EFFECT OF IRON-CONTAINING CATALYSTS ON THERMAL DECOMPOSITION OF CURED GAP-AP PROPELLANTS

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Abstract

The effects of various burning rate catalysts on thermal decomposition of cured glycidyl azide polymer (GAP)-ammonium perchlorate (AP) propellants have been studied by means of thermal analysis and a modified vacuum stability test (MVST). Four types of iron-containing catalysts examined in this paper are catocene, ferrocenecarboxaldehyde (FCA), ferrocene, and ferric oxide. Results of differential thermal analysis (DTA) and thermogravimetric analysis (TG) revealed that the catalysts play an important role in the decomposition of both AP and GAP. The peak decomposition temperature (T_m) of DTA curves and onset decomposition temperature (T_o) of TG patterns considerably shifted to a lower temperature as the concentration of catalysts increased in the propellants. The endothermic temperature of AP, however, is unaffected by the presence of burning rate catalysts in all cases. The activation energy of decomposition of the propellants in range of 80 to 120°C is determined, based on the MVST results.

Keywords: DTA, GAP-AP propellants, iron-containing catalysts, MVST, TG, thermal decomposition

Introduction

Corresponding to increase energy content of rocket or gun propellants, numerous researches have been done on the energetic ingredients, including binder, oxidizer, fuel and other additives. As a good energetic binder, glycidyl azide polymer (GAP) has received considerable attention in recent years. Kubota and Sonobe [1] found that the burning rate of GAP propellant is signifi-

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cantly higher than that of conventional solid propellants, though lower the adiabatic flame temperature. A GAP double-base propellant was studied by Nakashita and Kubota [2]. They found that the burning rate and temperature sensitivity are increased remarkably when diethylphthalate is replaced with GAP. Ho and Fong [3] investigated the fracture property of certain composite propellants under high (impact) strain rates. It was observed that GAP propellants are less sensitive to impact than comparable propellants with HTPB or poly(ether glycol) binders. By using simultaneous mass and temperature change (SMATCH)/FTIR spectroscopy, Chen and Brill [4] determined the kinetic parameters of GAP during programmed heating rate for thermal decomposition. Frankel *et al.* [5] reviewed the historical development of GAP from its conception. They concluded that GAP is an energetic, yet insensitive, thermally stable binder with potential applications in advanced solid propellants. Ammonium perchlorate (AP) is commonly used as an oxidizer in composite propellants. The burning rate catalyst is an important additive to adjust the combustion behaviour of propellants. Many investigations have been carried out on the effect of burning rate catalysts on AP-based propellants [6–9]. Although there are many studies related to the performance of GAP propellants, however, few reports have been published on the influence of burning rate catalysts to GAP-AP propellants up to now.

In order to elucidate the aforementioned behaviour, a series of experiments was performed in our laboratory. The effects of catocene on GAP-AP propellants containing different particle size of AP has been reported in the previous paper [10]. In the present study, attentions are paid to the effects of various iron-containing catalysts on thermal decomposition of cured GAP-AP propellants. Four kinds of burning rate catalysts were examined. The decomposition of GAP-AP propellants was carried out by both isothermal and non-isothermal methods. Therefore, the purpose of this article is to study the catalytic characteristics of burning rate catalysts on decomposition of GAP and AP in cured propellant.

Experimental

Propellant formulation

The GAP prepolymer examined in this study was laboratory synthesized. Each specimen was formulated by curing GAP with an isocyanate curative in a NCO:OH ratio of 1:1. Particle size of AP was 225 µm. The composition summary of tested samples was listed in Table 1. As Table 1 depicted all propellants contained 30 parts of GAP as binder and 70 parts of AP as filler. Different types of burning rate catalysts were added to the propellant with 0.5, 1.3 and

3.0 weight percent relative to AP, respectively. All ingredients were mixed well by a standard blending procedure. The composite slurries were then cured in an oven at 60°C for four days.

