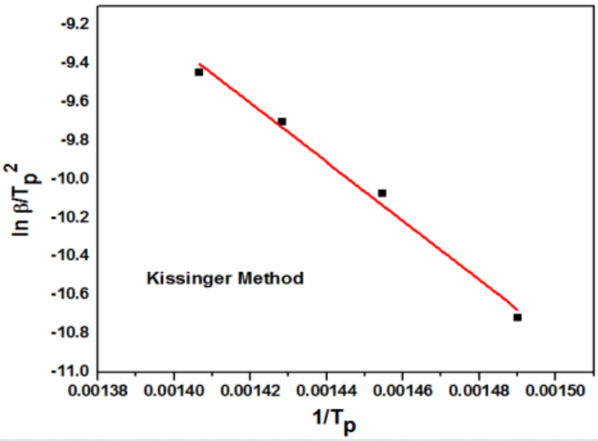
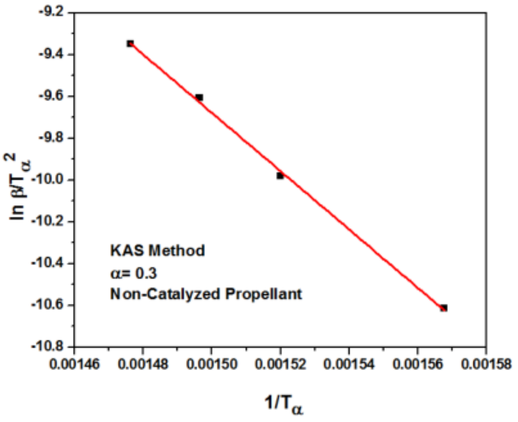
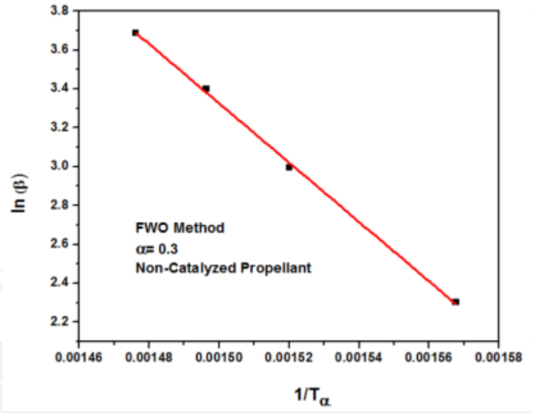


Fig. 6: The Kissinger graph for non-catalyzed composite propellant

It is important to highlight here that the thermal decomposition of the composite propellant is an intricate and multistep process. The decomposition process is temperature dependent due to which the activation energy is expected to show variations for different degrees of the sample conversion. Therefore, to clarify the mechanism of thermal decomposition and to quantify the variation of activation energy with respect to the conversion degree, kinetic evaluation has also been carried out by three isoconversional methods. Fig. 7(a), 7(b) and 7(c) shows the representative graphs of different isoconversional methods used for kinetic evaluation of the non-catalyzed composite propellant for (α=0.3).



(a)



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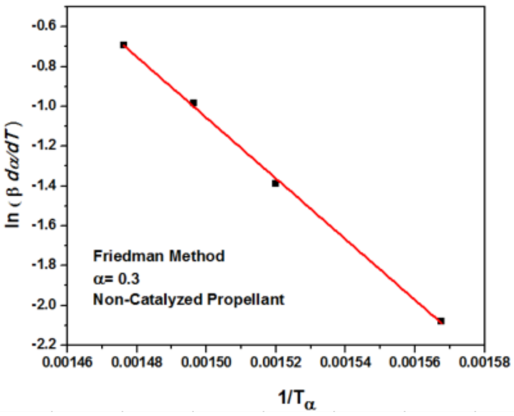


(c)

Fig. 7 (a,b,c) Representative graph of (a) Friedman,(b) Flynn–Wall–Ozawa and (c) Kissinger-Akahira-Sunose method for kinetic evaluation of the non-catalyzed composite propellant. The energy of activation for six different conversion degrees i.e. α = 0.2, α = 0.3, α = 0.4, α = 0.5, α = 0.6 and α = 0.7 has been calculated. It was found that the activation energy for composite propellant came out to be 116 kJ/mol, 126.9 kJ/mol and 133.5 kJ/mole for KAS, Friedman and FWO method respectively (α=0.3). The activation energy data for the different degrees of conversion has been shown in table 2 for all the three isoconversional methods.

