

Catalysed combustion of ammonium perchlorate, polystyrene and their composite propellants

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The combustion behaviours of ammonium perchlorate (AP), polystyrene (PS) and (AP+PS) propellant have been studied thermogravimetrically using $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($0 \leq x \leq 1$) phases as catalysts. Catalyst NiCr_2O_4 is found to be the most efficient amongst all the phases for thermooxidative degradation of PS. The phase, $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{O}_4$ facilitates thermal decomposition of AP and propellant to a greater extent as compared to other phases. Effect of catalyst in the enhancement of the combustion/burning rate of propellant is found to be through AP. The condensed phase reactions occurring at lower temperatures also affect the exothermic gaseous phase reactions at higher temperatures during the combustion of propellant.

The combustion of composite propellant containing oxidizer, ammonium perchlorate (AP), and polymeric fuel, polystyrene (PS) is affected in presence of small amount of the catalysts¹⁻³. The effect of additives on the combustion behaviour of AP and the catalytic effect of CuCr_2O_4 on decomposition/combustion reactions of AP, PS and (AP+PS) propellant have already been studied^{1,2,4-10}. It has been observed that some mixed spinel phases such as CuCrFeO_4 , $\text{CuCr}_{1.75}\text{Fe}_{0.25}\text{O}_4$, and $\text{CuCr}_{0.5}\text{Fe}_{1.5}\text{O}_4$ are found to be active catalysts for low temperature thermal decomposition of AP¹¹. It is also reported that mixed oxide phases such as $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($0 \leq x \leq 1$) and $\text{NiCr}_{2-x}\text{Fe}_x\text{O}_4$ ($0 \leq x \leq 2$) significantly catalyse the burning rate of (AP+PS) propellant¹.

The enhancement in the burning rate of the propellant may be due to the acceleration in several steps of propellant combustion such as decomposition of AP, degradation/decomposition of PS, condensed phase reactions between AP and PS prior to ignition and gas phase exothermic reactions between the pyrolytic products of oxidizer (AP) and fuel binder (PS) with appearance of flame due to subsequent reactions. In order to have a wider spectrum of the role of catalysts on the above mentioned steps of combustion, the present work on the thermal decomposition/degradation kinetics of AP, PS and (AP+PS) composite propellant has been carried out using $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($0 \leq x \leq 1$) catalysts.

Experimental Procedure

Basic nickel carbonate, basic copper carbonate, chromium carbonate and acetone (BDH grade)

were used for the preparation of catalysts. Ammonium perchlorate crystals of 99.1% purity were crushed in an agate mortar and sieved through 100-200 mesh. Styrene monomer was purified and polymerised as reported earlier¹².

Preparation of different catalysts and samples— To synthesize nickel(II) chromite catalyst, basic nickel(II) carbonate and chromium(III) carbonate were mixed in 1:3 molar ratio and the mixture was homogenised by grinding in an agate mortar using acetone. The homogenised mixture was dried, taken in a platinum crucible and calcined at $800 \pm 10^\circ\text{C}$ for 20h.

Copper(II) doped nickel(II) chromite catalyst was prepared by mixing basic nickel(II) carbonate, basic copper(II) carbonate and chromium(III) carbonate in 2:3:12 molar ratio. The mixture was homogenised and calcined in platinum crucible at $800 \pm 10^\circ\text{C}$ for 20h.

Copper(II) chromite catalyst was prepared by mixing basic copper(II) carbonate and chromium(III) carbonate in 1:2 molar ratio. The mixture was homogenised and calcined at $800 \pm 10^\circ\text{C}$ for 20 h.

The catalysts were characterised by gravimetric estimation of constituent metals and powder X-ray diffraction method as described earlier^{1,13,14}.

The samples of (AP+catalyst) were prepared by mixing AP homogeneously with different chromite catalysts (2% by mass) whereas to prepare (PS+catalyst) samples, a specific amount of polystyrene (PS) was taken in glass tube of about equal dimension and mixed homogeneously with catalyst (2% by mass). The tubes with content were kept in an incubator at $50 \pm 1^\circ\text{C}$ for fifteen

days and were broken after the solidification of the content. The PS strands thus obtained were cut into small pieces which were made smooth in the form of pellets. The samples of (AP+PS+catalyst) were prepared by mixing AP+PS (3:1 by mass) alongwith different catalysts (2% by mass) homogenously. This ratio was found to be the most suitable composition for the matrix formation. The homogenised mixture was filled in almost equal dimension glass tubes and cured in an incubator at $50 \pm 1^\circ\text{C}$ for fifteen days. The glass tube was broken after solidification of the contents and the propellant strands thus obtained were cut in small pieces.

The dynamic thermogravimeter (TG) of AP, PS and (AP+PS) propellant with catalysts was carried out using a manual thermogravimetric analyser at a heating rate of 2°C min^{-1} in air. The AP sample was used in powder form whereas PS and propellant as pellets of almost equal dimensions.

