

The thermal behavior of the carbohydrazide complexes of certain metals (VI)

Gases evolved in the system of the Mg complex with various oxidizing agents

by Miyako AKIYOSHI*, Yasuyuki IMANISHI*, Norimasa HIRATA**
Hidetsugu NAKAMURA* and Yasutake HARA*

Carbohydrazide (hereafter, CDH) metal complexes are expected to be a new gas generant for automobile air bags. In the previous report, the combustion reaction of the Mg complex with various oxidizing agents was investigated by thermal analysis and the measurement of the heat of combustion, the burning temperature and the burning rate.

In this report, the gas evolution behavior was investigated in the system of the Mg complex/oxidizing agent mixture. The oxidizing agents used were potassium perchlorate (KClO_4), potassium bromate (KBrO_3), potassium nitrate (KNO_3) and strontium nitrate ($\text{Sr}(\text{NO}_3)_2$). Furthermore, 10% CuO was added as an another oxidizing agent in all binary systems.

For the Mg complex / KBrO_3 mixture system, the initial temperature of the reaction was the lowest with the most vigorous reaction and the evolved amount of nitrogen and carbon dioxide gases was the largest of all systems. When using $\text{Sr}(\text{NO}_3)_2$ as the oxidizing agent, the amount of the N_2 gas evolved was the lowest and was increased with the addition of CuO. NH_3 and N_2H_4 gases were generated in all binary systems with the oxidizing agent, and the amount of these gases decreased remarkably with the addition of CuO.

1. Introduction

As a non-azide gas generant in an airbag system for safer driving, tetrazole derivatives¹⁾, urazole²⁾ and azodicarboamide³⁾ were the sub-

jects of this study. The authors evaluated carbohydrazide (hereafter, CDH), which is composed of four nitrogen atoms, a carbon atom and an oxygen atom; various CDH metal complexes were synthesized and their thermal decomposition behaviors were investigated in previous reports^{4~8)}.

In a fourth report⁷⁾, the combustion reaction for the Mg complex nitrate of CDH ($\text{Mg}(\text{CDH})_3(\text{NO}_3)_2$) with various oxidizing agents was investigated by thermal analysis and the measurement of the heat of the combustion, the burning temperature and the burning rate. The oxidizing agents were potassium perchlorate (KClO_4), potassium bromate (KBrO_3), potassium nitrate (KNO_3) and

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*Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology

Sensui-machi, Tobata-ku, Kitakyusyu-shi 804-8550, JAPAN

TEL 093-884-3308

FAX 093-884-3308

**Harima Plant, Daicel Chemical Industries, Ltd.

805 Umaba, Ibogawa-cho, Ibo-gun, Hyogo Prefecture 671-1665, JAPAN

TEL 0791-72-5422

FAX 0791-72-5450

Table 1 Compositions of mixtures

No	mixtures	mol/mol	wt./wt.
1	MgCDH*/CuO	12.5/87.5	42.9/57.1
2	MgCDH/KClO ₄ /CuO	29.3/44.9/25.8	59.7/30.3/10.0
3	MgCDH/KBrO ₃ /CuO	24.8/49.2/25.0	50.1/39.8/10.0
4	MgCDH/Sr(NO ₃) ₂ /CuO	31.7/38.4/29.9	55.8/34.2/10.0

*MgCDH = Mg(CDH)₃(NO₃)₂

Table 2 Conditions for gas chromatograph

Gases	N ₂ , CO	N ₂ O, CO ₂
Column	Molecular sieve 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.

strontium nitrate (Sr(NO₃)₂). Furthermore, for the Mg complex only, the gases evolved during the decomposition were already analyzed quantitatively in a previous report⁶⁾.

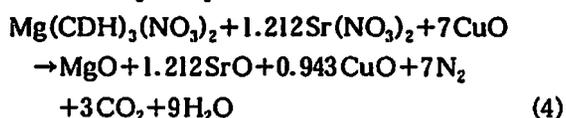
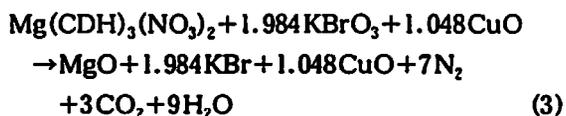
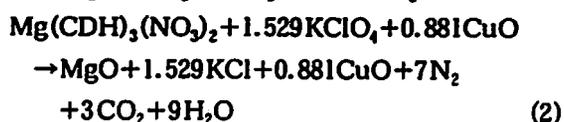
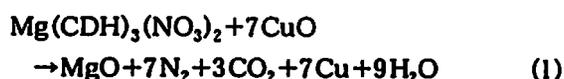
In this report, the gas evolution behavior in the mixture system of the Mg complex of CDH with the above-mentioned oxidizing agents was investigated, in which CuO was added as a part of the oxidizing agent in a weight ratio of 10% for all components.