Table 2: Activation energy data corresponding to different degrees of conversion for non- catalyzed and catalyzed composite propellant

		Activation Energy *(E_{α})					
	Method	$E_{0.2}$	$E_{0.3}$	$E_{0.4}$	$E_{0.5}$	$E_{0.6}$	$E_{0.7}$
Non catalyzed	KAS	115.8	116	121.9	116.6	112.7	114.5
	Friedman	126.5	126.9	133	127.8	124	125.9
	FWO	133	133.5	139.9	134.5	130.5	132.4
MgO Catalyzed	KAS	118.8	142.6	152.5	160.4	157.5	164.2
	Friedman	132.2	153.2	163.3	171.3	168.5	175.3
	FWO	139.1	161.2	171.8	180.1	177.2	184.4

***(Eα) represents the activation energy corresponding to a specific degree of conversion (α)**

The data presented in Table 2 shows that the activation energy calculated with different isoconversional methods is different from each other. However, the activation energy trend for different degrees of conversions is the same for all the three methods.

Kinetic analysis of the composite solid propellant revealed that activation energy values change as a function of degree of conversion (α). The "E" versus "α" curve of the non-catalyzed version of the composite propellant is shown in Fig. 8 which highlights the activation energy trend against the extent of conversion (α) by different kinetic evaluation methods.

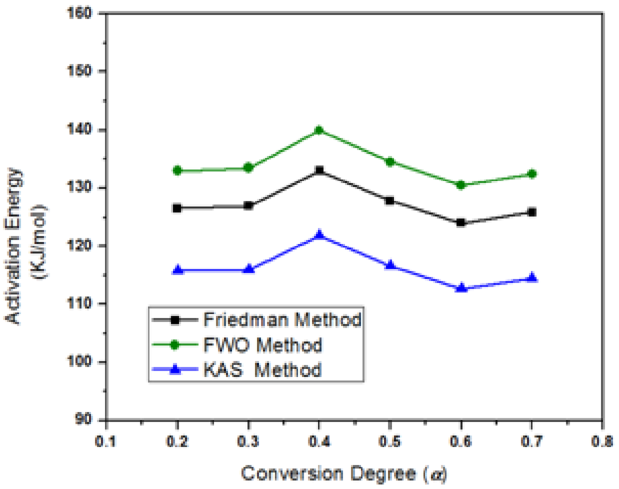


Fig. 8: The "E" versus "α" curve of the non-catalyzed version of the composite propellant

Kinetic Evaluation of Catalyzed Composite Propellant

Kinetic analysis of the MgO catalyzed composite solid propellant has also been carried out by four different methods. The multiple heating rate experiments were performed under exactly the same set of experimental conditions to investigate the effect of the catalyst on the kinetic behaviour of composite propellant. The Kissinger method for catalyzed version of the propellant has been depicted in Fig. 9.

Data presented in Table 1 shows that the activation energy calculated from the slope of the Kissinger graph came out to be 155.4 kJ mol^{-1} for the catalyzed propellant. This value is higher than the activation energy of 127.1 kJmol^{-1} for the non-catalyzed version of the propellant calculated by the Kissinger method. The average value of the frequency factor or the pre exponential factor in this case has been found to be 22.7 X 10^{9} and it is nearly three orders of magnitudes higher than the value obtained for non-catalyzed propellant. The rate constant in this case is 7.37 x 10^{-3} which is nearly 30 percent higher than that of the non- catalyzed propellant.

Generally speaking, the addition of catalyst should have lowered the value of activation energy but in our case the experimental results and the kinetic evaluation shows that it has rather increased. During the literature survey, it was found that the activation energy of AP may increase or decrease by the addition of catalyst and the results differ from case to case. Some researchers have reported on the basis of actual experimental results that the activation energy of ammonium perchlorate was found to increase after the catalytic activity [8, 30, 31]. It is important to note here that the rate constant has increased by 30 percent despite the increase in the activation energy. The main reason for this is that the rate constant has a very strong dependence on the frequency factor A which has increased by three orders of magnitude and therefore, the overall rate constant has increased.