The kinetics of the thermal decomposition/degradation of AP, PS and (AP+PS) propellant were measured by isothermal TG of AP, PS and propellants. Thermal decomposition of AP was studied in the temperature range $210\text{--}320^\circ\text{C}$, because no appreciable mass loss was observed below 210°C and deflagration occurred above 320°C in presence of catalysts.

The degradation kinetics of PS was studied in the temperature range $280\text{--}340^\circ\text{C}$ because no appreciable mass loss was observed below 280°C and almost complete mass loss occurred at 380°C with catalysts.

The kinetics of thermal decomposition of propellant was carried out in the temperature range $240\text{--}270^\circ\text{C}$. No experiments could be performed beyond this range due to inadequate mass loss below 240°C and deflagration of the propellant above 270°C with catalysts. Except for NiCr_2O_4 the deflagration of propellant occurred with catalysts at 260°C . Further, the propellant deflagrated at 280°C with NiCr_2O_4 and at 300°C without catalysts. Due to these limitations the decomposition of propellant with CuCr_2O_4 and $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{O}_4$ was studied only at 250°C .

Results and Discussion

On the basis of α -time plots for the catalysed and uncatalysed thermal decomposition of AP, it is suggested that upto 260°C (Fig. 1) the decomposition is predominantly acceleratory ($\alpha \leq 0.2$) followed by a deceleratory process. At temperature 280°C and onwards (Fig. 2) the decomposi-

tion is predominantly deceleratory ($\alpha \geq 0.2$) after a fast acceleratory process.

In order to establish the rate constants, k_a , for acceleratory decomposition in the temperature range $210\text{--}280^\circ\text{C}$. Avrami-Erofeev equation has been used for uncatalysed thermal decomposition of AP (Fig. 3). Similar plots were obtained for catalysed thermal decomposition of AP. The values of activation energy (E) and collision frequency

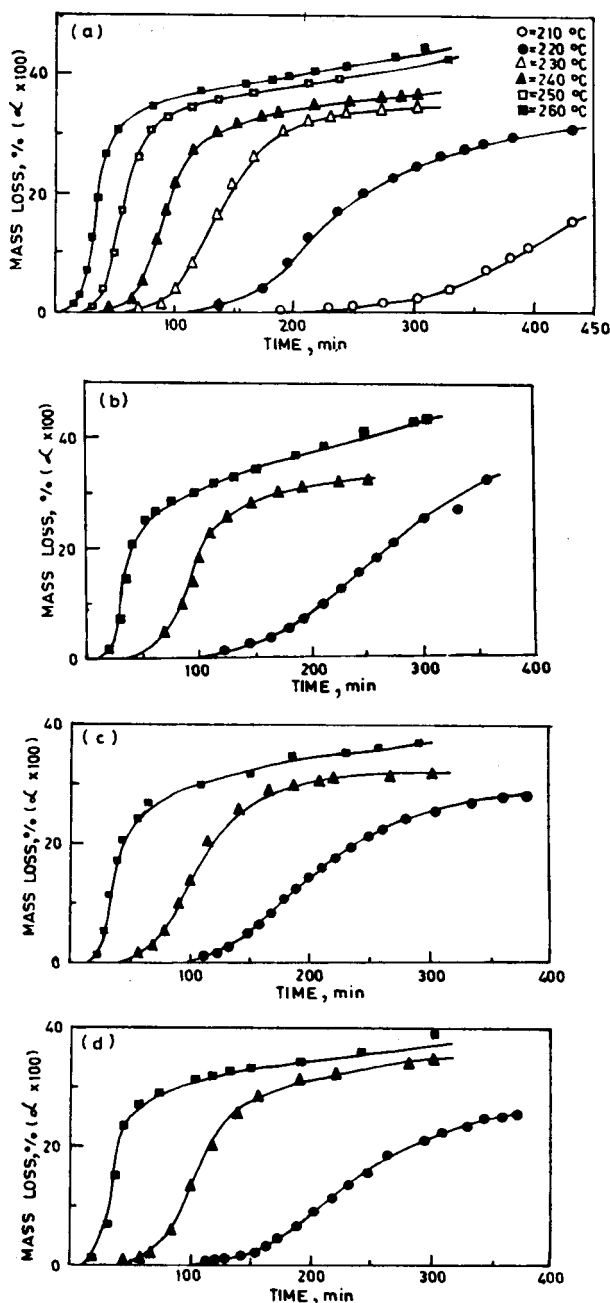


Fig. 1—Thermal decomposition (α -time plots) of AP and (AP+catalysts) in temperature range $220\text{--}260^\circ\text{C}$. (a) Uncatalysed AP, (b) AP+ NiCr_2O_4 , (c) AP+ $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{O}_4$ and (d) AP+ CuCr_2O_4

factor (A) for uncatalysed and catalysed thermal decomposition of AP have been calculated. For determining the rate constants, k_d , for deceleratory process in the temperature range 280–320°C, the equation $[1 - (1 - \alpha)^{1/n}] = kt$ with $n=3$ (contracting cube equation) was used for uncatalysed and $n=2$ (contracting area equation) for catalysed thermal decomposition of AP (Figs 4a and 4b). In these equations, α is the fraction decomposed at time, t . The activation energy and collision frequency factor for acceleratory and deceleratory processes calculated from Arrhenius plots are given in Table 1.

