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Article

Thermal behavior of 5-amino-1H-tetrazole
— Influence of the additive on the ignitability —

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A fundamental study on ignitability improvement was investigated by the addition of various metal oxides (MoO_3, V_2O_5, WO_3, TiO_2, NiO, AgO, Ag_2O, BaO_2) to the 5-amino-1H-tetoirazole (HAT) $-Sr(NO_3)_2$ (SrN) mixture, which has already been used in practical application as a non-azide gas generant.

The 10wt.% addition of MoO_3 or V_2O_5 was found to lower the ignition temperature compared with that of the HAT-SrN binary mixture (425℃); ignition temperature was 195℃ by addition of MoO_3 and 260℃ by addition of V_2O_5. It was clear that these oxides improved ignitability, acting not as an oxidizing agent but as a catalysis. An oxide with high oxidizability, such as AgO, does not always contribute to improvement of the ignitability.

The kinetics parameter of the decomposition was investigated for the HAT and its mixtures by carrying out of isothermal decomposition. The addition of MoO_3 or V_2O_5 changed the rate equation of the decomposition from a first order equation to an autocatalytic one. These oxides seemed to be concerned involved in the cleavage reaction of the tetrazole ring by the same catalyst mechanism, though the mechanism was not clear.

The decomposition temperature of the oxidizing agent was lowered by the addition of most metal oxides used in this experiment, and was most lowered by addition of V_2O_5. The reactivity of SrN with HAT was promoted due to the decomposition of SrN at the lower temperature, which might explain the lower ignition temperature.

1. Introduction

Automobiles sold in Japan are generally have been equipped with airbag systems for greater safety driving in the event of an accident. A non-azide gas generant as a substitute for sodium azide in airbag system has been studied. For use in this capacity, tetrazole derivatives[1], urazole[2], and azodicarbonamide[3], were investigated in this study.

5-Amino-1H-tetrazole (hereafter, HAT) has already been used in practical application in a mixture system utilizing strontium nitrate (hereafter, SrN) of non-halogen nitrate. The HAT-SrN binary mixture has problematically low thermal reactivity resulting in bad ignitability and

poor combustion performance, though HAT has no toxicity and its mixture generates a great deal of gas during the combustion reaction. Resolution of this trouble is expected for the HAT mixture.

In this paper, a fundamental study on ignitability improvement by the addition of various metal oxides (MoO_3, V_2O_5, WO_3, TiO_2, NiO, AgO, Ag_2O, BaO_2) to the HAT-SrN mixture was conducted. The oxides were considered in terms of their ability as catalysts for the oxidation reaction and of their degree of oxidizability.

2. Experiment
2.1 Reagents

HAT was made by Toyo Chemical Co., Ltd. SrN of the oxidizing agent and various metal oxides (V_2O_5, WO_3, TiO_2, NiO, AgO, Ag_2O, BaO_2) except for MoO_3 was Wako Pure Chemical Industries, Ltd. NiO was also synthesized by the decomposition of $NiCO_3$ in order to prepare a non-stoichiometric NiO (hereafter, actNiO). MoO_3 was made by Nippon Special Chemical Co., Ltd. Reagents screened to under 63 μm were mixed for sixty

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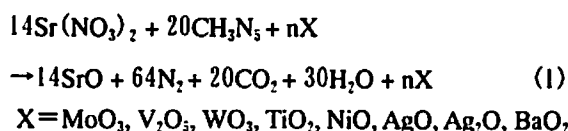TEL +81-93-884-3334
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minutes using splittable chopsticks on parchment paper. Several kinds of samples were prepared by mixing. Table 1 shows these compositions. 10 wt.% of a metal oxide was added for the HAT-SrN stoichiometric composition, based on eq.1. The binary mixture with the metal oxide was prepared so that the weight ratio of the two compositions became equal to their weight ratio in the tertiary mixture.

