研究論文

Combustion catalysts of non-pollutant solid rocket propellant

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The thermal reaction and the combustion of non-pollutant solid rocket propellant containing ammonium perchlorate (NH_4ClO_4)were studied by thermal analysis, combustion experiments and analyses of the reaction residue in order to clarify the mechanism of combustion of non-pollutant solid rocket propellant. The results obtained are as follows.

Iron oxide is a representative catalyst of usual solid rocket propellant containing ammonium perchlorate. The mechanism of this catalytic effect was estimated as that the formation of an unstable iron perchlorate in the course of reaction. But, it had no catalytic effect on the NH_4ClO_4 Sodium nitrates –($NaNO_3$)- Al-binder propellant and NH_4NO_3-Al/Mg-binder propellant from the experiments of thermal reaction and combustion. This reason was ascribed to the formation of sodium perchlorate and ammonium nitrate which were more stable compared to ammonium perchlorate because of the double decomposition between ammonium perchlorate and sodium nitrate in NH_4ClO_4 -$NaNO_3$-Al-binder propellant on heating. Then, iron oxide or other iron containing catalyst had also no catalytic effect on sodium perchlorate and ammonium nitrate.

Active carbon had a catalytic effect both on the thermal reaction and combustion of NH_4ClO_4 -$NaNO_3$-Al-binder propellant. Moreover, pressure index calculated from Vieille's equation was a small value of 0.43~0.52 compared to that without catalyst. Oxides, which had the structure of perovskite type also, had a catalytic effect on the NH_4ClO_4 -$NaNO_3$-Al-binder propellant, though its effect was smaller than that compared to active carbon.

1. Introduction

Ammonium perchlorate (NH_4ClO_4) has been mainly used as an oxidizer of solid rocket propellant in practical use. However, it has the problem of producing local acid rain over the launching district and ozone destruction in the stratosphere due to hydrochloric acid formation. Ammonium perchlorate - sodium nitrate($NaNO_3$)- aluminum (Al) - binder (glysidyl azide polymer GAP or hydroxy terminated polybutadiene HTPB) (abbreviated as NH_4ClO_4-$NaNO_3$-Al-GAP propellant or scavenged propellant), ammonium nitrate (NH_4NO_3)- magnarium (Al/Mg alloy)-binder (NH_4NO_3-Al/Mg-GAP propellant) and NH_4ClO_4-Al/Mg-binder propellant (neutralized propellant) are candidates for a chlorine free non-polluting solid propellant. Though the combustion of these type of propellants have been studied by some workers [1-4], there are few which evaluated a catalyst for the propellants [5].

Iron compound is a representative catalyst of usual ammonium perchlorate containing solid rocket propellant. But, the mechanism of this catalytic effect on the propellant was not clearly known till now. In this experiment, the reaction mechanism of iron compounds on the solid rocket propellant was studied at first, and then the effect of iron compound catalysts was estimated with regard to the combustion catalysts on the NH_4ClO_4-$NaNO_3$-Al-binder propellant. At last, some effective catalysts were proposed for a chlorine free non-polluting solid propellant.

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2. Experimental

2.1 Materials

The aluminum used in this study was obtained from Alcoa, Inc., in the USA. Its particle size is below 5μm and the purity is 99.5 %. Ammonium perchlorate and sodium nitrate were reagent grade, and their particle sizes were about 150μm after pulverizing and sieving. The iron oxide catalyst (α-Fe_2O_3) was obtained from Tohoganryou K.K. and its particle size is about 0.2μm. The catocene catalyst was industrial grade obtained from Arapahoe Co. Ltd. Lanthan containing perovskite catalysts were made from calcium nitrate, manganese nitrate, cobalt nitrate and lanthanum nitrate. Active carbons of AC1(speccific surface area;865 m^2/g, average particle size; 3.6μm), AC2(1477 m^2/g, 1.8μm) and AC3(1516 m^2/g, 30.9μm), were obtained from Mitubishi Chemical Corporation.