It is interesting to note that the rate of thermal decomposition of AP with catalysts in the temperature range 220–260°C is lowered with reduction in energy barrier whereas in temperature range 280–320°C, it increases with increase in activation energy. This is in contrast to the Arrhenius equation, where the energy barrier should decrease with increase in specific rate constant. However, these observations are in agreement with earlier reports¹⁵⁻¹⁸. It is seen from Table 1 that collision frequency factor (A) appreciably increases for catalysed decomposition as compared to uncatalysed decomposition. Further, lowering in the value of A

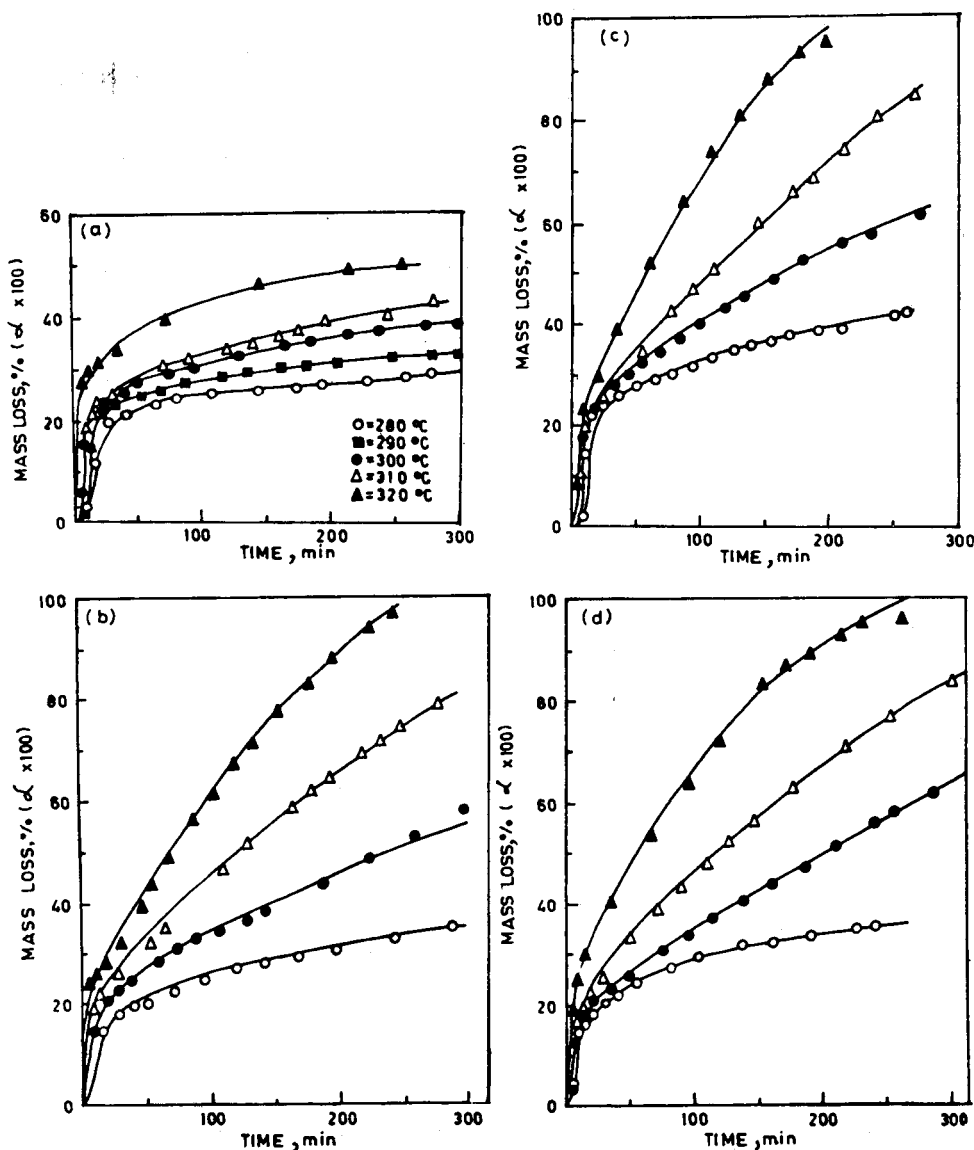


Fig. 2—Thermal decomposition (α -time plots) of AP and (AP+catalysts) in temperature range 280–320°C. (a) Uncatalysed AP, (b) AP+NiCr₂O₄, (c) AP+Ni_{0.5}Cu_{0.5}Cr₂O₄ and (d) AP+CuCr₂O₄.