Table 1 Summary of propellants compositions

Sample No.	GAP	AP	Catalyst content / wt% of AP			
			I	II	III	IV
A1	30	70	0.5			
A2	30	70	1.3			
A3	30	70	3.0			
B1	30	70		0.5		
B2	30	70		1.3		
B3	30	70		3.0		
C1	30	70			0.5	
C2	30	70			1.3	
C3	30	70			3.0	
D1	30	70				0.5
D2	30	70				1.3
D3	30	70				3.0

Note: I = Catocene; II = Ferrocenecarboxaldehyde; III = Ferrocene; IV = Fe_2O_3

DTA, TG and MVST measurements

Thermal analysis measurements were accomplished by a DuPont Instruments 9900 thermal analyzer system with 951 TGA and 1600 DTA modules. Sample weight was set around 2–4 mg. A heating rate of 10 deg·min^{-1} from room temperature up to 400°C was used for each run. All DTA and TG experiments were conducted with a nitrogen flowing rate of 50 ml/min.

The modified vacuum stability test (MVST) was designed to monitor the pressure change during the decomposition period of the propellants. The MVST apparatus consists of a metal heating block (Julius Peter) with a temperature controller (West 3000), pressure transducers with a data acquisition system and a personal computer (Acer 915P). Samples less than one gram placed into tubes were evacuated before testing. The tubes were then put into the heating device for 40 h at the desired temperature. Afterwards, the tubes were drawn out of the heating device for cooling to room temperature. The histories of pressure during experiments were recorded by the computer. The readings of pressure were converted to volume under standard conditions by using the ideal gas law. The detailed description about the MVST had been reported earlier [11].
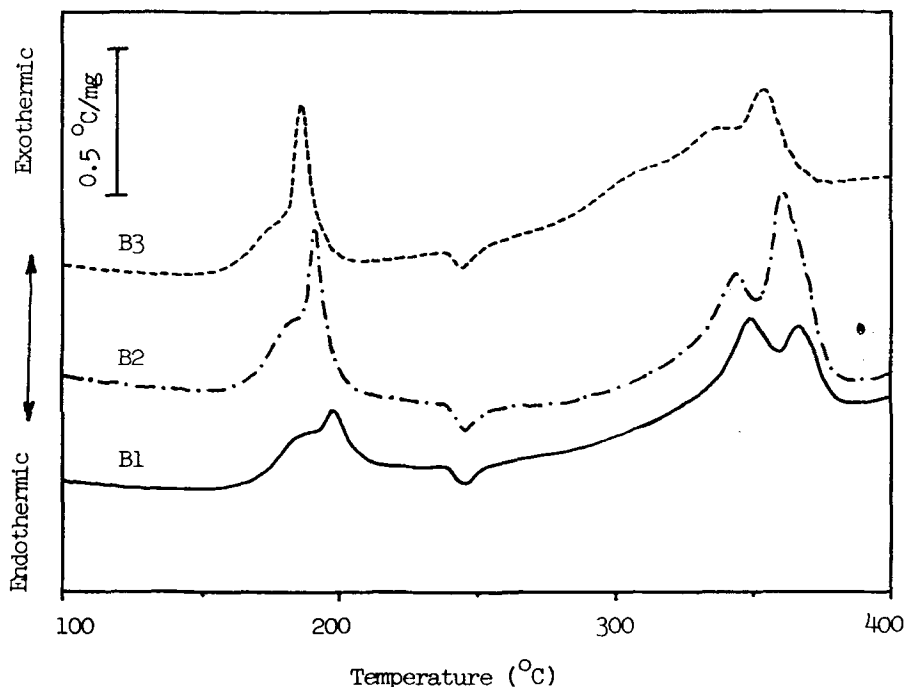
Fig. 1 DTA curves of GAP-AP propellants containing different concentrations of ferrocene-carboxaldehyde

Results and discussion

The thermal decomposition of AP has been extensively investigated [12–15]. It is found that the decomposition of AP is characterized by a phase transition from orthorhombic to cubic crystal structure at about 240°C, followed by two stages of exothermic decomposition in the range of 300–330°C and 380–460°C, respectively. Most researchers believed that the second exothermic reaction is the predominate decomposition of AP.

Figure 1 shows the typical DTA curves of propellants containing various concentrations of ferrocenecarboxaldehyde (FCA). An endothermic peak temperature around 246°C is found for each specimen. The heat absorbed is attributed to provide the phase transition as mentioned above. It is interesting that this endotherm is independent of FCA concentration. In other words, the endothermic temperature of AP remains constant and is unaffected by FCA. A similar result has been observed by Thomas and Nandi [16] and by Saito et al. [17]. By using DSC, Shen et al. [18] reported that the maximum exothermic peak temperatures (T_m) for uncured and cured GAP are near 251 and 240°C, respectively. Recently, it has been proved that the T_m value of cured GAP propellants

