Effect of metal complex catalysis of tetraaza-(14)-anurene on the thermal decomposition of ammonium nitrate and ammonium perchlorate

Hidetsugu NAKAMURA*, Miyako AKIYOSHI*, Kazunori SAKATA* and Yasutake HARA*

The effect of various metal complex catalysts of tetraaza-(14)-anurene on the thermal decomposition of ammonium nitrate, ammonium perchlorate and a solid propellant containing ammonium perchlorate as an oxidizer was studied by thermal analysis and burning rate measurements. The following results were obtained.

A metal complex, which had iron or vanadium as a central metallic ion, showed high activity during the thermal decomposition of ammonium nitrate. Especially, this activity became high when chloride and perchlorate ions were combined with iron or vanadium ions.

Iron and vanadium catalysts also had high activity during the thermal decomposition of ammonium perchlorate and its solid propellant. For the solid propellants which contained iron or vanadium complexes as catalysts, the burning rate increased by 1.6 times and their n index decreased to 80 % compared to the burning experiments without a catalyst at a pressure of 5.0 MPa.

1. Introduction

There have been a wide variety of studies on decomposition catalysts of ammonium perchlorate (NH_4ClO_4; AP) and burning catalysts of AP containing composite propellants, even though basic or practical they were. For examples, Jacobs et al. and Solymosi summarized the action of metallic oxides, oxyacids, halides and so on[1,2]. With regard to the decomposition catalysts of ammonium nitrate (NH_4NO_3; AN), which are extensively used as oxidizers of industrial explosives and propellants, there have been many reports which were summarized by Urbanski[3].

It is well known that the activity of solid catalysts are significantly influenced by their method of preparation or raw materials, because catalytic activities are controlled by surface properties such as surface area, surface structure and impurities. Especially, a metallic oxide is strongly affected, because it may be calcined or ground during preparation. In the case of the catalytic activities of metallic oxides on the thermal decomposition of AP, Solymosi reported a discrepancy in the order of activities of metallic oxides[2].

In this paper, the effect of various metal complex catalysts of tetraaza-(14)-anurene on the thermal decomposition of ammonium nitrate, ammonium perchlorate and solid propellant containing ammonium perchlorate as an oxidizer was studied by thermal analysis and burning rate measurements. Moreover, the order of catalytic activities with regard to metal species were also discussed. Catalysts used are the complexes which coordinate metallic species on the central part of the tetraaza-(14)-anuren ligand. These catalysts take the form of a powder. The most important advantages for using these types of catalysts are that (1) compatibility among physical properties such as particle size, molecular weight and melting point with each other because of the strong effect of a large ligand field and (2) a capability of the ligand's action as an oxy-

Received on November 11, 1999
*Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Sensui, Tobata, Kitakyushu, 804-8550 JAPAN
TEL 093-884-3319
FAX 093-884-3300

Table 1 Propellant compositions tested in this study

Prop.	AP	HTPB	Complex			
			Ni	Mn·NCS	Fe·Cl	V=O
Ref.	86	14	—	—	—	—
Ni	84	14	2	—	—	—
Mn·NCS	84	14	—	2	—	—
Fe·Cl	84	14	—	—	2	—
V=O	84	14	—	—	—	2

gen carrier.

2. Experimental

2. 1 Materials

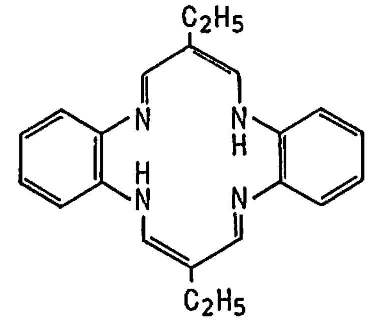
Ammonium nitrate and ammonium perchlorate were prepared by recrystallization of commercial reagents from pure water. Composite propellants for burning rate measurements consisted of ammonium perchlorate having an average particle size of 200 μm and hydroxyl-terminated poly butadiene (HTPB) as a binder.