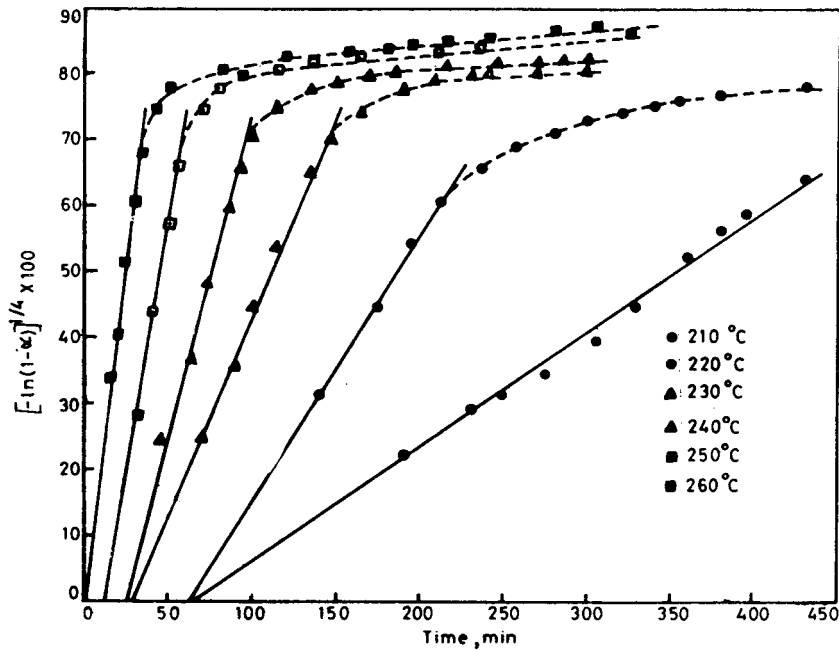


Fig. 3—Kinetics of thermal decomposition of AP in temperature range 210-260°C using equation $[-\ln(1-\alpha)]^{1/4} = kt + C$

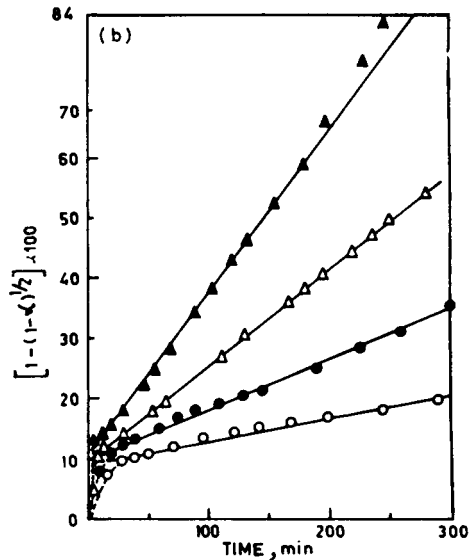
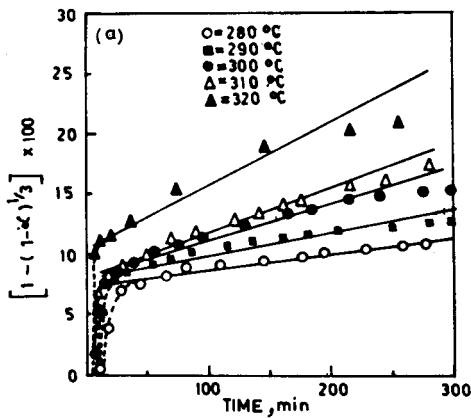


Fig. 4—(a) Kinetics of thermal decomposition of AP in temperature range 280-320°C using equation $[1-(1-\alpha)^{1/3}] = kt + C$. (b) Kinetics of thermal decomposition of AP+NiCr₂O₄ in temperature range 280-320°C using equation $[1-(1-\alpha)^{1/2}] = kt + C$

has been observed for inhibited decomposition of AP. Therefore, it appears that frequency factor, which is related to the concentration of reactant molecules on catalyst surface, plays a significant role in catalysed reactions.

It has been found that *p*-type semiconductors are most effective catalysts whereas *n*-type semi-

conductors and insulators are less effective or completely inactive for the thermal decomposition of AP^{19,20}. Being *p*-type semiconductors¹⁴, the chromite catalysts employed under the present investigation are likely to accelerate the electron transfer process^{19,20}. The mechanism can be shown as:

Table 1—Energy of activation (E) and collision frequency factor (A) for the catalysed thermal decomposition of AP Systems

Systems	Temperature range 210-260°C		Temperature range 280-320°C	
	E_a , kJ mol ⁻¹	A_a , min ⁻¹	E_d , kJ mol ⁻¹	A_d , min ⁻¹
AP	102.4	8.381×10^8	93.2	1.88×10^4
AP+NiCr ₂ O ₄	98.2	7.86×10^7	131.6	1.90×10^{10}
AP+Ni _{0.5} Cu _{0.5} Cr ₂ O ₄	86.1	6.668×10^6	141.2	5.53×10^{10}
AP+CuCr ₂ O ₄	90.7	7.083×10^7	144.2	7.94×10^{10}