2. Experiment

2.1 Reagents

The Mg complex of CDH was synthesized by a previously reported method⁴⁾. The oxidizing agents were Wako Pure Chemical reagent grade. Reagents screened to under 63 μm were mixed for sixty minutes by the splittable chopsticks on parchment paper.

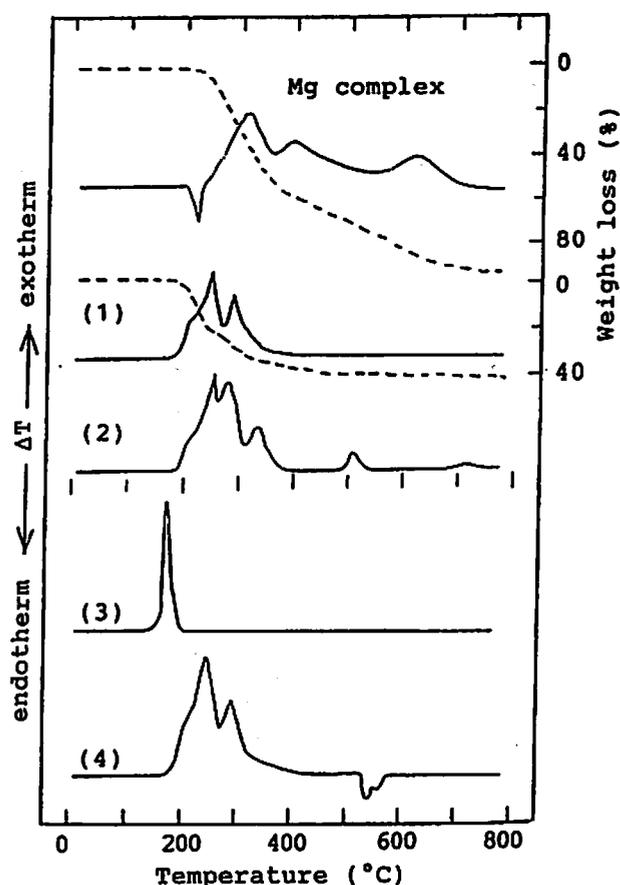
The mixture composition was a stoichiometric one based on the following eq. 1~4 in addition to eq. 1, 2 and 4 in the fourth report⁷⁾. Table 1 shows the mixture composition except for the compositions mentioned in the fourth report⁷⁾.



2.2 Apparatus and method

Differential thermal analysis and thermogravimetry were carried out using a Rigaku TAS-200 Thermal Analyzer. The sample container was an open alumina cell and the sample amount was five mg. The sample was heated to 800°C at a heating rate of 20°C/min. under air.

The analysis of the evolved gas was carried out by two methods. One was a method in which the sample was decomposed under isothermal conditions. The other one was the method in which the sample was burned in a tube. For the former, a glass tube (A) (16 mm, inside diameter) was fixed in a furnace kept at 400°C. 50 mg of the sample was weighed into a boat-shaped container and the container was inserted into the glass tube (A). The decomposition was carried out under flowing He gas at 20 ml/min. The evolved gases were collected in a collection bag (Tedlar bag, 350ml capacity). The amounts of the N₂, CO, CO₂ and N₂O gases evolved were quantified using a Shimadzu GC-4C Gas Chromatograph (hereafter, GC). Table 2 shows the



(1)-(4); Mixtures of Table 1
 Fig. 1 DTA and TG curves of the Mg complex and mixtures

measurement conditions for the GC. The NO and NO₂ gases were quantitatively analyzed using a Gastec gas detector tube. The NH₃ and N₂H₄ gases were quantified by the indophenol method⁹⁾ ($\lambda = 630 \text{ nm}$) and the P-aminobenzaldehyde method¹⁰⁾ ($\lambda = 458 \text{ nm}$), respectively. For the latter, 1 g of the sample was loaded at a 0.6 packing fraction in a 6 mm I.D. aluminum burning tube. The sample was ignited in the burning container (18.3 mm, inside diameter; 93.2 mm, height). The evolved gas was quantitatively analyzed by the above-mentioned method.