Twelve types of propellants were prepared using 20.0 wt.% GAP (or HTPB)) as the binder, 62.4 wt.% oxidizer and 17.6 wt.% aluminum, and 0~5 wt.% catalysts were added to the propellants.

2.2 Analysis

Thermal analyses were performed using a RIGAKU DTA-TG simultaneous analyzer, in which the sample weight was 5 mg and the heating rate was 20 ℃/min under an argon gas stream. The sample container was an open alumina crucible (5 mm i.d.× 5 mm height).

A qualitative analysis of the reaction products was performed using X-ray powder diffraction.

A quantitative analyses of water soluble iron was performed using UV-visible spectrophotometer for the reaction product of the mixture of ammonium perchlorate (90 mg), catocene (10 mg) and α-Al_2O_3 (200 mg). Before analyses, the mixture was heated to a given temperature or for a given time and the cooled sample was dissolved in 100 ml of distilled water. Then, this solution was filtrated through membrane filter (pore size; 0.45 μm).

2.3 Combustion experiment

The linear burning rate was measured for the strands formed in a 6 mm x 6 mm shape. The time needed for the 40 mm burning of the strands was measured by means of a chimney type strand burner under pressurized nitrogen ranging from 3 to 12 MPa.

3. Results and discussion

3.1 Reaction mechanism of iron compound catalyst of the ammonium perchlorate containing solid rocket propellant

Iron oxide is a representative catalyst of usual ammonium perchlorate-containing solid rocket propellant. But, the mechanism of this catalytic effect on the propellant was not cleanly known till now. Figure 1 shows the results of thermal analyses of ammonium perchlorate and its mixture with catocene catalyst under atmospheric and pressurized condition of nitrogen. Under atmospheric condition, ammonium perchlorate with 5wt% catocene catalyst caused four exothermic reactions at lower temperature compared to that without catalyst. Under pressurized condition, catocene also showed catalytic effect of ammonium perchlorate decomposition.

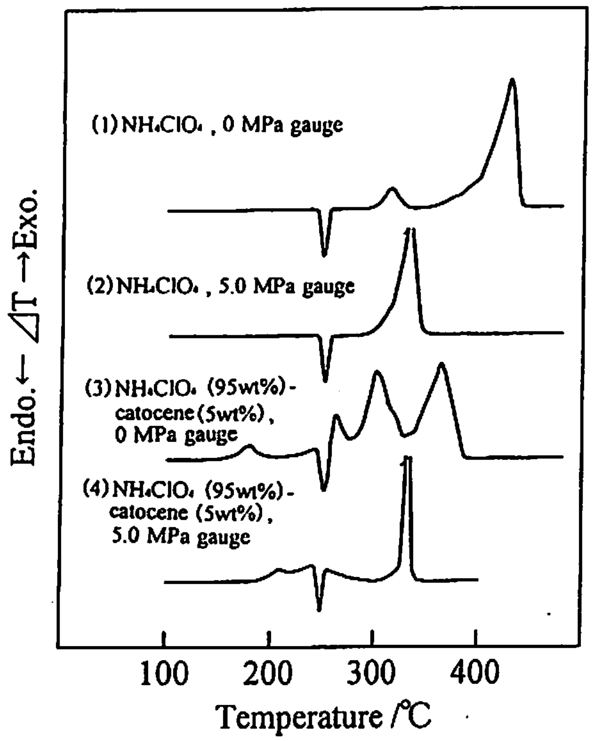

Fig. 1 DTA curves of NH_4ClO_4 and its mixture with catocene under atmospheric and pressurized condition of nitrogen

From the X-ray powder diffraction of the reaction product, catocene changed to iron oxide at 400℃.

