

Thermal behavior of various metal complex nitrates (V)

— Co complex nitrates —

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The thermal behavior of Co complex nitrates of carbohydrazide and ammine (hereafter, CoCDH and CoAM, respectively) was investigated when mixed with two kinds of the oxidizing agent, strontium nitrate (hereafter, SrN) and copper nitrate basic (hereafter, CNB).

The thermal stability of CoCDH was slightly lower than that of CoAM, while its thermal reactivity was higher, as demonstrated by the results of differential thermal analysis. Both complexes reacted more strongly to CNB in comparison with SrN.

Neither ignition nor burning occurred in the CoAM-SrN mixture during the combustion experiment. The CoCDH-CNBN mixture was the most easily ignited of all the mixtures. The positive energy necessary for igniting the mixtures except for the CoCDH-CNBN was thought to be offset by melting and endothermic reaction.

In regard to combustion reactivity, the CoCDH-CNBN mixture was thought to be the most effective as a gas generant because of its small pressure exponent and low burning temperature. The CoAM complex did not easily react with the two kinds of oxidizing agent used in this experiment, necessitating the addition of another component in order to improve the reactivity.

In the CoCDH complex mixtures, the use of CNB as an oxidizing agent considerably reduced the generation of the NO_x gas, while the generation of CO gas increased due to the temperature reduction. For the CoAM mixture, a relatively high amount of NO_x gases were generated, because the combustion temperature was high. On the other hand, CO gas was not generated.

1. Introduction

Recently, automobiles sold in Japan are equipped with airbag systems for safer driving. A non-azide gas generant as a substitute for sodium azide has been studied, and tetrazole derivatives¹⁾, urazole²⁾ and azodicarboamide³⁾, were the subjects of this study.

The authors evaluated the metal complexes of organic compounds, which are composed of many nitrogen atoms, as the new gas generant. In previous reports⁴⁾⁻¹²⁾, the thermal decomposition behavior of metal complexes of carbohydrazide was investigated.

In this report, the Co complex nitrates of carbohydrazide (Co(NH₂NHCONHNH₂)₃(NO₃)₃, CoCDH) were synthesized, and the thermal behavior was investigated in a mixed system with two kinds of the oxidizing agent: Strontium nitrate

(Sr(NO₃)₂, SrN) and copper nitrate basic (Cu(OH)(NO₃), CNB). The thermal behavior of these mixtures were compared with that of the mixture of the Co ammine complex nitrate (Co(NH₃)₆(NO₃)₃, CoAM) already in use.

2. Experiment

2.1 Reagents

CoCDH was synthesized based on the method described by Ivanov et al.¹³⁾ For the CoAM, Co ammine complex chloride was synthesized from cobalt chloride and aqueous ammonia, and the hydrochloride was then converted into the nitrate¹⁴⁾. The obtained complexes were identified using elemental analysis and polarized light zeman atomic absorption spectrometry due to their insolubility in water.

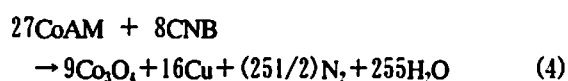
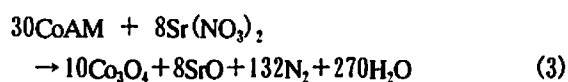
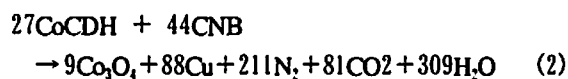
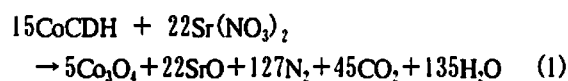
The Sr nitrate of the oxidizing agent was Wako pure chemical reagent grade. The copper nitrate basic was synthesized referring to the method described in Gemelin's handbook¹⁵⁾. Reagents screened to under 63 μm were mixed for sixty minutes using splittable chopsticks on parchment paper. Several kinds of samples were prepared by mixing: a

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stoichiometric composition and a few compositions each with positive and negative oxygen balances based on eqs.1 to 4. Table 1 shows these compositions.



2. 2 Apparatus and method

2. 2. 1 Thermal analysis

The differential thermal analysis and the Thermal gravimetric analysis were carried out using a Rigaku Thermal Analyzer ThermoPlus. The sample container was an alumina cell and the sample amount was three mg. The sample was heated to 800°C at a heating rate of 20K/min under Ar.

2. 2. 2 Ignition test

The ignition test was carried out according to the croup method⁶⁾. 8 mg of the sample of the pellet was put in glass vessel of 250ml capacity. The ignition delay period was measured.