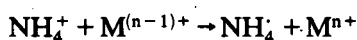
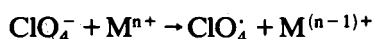
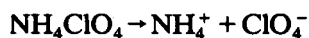
a = acceleratory, d = deceleratory

Table 2—Effect of catalysts on the rate of the thermal decomposition/degradation of AP, PS and AP+PS propellant

Temperature °C	Sample	Equation used	Rate constant min ⁻¹	Catalytic activity C_A^*
220	AP	AE	3.80×10^{-3}	—
	AP+NiCr ₂ O ₄	AE	2.67×10^{-3}	Negative
	AP+Ni _{0.5} Cu _{0.5} Cr ₂ O ₄	AE	2.63×10^{-3}	Negative
	AP+CuCr ₂ O ₄	AE	3.15×10^{-3}	Negative
320	AP	CC	5.24×10^{-4}	—
	AP+NiCr ₂ O ₄	CA	2.75×10^{-3}	5.3
	AP+Ni _{0.5} Cu _{0.5} Cr ₂ O ₄	CA	3.86×10^{-3}	7.3
	AP+CuCr ₂ O ₄	CA	3.00×10^{-3}	5.7
280	PS	CA	2.10×10^{-4}	—
	PS+NiCr ₂ O ₄	CA	3.03×10^{-4}	1.4
	PS+Ni _{0.5} Cu _{0.5} Cr ₂ O ₄	CA	2.61×10^{-4}	1.2
	PS+CuCr ₂ O ₄	CA	2.41×10^{-4}	1.1
340	PS	CA	1.39×10^{-3}	—
	PS+NiCr ₂ O ₄	CA	2.76×10^{-3}	2.0
	PS+Ni _{0.5} Cu _{0.5} Cr ₂ O ₄	CA	1.80×10^{-3}	1.3
	PS+CuCr ₂ O ₄	CA	1.71×10^{-3}	1.2

AE = Avrami Erofeev Equation; CC = contracting cube equation; CA = contracting area equation,

$$C_A^* = \frac{\text{Rate of decomposition with catalyst}}{\text{Rate of decomposition without catalyst}}$$



where M^{n+} represents the positive hole present in the catalyst. The reason for their rate accelerating effect may be that the positive holes acting as electron acceptors trap the electrons of perchlorate ion, (ClO_4^-) and increase the life of perchlorate radicals (ClO_4), thereby, facilitating the thermal decomposition process. The values of activation energy for the deceleratory catalysed decomposition of AP is very nearly equal to the value

($E = 133.9 \text{ kJ mol}^{-1}$) for electron transfer process²¹. This supports the proposed argument in favour of electron transfer mechanism for thermal decomposition of AP. The order of catalytic activity (C_A) of chromites was calculated from the expression,

$$C_A = \frac{\text{Rate of catalysed reaction}}{\text{Rate of uncatalysed reaction}}$$

Thermal decomposition of AP in the temperature range 220-320°C (Table 2) follows the order $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{O}_4 > \text{CuCr}_2\text{O}_4 > \text{NiCr}_2\text{O}_4$. The plots of α -time for thermo-oxidative degradation of PS and PS+catalyst (Fig. 5) have been observed to be deceleratory throughout. A kinetic equation, $[1 - (1 - \alpha)^{1/2}] = kt + C$ described for deceleratory

process, has been used to determine the rate constants for both uncatalysed and catalysed degradation of PS. Plots between $[1 - (1 - \alpha)^{1/2}]$ and time for uncatalysed thermal decomposition of PS are shown in Fig. 6. Similar plots were obtained for catalysed thermal decomposition. The value of activation energy (E) and collision frequency factor (A) have been shown in Table 3. Like AP, the rate of catalysed degradation of PS increases with increase in activation energy which may also be attributed to an increase in collision frequency factor which makes greater probability of collision between reacting species. Thus, it may be suggest-

ed that the chromite catalysts enhance the thermooxidative degradation of polymer via free radical formation and their subsequent combination/disproportionation leading to the formation of final reaction products. For the thermal degradation of PS, the catalytic activity of chromites follows the order $\text{NiCr}_2\text{O}_4 > \text{Ni}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{O}_4 = \text{CuCr}_2\text{O}_4$.