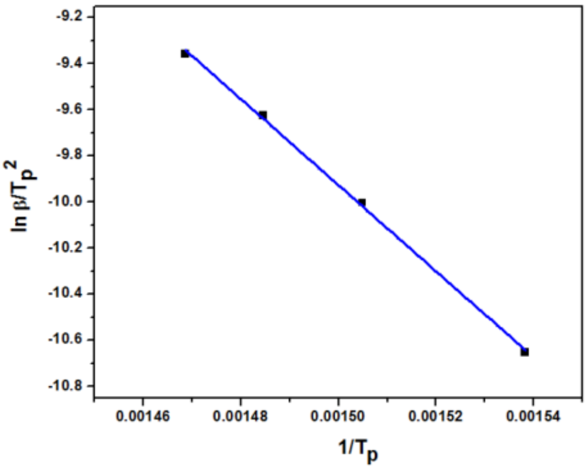
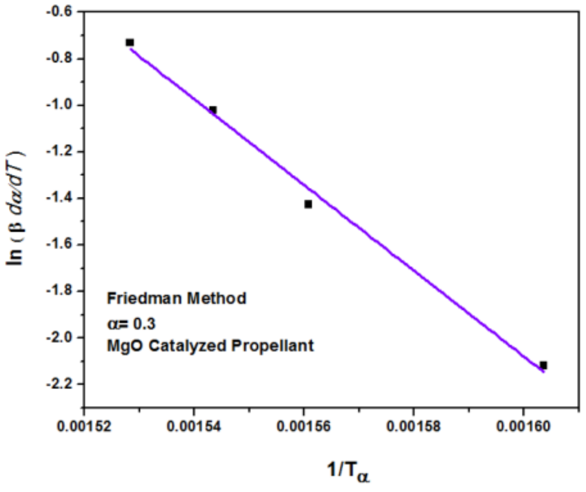


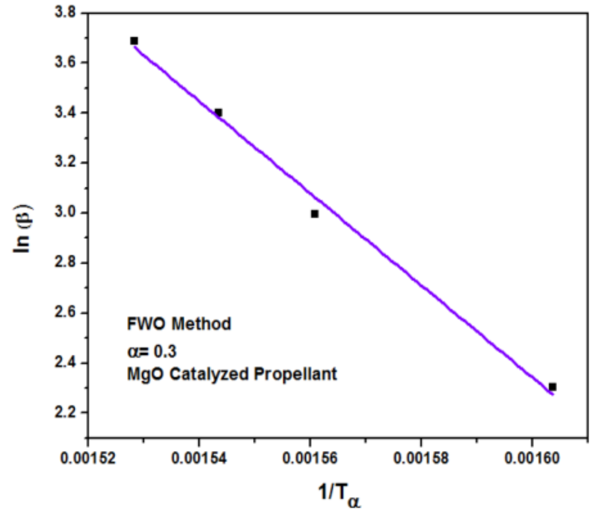
Fig. 9: The Kissinger graph for catalyzed version of the propellant

The rate constant further increases with the increase in the peak temperatures. The comparative analysis of the two versions of the propellant by Kissinger method clearly indicates that the kinetic behaviour of the composite propellant has significantly changed by the addition of nano magnesium oxide as a catalyst. The activation energy of the catalyzed propellant has increased by 22 percent and the frequency factor has increased tremendously by 3 orders of magnitude. It is worth mentioning here that the overall reactivity of the composite propellant has increased due to addition of the catalyst because the rate constant has increased by nearly 30 percent.

The isoconversional analysis of the non-catalyzed propellant showed that the activation energy value changes as the degree of conversion increases. Therefore, it was obligatory to carry out the isoconversional kinetic analysis of the catalyzed propellant as well to elucidate the changes caused by the catalyst. Three different isoconversional methods have been used for the analysis which includes Friedman method, Flynn–Wall–Ozawa method and Kissinger-Akahira-Sunose method. With each kinetic method, activation energy has been calculated at six different values of conversion (α) i.e. $\alpha = 0.2$, $\alpha = 0.3$, $\alpha = 0.4$, $\alpha = 0.5$, $\alpha = 0.6$ and $\alpha = 0.7$. The representative graphs of all the three kinetic evaluation method are presented in Fig. 10(a), 10(b) and 10(c).



(a)



(b)

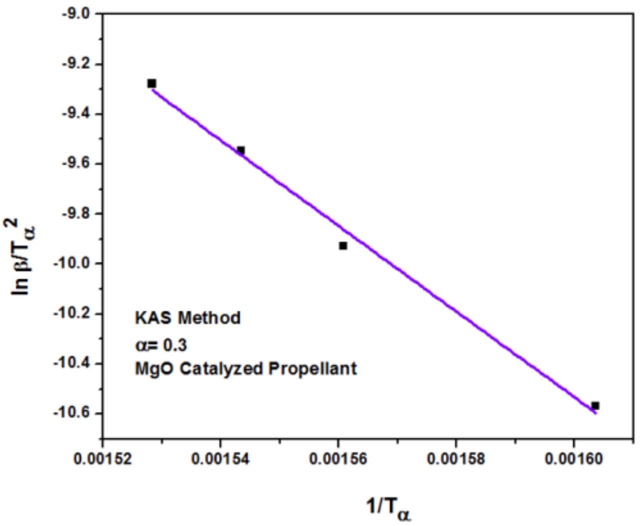


Fig.10: (a,b,c) Representative graph of (a) Friedman,(b) Flynn–Wall–Ozawa and (c) Kissinger-Akahira-Sunose method for kinetic evaluation of the catalyzed composite propellant