shifts to a lower value as catocene is added [10]. Therefore, the first exothermic peak in Fig. 1 is believed to be caused by the decomposition of GAP. The other exothermic peak is due to the decomposition of AP. As Fig. 1 shows, the T_m of GAP is significantly dropped even lower than the endothermic temperature of AP. Comparing DTA curves in Fig. 1, it is found that the T_m values of both GAP and AP decrease with increasing the FCA concentration. It is worthy to note that the decomposition curves of AP change from one with two maximum peaks to one with a single major peak with a shoulder on the lower temperature side. This implies that FCA has a greater catalytic effect on the second stage decomposition of AP than on the first stage. As a result, the second peak overlaps with the first peak as FCA content increasing up to 3 wt.%. On the other hand, the effect of FCA on GAP is different from that on AP. The shoulder of decomposition peak of GAP is gradual narrowing as the concentration of FCA increasing.
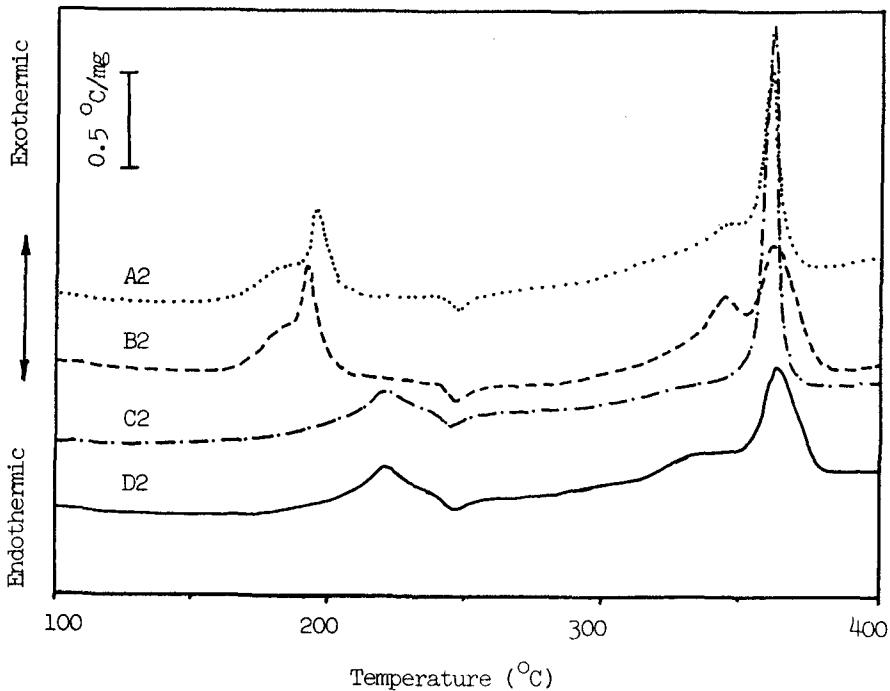

Fig. 2 DTA curves of GAP-AP propellants containing various catalysts with 1.3 wt.% corresponding to AP

Figure 2 illustrates the DTA curves of propellants containing 1.3 wt.% of different burning rate catalysts. It is observed that the catalytic effect of burning rate modifier on GAP can be categorized into two types: the first type is formed