$$14Sr(NO_3)_2 + 20CH_3N_5 + nX$$

$$\rightarrow 14SrO + 64N_2 + 20CO_2 + 30H_2O + nX \qquad (1)$$

$$X = MoO_3, V_2O_5, WO_3, TiO_2, NiO, AgO, Ag_2O, BaO_2$$

2. 2 Apparatus and method
2. 2. 1 Thermal analysis

The differential thermal analysis (hereafter, DTA) and the gravimetric analysis were carried out using a Rigaku Thermal Analyzer ThermoPlus. The sample container was an alumina cell and the sample amount was 2 mg. The sample was heated to 800℃ at a heating rate of 20 K/min under Ar.

Further, the isothermal decomposition experiment was also carried out using a Rigaku Thermal Analyzer ThermoPlus. The 2mg sample was heated to 195℃ at a heating rate of 100 K/min. and was kept at 195℃ for several hours. The weight loss of the sample over time was measured, and an applicable rate equation was investigated from the fractional decomposition; the n-order reaction and an autocatalytic equation, etc.

2. 2. 2 Ignition test

The ignition test was carried out according to the Krupp method[5]. 10 mg of the sample pellet was put in a glass vessel with a 200ml capacity. The ignition delay period was measured. The criterion of ignition was whether the sample ignited within 30 seconds from the time it was dropped into the vessel. The ignition residue was analyzed by X-ray diffraction using a Rigaku rotaflex RU-200.

3. Results and Discussion
3. 1 Thermal behavior of the HAT-SrN with adding the metal oxide
3. 1. 1 Thermal analysis

Figure 1 shows the results of the thermal analysis of (a) HAT and (b) its binary mixture with SrN. The HAT started to melt at 200 ℃ and then decomposed

Table 1 Composition of SrN/HAT/X mixtures
$X = MoO_3, V_2O_5, WO_3, TiO_2, NiO, AgO, Ag_2O, BaO_2$

Composition	Weight ratio (wt./wt/wt.)
SrN/HAT	63.52/36.48
SrN/HAT/X	63.52/36.48/10.00
HAT/X	36.48/10.00
SrN/X	63.52/10.00

exothermally over a wide temperature range.

For the mixture with $Sr(NO_3)_2$ of the oxidizing agent, slight difference in apparent thermal behavior was shown compared with that of the HAT alone, though a sharp exothermal peak was observed at 500℃. The unreactive $Sr(NO_3)_2$ was also found to decompose at 560℃.

Figure 2 shows the results of the thermal analysis of various HAT-SrN-additive tertiary mixtures. In the mixture to which MoO_3 was added, the exothermic reaction was observed immediately after a very slight endothermic peak at 200℃. When V_2O_5 or WO_3 was used as the additive, the exothermic peak was confirmed after the melting. On the other hand, in the HAT-SrN mixture with TiO_2 or NiO, there was only a slight difference in apparent thermal behavior compared with that of the HAT-SrN mixture alone. It was interesting to note that the use of ActNiO cause an exothermic reaction at the initial stage, in contrast with the
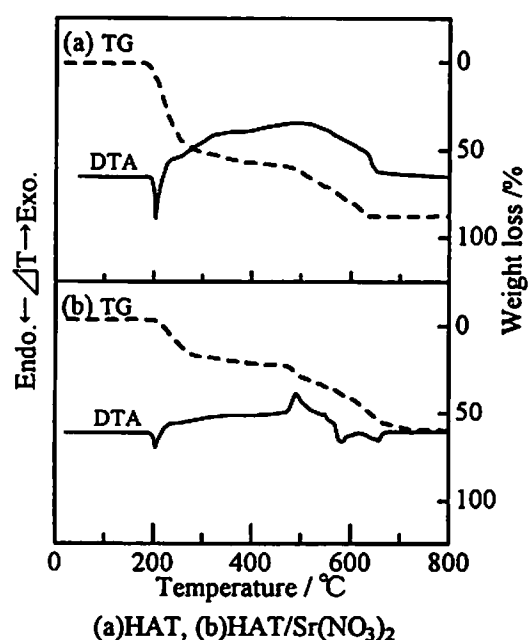

