Research paper

Thermal decomposition properties of energetic compositions of guanidine nitrate and azodicarbonamide

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Abstract

To obtain a better understanding of the thermal decomposition properties of energetic compositions of guanidine nitrate (GN) and azodicarbonamide (ADCA), differential scanning calorimetry (DSC) and thermogravimetry-differential thermal analysis connected with infrared spectroscopy (TG-DTA-IR) and with mass spectrometry (TG-DTA-MS) were carried out, and the onset temperature, heat of decomposition and evolved gas were determined. Furthermore, residue of thermal decomposition at various conditions was identified with Fourier transformation infrared spectroscopy (FT-IR) analysis. Experimental results suggested that the thermal decomposition of GN proceeded with the balance between the rates of vaporization and decomposition above a certain temperature and evolved gas products of thermal decomposition of GN/ADCA compositions are influenced by the mixing ratio.

Keywords : thermal decomposition, guanidine nitrate, azodicarbonamide, gas analysis

1. Introduction

Energetic compositions release large amount of gaseous products with heat in a short time and they have been widely used as propellants, fireworks or blasting agents and so on. Especially gas generants for smoking agents need to decompose with large amount of gas and heat release and vaporize active ingredients without decomposition, hence detailed characterization is needed. However, since gas generants are usually used in public space or houses, they also need appropriate combustion performance, non-toxic gaseous products and cleaner residue from the view point of safety, health and environment, and detail characterization is needed to lower the physical and chemical risk[1)-6)]. As compositions of guanidine nitrate (GN) and azodicarbonamide (ADCA) are expected to be alternative gas generants of next generation[7)-10)], there are still many unknown characteristics to be investigated. In this paper, thermal decomposition properties of GN and ADCA compositions are investigated with differential scanning calorimetry (DSC), simultaneous measurement of thermogravimetry - differential thermal analysis - Fourier transformation infrared spectroscopy (TG-DTA-IR) and thermogravimetry - differential thermal analysis - mass spectroscopy system (TG-DTA-MS). The reaction residues are analyzed with Fourier transformation infrared spectroscopy (FT-IR) and thermal decomposition mechanism was discussed.

2. Materials

Materials used in this study were commercially available reagents GN and ADCA purchased from Chugokukayaku Co., Ltd. and Dainichiseika Color and Chemicals Mfg. Co., Ltd., respectively and they were used as provided without further purification. Purities of GN and ADCA were 94 mass % and 99.9 mass %, respectively and average particle size of ADCA was 11.9 μm. Testing compositions were made as GN/ADCA=0/10, 3/7, 5/5, 7/3 and 10/0. Chemical structures of GN and ADCA are shown in Figure 1.

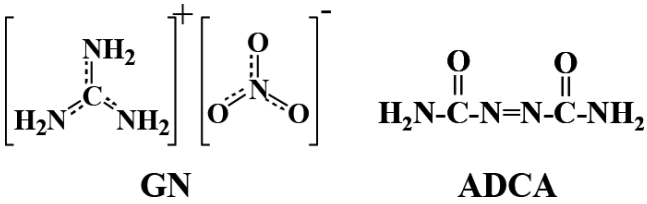

Figure 1 Chemical structures of GN and ADCA.

3. Experimental

3.1 Thermal analysis of GN/ADCA mixtures

Simultaneous TG-DTA was carried out for each sample with Shimadzu DTG-50. Samples were heated up to 400 °C at a heating rate of 10 K min^{-1} under 0.1 MPa air atmosphere. DSC (Mettler Toledo International Inc., HP DSC827e) was carried out for samples (1 mg) in a stainless steel sealed cell (Seiko Instruments Inc.) at a heating rate of 5 K min^{-1} over the measurement range of 30 - 500 °C.