2. 2. 3 Combustion reactivity

The heat of the reaction was measured using a Shimadzu CA-4 Type Automatic Bomb calorimeter in argon. The results of the investigation at ambient pressure showed a variation in the measured values of 3% to 4% over the pressure range of 1.1 MPa to 3.1MPa. A case existed in which no combustion occurred depending on the composition at 0.1 MPa.

The measurement of the burning rate was carried out under the following conditions. A preliminary investigation showed that the linear burning rate in the theoretical density range of 0.65 to 0.70 decreased as the theoretical density increased, while the weight burning rate was independent of the theoretical density. Also, when the diameter of the burning tube was 6 mm, the burning rate showed its maximum value.

Table 1 Compositions of mixtures

		Co complex /oxidizing agent		Oxygen balance g(100g) ⁻¹
		mol/mol	wt./wt.	
CoCDH	SrN	0.441/0.559	0.628/0.372	- 2.66
		0.417/0.583	0.605/0.395	- 0.85
		0.405/0.595	0.594/0.407	0
		0.395/0.604	0.583/0.417	+ 0.82
		0.375/0.625	0.562/0.438	+ 2.38
	CNB	0.397/0.603	0.554/0.446	- 0.98
		0.386/0.614	0.542/0.458	- 0.32
		0.380/0.620	0.536/0.463	0
		0.375/0.625	0.531/0.469	+ 0.31
		0.365/0.635	0.520/0.480	+ 0.92
CoAM	SrN	0.857/0.143	0.908/0.092	- 2.51
		0.811/0.189	0.876/0.125	- 0.87
		0.790/0.210	0.860/0.140	0
		0.769/0.231	0.845/0.155	+ 0.78
		0.732/0.268	0.817/0.183	+ 2.26
	CNB	0.844/0.156	0.887/0.113	- 2.74
		0.818/0.182	0.867/0.133	- 1.78
		0.794/0.206	0.848/0.152	- 0.87
		0.771/0.229	0.830/0.170	0
		0.750/0.250	0.813/0.187	+ 0.83
		0.711/0.289	0.780/0.220	+ 2.40

Consequently, the sample was loaded at 0.6 of the theoretical density in a 6 mm i.d. aluminum tube. The pressure dependence was measured over a pressure range of 0.1 to 4.1 MPa and the influence of the composition on the burning rate was investigated at 1.1 MPa. The burning rate was determined in terms of the time that was needed for the combustion wave to proceed 10 mm.

The burning temperature was also measured using the same theoretical density and tube diameter as that used for the measurement of the burning rate. A 0.25 mm diameter W/Re thermocouple was vertically inserted into the burning tube against the combustion direction and was connected to a Yokogawahokusinn Analyzing Recorder.

The combustion residue was analyzed by X-ray diffraction using a Rigaku rotaflex RU-200.

2. 2. 4 The evolved gas

The evolved gases, produced when the heat of reaction was measured, were collected in a collection bag (Tedlar bag, 350ml capacity). The amounts of N_2 , CO, CO_2 and N_2O gases evolved were quantified using a Shimadzu GC-4C Gas Chromatograph (hereafter, GC). Table 2 shows the measurement conditions for the GC. The NO and NO_2 gases were quantitatively analyzed using a Gastec gas detector tube. The NH_3 and N_2H_4 gases were quantified using the indophenol's method¹⁷⁾ ($\lambda = 630$ nm) and the p-aminobenzaldehyde method¹⁸⁾ ($\lambda = 458$ nm), respectively.

3. Results and discussion

3. 1 Thermal analysis

Fig.1 shows the results of the thermal analysis of CoCDH and CoAM. The CoCDH started to melt at 210°C, and then decomposed exothermally at 250°C after the endothermic decomposition. The CoAM complex was slightly more stable than the CoCDH because of a moderately higher melting point (220 °C) and initial temperature of exothermic decomposition (275 °C). The thermal reactivity of the CoCDH was guessed to be higher than that of the CoAM considering the weight loss during the endothermic decomposition. The final residue was Co_3O_4 , which was confirmed using the powder X-ray diffraction and the final weight loss.

Fig.2 shows the results of thermal analysis of the CoCDH and its mixtures at the stoichiometric composition, representatively. For the mixture with $Sr(NO_3)_2$ of the oxidizing agent, there was a little difference in apparent thermal behavior compared with that of only the complex (as

Table 2 Gas chromatograph conditions

Gases	N_2 , CO	N_2O , CO_2
Column	molecular sieves 5A	activated charcoal
Particle size	60~80 mesh	60~80 mesh
Length	2 m	1 m
Temp.	40°C	40°C
Carrier gas	He, 20 ml/min.	He, 60 ml/min.