(a)HAT, (b)HAT/Sr(NO₃)₂

Fig.1 DTA-TG curves of HAT and its mixture with SrN

result in the reagent grade NiO, as shown in Fig.2 (f). The metal oxides (AgO, Ag$_2$O, and BaO$_2$), which show large oxidizability, did not always affect the oxidation –reduction in the HAT-SrN mixture under the measurement condition used in the thermal analysis. A slight exothermic peak before melting was observed only in the HAT-SrN-AgO mixture. It was expected that the size of the calorific value in the initial reaction was related to the ignitability.

3. 1. 2 Burning rate characteristics

Figure 3 shows the plots of the minimum ignition temperature in various tertiary systems. The minimum ignition temperature was 425℃ in the HAT-SrN binary mixture. The addition of MoO$_3$ was the most effective for the minimum ignition temperature reduction. The ignition temperature was also lowered by addition of V$_2$O$_5$ or NiO. In the other systems investigated herein, there was no addition effect for the ignition temperature reduction. Using WO$_3$ or AgO as the additive did not lead to ignition temperature reduction, though an exothermic reaction was observed in the initial reaction in DTA curve for these systems (Fig.2). Similarly, not ActNiO but NiO was effective for ignition temperature reduction. Therefore, the tendency of the ignition temperature reduction did not always agree with one of the exothermic peaks in the initial reaction in DTA. In addition, the oxidizability of the additives seemed to not affect the ignition temperature reduction.

Figure 4 shows the results of the X-ray diffraction of the combustion residue for six kinds of tertiary mixture as representative examples; in these cases, the addititives were MoO$_3$, V$_2$O$_5$, WO$_3$, NiO, ActNiO, and AgO, respectively. Fundamentally, most of the additives used in this experiment did not react with the others, and each finally formed a composite oxide with SrO.

However, the additives showing high oxidizability acted as an oxidizing agent in the reaction, so that a considerable amount of unreactive SrN remained as representative of the result of the AgO mixture (Fig.4 (f)). On the other hand, the diffraction intensity of SrN was small in the HAT-SrN-WO$_3$ mixture. The addition of WO$_3$ seemed to promote the oxidation-reduction reaction between HAT and SrN, so that this was thought to cause an initial exothermal reaction in DTA curve for the tertiary mixture. Further, it is interesting that the effect of the additives was different between the reagent grade NiO and the ActNiO. Use of ActNiO allowed SrN of the
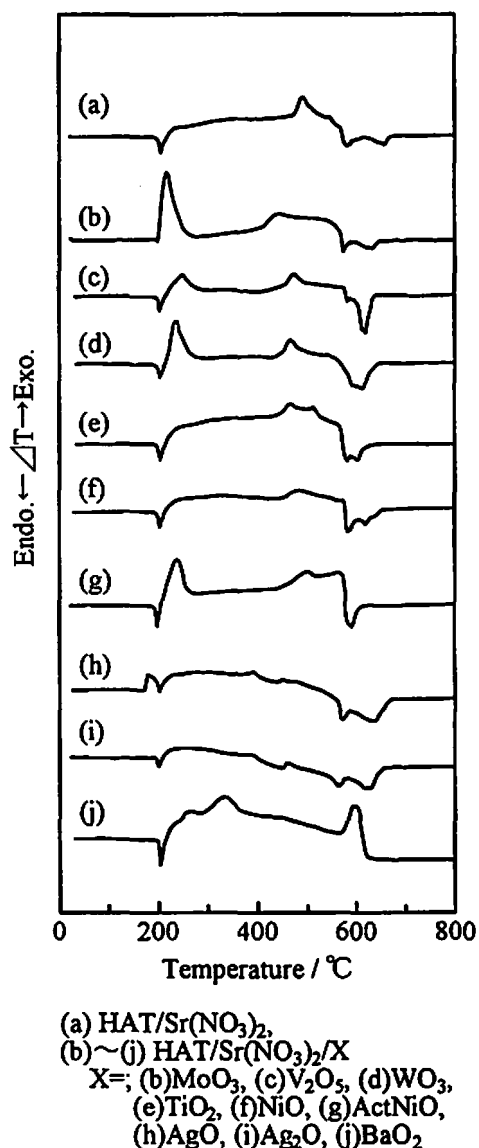