The decomposition and combustion residue was analyzed by the X-ray diffraction using a Nippon Detam JDX-3500.

3. Results and discussion

3.1 Thermal analysis

Fig. 1 shows the results of the thermal analysis for the Mg complex and the stoichiometric mixtures with various oxidizing agents according to

eq. 1~4. The Mg complex gradually decomposed after melting at 220°C, and the final residue was MgO. For its decomposition behavior, such as the gas evolution behavior, the detailed description is omitted in this report, because it was reported already^{4~7)}. In the binary system with various oxidizing agents, it was reported the decomposition vigorously progressed at low temperature only when using KBrO₃ as the oxidizing agent⁷⁾.

In the binary system of the Mg complex of CDH/CuO, the exothermic decomposition occurred at a lower temperature (185°C) than the melting point for the complex only, and the decomposition reaction finished at 350°C. The final weight loss was 41%, which was inconsistent with the calculated value for the MgO and Cu of the residue (50.3%). This value was close to the calculated value for the MgO and CuO of the residue (38.8%). Most of the CuO remained unreacted, and CuO seem to contribute to the reaction not as an oxidizing agent but as a catalyst. As seen in Fig. 6, the X-ray diffraction pattern of CuO was confirmed in the decomposition residue.

With the addition of CuO to the binary systems with various oxidizing agents, the initial temperature of decomposition became lower and the exothermic decomposition peak became sharp in comparison with the results for the binary system⁷⁾.

When using Sr(NO₃)₂ as the main oxidizing agent, unreacted Sr(NO₃)₂ remained and decomposed above 500°C (temperature of the decomposition, 570°C¹¹⁾). However, the amount of unreacted Sr(NO₃)₂ in the Mg complex /Sr(NO₃)₂/CuO was thought to be less than that in the binary system without CuO⁷⁾, considering the size of the endothermic peak.

3.2 Analysis of the gas evolved

3.2.1 qualitative analysis of the gas evolved using TG-MS

As previously reported⁶⁾, the gas behavior in the Mg complex corresponded to the thermal behavior in the DTA curve, and mainly N₂, NH₃, N₂O, CO and CO₂ gases were evolved during the decomposition.

Fig. 2 shows the amount of various fragment

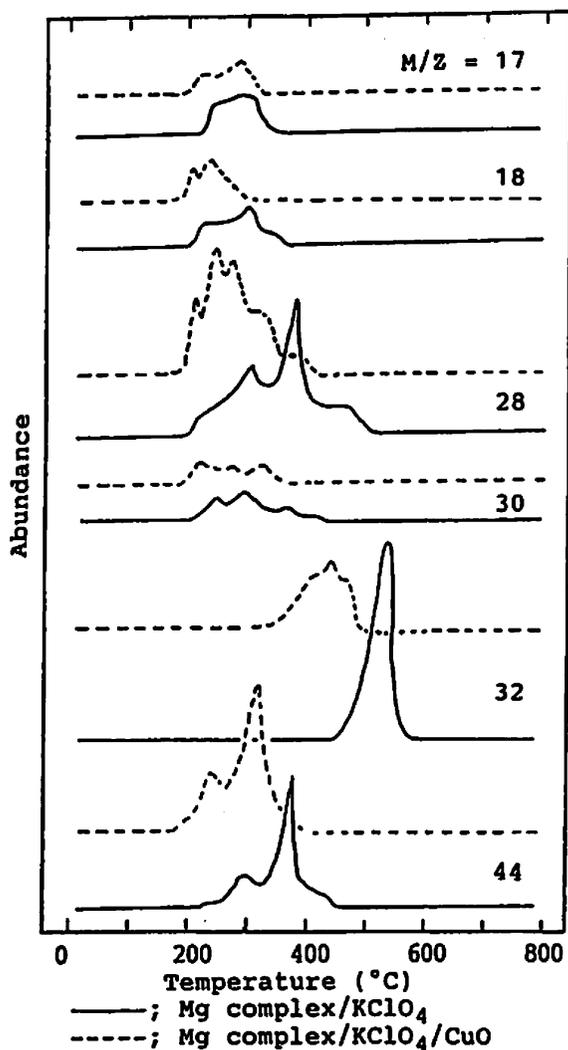


Fig. 2 Amount of fragment ions of the evolved gas for the mixtures with KClO_4

ions versus temperature from the results of TG-MS analysis in the Mg complex/ KClO_4 and the Mg complex/ KClO_4/CuO .