The formulations of ammonium perchlorate composite propellants are shown in Table 1 and the structural formula of the complex and the ligand used in this experiment are shown in Fig.1. The ligand, nickel complex, iron complex and cobalt complex were synthesized by a previously reported method[4,5] and the other complexes were prepared by a method similar to that previously stated.

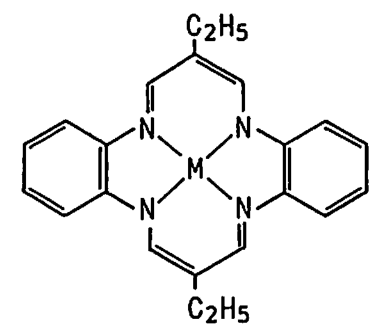
2. 2 Thermal analysis and burning characteristic measurements

Thermal analyses were carried out using a Rigaku Simultaneous DTA-TG Analyzer and a Rigaku High Pressure DTA Analyzer which can be operated under pressurized conditions. Small cylindrically shaped aluminum crucibles were used in this experiments which had an internal diameter of 4 mm ϕ and a height of 5 mm, and were sealed with a aluminum cover which had an pin-hole at the center. Heating rates were 20 ℃/min for the analysis of ammonium nitrate mixtures and 10 ℃/min for ammonium perchlorate mixtures.

Ignition temperature was measured by the Krupp method under an atmosphere of argon, using a sample of about 30 mg which has a dimension of 1 mm thickness and 3 mm × 3 mm width.



Ligand($C_{22}H_{22}N_4H_2$; RH_2)
5,14-dihydro-7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine



Complex($C_{22}H_{22}N_4M$; RM)
M= Cu, Co, Ni, Mn·NCS, Mn·ClO_4, Fe·Cl, Fe·ClO_4, V=O

Fig. 1 Structural formula of ligand and its metal complexes tested in this study

The burning rate measurements were carried out using a chimney type strand burner pressurized with nitrogen.

3. Results and Discussion

3. 1 Effect of metallic complexes on the thermal decomposition of ammonium nitrate

Thermal analysis experiments for ammonium nitrate and its mixtures were carried out under pressurized conditions because ammonium nitrate evaporates without decomposition under atmospheric conditions. Fig.2 and Fig.3 show DTA curves of ammonium nitrate, ligand, metallic complex catalysts and ammonium nitrate added with 10 wt% metallic complex catalysts.

Ligands show an endothermic peak at about 230 ℃ corresponding to its melting (melting point; 232 - 233.5 ℃) and an exothermic peak initiating at about 310 ℃ corresponding to the thermal decom-

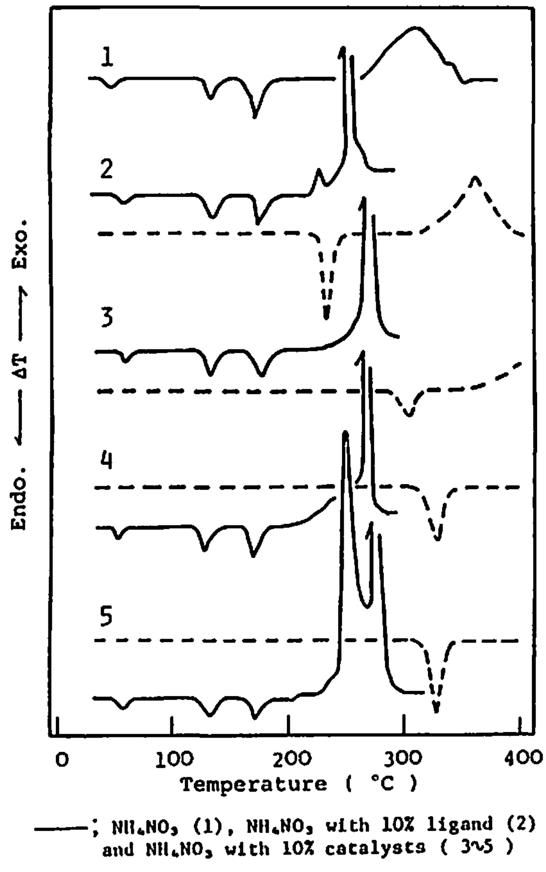


Fig. 2 DTA curves of NH_4NO_3, catalysts and NH_4NO_3 with catalysts under a pressure of 5.0 MPa gauge (1)