Table 1 Fraction of water soluble iron formation on dynamical heating of the mixture of ammonium perchlorate and catocene up to 300℃

Temperature	(℃)	200	230	260	280	300
[Soluble Fe]/ [Total Fe]	(%)	0.8	8.1	19.4	27.6	1.1

Sample ; NH_4ClO_4 (90 mg), Catocene (10 mg), α-Al_2O_3 (200 mg)

Table 2 Fraction of water soluble iron formation on isothermal heating of the mixture of ammonium perchlorate and catocene

Temperature (℃)	Heating Time (hours)	[Soluble Fe]/ [Total Fe] (%)
240	1.0	19.2
	2.0	21.0
	3.0	21.8
	6.0	12.7
245	3.0	49.0
	4.0	52.5
	6.0	56.2
	10.0	0.1
250	1.5	56.5
	3.0	3.2

Sample ; NH_4ClO_4 (90 mg), Catocene (10 mg), α-Al_2O_3 (200 mg)

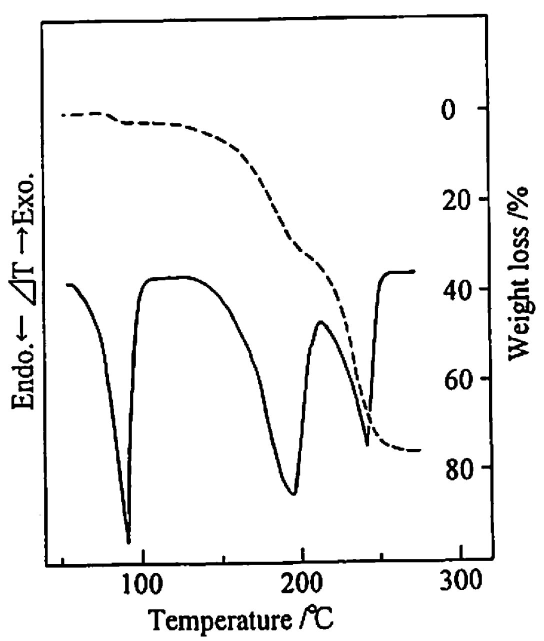

Fig.2 Thermal analysis of $Fe(ClO_4)_3 \cdot 6H_2O$

But, ammonium perchlorate with 5wt% catocene catalyst produced water soluble iron compound in the course of the reaction. Table 1 shows the fraction of water soluble iron on dynamical heating up to 300℃. Much more water soluble iron was produced on isothermal heating and 56.5% of iron in catocene changed to ionic iron compound on heating for 1.5 hours at 250 ℃(Table 2). Though it was not identified by X-ray powder diffraction of the reaction residue in the course of the reaction, this water soluble intermediate was estimated as iron perchlorate. Figure 2 shows the results of thermal analysis of iron perchlorate ($Fe(ClO_4)_3 \cdot 6H_2O$). Iron perchlorate hydrate underwent a partial dehydration of water of crystallization at about 60 ℃ and a decomposition with dehydration at about 120℃. From these results, it was estimated that catalytic effect of iron compounds was ascribed to the formation of an unstable iron perchlorate in the course of reaction.