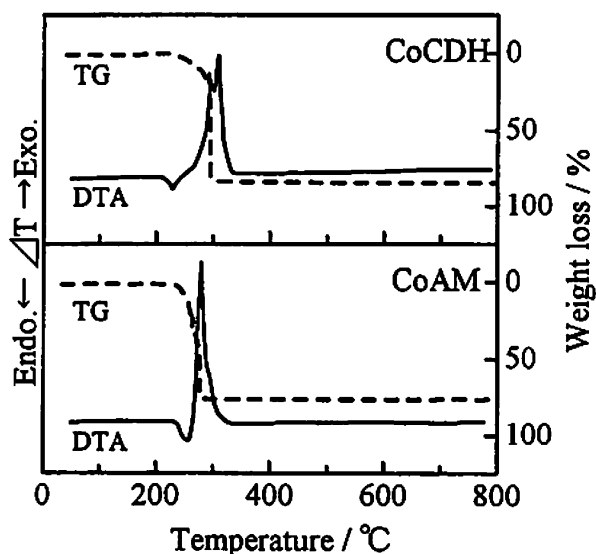


Fig.1 DTA-TG curves for the Co complex nitrates

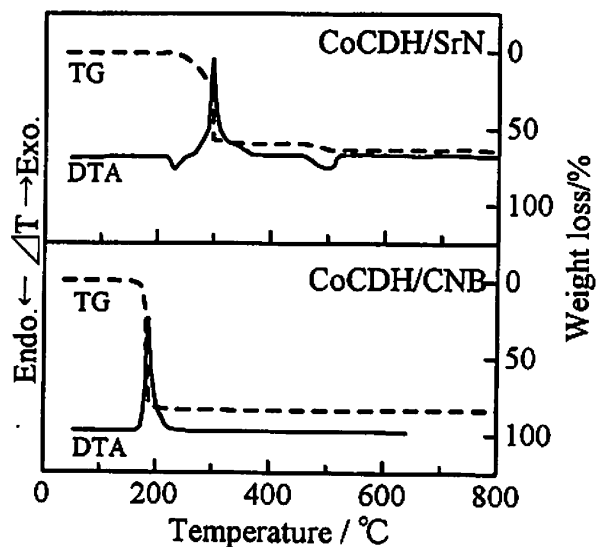


Fig.2 DTA-TG curves for the Co complex mixtures

seen in Fig.1), though the separated peak became the sharp one. The unreactive $Sr(NO_3)_2$ was found to decompose at 560°C. The mixture with CNB started to react at 190°C before the melting. On the other hand, in the CoAM system, the temperature reduction of the melting before the

exothermic reaction was confirmed by using the CNB as the oxidizing agent. The reactivity with the CNB was expected to be higher than that with $Sr(NO_3)_2$ in both complexes.

3. 2 Heat of combustion

Fig.3 shows the composition dependence of the heat of reaction. The composition dependence was small in all systems. The small composition range was considered to be one of the reasons for this, because the CoAM mixture didn't especially ignite in the wide composition range. Fig.4 shows the XRD patterns of the combustion residue at the stoichiometric composition. In the mixture with $Sr(NO_3)_2$, various cobalt oxides were confirmed and Co_2O_3 formed the composite oxide with SrO. On the other hand, CoO was confirmed only in the mixture with CNB. $SrCO_3$ was produced by the reaction of SrO and CO_2 .

In the CoAM-CNBN mixture, the heat of combustion had a maximum value at $-1.776g(100g)^{-1}$ of the oxygen balance. This was caused by the formed oxide was not being Co_3O_4 , but CoO. The stoichiometric equation was set up assuming that the residue was Co_3O_4 , confirmed during the decomposition at the heating rate of 20K/min.; eqs.1 to 4. In this system, the combustion reactivity in a tube was investigated for the composition of $-1.776g(100g)^{-1}$, as described later in section 3.3. In all systems except for the CoAM-CNBN mixture, it was unknown whether the heat of combustion reaches its maximum value at any oxygen balance because of a small composition dependence. The heat of combustion in the CoCDH-CNBN mixture had the smallest value of all the mixtures.