It has been observed that the decomposition of propellant is significantly affected by the catalysts (Tables 4-6). The deflagration of propellant occurred at lower temperature in presence of the catalysts. The nature of α -time plots for thermal decomposition of propellant and propellant + catalyst

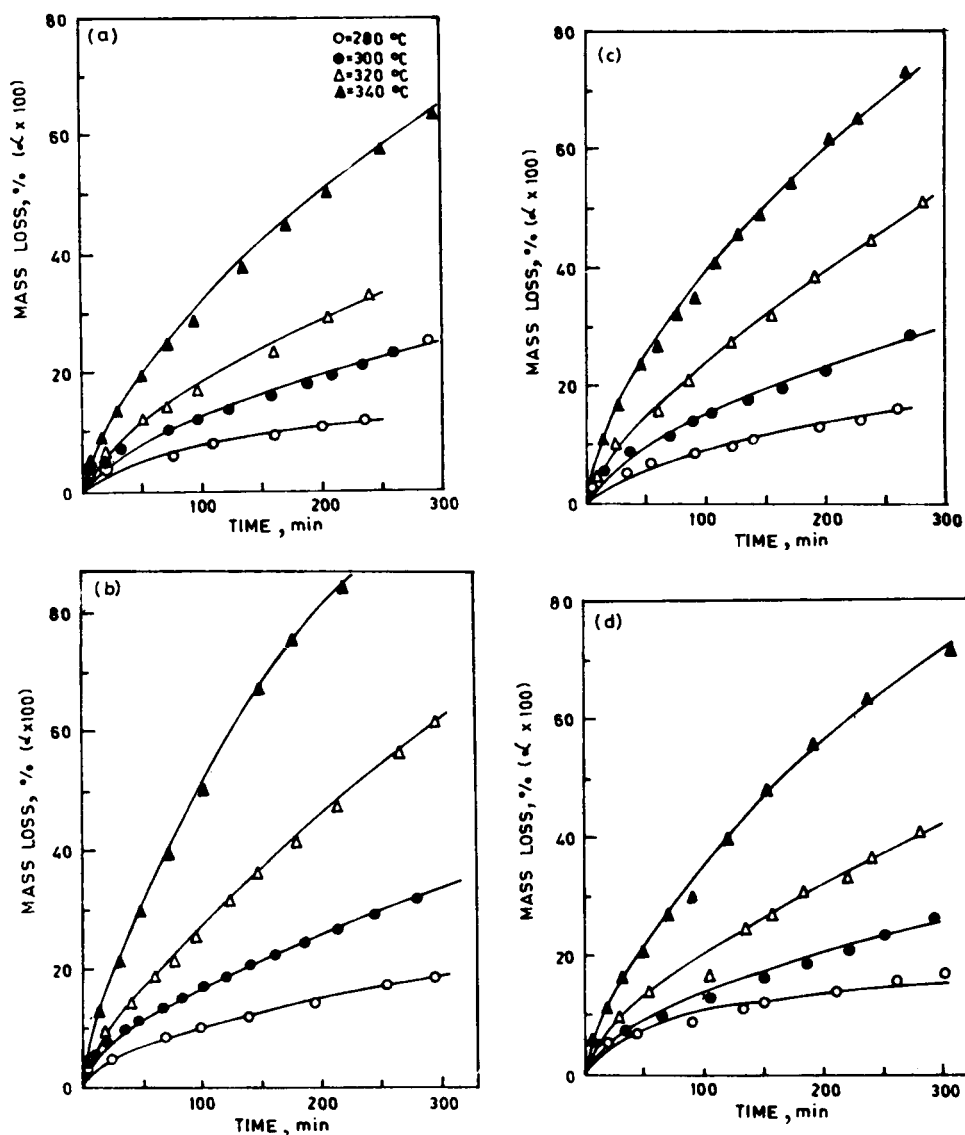


Fig. 5—Thermal decomposition (α -time plots) of PS and (PS+catalysts) in temperature range 280-340°C. (a) Uncatalysed PS, (b) PS+ NiCr_2O_4 , (c) PS+ $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{O}_4$ and (d) PS+ CuCr_2O_4

(Fig. 7) was found to be sigmoid. This indicates that the decomposition is predominantly acceleratory ($\alpha \leq 0.2$) followed by a deceleratory process as obtained in case of AP. The Avrami-Erofeev equation has been used for determination of rate

Table 3—Energy of activation (E) and collision frequency factor (A) for catalysed thermooxidative degradation of PS

System	E , kJ mol ⁻¹	A , min ⁻¹
PS	84.9	4.45×10^5
PS + NiCr ₂ O ₄	103.8	1.95×10^7
PS + Ni _{0.5} Cu _{0.5} Cr ₂ O ₄	94.6	1.20×10^6
PS + CuCr ₂ O ₄	91.6	9.30×10^5

Table 4—Dynamic TG data for AP and AP + Ni_{1-x}Cu_xCr₂O₄ ($0 \leq x \leq 1$) catalysts