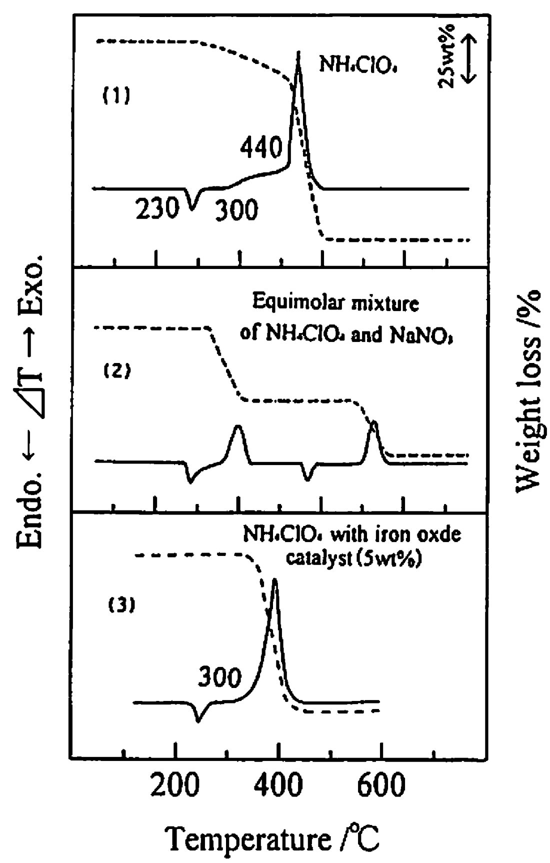

Fig.3 Thermal analysis of NH_4ClO_4, the mixture of NH_4ClO_4 with $NaNO_3$ and NH_4ClO_4 with iron oxide catalyst in air

3.2 Reation mechanism of scavenged propellant

Figure 3 shows the results of the thermal analyses of ammonium perchlorate and the mixture of ammonium perchlorate with sodium nitrate in air. The DTA trace of the mixture of ammonium perchlorate with sodium nitrate showed two exotherms at 300 ℃ and 560℃, and an endotherm at 455 ℃. X-ray powder diffraction analyses of the reaction residue were carried out at 360 and 650℃. The reaction residue at 360 ℃ was sodium perchlorate and that at 650℃ was sodium chloride. The observed weight loss of 41 % corresponded well to the calculated one of 40 % according to equation (1), in which ammonium nitrate formed was assumed to decompose and gasify:

$$NH_4ClO_4 + NaNO_3 \rightarrow NaClO_4 + NH_4NO_3 \qquad (1)$$

This double decomposition was confirmed by the fact that the observed endotherm at 455 ℃, which was accompanied by no weight change, corresponded to the melting point of the formed sodium perchlorate [4]. The observed final weight remaining of 27 % was in good agreement with the calculated value of the sodium chloride formation described by equation (2):

$$NaClO_4 \rightarrow NaCl + 2O_2 \qquad (2)$$

Figure 3-3 shows the results of the thermal analysis of ammonium perchlorate with 5 wt. % iron oxide catalyst. Unlike the case without a catalyst in which a two-step decomposition occurred, ammonium perchlorate with the iron oxide catalyst underwent an intense decomposition at 300℃.

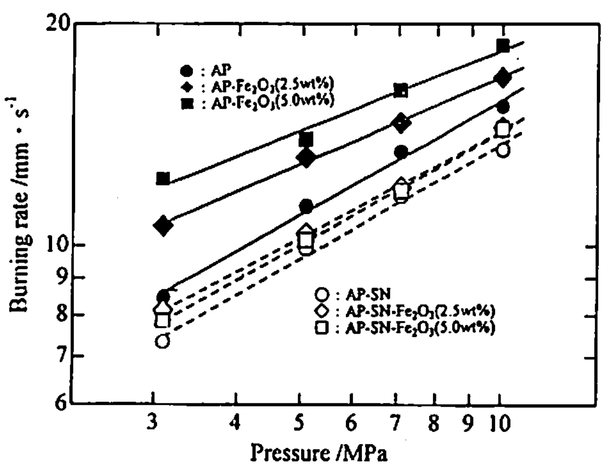

Fig.4 Effect of iron oxide catalyst on linear burning rate of NH_4ClO_4-Al-GAP and NH_4ClO_4 · $NaNO_3$-Al-GAP composite solid propellants under pressurized nitrogen

Figure 4 shows the results of the linear burning rate measurements for an ammonium perchlorate - aluminum - glysidyl azide polymer- iron oxide catalyst and an ammonium perchlorate- sodium nitrate-aluminum- glysidyl azide polymer - iron oxide catalyst composite solid propellant under pressurized nitrogen, in which the catalyst level was from 0 to 5 wt. % of the total amount of oxidizer. The linear burning rate of an ammonium perchlorate- aluminum- glysidyl azide polymer composite solid propellant increased with increasing amount of additive level and ambient pressure. On the other hand, the effect of iron catalysts on the combustion of the sodium nitrate-containing propellant was different from that without sodium nitrate; that is, the linear burning rate of a sodium nitrate- containing propellant increased with ambient pressure, but did not change with an increasing amount of additive.