(a) HAT/Sr(NO$_3$)$_2$,
(b)~(j) HAT/Sr(NO$_3$)$_2$/X
  X=; (b)MoO$_3$, (c)V$_2$O$_5$, (d)WO$_3$,
  (e)TiO$_2$, (f)NiO, (g)ActNiO,
  (h)AgO, (i)Ag$_2$O, (j)BaO$_2$

Fig.2 DTA curves for various HAT/SrN/ X mixtures (X: metal oxide)

(a) HAT/SrN
(b)~(j) HAT/SrN/X
  X=; (b)MoO$_3$,(c)V$_2$O$_5$,(d)WO$_3$,
  (e)TiO$_2$,(f)NiO,(g)activated NiO,
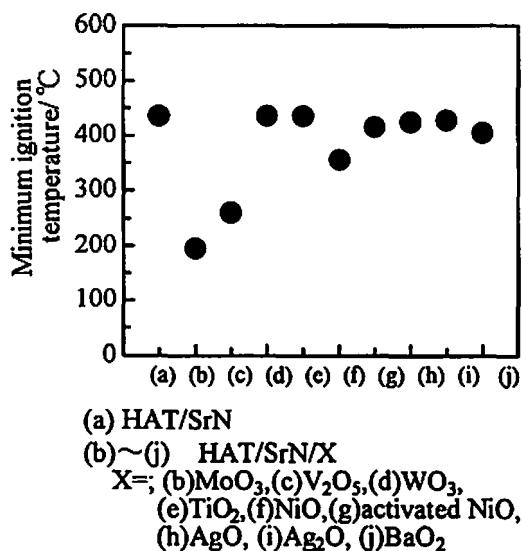 (h)AgO, (i)Ag$_2$O, (j)BaO$_2$