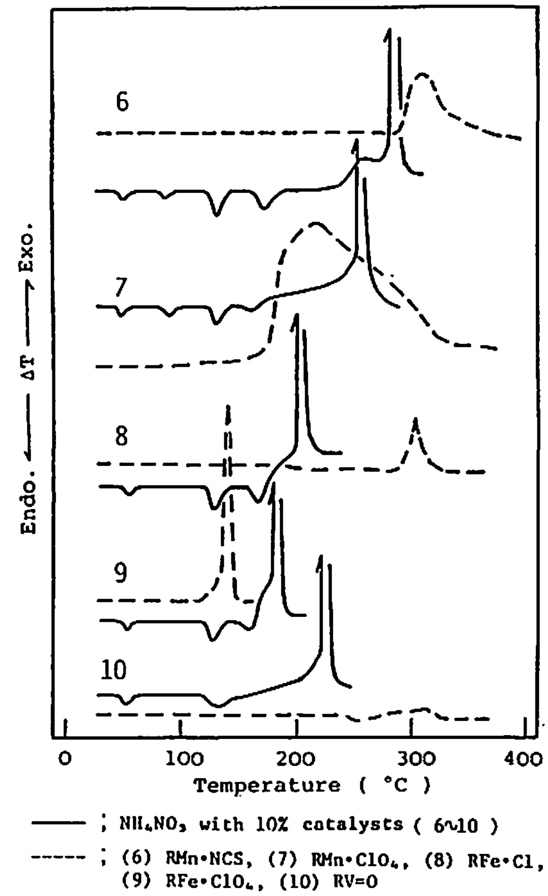
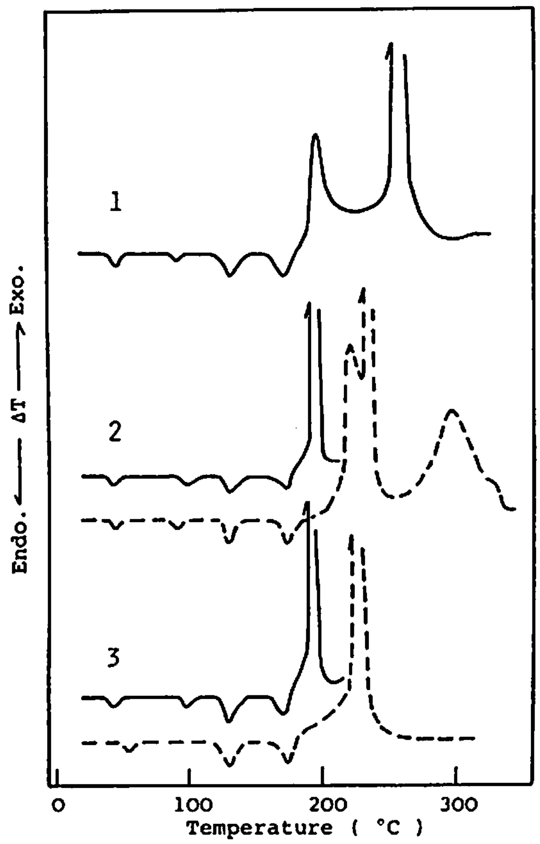


Fig. 3 DTA curves of NH_4NO_3, catalysts and NH_4NO_3 with catalysts under a pressure of 5.0 MPa gauge (2)

position. The thermal behaviors of metallic complexes are strongly dependent on a central metallic ion and are classified into two categories. One is the complex which gave rise to an endothermic decomposition such as the vanadium complex shown in Fig.3, and the other is the complexes which gave rise to the exothermic decomposition shown in Fig.2 and 3. Especially, both manganese complexes and iron complexes which coordinate perchlorate ion showed characteristic features in thermal behavior. That is, the former had a large heat evolution and the latter had a low decomposition temperature.