Temperature °C	Mass loss, %			
	AP	AP + NiCr ₂ O ₄	AP + Ni _{0.5} Cu _{0.5} Cr ₂ O ₄	AP + CuCr ₂ O ₄
140	0.46	0.47	1.45	—
160	0.91	0.94	1.94	0.45
180	1.36	2.83	2.90	2.35
200	2.27	4.72	3.87	2.70
220	2.72	6.60	4.35	4.05
240	3.62	10.38	22.22	23.88
260	9.51	27.36	29.96	28.38
280	28.51	42.45	37.69	41.90
300	32.13	64.15	53.14	55.41
320	35.75	80.56	86.58	82.43
340	43.90	d*	d*	d*
360	52.04	—	—	—
380	59.28	—	—	—
400	d*	—	—	—

*deflagration

constants. Plots between $[-\ln(1-\alpha)]^{1/4} \times 100$ and time for uncatalysed thermal decomposition of AP+PS propellant are shown in Fig. 8. Similar plots were obtained for catalysed decomposition also. The values of energy of activation for uncatalysed and catalysed thermal decomposition of propellant is practically the same [$E = 150.6$ kJ mol⁻¹]. Similarly, the value of collision frequency factor for thermal decomposition of the propellant under the two conditions is almost the same ($A = 3.58 \times 10^{13}$ and 4.14×10^{13} min⁻¹). A comparison of catalytic effect of the chromites has been made by studying the thermal decomposition of

Table 5—Dynamic TG data for PS and PS + Ni_{1-x}Cu_xCr₂O₄ ($0 \leq x \leq 1$) catalysts

Temperature °C	Mass loss, %			
	PS	PS + NiCr ₂ O ₄	PS + Ni _{0.5} Cu _{0.5} Cr ₂ O ₄	PS + CuCr ₂ O ₄
120	0.97	0.95	0.49	0.45
140	1.45	1.42	0.95	0.90
160	1.45	1.89	1.42	1.82
180	2.43	2.37	1.90	2.73
200	3.39	2.87	2.85	3.18
220	3.88	3.79	4.76	3.63
240	4.36	5.68	6.19	4.54
260	6.79	9.00	8.56	7.05
280	11.16	12.82	12.38	10.00
300	18.44	21.32	19.05	17.64
320	31.55	37.91	35.71	34.11
340	48.54	66.82	70.48	62.35
360	77.18	89.85	85.68	79.65
380	88.62	97.86	97.50	92.76
400	98.50	—	—	97.82

Table 6—Dynamic TG data for (AP+PS) and AP+PS + Ni_{1-x}Cu_xCr₂O₄ ($0 \leq x \leq 1$) catalysts

Temperature °C	Mass loss, %			
	AP+PS	AP+PS + NiCr ₂ O ₄	AP+PS + Ni _{0.5} Cu _{0.5} Cr ₂ O ₄	AP+PS + CuCr ₂ O ₄
120	0.98	1.36	1.91	1.19
140	1.46	1.53	2.07	1.48
160	1.97	1.87	2.54	2.08
180	2.46	2.21	2.70	2.37
200	2.95	2.72	3.02	2.67
220	3.94	3.40	4.13	3.26
240	7.39	7.80	5.72	7.42
260	9.85	11.22	d*	d*
280	12.65	d*		
300	d*			

d* = deflagration

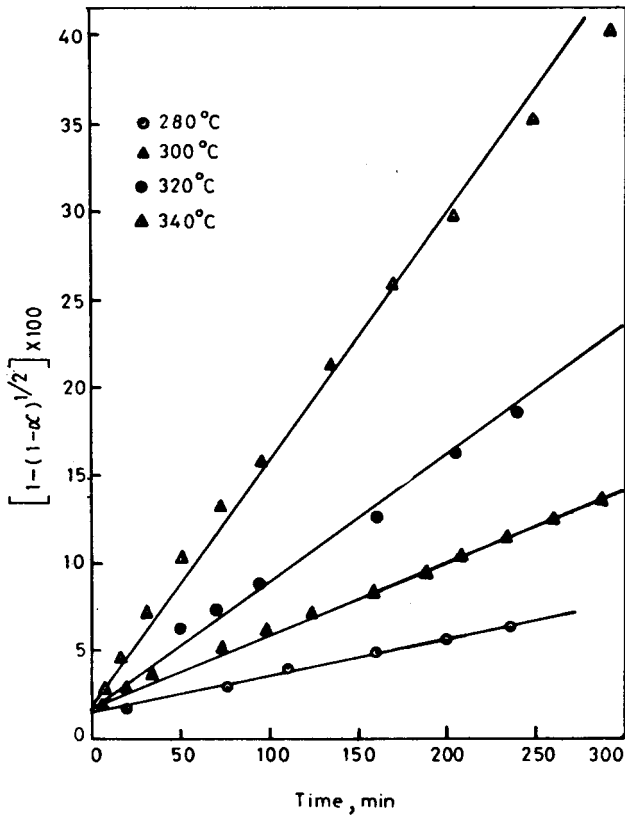


Fig. 6—Kinetics of thermal decomposition of PS in temperature range 280-340°C using equation $[1-(1-\alpha)^{1/2}] = kt + C$