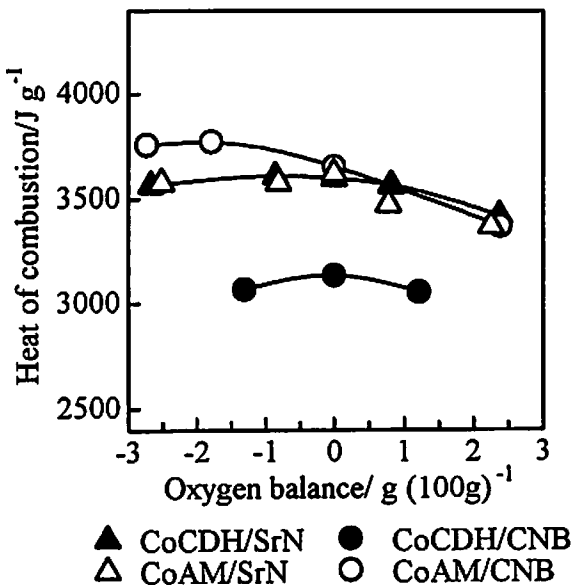


Fig.3 Heat of combustion for the Co complex mixtures

Furthermore, for the CoAM mixture system, an intense ammonium smell was detected in opening the pressure-proof combustion vessel after the end of the experiment. These systems didn't seem to burn completely.

3. 3 Ignition temperature

Fig.5 shows the relationship between the ignition delay period and the temperature in the CoCDH-CNBN mixture, as a representative example. The minimum ignition temperature and the ignition temperature in a 4s delay is listed in Table 3, in which the active energy of the ignition is also shown. No ignition occurred in the CoAM-SrN mixture. The minimum ignition temperature T_{min} in the CoCDH-SrN mixture has a high value compared with the initial temperature of

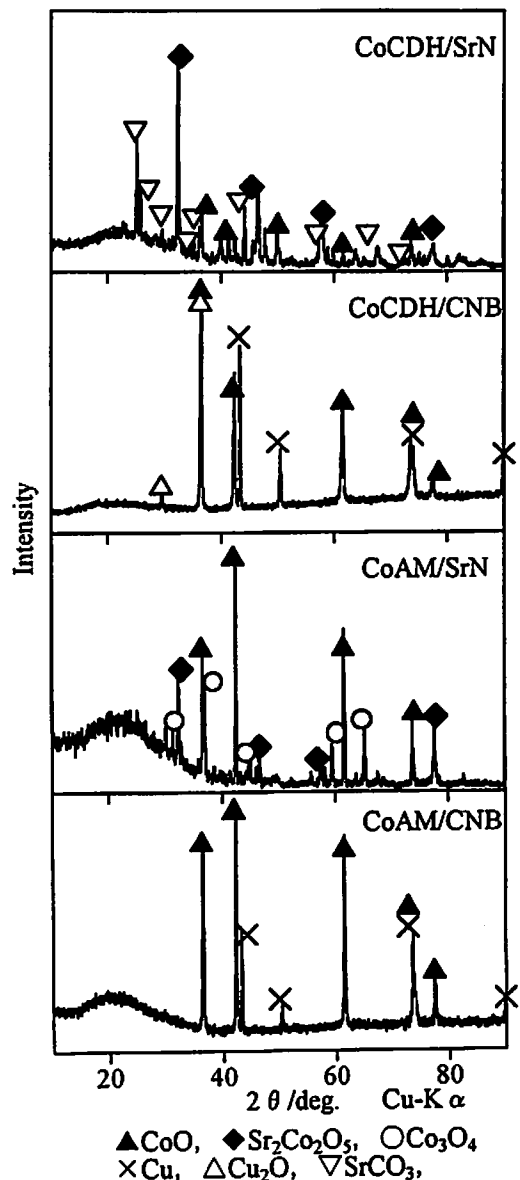


Fig.4 XRD patterns during the combustion for the Co complex mixtures

exothermal reaction in the DTA curve; 250°C (Fig.2). In this system, the sound with the sample melting was clearly heard before the ignition. The material ignites by applying the necessary energy from the outside. The positive energy necessary for the ignition was assumed to be offset by the melting and the endothermic reaction. A similar phenomenon was observed also in the CoAM-CNB mixture.

In a comparison of the oxidizing agents, the mixture with CNB was easier to ignite from that with SrN. The CoAM mixture used already in actual operation was difficult to ignite in a two-component system comprised of simple reducing and oxidizing agent.