The evolution of NH_3 , H_2O , N_2 , NO , N_2O , CO and CO_2 was supposed from the fragments (m/z) of 17, 18, 28, 30 and 44. In the case of the tertiary system (the dotted line in Fig. 2), the evolution of N_2 seems to occur mainly over the temperature range of 200 to 300 °C, because the peak behavior of $m/z=28$ was inconsistent with that of $m/z=44$. However, after 300 °C, the evolution of CO and CO_2 was supposed to become the main reaction from the similar behavior for $m/z=28$ and 44. The amount of NO evolved seemed to be small because of the small peak for $m/z=30$. The peak for $m/z=32$ observed in both systems above 400 °C indicates the evolution of O_2 due to the decomposition of unreacted KClO_4 .

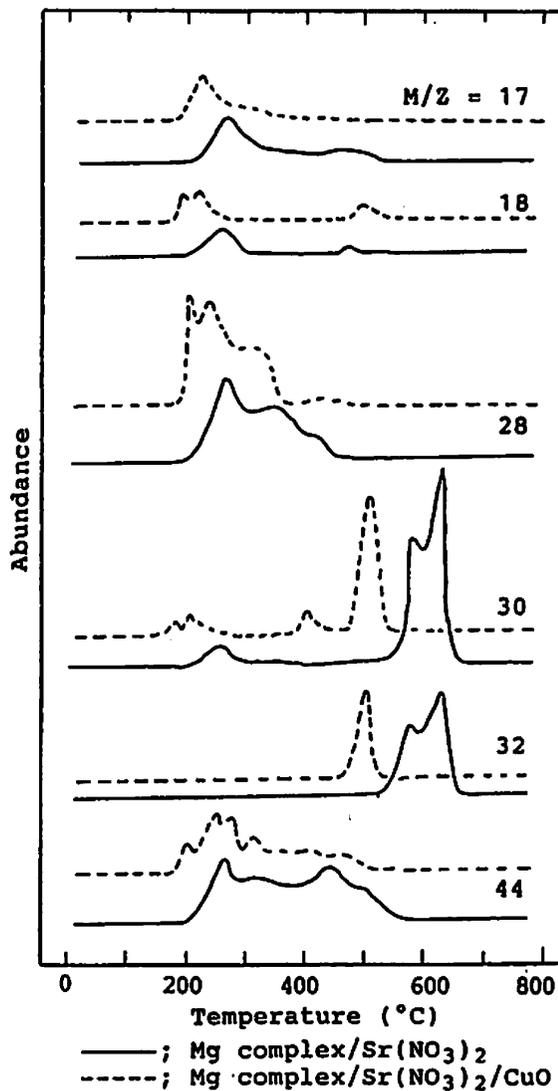


Fig. 3 Amount of fragment ions in the gas evolved for the mixtures with $\text{Sr}(\text{NO}_3)_2$

Fig. 3 shows the amount of various observed fragment ions versus temperature in the binary system and the tertiary system with CuO , when using $\text{Sr}(\text{NO}_3)_2$ as main oxidizing agent. In this case, CO_2 seemed to evolve over a wide temperature range of 220 to 550 °C, as supposed from an similar behavior for $m/z=28$ and 44. Furthermore, the peak for $m/z=32$ and 30 observed in both systems at above 500 °C indicates the evolution of O_2 and NO due to the decomposition of unreacted $\text{Sr}(\text{NO}_3)_2$.

In the tertiary system with KBrO_3 also, the gas behavior corresponded to that in the DTA curve; the gas evolution curve has a sharp peak. Fig. 4 shows the mass spectrum at the temperature at which the maximum amount of the gas was evolved. It was known that the various gases