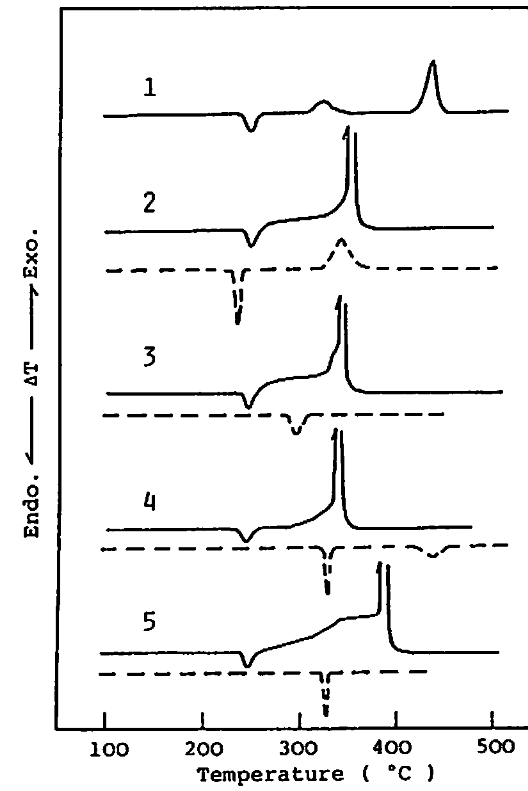
Ammonium nitrate undergoes phase transitions, melting at 169 ℃ and exothermic decomposition above approximately 265 ℃ upon heating under pressurized conditions. Addition of the above metallic complex catalysts to ammonium nitrate made its decomposition temperature lower and its exothermicity larger. When the organic compounds were added to ammonium nitrate, a violent exothermic reaction occurred at about 220 ℃ according to a mutual redox reaction. Therefore, it can be understood that the ligand acts similar to organic compounds if they are added to ammonium nitrate. Metallic complex catalysts having Cu, Co, Ni or Mn-NCS as a central metallic ion showed the same thermal behavior as the ligand. Although the Mn-ClO_4 complex itself underwent an exothermic decomposition at about the same temperature at which ammonium nitrate commenced melting, it could not cause such a violent exothermic reaction judging from the amount of low level addition as in these experiments.

Both iron and vanadium complexes showed a remarkable catalytic effect during the thermal reaction. The oxides of iron or vanadium such as Fe_2O_3 and V_2O_5 are known to have a slight catalytic effect on the thermal decomposition of ammonium nitrate[6]. Therefore, the catalytic effects of iron and vanadium in complexes were considered to be caused



——; NH_4NO_3 with RFe·Cl
-----; NH_4NO_3 with RV=O
catalysts levels; (1) 1%, (2) 3%, (3) 5% by weight

Fig. 4 Effect of catalysts levels on DTA curves of NH_4NO_3 with catalysts



——; NH_4ClO_4 (1), NH_4ClO_4 with 10% ligand (2) and NH_4ClO_4 with 10% catalysts (3∿5)
-----; (2) Ligand, (3) RCu, (4) RCo, (5) RNi

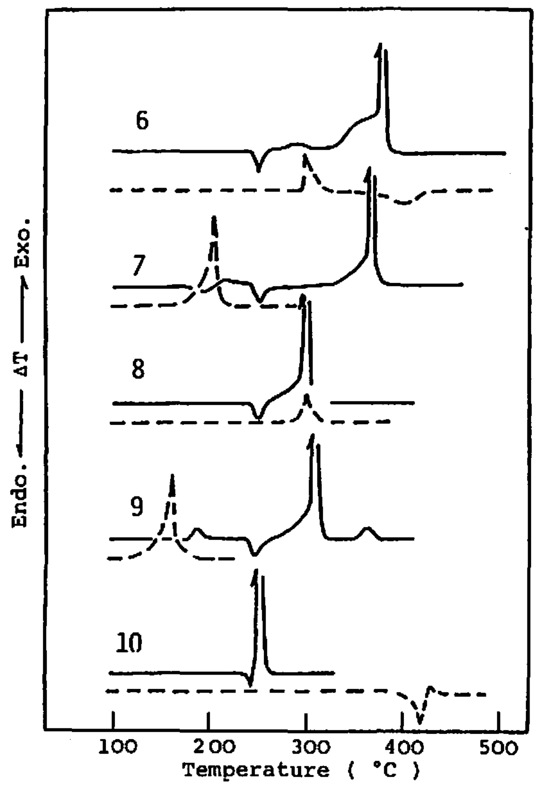
Fig. 5 DTA curves of NH_4ClO_4, catalysts and NH_4ClO_4 with catalysts under an atmospheric pressure (1)