Fig.3 Minimum ignition temperature for various HAT-SrN-X mixtures (X: metal oxide)
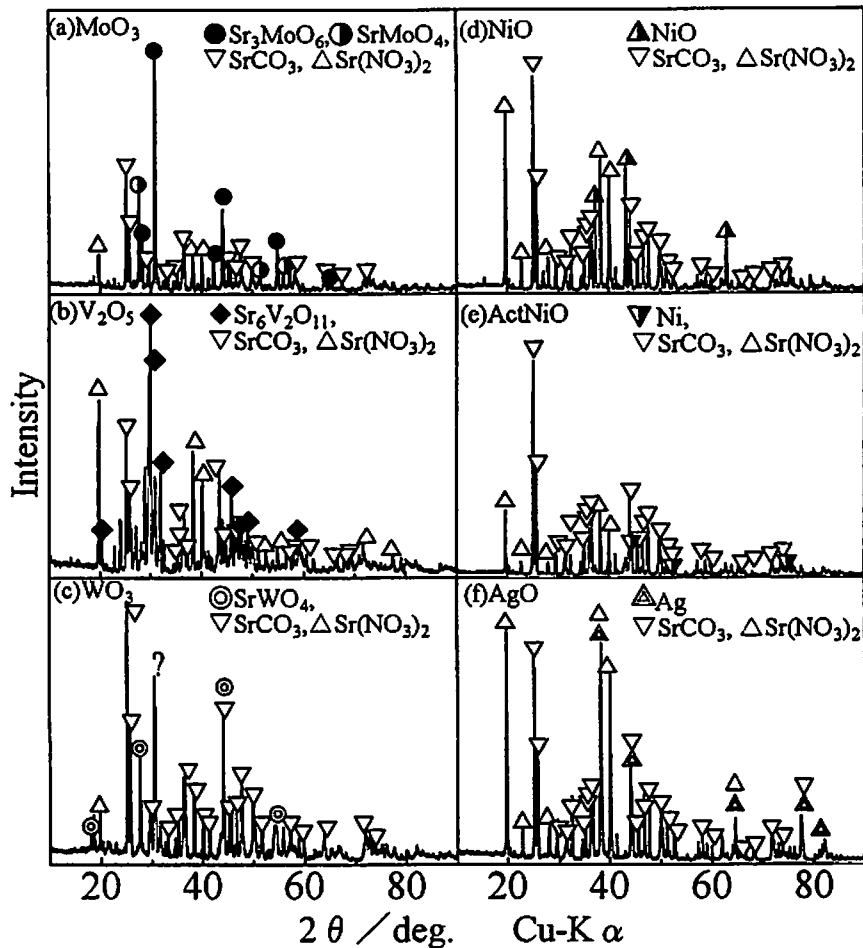
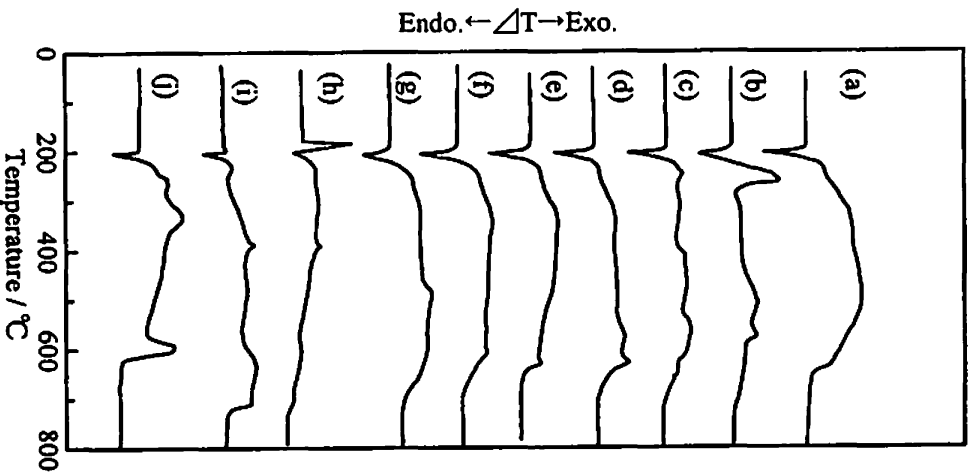Fig.4 X-ray diffraction of the combustion residue

oxidizing agent to contribute more to the reaction, and ActNiO also decomposed to Ni.

From these results, the oxidation of HAT or the promotion of the oxidation-reduction between HAT and SrN seemed not to be effective method in order to lead to the improvement in the ignitability.

3. 2 Influence of the metal oxide on the reactivity of the HAT

Figure 5 shows the result of the thermal analysis of the binary HAT mixtures to which various metal oxides were added. The remarkable exothermic reaction after the melting was confirmed in the initial reaction by the addition of MoO_3 or V_2O_5. These oxides were thought to promote the decomposition of HAT. In HAT-WO_3 binary mixture, the initial exothermic reaction was not confirmed unlike the result in the tertiary mixture (Fig.2(d)). WO_3 was thought to seldom affect the decomposition of the HAT. From these results, it might be effective to promote the decomposition of HAT for the ignitability improvement.