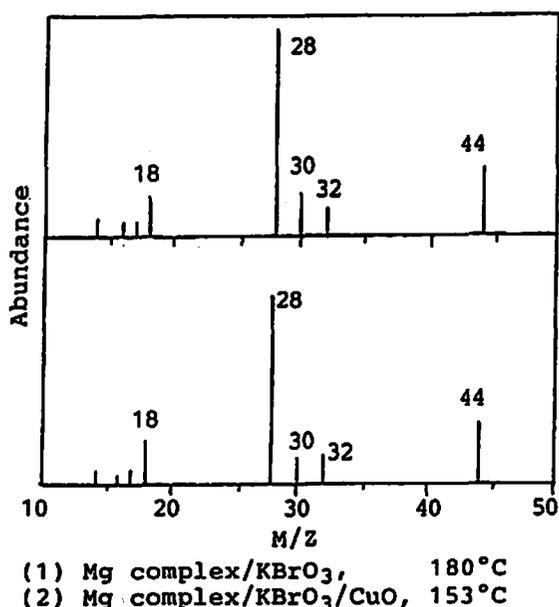


Fig. 4 Mass spectrum of the gas evolved for the mixtures with KBrO₃

observed over a wide temperature range in the other systems were evolved at the same time in this system.

3. 2. 2 Gas evolved upon igniting under isothermal conditions

Table 3 shows the analysis results of the gas evolved upon ignition at 400°C. In this table, the results for the Mg complex of CDH is also shown because hydrazine was not analyzed in the third report⁶⁾.

In the mixture system with various oxidizing agents, the amount of N₂ evolved increased remarkably compared with the results for the Mg complex of CDH only. This might be caused by the increase in the effect of the oxidizing agent on the ignition, which was inconsistent with the tendency in the DTA curve under a moderate condition. Furthermore, the amount of NH₃ evolved changed little, while that of N₂H₄ decreased. A strong reductive N₂H₄ was thought to react with the oxidizing agent.

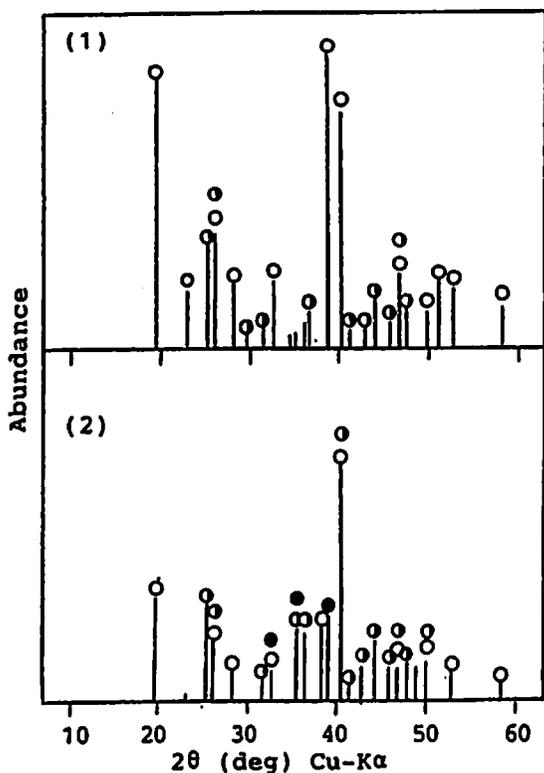
The effect of the oxidizing agent when using KBrO₃ was the largest of all systems, and most of the nitrogen atoms in the complex became N₂ gas without formation of NH₃ and N₂H₄ gases. 80% of the carbon atoms were oxidized to CO₂ gas. (the remainder of the product was CO gas.) The mass balance for these atoms was approximately good, about 100%, as shown in Table 3. KBrO₃ decomposed completely to KBr and O₂; KBr was confirmed by X-ray diffraction of the decomposition residue. Based on the residue and the gas behavior, KBrO₃ was supposed to react sufficiently with the Mg complex as the oxidizing agent.

The effect of the oxidizing agent decreased in the order of KBrO₃, KClO₄ and Sr(NO₃)₂ as the oxidizing agent. The mass balance of nitrogen

Table 3 Amount of gas evolved for the Mg complex and two component mixtures with various oxidizing agents (unit: mol/mol)

Gases	Mixtures of Table 1			
	MgCDH*	MgCDH/KClO ₄	MgCDH/KBrO ₃	MgCDH/Sr(NO ₃) ₂
N ₂	4.57	6.13	7.01	5.99
NH ₃	0.97	0.65	0.10	0.79
NH ₂ NH ₂	1.34	0.16	0.003	0.06
N ₂ O	0.50	0.00	0.00	0.00
NO	0.005	0.021	0.050	0.025
NO ₂	0.0014	0.00003	0.00003	0.00060
CO	1.76	0.19	0.64	0.53
CO ₂	0.57	1.68	2.39	0.71
N number	13.79	13.23	14.13	12.92
%	98.5	94.5	100.9	76.9
C number	2.33	1.87	3.03	1.24
%	77.7	62.3	101.0	41.3