by catocene and FCA and the other is by ferrocene and Fe_2O_3. There is a distinguishable shoulder on the first type GAP decomposition peak of DTA curves. However, the shoulder does not appear in the second type. The T_m values of GAP decomposition of first type DTA curves are much lower than those of second type. In other words, the decomposition of GAP affected by catocene or FCA does more significantly than by ferrocene or Fe_2O_3. The second exothermic peak is due to the decomposition of AP. Two distinct peaks were found for B-2 propellant containing FCA. One peak with a shoulder was observed for A-2 propellant containing catocene and D-2 propellant containing Fe_2O_3. However, only one sharp peak was detected for C-2 propellant containing ferrocene. It should be noted that the endothermic valley caused by AP phase transition is kept the same for all propellants with various catalysts.
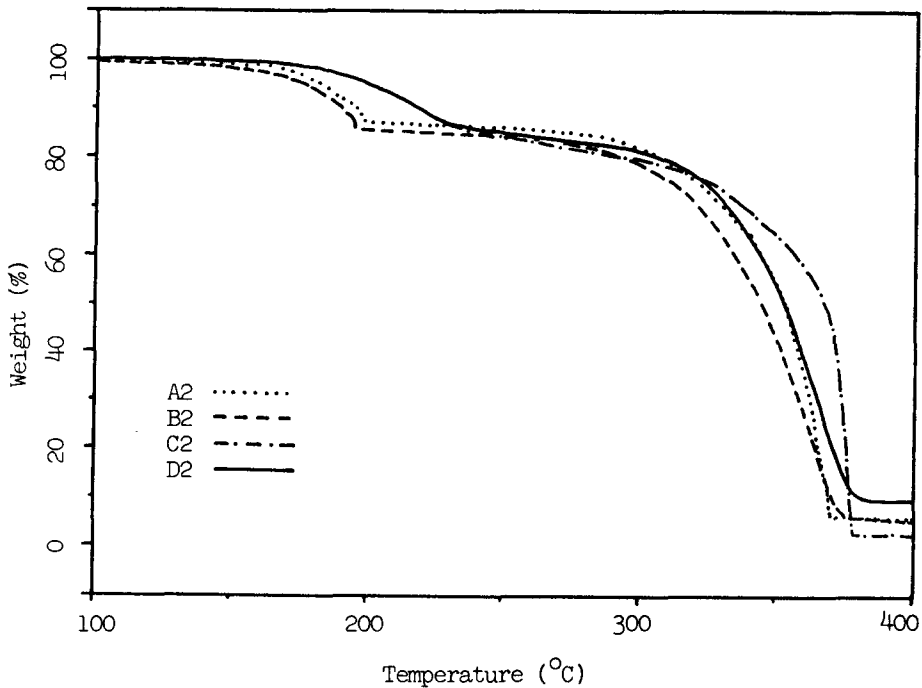

Fig. 3 TG curves of GAP-AP propellants containing various catalysts with 1.3 wt.% corresponding to AP

Figure 3 shows the typical TG curves of GAP-AP propellants contained various catalysts. As can be seen in Fig. 3, two major stages of weight loss occur in the decomposition for all the observations. About 15% of the total weight loss occur in the first stage of decomposition. It is believed that the first stage of weight loss is due to the decomposition of GAP. As obtained in Fig. 2, the first

stage weight loss of TG curves can be categorized into two groups. The second stage of weight loss is mainly caused by the decomposition of AP. From Fig. 3, the decomposition of AP for C-2 propellant is the smallest before 350°C. But, about 65% of total weight lost in the range of 350–376°C. In other words, the weight loss in this range is drastically rapid. This result is consistent with the DTA curve shown in Fig. 2.

Results of both DTA and TG measurements are tabulated in Table 2. Both T_m and T_o of GAP-AP propellants are consistently dropped to the lower values as increasing the content of the catalysts. The decomposition of both GAP and AP, presented in the propellants, are apparently affected by these four iron-containing catalysts. As the data shown, the effect on decomposition of GAP by FCA or by catocene is stronger than that by ferrocene or by Fe_2O_3. The two stages decomposition of AP are jointed together in presence of catalysts, except for FCA. Nevertheless, the endothermic temperature of AP is independent of the presence of catalyst in all cases.

The vacuum stability test is one of standard methods for determining the stability of explosives and propellants. However, there are several disadvantages of this old conventional test method. Some of its limitations have been successfully improved by a modified manometric vacuum stability test apparatus (modified
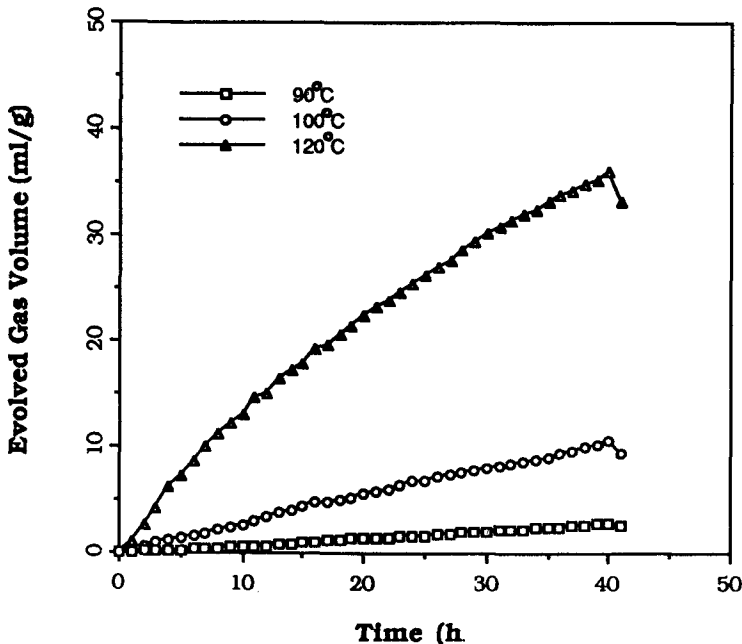