On the other hand, AgO addition did not show an ignition temperature reduction in spite of the existence of the exothermic reaction before the melting in the DTA curve for the binary mixture. AgO reacted with HAT not as a catalyst but as an oxidizing agent due to its high oxidizability. The material, which caused the oxidation-reduction reaction with HAT, does not always lower the ignition temperature. Further, the isothermal decomposition was carried out in order to clarify the effect of the oxide addition on the HAT decomposition. Figure 6 shows the fractional decomposition versus time curve during the isothermal decomposition at 195°C. Data on several binary mixtures is arranged as simply as possible, and the result of the HAT alone is also shown for reference. The fractional decomposition was derived from the weight loss of the sample. For the mixture system to which was added the oxide showing high oxidizability, the isothermal experiment was not executed. The form of the curve for the mixture to which MoO_3 or V_2O_5 were added was clearly different than that of HAT alone. An applicable rate equation was investigated by

Endo.←△T→Exo.

Temperature / ℃

(a) (b) (c) (d) (e) (f) (g) (h) (i)

Fig.5 DTA curves for various HAT-X mixtures
(X: metal oxide)

(a) HAT,
(b)~(i) HAT/X
X=, (b)MoO$_3$, (c)V$_2$O$_5$, (d)WO$_3$,
(e)TiO$_2$, (f)NiO, (g)activated NiO,
(h)Ag$_2$O, (i)BaO$_2$

Fractional decomposition

Time / min.
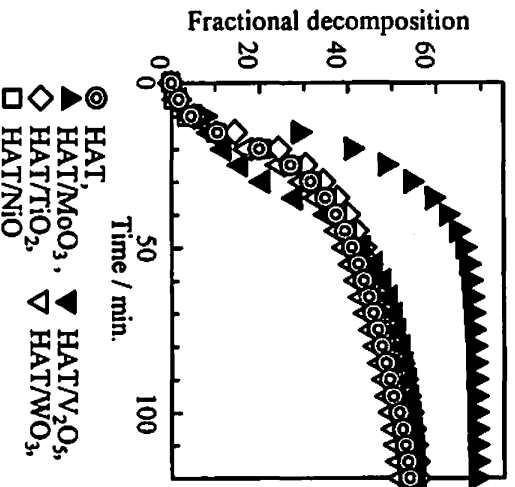
Fig.6 Fractional decomposition versus time curves for various HAT-metal oxide

◎ HAT,
▲ HAT/MoO$_3$, ▼ HAT/V$_2$O$_5$,
◇ HAT/TiO$_2$, ▽ HAT/WO$_3$,
□ HAT/NiO

−ln(1−X)

ln(x/(1−x))

Time / min.
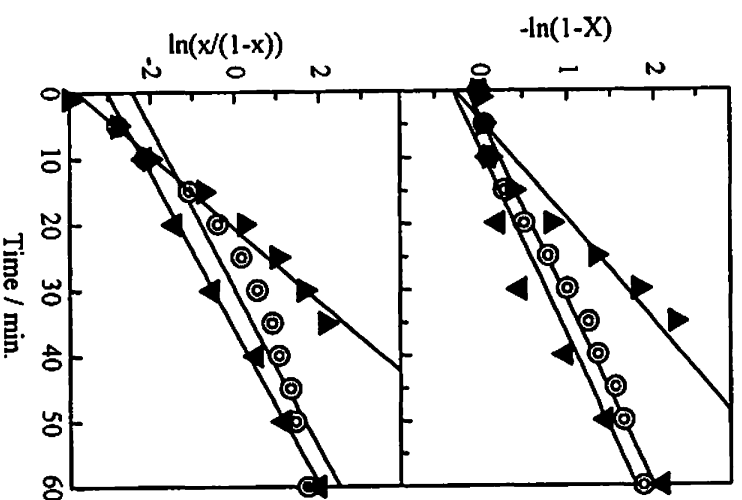
Fig.7 Plots of −ln(1−X) and ln(X/(1−X)) versus time for the binary mixtures

◎ HAT,
▲ HAT/MoO$_3$, ▼ HAT/V$_2$O$_5$,
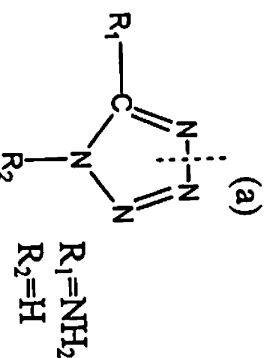

R_1
R_2

R_1=NH$_2$
R_2=H

(a)