by either the reaction products forming during the thermal decomposition of the complexes or the mutual reaction of the metallic ion with a ligand as a fuel. Furthermore, having been known that the catalytic effect of chloride ion on the thermal decomposition of ammonium nitrate, it is considered that two types of catalysts which contain chloride or perchlorate ions showed the catalytic effect because chloride ion is formed by its thermal decomposition.

In order to clarify the catalytic effect of complexes in detail, the 1, 3, 5 wt% addition of catalyst was tested in the above experiments. Fig.4 shows the effect of the amount of addition of Fe·Cl or V=O catalysts on the thermal reaction of ammonium nitrate. It was found from these results that the addition of 3 wt% catalysts gave an adequate effect.

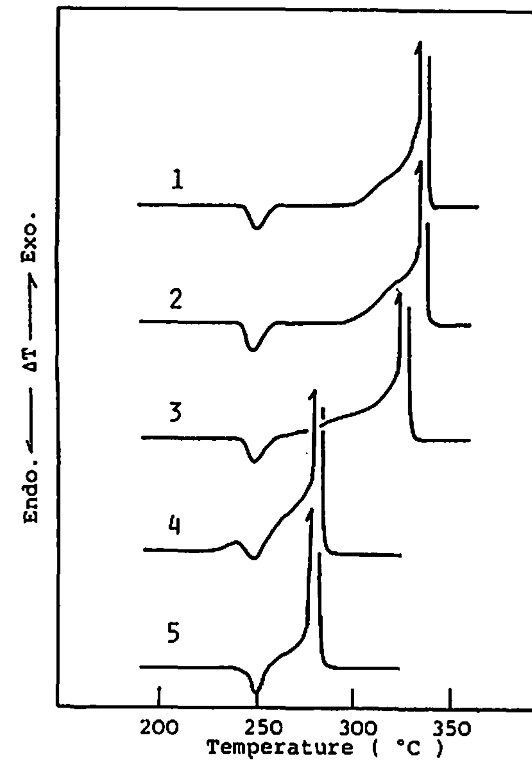
3. 2 Effect of metallic complexes on the thermal decomposition of ammonium perchlorate

As in the case of ammonium nitrate, the effect of metallic complexes on the thermal decomposition of ammonium perchlorate was examined and the results are shown in Fig.5 and Fig.6. Since the vapor pressure of ammonium perchlorate is not very large compared to ammonium nitrate, these experiments were carried out under atmospheric conditions. Therefore, the DTA traces of catalysts were somewhat different from those obtained for pressurized conditions in Fig.2 or Fig.3. With regard to the activity of the catalysts, the same catalysts have a similar effect on the thermal decomposition of ammonium perchlorate. When a V=O-complex was added, ammonium perchlorate underwent violent thermal decomposition immediately after the phase transition. The Fe-complexes have higher activity than the V=O-complex in the thermal decomposition of ammonium nitrate, but in the case of ammonium perchlorate, the V=O catalysts have higher activity than the Fe-complex.