Fig. 4 The MVST results for C-series propellants with different contents of ferrocene under 100°C heating

MVST) developed by Huang and his co-workers [19]. Typical patterns of the MVST measurements are presented in Fig. 4. The evolved gas volumes from partial decomposition of propellants have already been converted to the values under the standard conditions (0°C and 1 atm). The data at 41th h are the volumes of evolved gas after cooling to room temperature. Because of partial condensation and the temperature decrease, the evolved gas volume dropped slightly. Figure 4 shows the MVST measurements of samples C1-C3 heated at 100°C. It is observed that the evolved gas volumes of all three propellants stably increase along with heating time. As Fig. 4 shows, the evolved gas volume at any time increases with increasing ferrocene content.

It is known that the heating temperature is an important factor in a thermal decomposition reaction. Figure 5 shows the decomposition pattern of C2 at 90, 100, and 120°C. The corresponding final evolved gas volumes are 2.65, 9.40 and 33.10 ml/g, respectively. The values of evolved gas volume at 120°C is as high as twelve-fold of that at 90°C. Under 90 and 100°C heating, the propellants decompose at a constant rate. As the heating temperature increases to 120°C, the curve becomes slightly concave. In other words, the liberation of gas is relative rapid during the earlier period of heating time. Subsequently, the decompose reaction progress slows down. This indicates that the evolved gas products do not promote further decomposition.
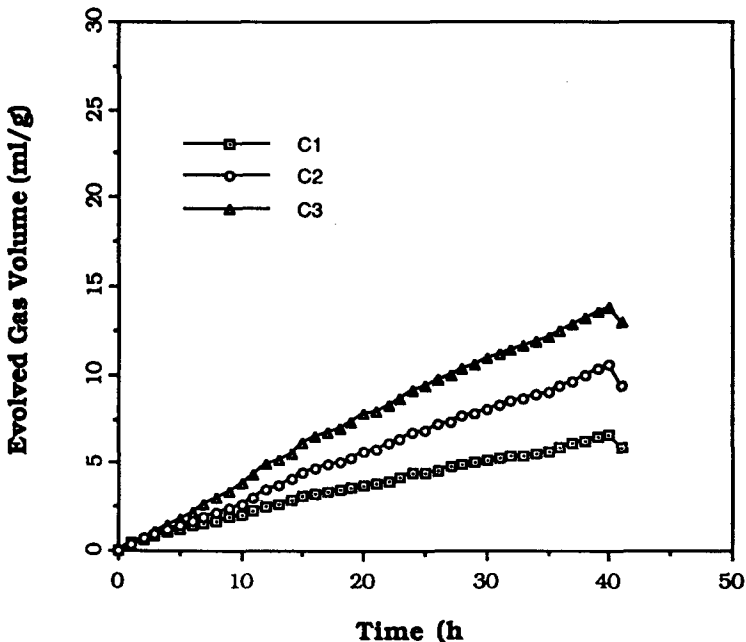

Fig. 5 Comparison of MVST curves of C2 propellant at various heating temperatures