Fig.8 The cleavage of the hetero ring of the HAT

the fractional decomposition. As shown in Fig.7, an autocatalytic equation can describe the reaction in the mixture with MoO$_3$ or V$_2$O$_5$, whereas a first order equation can describe the reaction in the HAT alone. A first order equation was also the best suited to mixture with all additives excepting MoO$_3$ and V$_2$O$_5$. From these results, MoO$_3$ and V$_2$O$_5$ might act on the decomposition of the HAT by the same catalyst mechanism.

J. Z. Wu et al. reported[6] that the N-N bond cleave first in hetero ring of HAT, as represented by the dotted line (a) in Fig.8. In our further investigation, it became clear that MoO$_3$ affected the decomposition of the tetrazole compound in the case that the electron-withdrawing groups, such as NH$_2$ group or OC$_6$H$_5$ group, exist in the

tetrazole ring. It was indicated that the tetrazole ring was made unstable by that Mo^{5+} or Mo^{4+} pulled the lone pair of the electro-withdrawing group. V^{4+} exists for V_2O_5 considering from this viewpoint. Catalyst effect of both oxides might be the promotion of the cleavage of the N-N bond (the dotted line (a) in Fig.8). More detailed investigation results on the catalyst mechanism will be reported.

3. 3 Influence of the metal oxide on the reactivity of the SrN

Figure 9 shows the results of the thermal analysis for various SrN-metal oxide mixtures. The arrow in figure indicates the temperature at which weight loss began; the decomposition of SrN alone is shown in Fig.9 (a).
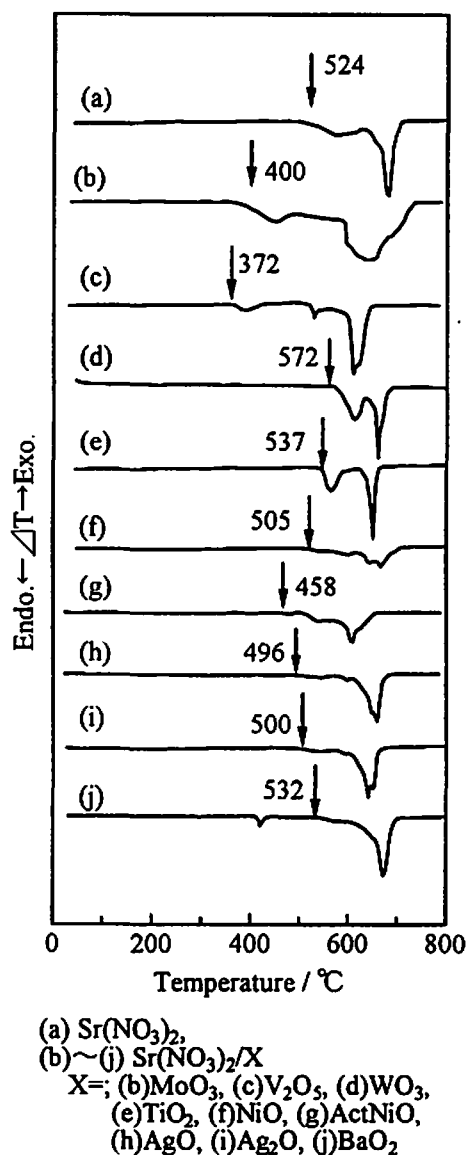

(a) Sr(NO₃)₂,
(b)~(j) Sr(NO₃)₂/X
  X=; (b)MoO₃, (c)V₂O₅, (d)WO₃,
     (e)TiO₂, (f)NiO, (g)ActNiO,
     (h)AgO, (i)Ag₂O, (j)BaO₂

Fig.9 DTA curves for various SrN-the metal oxide mixtures

In mixture systems with the oxide except for WO_3, TiO_2 and BaO_2, the decomposition temperature was lowered the most by addition of V_2O_5. The decomposition promotion of the oxidizing agent was thought to affect the lowering of the ignition temperature. However, the material, which greatly promotes the decomposition of not the oxidizing agent but the HAT, as mentioned in 3.2, was guessed to more greatly work for the ignition temperature reduction considering from the effect for the ignitability.