*MgCDH = Mg(CDH)₃(NO₃)₂



(1) Mg complex/ $\text{Sr}(\text{NO}_3)_2$
 (2) Mg complex/ $\text{Sr}(\text{NO}_3)_2/\text{CuO}$
 ○ ; $\text{Sr}(\text{NO}_3)_2$, ◐ ; SrCO_3 , ● ; CuO
 Fig. 5 XRD patterns of the residue for $\text{Sr}(\text{NO}_3)_2$ mixtures

and carbon atom was low when $\text{Sr}(\text{NO}_3)_2$ was used. The low mass balance for the nitrogen atom was thought to be caused by including of the nitrogen atom in the $\text{Sr}(\text{NO}_3)_2$ oxidizing

agent. Namely, in this case, part of the oxidizing agent remained unreacted, because the X-ray diffraction pattern (Fig. 5) of $\text{Sr}(\text{NO}_3)_2$ was confirmed in the decomposition residue. As for the mass balance of the carbon atom, the evolved carbon dioxide was fixed as SrCO_3 , as seen in Fig. 5. SrCO_3 was formed by the reaction of SrO with H_2O and CO_2 of the decomposition product, as previously reported⁷⁾.

In the binary system with KClO_4 , the gas behavior was close to the results in the mixture system with $\text{Sr}(\text{NO}_3)_2$. In this case also, unreacted KClO_4 was confirmed in the decomposition residue. The results of X-ray diffraction of the residue were omitted. Consequently, KClO_4 did not seem to react sufficiently with the complex, as in the case of $\text{Sr}(\text{NO}_3)_2$. In the case of (1) (the binary system of the Mg complex with CuO), the amount of the N_2 evolved increased compared with that in the Mg complex only. The amount of NH_3 evolved increased more or less, and that was thought to be caused by the action of CuO as a catalyst of the decomposition, as mentioned in 3. 1. Namely, the oxidation of NH_3 was thought to be insufficient. Fig. 6 shows the X-ray diffraction of the decomposition residue in the Mg complex/ CuO . The X-ray diffraction pattern of CuO was confirmed, though a part of the CuO was reduced to Cu_2O . The NH_3 evolu-

Table 4 The effect of CuO on the amount of gas evolved
 (unit: mol/mol)

Gases	Mixtures of Table 1			
	(1)	(2)	(3)	(4)
N_2	5.82	6.13	6.81	6.69
NH_3	2.10	9.21×10^{-5}	0.000462	8.54×10^{-5}
NH_2NH_2	0.00	0.000482	0.000251	0.00037
N_2O	0.07	0.00	0.00	0.00
NO	0.023	0.020	0.0254	0.025
NO_2	0.0006	2.82×10^{-5}	3.91×10^{-5}	3.55×10^{-5}
CO	0.99	1.10	0.81	1.09
CO_2	1.90	1.68	2.01	1.24
N number	13.90	13.18	13.65	13.38
%	99.3	94.1	97.5	81.5
C number	2.89	2.69	2.82	2.33
%	96.3	89.7	94.0	77.7

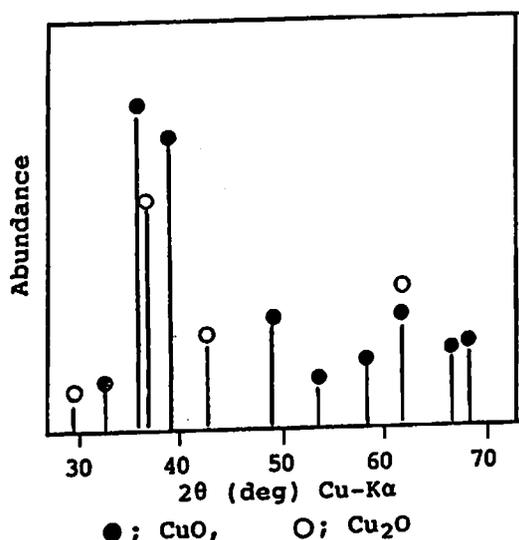


Fig. 6 XRD patterns of the residue for the Mg complex/CuO

tion decreased remarkably by the addition of another oxidizing agent with a decrease in N_2H_4 evolution.