Table 2 Results of DTA and TG measurements

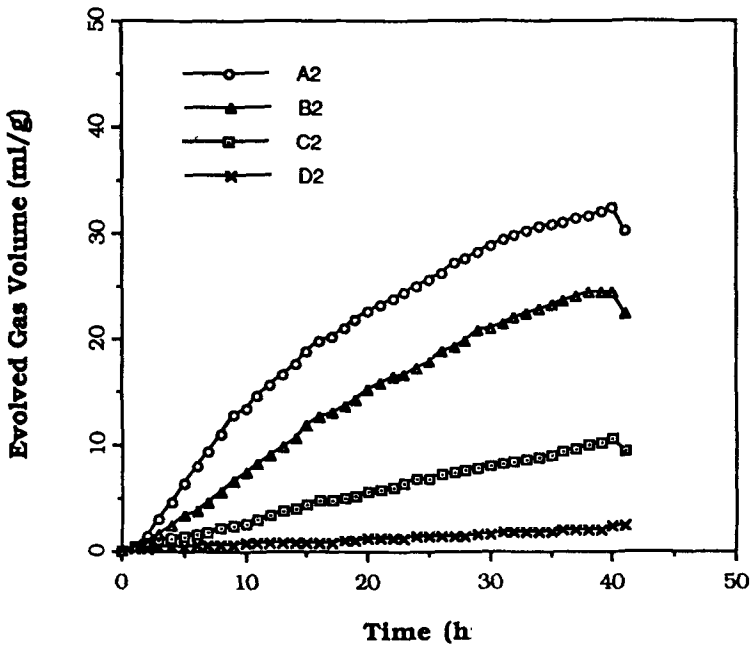| Sample No.	DTA				TG			
	1st exoth. peak, T_m / °C	endothermic peak, T_m / °C	2nd exothermic peak, T_m / °C		1st stage T_o / °C	weight loss / wt%	2nd stage T_o / °C	weight loss / wt%
A1	207.4	246.0	369.1		177.0	14.37	340.0	78.68
A2	194.6	246.8	359.4		172.0	12.19	336.3	81.50
A3	187.1	246.2	355.8		170.1	13.83	316.4	79.16
B1	198.0	245.5	348.0	366.7	177.3	13.70	328.3	77.66
B2	192.0	245.4	344.0	360.9	171.6	14.05	323.2	79.16
B3	186.4	245.0	353.7		166.9	15.37	323.5	76.76
C1	224.3	244.1	367.8		192.4	12.91	352.5	86.43
C2	219.5	243.9	360.8		191.2	14.86	355.2	82.44
C3	214.8	245.0	356.0		191.5	13.57	348.9	83.10
D1	225.1	242.66	368.9		198.0	13.99	339.4	74.01
D2	220.2	245.1	363.0		191.0	14.11	335.0	76.18
D3	220.2	245.9	358.4		190.8	13.46	337.8	76.07

Fig. 6 MVST results of propellant added with 1.3 wt.% of various catalysts at 100°C

Table 3 Final results of modified vacuum stability tests

| Sample | Evolved gas volume after cooling / ml·g^{-1} | | | | E_a / |
No.	80°C	90°C	100°C	120°C	kcal·mol^{-1}
A1	2.19	8.78	19.23	37.66	26
A2	4.86	15.12	30.27	44.34	27
A3	7.97	18.43	30.70	45.67	24
B1	–	6.06	16.21	40.08	31
B2	–	11.11	22.43	43.90	29
B3	–	17.53	33.23	44.67	27
C1	–	1.72	5.89	33.62	28
C2	–	2.65	9.40	33.10	29
C3	–	4.66	12.93	48.91	32
D1	–	0.59	1.63	16.61	20
D2	–	0.54	2.32	14.82	22
D3	–	0.84	2.71	19.85	22

Figure 6 shows the MVST measurements of propellants containing 1.3 wt.% various catalysts at 100°C. The curves of C2 and D2 propellants seemingly pre-

sent linear. But, for A2 and B2 propellants, the curves are slightly concave. From Fig. 6, the evolved gas volumes by partial decomposition of propellants are in the order of A2, B2, C2 and D2. In other words, the catalytic effect on propellants decomposition by addition with catocene or FCA is more significant than with ferrocene or Fe_2O_3. This result is similar to that determined by DTA or TG.