Iron oxide is a well-known catalyst for ammonium perchlorate and ammonium perchlorate containing propellants. However, it has no effect on the decomposition of the mixture of ammonium perchlorate with sodium nitrate and a sodium nitrate-containing propellant. In this experiment, a detailed investigation was not carried out, but the mixture of ammonium perchlorate with sodium nitrate did produce a sodium perchlorate intermediate. This intermediate was less reactive compared to the original ammonium perchlorate. This may be one reason for the difference in the combustion characteristics between a sodium nitrate-containing propellant and that without sodium nitrate.

3.3 Effect of the catalyst on scavenged propellant

Figure 5 shows the effect of lanthan containing-perovskite-type oxide catalysts on the thermal analysis of the equimoler mixture of ammonium perchlorate and sodium nitrate under atmospheric condition. Though the mixture of ammonium perchlorate and sodium nitrate caused none of remarkable exothermic reaction, the mixture with perovskite catalysts showed an intense exotherm

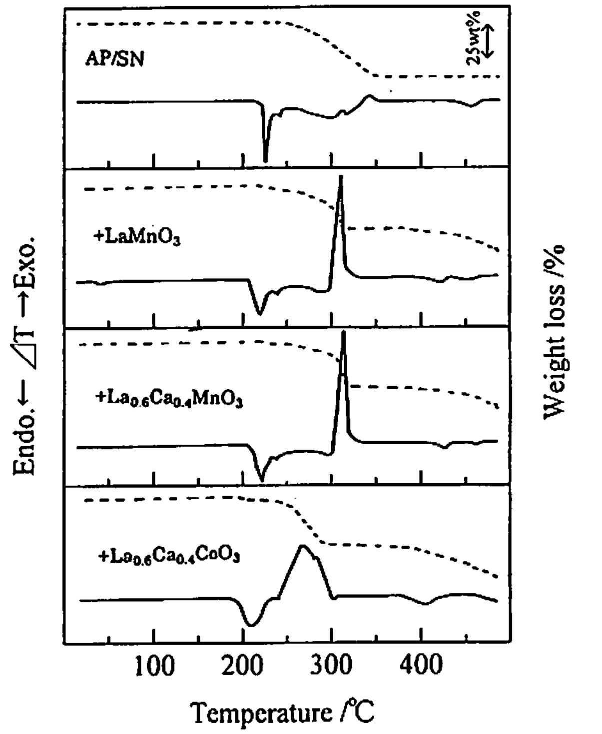

Fig.5 Thermal analysis of the mixture of NH_4ClO_4 and $NaNO_3$ with and without perovskite-type oxide catalysts

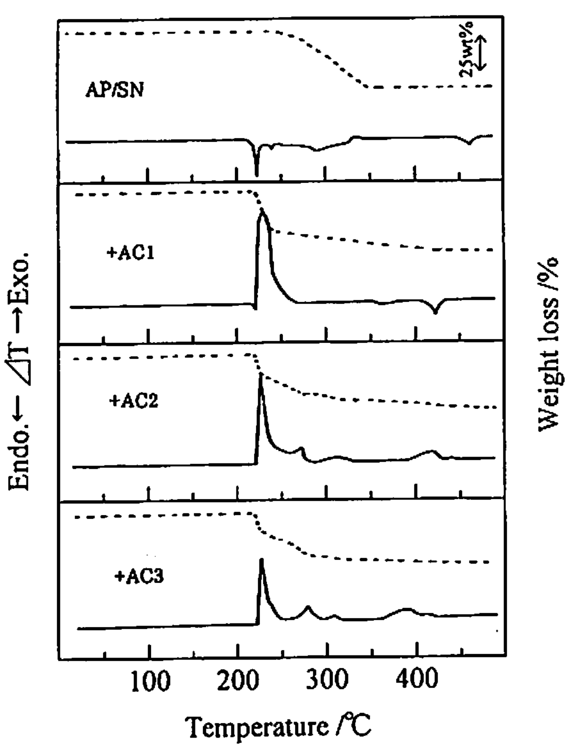

Fig.6 Thermal analysis of the mixture of NH_4ClO_4 and $NaNO_3$ with and without active carbon catalysts

at 240 ~320℃ that corresponded to the low temperature decomposition of ammonium perchlorate. So, it can be concluded that lanthan