In the tertiary system with CuO, the N_2 evolution increased except for the system with $KBrO_3$, though the evolved amount of it was insufficient based on the stoichiometric equation. In the system with $KBrO_3$, the amount of N_2 evolved and the mass balance of nitrogen atom become smaller with the addition of CuO. The reaction might be insufficient due to the scattering of the

sample because of the vigorous reaction. On the other hand, in the case of $Sr(NO_3)_2$, the reactivity become greater with the addition of CuO; the amount of N_2 evolved increased by 5%. In addition, the relative intensity of the X-ray diffraction of $Sr(NO_3)_2$ become smaller with the addition of CuO, as seen in Fig.5.

3.2.3 Evolved gas during combustion

Table 5 shows the amounts of the gases evolved during combustion in the system using $Sr(NO_3)_2$. The gas behavior during the combustion only in this system was investigated; the mass balance of nitrogen was low during the ignition at 400°C. In the case of the combustion, the mass balance of nitrogen increased about 4% in both systems. When using $Sr(NO_3)_2$ as the oxidizing agent, the investigation of the change in the combustion form and the use of a combustion catalyst is necessary, considering the mass balance of nitrogen. The use of $Sr(NO_3)_2$ is advantageous from the view point of a non-halogen agent and a reaction product having a higher melting point (the oxide, the carbonate), and its practical use will be investigated subsequently.

4. Conclusions

The thermal behavior and the gas evolution behavior was investigated in the Mg complex

Table 5 Amount of gas evolved for combustion of the Mg complex- $Sr(NO_3)_2$ mixtures (unit: mol/mol)

Gases	Mixtures of Table 1	
	MgCDH/ $Sr(NO_3)_2$	MgCDH/ $Sr(NO_3)_2$ /CuO
N_2	6.82	7.02
NH_3	0.00027	0.0019
NH_2NH_2	4.02×10^{-5}	2.64×10^{-5}
N_2O	0.016	0.013
NO	0.00030	0.00038
NO_2	0.00040	0.00077
CO	0.38	0.41
CO_2	0.96	1.08
N number	13.67	14.07
%	81.4	85.7
C number	1.34	1.49
%	44.7	49.7

*MgCDH = $Mg(CDH)_3(NO_3)_2$

with various oxidizing agents or in a tertiary system with 10% added CuO as another oxidizing agent. The oxidizing agents were potassium perchlorate, potassium bromate and strontium nitrate.

For the Mg complex / KBrO_3 mixture system, the initial temperature of the reaction was the lowest with the most vigorous reaction, and the amount of nitrogen and carbon dioxide gases were the largest of all systems. When using $\text{Sr}(\text{NO}_3)_2$ as the oxidizing agent, the amount of the N_2 gas evolved was the lowest. However, the reactivity was thought to be improved by the change in the combustion form and the addition of a combustion catalyst. NH_3 and N_2H_4 gases were generated in all binary systems with various oxidizing agents, and the amounts of these gases decreased remarkably with the addition of CuO.

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カルボノヒドラジド金属錯体硝酸塩の熱挙動(第6報) —マグネシウム錯体と酸化剤混合系のガス発生挙動—

秋吉美也子*, 今西康之*, 平田哲正**
中村英嗣*, 原 泰毅*

自動車用エアバッグのガス発生剤として、カルボノヒドラジドのマグネシウム錯体を取り上げ、その性能を評価する目的で、第4報では酸化剤との混合物の熱分析、燃焼熱、燃焼温度や燃焼速度を測定して考察した。本報告では、マグネシウム錯体と過塩素酸カリウム、臭素酸カリウムおよび硝酸ストロンチウムの酸化剤に一部酸化銅を加えた系のガス発生挙動を比較検討した。

マグネシウム錯体は臭素酸カリウムと混合するとき最も低温で、しかも激しく反応し、窒素および二酸化炭素の発生量が最も大きくなった。硝酸ストロンチウムを用いた系では、窒素の発生量は最も少なかったが、酸化銅を添加することによって、その発生量は増大した。いずれの系においても、酸化剤との2成分系ではアンモニウムやヒドラジンを発生するが、酸化銅を加えることによってこれらの発生量は著しく小さくなった。

(*九州工業大学応用化学教室 〒805-8550 北九州市戸畑区仙水町1-1

**ダイセル化学工業(株)技術開発センター 〒671-1665 兵庫県揖保郡揖保川馬場805)