A pseudo-zeroth order decomposition could be reasonably assumed for the linear region of the MVST curve [19]. The decomposition rate is simply calculated as the first derivative of the evolved gas volume with respect to time. In addition, the activation energy of decomposition is obtained according to the Arrhenius law with rates (r) determined at various temperatures (T). The relationship between $\ln r$ vs. $1/T$ is illustrated in Fig. 7. Obviously, the data are fairly well correlated by a straight line. This result indicates that the Arrhenius law is suitable to describe the relationship between the decomposition rate and heating temperature. The activation energy is then simply calculated from the slope of the regression line. The results of MVST measurements as well as the calculated activation energy (E_a) are listed in Table 3. From Table 3, it can be seen that the evolved gas volume increases along with the heating temperature,
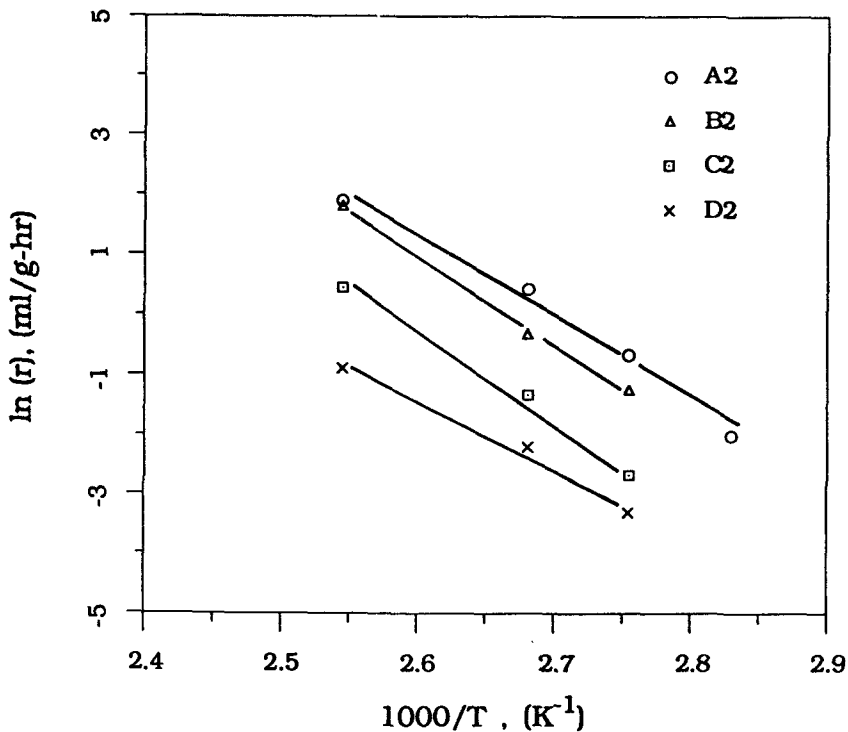

Fig. 7 Relationship between the decomposition rates of propellants and heating temperature

especially as the heating temperature is higher. It should be noted that the evolved gas volumes of D-series propellants are always kept relative small for all cases.

Conclusions

The effects of burning rate catalysts on decomposition of GAP and AP in cured propellants were studied by DTA, TG and MVST. Four kinds of iron-containing catalysts examined were catocene, ferrocenecarboxaldehyde (FCA), ferrocene and ferric oxide. From DTA measurements, the T_m values of both GAP and AP decrease with increasing content of catalyst. Similar observations are obtained for T_o by TG. The catalytic behaviours on GAP have two types: one type is formed by catocene and FCA and the other type is formed by ferrocene and Fe_2O_3. The former has the larger effect on GAP decomposition than the latter. The predominate effect of tested catalysts is acting on the second exothermic decomposition of AP. On the other hand, the endothermic temperature of AP phase transition is independent of the existence of catalyst. According to the MVST measurements, the evolved gas volume for ferric oxide is the smallest. The activation energies are obtained by the Arrhenius law with the MVST data. Evolved gas volume increases as the catalyst content increases.

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Zusammenfassung — Mittels Thermoanalyse und einem modifizierten Vakuumstabilitätstest (MVST) wurde der Einfluß von verschiedenen Brenngeschwindigkeitskatalysatoren auf die thermische Zersetzung von Glycidylazidpolymer (GAP)-Ammoniumperchlorat (AP)-Treibstoffen untersucht. Vier der vorliegend untersuchten eisenhaltigen Katalysatoren waren Katocen, Ferrocencarboxaldehyd (FCA), Ferrocen und Eisentrioxid. Die Ergebnisse von DTA und TG zeigen, daß die Katalysatoren eine bedeutende Rolle bei der Zersetzung von sowohl AP als auch GAP spielen. Bei ansteigender Katalysatorenkonzentration in den Treibstoffen wird die zum Peak gehörende Zersetzungstemperatur (T_m) der DTA-Kurven und die Temperatur für die einsetzende Zersetzung (T_o) des TG-Verlaufes beträchtlich zu niedrigeren Temperaturen verschoben. Die Endothermentemperatur von AP bleibt von der Gegenwart von Brenngeschwindigkeitskatalysatoren in allen Fällen unverändert. Anhand der MVST-Ergebnisse wurde die Aktivierungsenergie der Zersetzung der Treibstoffe im Intervall 80–120°C ermittelt.