On the other hand, the initial temperature of decomposition rose slightly little by addition of WO_3 or TiO_2. These metal oxides might inhibit the decomposition of the nitrate, though the reason the slightly raised temperature in these cases was not clear.

4. Conclusions

Improvement of ignitability of the 5-amino-1H-tetoirazole (HAT) -strontium nitrate (SrN) mixture, which has already been use as a non-azide gas generant, by addition of various metal oxide to the HAT-SrN mixture was investigated.

The 10 wt.% addition of MoO_3 or V_2O_5 lowered the ignition temperature compared with that of the HAT-SrN binary mixture; the ignition temperature was lowered to 225°C by addition of MoO_3 and to 165°C by addition of V_2O_5. It was clear that these oxides improved ignitability. Oxides such as AgO, which has a high oxidizability, caused the oxidation-reduction reaction with HAT, and did not always contribute to improvement of ignitability. the oxidation of HAT or the promotion of of the oxidation-reduction between HAT and SrN seemed not to be effective method in order to lead to the improvement in the ignitability.

For HAT and its mixtures with various oxides, experiment of the isothermal decomposition was carried out at the initial temperature of the decomposition of HAT. An autocatalytic equation could describe the reaction in the mixture with MoO_3 or V_2O_5, whereas a first order equation could describe the reaction in the HAT alone. A first order equation was also best suited to the mixtures with all additives excepting MoO_3 and V_2O_5. MoO_3 and V_2O_5 might act on the decomposition of the HAT by a similar catalytic mechanism. MoO_3 and V_2O_5 seemed to be involved in the cleavage reaction of the tetrazole ring, though the mechanism of involvement was not clear.

On the other hand, the decomposition temperature of

SrN was lowered by the addition of most metal oxides in this experiment, and particularly by the addition of V_2O_5 in all mixtures. Decomposition promotion of the oxidizing agent was also thought to affect the lowering of the ignition temperature. The reactivity of SrN with HAT was speculated to be improved as a result of the occurrence of the decomposition of SrN at the lower temperature.

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5 - アミノ - 1 H - テトラゾールの熱挙動
－着火性に及ぼす添加物の影響－

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エアバッグ用ガス発生剤として既に実用化されている5－アミノ1H－テトラゾール (HAT) 組成物に関して，着火性改良を目的として種々の金属酸化物 (MoO_3, V_2O_5, WO_3, TiO_2, NiO, AgO, Ag_2O, BaO_2) が添加された.添加量は、HAT-SrN 2成分混合物に対して外割で 10Wt.%とした。

HAT－Sr(NO_3)$_2$混合物系の最低発火温度は，MoO_3の添加によって 425℃から 195℃へ，V_2O_5の添加によって 260℃まで低下した.これらの酸化物は酸化剤としてではなく，触媒として系に作用した.AgO のような高い酸化力を持つ酸化物は，最低発火温度の低下に必ずしも寄与するわけではないことが明らかとなった。

HAT ならびに金属酸化物との2成分混合物について等温分解を行い，分解の速度パラメータを検討した.分解反応は，発火温度の低下に寄与する MoO_3,V_2O_5添加系では自触媒反応の式に，HAT 単体ならびに他の酸化物添加系では1次反応の式に最もよく適合した.MoO_3,V_2O_5は，HAT の分解に対して同じ触媒作用を持つことが推測された。

一方，酸化剤である Sr(NO_3)$_2$の分解温度も種々の金属酸化物の添加によって低下する結果となり，V_2O_5の添加効果が最も大きかった.より低い温度で Sr(NO_3)$_2$が分解することで，HAT との反応性が促進されると推測された。

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