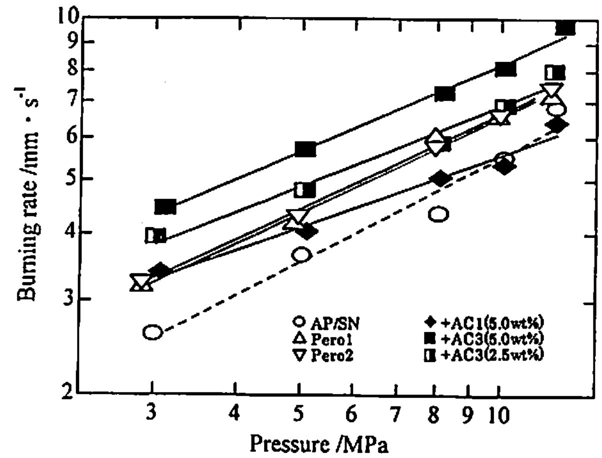

Fig.7 Effect of catalysts on linear burning rate of NH_4ClO_4-$NaNO_3$-Al-GAP composite solid propellants under pressurized nitrogen

containing-perovskite-type oxide catalysts have a catalytic effect on the thermal reaction of the mixture ammonium perchlorate and sodium nitrate. Figure 6 shows the results of the thermal analysis of the mixture of ammonium perchlorate and sodium nitrate with and without active carbon catalysts. When active carbon was added to the mixture, the DTA trace showed an intense exotherm at about 220 ℃ that corresponded to the eutectic temperature of the binary mixtures.

Figure 7 shows the effect of catalysts on linear burning rate of NH_4ClO_4-$NaNO_3$-Al-HTPB composite solid propellants with and without catalysts under pressurized nitrogen, in which the catalyst levels were from 0 to 5 wt. % of the total amount of propellant. The linear burning rate of a scavenged propellant increased with increasing ambient pressure and showed an increase compared to that without a catalyst. The pressure index calculated from Vieille's equation had the value of 0.46~0.47 for perovskite catalysts and of 0.43~0.52 for active carbon with different catalyst levels, which was smaller than that of a scavenged propellant without catalyst(n = 0.63). From these result, it was concluded that active carbon had a catalytic effect both on the thermal reaction and combustion of a scavenged propellant.

4. Conclusion

The reason why iron compounds had the catalytic effect to ammnium perchlorate and ammonium perchlorate containing - solid rocket propellant was ascribed to the formation of an unstable iron perchlorate in the course of reaction. But, it had no catalytic effect on the scavenged propellant (NH_4ClO_4-$NaNO_3$-Al- binder propellant) and a neutralized propellants (NH_4NO_3-Al/Mg-binder or NH_4ClO_4-Al/Mg -binder). The reason of this fact was considered as follows. That is, sodium perchlorate and ammonium nitrate which were more stable compared to ammonium perchlorate were formed because of the double decomposition between ammonium perchlorate and sodium nitrate in NH_4ClO_4 -$NaNO_3$-Al-binder propellant on heating. Then, iron oxide or other iron containing catalyst had also no catalytic effect on sodium perchlorate and ammonium nitrate. On the other hand, active carbon had a catalytic effect both on the thermal reaction and combustion of a scavenged propellant. Moreover, the pressure index had the value of 0.43~0.52 for active carbon with different catalyst levels. Oxides, which had the structure of perovskite type, also had a catalytic effect on the NH_4ClO_4-$NaNO_3$-Al-binder propellant combustion and a small pressure index of 0.46~0.47, though its effect was smaller than that compared to activated carbon.

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