The detailed analysis of the catalyzed propellant showed that the activation energy has increased by the addition of the catalyst throughout the decomposition process. The increase in activation energy was confirmed by all the three isoconversional methods. For instance the activation energy of the non-catalyzed propellant at 30 percent conversion ($\alpha = 0.3$) was found to be 116 kJ/mol, 126.9 kJ/mol and 133.5 kJ/mol for KAS, Friedman and FWO method respectively. Whereas, for the same degree of conversion ($\alpha = 0.3$), the activation energy values of the catalyzed propellant were found to be 142.6 kJ/mol, 153.2 kJ/mol and 161.2 kJ/mol respectively KAS, Friedman and FWO method. Similar kind of increase can be seen for the other degrees of conversion from Table 2.

We had noted for the non-catalyzed propellant that the activation energy depends on the degree of conversion and shows the variation. Similarly, the catalyzed propellant also shows variation in the activation energy values for different conversions. The "E" versus "α" curve of the catalyzed version of the composite propellant has been shown in Fig. 11 which indicates the activation energy trend against the degree of conversion (α) by three isoconversional methods. The degree of conversion (α) is determined from the experimental TG data. It is fraction of the mass converted to products.

It is evident from the thermal and kinetic analysis presented above that the magnesium oxide nano particles play an important role in catalyzing the thermal decomposition of the composite propellants. Similarly some other transition metal oxides (TMOs) are also reported in literature for catalyzing the decomposition of the AP and AP containing composite propellants. However, the mechanism of effect by which these TMOs influence the thermal cum kinetic behaviour of composite solid propellant is not yet clearly established even today. Ebrahim et al has suggested

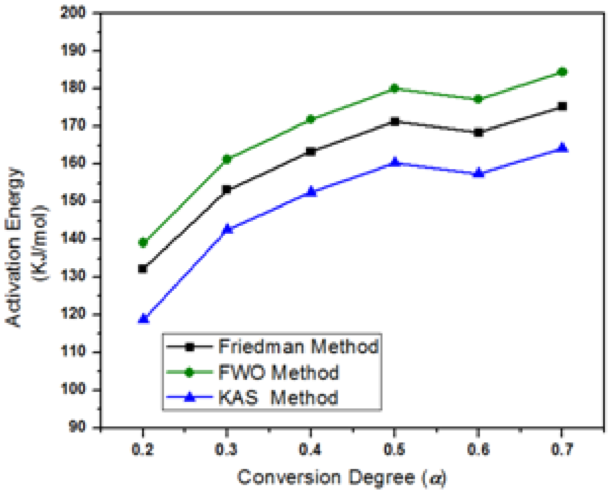


Fig. 11: The "E" versus "α" curve of the catalyzed version of the composite propellant

an electron transfer mechanism for the thermal decomposition of AP by using p type semiconductors as a catalyst (CuO in their case). The authors proposed that catalyzed thermal decomposition of AP involves transfer of electron from perchlorate ion to ammonium ion [32]. There are many holes on the surface of 'p' type semiconductors such as MgO in this case and these holes help in accelerating the electron transfer process.

$$ClO_4^- + e^-_{oxide} \rightarrow ClO_3^- + O_{oxide} \rightarrow ClO_3^- + e^-_{oxide} + \tfrac{1}{2}O_2 \qquad (9)$$

"O_{oxide}" represents an oxygen atom abstracted from the oxide and "e^-_{oxide}" is the positive hole in the valence band of the oxide.

Conclusions

The thermal cum kinetic analysis of the two versions of the composite propellant indicates that magnesium oxide nano particles have a strong catalytic effect on both the thermal as well as the kinetic behaviour of the composite solid propellant. DSC results show that the peak temperature of the thermal decomposition of the composite propellant has decreased by 22°C due to the catalytic activity. Lowering of the peak temperature is also confirmed by the TG results. The kinetic data showed that the activation energy value in the catalyzed propellant has increased. The frequency factor of the catalyzed propellant was found to be three magnitudes higher than the non-catalyzed version. The overall rate constant increased by nearly 30 percent despite increase in the activation energy due to a noticeable increase in the frequency factor A. Isoconversional kinetic analysis of both versions of the propellant revealed the variation of activation energy with respect to the degree of conversion (α). The isoconversional analysis also confirmed the increase in activation energy of the catalyzed propellant. The decrease in peak temperature and increase in the rate constant of the catalyzed propellant reflect the effectiveness of the catalyst. The effect of heating rate is similar for both the versions and the decomposition peaks are shifted to higher temperatures as the heating rates are increased.

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