3. 4 Combustion reactivity

Fig.6 shows the pressure dependence of the burning rate in three mixtures except for the CoAM-SrN mixture. No ignition and combustion occurred in the CoAM-SrN mixture. Table 4 lists the pressure exponent calculated based on Vieille's equation ($V=aP^n$) and the burning temperature at the stoichiometric composition. The burning rate at 1.01 MPa showed the highest value in the CoAM-CNB mixture, followed by the CoCDH-SrN mixture and the CoCDH-CNB mixture. The CoCDH-CNB mixture was thought to be advantageous as the gas generant because of its small

pressure exponent and low burning temperature. The CoAM complex did not easily react with the two kinds of oxidizing agent used in this experiment.

A non-stoichiometric CoO formed during the decomposition of the complex might cause also the difference in the combustion reactivity¹⁹⁾.

4. Gas evolution behavior.

Table 5 lists the analytical results of the evolved gases during combustion. The CoAM-SrN mixture did not ignite.

The CoAM-CNB mixture did not generate the carbon-containing CO_x gas, as predicted from the molecular formula of CoAM. However, it is necessary to add at another component due to the difficulties of ignition and burning, as already described.

N₂ and CO₂ gases account for about 99 % of all evolved gases in the CoCDH mixtures. Using the CNB of the oxidizing agent considerably reduced the generation of NO_x gas. The evolution of NO gas in the CoCDH-CNB mixture

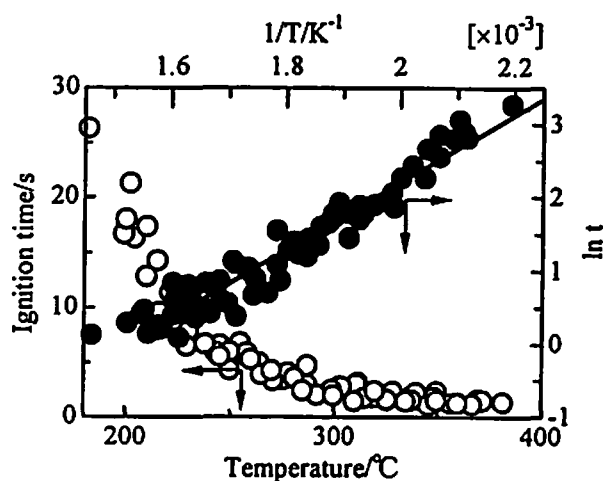


Fig.5 Ignition test for the CoCDH-CNB mixture

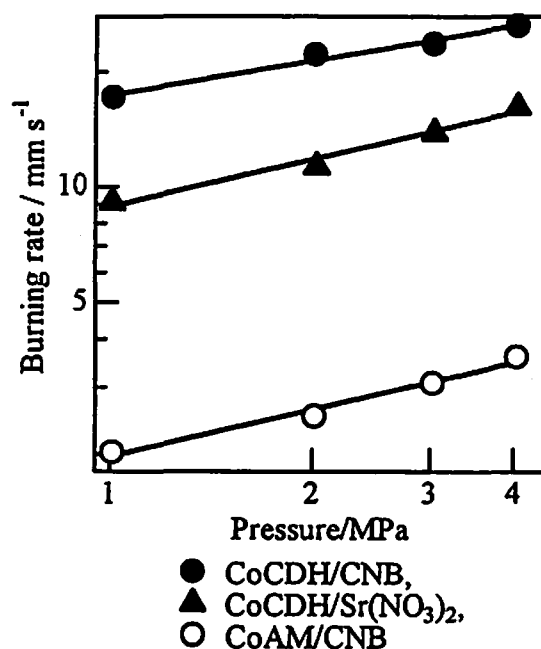


Fig.6 The burning characteristics for the Co complex mixtures

Table 3 Various characteristics in the ignition test

	$T_{\min} / ^\circ\text{C}$ (sec.) [*]	$T_{4s} / ^\circ\text{C}$	$\Delta E / \text{kJ}(\text{mol})^{-1}$
CoCDH/SrN	324 (24.1)	372.3	75.6
CoCDH/CNB	182 (26.3)	266.8	38.3
CoAM/CNB	323 (23.8)	477.6	35.5

^{*} T_{\min} ; The minimum temperature when the ignition occurred. The value in the parenthesis means the ignition delay period at this temperature.