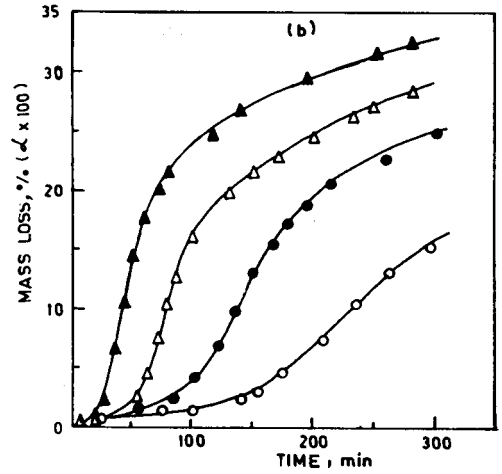
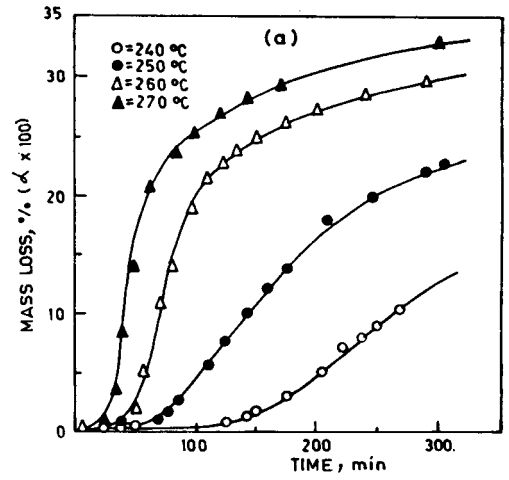


Fig. 7—Thermal decomposition (α -time plots) of (a) (AP+PS) propellant and (b) (AP+PS) propellant + NiCr_2O_4 in temperature range 240-270°C

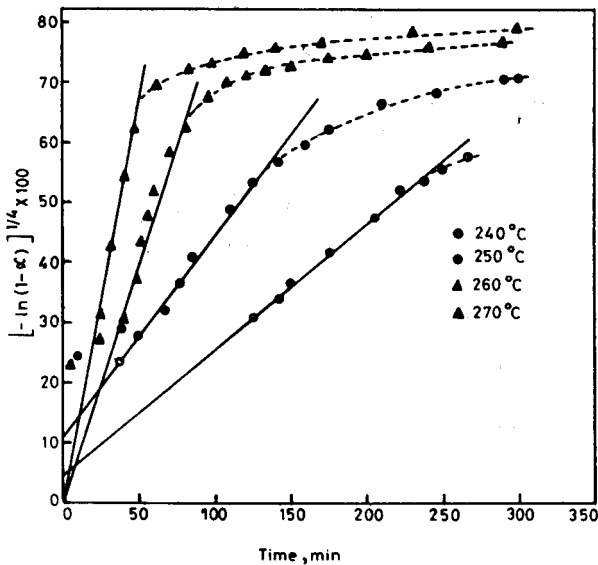


Fig. 8—Kinetics of thermal decomposition of AP+PS (3:1) propellant using equation $[-\ln(1-\alpha)^{1/4}] = kt + C$

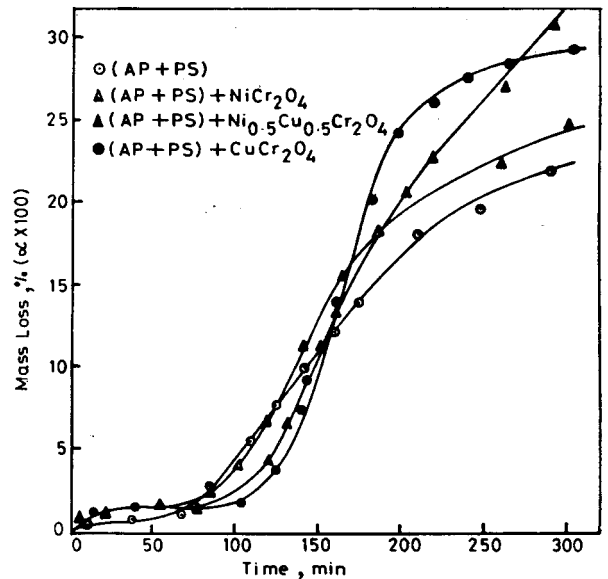


Fig. 9—Thermal decomposition (α -time plots) of (AP+PS) propellant + $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($x=0.0, 0.5, 1.0$) at $250 \pm 1^\circ\text{C}$

propellant at $250 \pm 1^\circ\text{C}$ (Fig. 9). The extent of decomposition clearly indicates that the order of catalytic activity is, $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{O}_4 > \text{CuCr}_2\text{O}_4 > \text{NiCr}_2\text{O}_4$.

Conclusion

On the basis of above observations it may be concluded that the effect of catalysts during the combustion of propellant is mainly governed by AP decomposition/combustion and the condensed phase reactions occurring at low temperatures affect the reactions occurring at high temperatures during the propellant burnings.

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