——;NH_4ClO_4 with 10% catalysts (6~10)
-----;(6) RMn•NCS, (7) RMn•ClO_4, (8) RFe•Cl, (9) RFe•ClO_4, (10) RV=O

Fig. 6 DTA curves of NH_4ClO_4, catalysts and NH_4ClO_4 with catalysts under an atmospheric pressure (2)



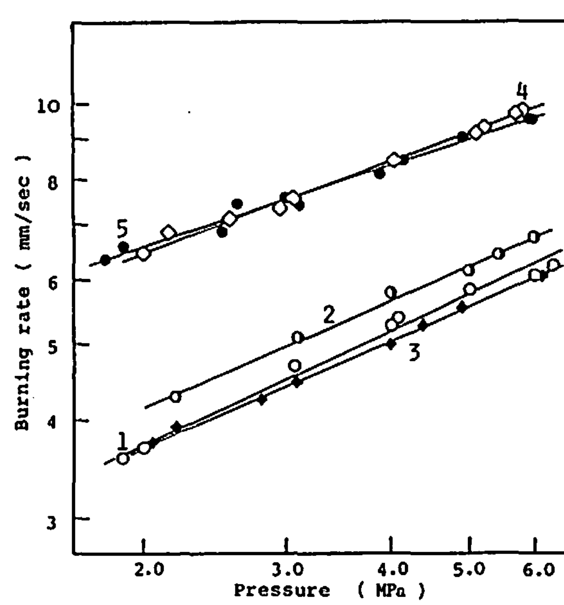
(1) Reference propellant (without catalysts), (2) propellant with RNi, (3) RMn•NCS, (4) RFe•Cl, (5) RV=O

Fig. 7 Effect of catalysts on DTA curves of propellants under a pressure of 5.0 MPa gauge

3. 3 Effect of metallic complexes on the thermal decomposition of solid propellant and its deflagration

Fig.7 showed the effect of metallic complex catalysts on the thermal decomposition of the solid propellants. Ni- or Mn-complexes had no influence on the thermal reaction of a solid propellant as in the case of ammonium perchlorate. Addition of Fe- or V-complex catalysts to the solid propellants caused a violent exothermic reaction immediately after the phase transition of ammonium perchlorate during heating.

Fig.8 shows the results of burning rate measurements for the solid propellant with and without catalysts under pressurized conditions. The burning rate increased with increasing pressure and showed a linear relation between the natural logarithm of the burning rate and pressure. The Ni-complex or Mn•NCS-complex had no influence on the deflagration of solid propellants. Addition of Fe•Cl- or V=O-complexes increased the burning rate about 60% at a pressure of 5.0 MPa. Therefore, it is



(1) Reference propellant, (2) Propellant with RNi, (3) RMn•NCS, (4) RFe•Cl (5) RV=O

Fig. 8 Effect of catalysts on burning characteristics of propellant

shown that the catalysts which catalyzed the thermal reaction of solid propellants also have a catalytic effect on its deflagration. The pressure expo-

Table 2 Effect of metal complex catalysts on the ignition test of solid propellants

Prop.	Ti(℃)	Ea(kJ/mol)	-ln A
Ref.	360	48.7	4.32
Ni	325	64.1	8.51
Mn·NCS	290	57.0	7.71
Fe·Cl	265	32.3	3.05
V=O	260	43.0	5.11

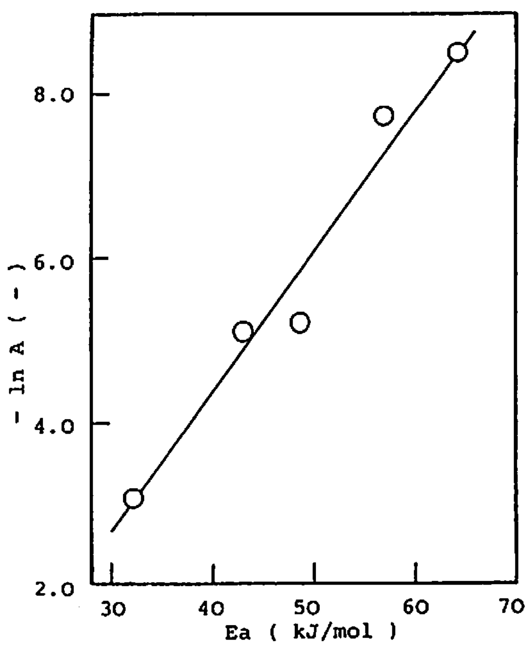


Fig. 9 Linear relationship between Ea and ln A in the ignition test for the propellants with and without metal complex catalysts

nents, which were obtained from the slope in Fig.8, are 0.45 - 0.47 for Mn:NCS- and Ni-complexes, and 0.34 - 0.38 for Fe·Cl- and V=O-complexes. The mechanism of the catalytic activity of these metallic complexes was considered to resemble that of ferrocene derivatives such as catocene because of the same effect of both catalysts on the thermal reaction and deflagration of solid propellants.