Table 4 Constants of the burning rate

Complex	Oxidizing agent	a	n	Burning temperature / °C
CoCDH	SrN	1.729	0.410	1300
	CNB	0.884	0.305	1170
CoAM	CNB	0.197	0.410	1360

Table 5 The amount of the evolved gases (unit: mol/mol-complex)

	CoCDH		CoAM
	SrN	CNB	CNB
N ₂	8.3	8.3	7.4
NH ₃	≒0.0	≒0.0	≒0.0
N ₂ H ₄	≒0.0	≒0.0	≒0.0
NO	412.0 × 10 ⁻⁴	8.7 × 10 ⁻⁴	61.9 × 10 ⁻⁴
NO ₂	1.2 × 10 ⁻²	≒0.0	≒0.0
N ₂ O	0.0	≒0.0	≒0.0
HCN	1.4 × 10 ⁻³	≒0.0	≒0.0
CO ₂	1.8	2.6	0.0
CO	0.08	0.26	0.0
N number	16.7	14.8	9.0
%	98.4	94.7	96.9
C number	1.9	1.38	-
%	62.7	95.3	-

was slight compared with that in the CoAM-CNB mixture. However, the generation of CO gas increased due to the reduction in temperature. A reduction in CO gas is required in the future. The low mass balance of C molecules was due to the formation of SrCO₃ by the reaction of SrO and CO₂ in the mixture with SrN.

5. Conclusion

A new gas generant, Co complex nitrates of the carbohydrazide (CoCDH), was synthesized, and the thermal behavior was investigated in a mixed system composed of two kinds of oxidizing agent: strontium nitrate (Sr(NO₃)₂; SrN) and copper nitrate basic (Cu(OH)(NO₃); CNB). The thermal behavior of these mixture was compared with that in a mixture of the Co ammine complex nitrate used in actual operation.

The thermal stability of CoCDH was lower a little than that of CoAM, while its thermal reactivity was higher, as demonstrated by the results of the differential thermal analysis. Both complexes reacted more strongly when containing CNB in comparison with SrN.

Neither ignition nor burning occurred in the CoAM-SrN mixture during the combustion experiment. The minimum

ignition temperature in the mixture except for the CoCDH-CNB has a high value of approximately 100°C compared with the initial temperature of the exothermal reaction in the DTA curve. The positive energy necessary for the ignition was thought to be offset by endothermic reactions such as melting and endothermic decomposition. The CoCDH-CNB mixture was most easy to be ignited in all mixtures.

In regard to combustion reactivity, the CoCDH-CNB mixture was thought to be the most effective as a gas generant because of its small pressure exponent and low burning temperature. The CoAM complex did not easily react with the two kinds of oxidizing agent used in this experiment, necessitating the addition of another component to facilitate ignition and burning.

N₂ and CO₂ gases account for about 99 % of all evolved gases in the CoCDH complex mixtures. Using CNB as an oxidizing agent considerably reduced the generation of the NO_x gas. However the generation of CO gas increased due to the temperature reduction. The CoAM mixture generated a considerable amount of NO_x gases due to high combustion temperature, though CO gas was not generated.

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種々の金属錯体硝酸塩の熱的挙動 (第 5 報) —コバルト錯体硝酸塩—

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カルボノヒドラジドならびにアンミンの Co 錯体硝酸塩(各々 CoCDH, CoAM)の熱的挙動を酸化剤混合系にて比較検討した。酸化剤としては $\text{Sr}(\text{NO}_3)_2$, $\text{Cu}(\text{OH})(\text{NO}_3)$ (SrN , CNB)の 2 種類が選択された。

示差熱分析より, CoCDH 錯体の熱安定性は, CoAM 錯体に比べやや低いが, 熱反応性は高いことが推測された。両錯体ともに酸化剤として CNB を用いた方が熱反応性は高かった。

着火性は CoCDH-CN B 混合物が最も良好で, CoAM-SrN 混合物では着火, 燃焼しなかった。CoCDH-CN B 混合物以外の系では, 発火に必要なエネルギーが融解や吸熱反応により相殺され, 着火しにくくなることが推測された。

さらに CoCDH-CN B 混合物系は燃焼速度の圧力依存性が小さく, 燃焼温度が低い結果が得られ, ガス発生剤として有効な性質をもつ組成物であることが明らかとなった。CoAM 系は, 本実験で使用した 2 種類の酸化剤との燃焼反応性が低い結果で, 反応性改良の為に第三成分の添加が必要であると考えられる。

燃焼時の発生ガスは CoCDH-CN B 混合物系では NO_x ガスは低減するが, 燃焼温度が低いために CO ガスが増加した。CoAM 混合物では CO ガスは発生しないが, 燃焼温度が高いために NO_x ガスの発生は多い結果となった。

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