It is known that an Arrhenius type equation described by equation (1) can exist between delay time t and temperature T for the ignition test.

$$\text{Ln}\, t = Ea/RT - \ln A \quad (1)$$

The obtained Ea and ln A are shown in Table 2. Fig.9 shows the linear relationship between apparent activation energy, Ea, for ignition and logarithm of pre-exponential factor A in this experiment. For an ordinary catalytic reaction, a compensation effect (a linear relationship between activation energy and logarithm of pre-exponential factor) frequently holds if the rate constant is described by the Arrhenius equation and the reaction proceeds through the same reaction mechanism. In this experiment, for the catalytic combustion of solid propellant, it was found that the same compensation effect can hold as in the catalytic reaction.

4. Conclusion

The effect of various metal complex catalysts of tetraaza-(14)-anurene on the thermal decomposition of ammonium nitrate, ammonium perchlorate and solid propellant containing ammonium perchlorate as an oxidizer were studied by thermal analysis and burning rate measurements and the following results were obtained.

A metal complex, which has iron or vanadium as a central metallic ion showed high activity during the thermal decomposition of ammonium nitrate. Especially, this activity becomes higher when chloride and perchlorate ions are combined with iron or vanadium ions.

Iron and vanadium catalysts also have high activity during the thermal decomposition of ammonium perchlorate and its solid propellant. Solid propellants which contain iron or vanadium complexes as catalysts increase the burning rate by 1.6 times and the n index decreases to 80 % compared with the burning experiments without a catalyst under a pressure of 5.0 MPa.

The addition of Fe·Cl- and V=O-complexes increased the burning rate about 60% and decreased the pressure exponents to 80% at a pressure of 5.0 MPa compared with no catalysts.

A compensation effect holds between an apparent activation energy and logarithm of pre-exponential factor for the catalytic combustion of solid propellant if an Arrhenius type equation is applied to the ignition test data.

References

1) P. E. M. Jacobs, H. M. Whitehead, Chem. Rev., 69, 551(1969)

2) F. Solymosi, "Structure and Stability of Salts of

Halogen Oxyacid in the Solid Phase", John Wiley & Sons(1977)p.195
3) T. Urbanski, "Chemistry and Technology of Explosives, Vol.2", Pergamon Press(1965)P.457
4) K. Sakata, M. Hashimoto and T. Naganawa, Inorg. Chim. Acta, 98, L11(1985)
5) K. Sakata, T. Annoura and M. Hashimoto, Inorg. Chim. Acta, 150, 153(1988)
6) J. H. Koper, O. J. Janren, P. J. Von den Berg, Explosivesstoff, 8, 181(1970)

硝酸アンモニウムおよび過塩素酸アンモニウムの熱分解に及ぼすテトラアザー14－アヌレン金属錯体触媒の効果

中村英嗣*, 秋吉美也子*, 坂田一矩*, 原　泰毅*

硝酸アンモニウム，過塩素酸アンモニウムおよび過塩素酸アンモニウムを含む固体推進薬の熱分解に及ぼすテトラアザー14－アヌレンの種々の金属錯体触媒の効果を，熱分析や燃焼実験によって検討した。

硝酸アンモニウムの熱分解には中心に鉄やバナジウムを配位した触媒が高活性を示した。その際，鉄やバナジウムに塩素や過塩素酸イオンを結合させた錯体の活性が特に高かった。過塩素酸アンモニウムの熱分解や過塩素酸アンモニウムを含む固体推進薬の熱分解や燃焼反応にも鉄やバナジウム錯体が高活性を示した。

(*九州工業大学 工学部 応用化学教室　〒804-8550 北九州市戸畑区仙水町１－１)