3.2 Thermal decomposition of GN

Mettler Toledo pressure type DSC HP 827e was used to investigate the influence of ambient pressure on the thermal decomposition GN. 2 mg of GN in aluminum open crucible was heated up to 400°C at a heating rate of 10 K min^{-1} and the ambient pressure was chosen as 0.1, 0.3, 0.5, 0.7 or 0.9 MPa.

To confirm whether the endothermic peak at 0.1 MPa is due to vaporization or decomposition, the ratio of mass loss of GN up to the specific temperature against the total mass loss of GN were determined by stopping TG-DTA operation at a specific temperature and scanning again from room temperature (R.T.; 25 - 30°C) to 400 °C. Furthermore, FT-IR analysis was carried out with JASCO Co. FT-IR-420 for GN and its decomposition residue which were pre-heated and stopped at a specific temperature.

3.3 Evolved gas analysis of GN/ADCA compositions

To obtain information on gas products of GN/ADCA compositions, TG-DTA-IR and TG-DTA-MS analyses were performed. Samples (2 mg) were measured in an aluminum pan at a heating rate of 10 K min^{-1} in the range of R.T. to 500 °C.

TG-DTA-IR was used to identify the gases evolved during pyrolysis of samples. The apparatus consisted of a TG system (Shimadzu Co. Ltd., DTG-50) and an IR spectrometer (Shimadzu Co. Ltd., IR Prestige-21). The gases evolved after pyrolysis of the samples during the TG measurements were fed to a gas cell for IR analysis through a stainless steel transfer line. TG-DTA-IR analysis was carried out using an aluminum pan under an argon gas flow of 20 mL min^{-1}, a heating rate of 10 K min^{-1}, a measurement range of R.T. to 400 °C, and with a scanning resolution of 8 cm^{-1}. All spectra were integrated 15 times.

TG-DTA-MS was used for real-time analysis of the gases evolved during the pyrolysis of samples. This apparatus consisted of a TG system (Rigaku Co., TG8120) and a mass spectrometer (Shimadzu Co. Ltd., GCMS-QP 2010). Measurements were carried out using an aluminum pan under a helium gas flow of 200 mL min^{-1}, with a heating rate of 10 K min^{-1}, a measurement range of R.T. to 400 °C, and an oven temperature of 200 °C. The evolved gas components were identified on the basis of IR and MS reference spectra, available in the spectral libraries of the National Institute of Standards and Technology (NIST)[11] and from previous studies[3)–5), 12)–14)].

4. Results and descussions

4.1 Thermal analysis of GN/ADCA mixtures

Figure 2 shows simultaneous TG-DTA results of GN (10/0), ADCA (0/10), and GN/ADCA=5/5. ADCA initially undergoes an exothermic decomposition with mass loss at above 200 °C, followed by an endothermic decomposition of decomposition products : biurea at 230 °C[15]. Meanwhile, GN melts at 209 °C and decomposes at above 280 °C. At 195 °C, DTA curve of GN/ADCA=5/5 exhibited sharp exotherm with mass loss. Since GN dissociates into nitric acid and guanidine after melting[4), 5), 16),17)], the exothermic peak at 195 °C is suggested to be caused by a reaction between ADCA and nitric acid that dissociated from GN. Figure 3 shows sealed cell DSC results of GN, ADCA and GN/ADCA=7/3, 5/5, 3/7 compositions. The results of DSC were summarized in Table 1. Onset temperatures of GN and ADCA were 290 °C and 209 °C, respectively and those of GN/ADCA compositions were lower than pure materials. The heat of reaction of GN/ADCA compositions increased with an increase in the amount of ADCA.

It was found that the endothermic decomposition of GN and ADCA was suppressed in a closed cell. And it was found that the decomposition of ADCA shows violent and lower onset temperatures than those of ADCA and GN in the presence of GN.

4.2 Thermal decomposition of GN

Figure 4 shows the influence of ambient pressure on the thermal decomposition GN. Endothermic peak as seen in each composition at around 210 °C was due to the melting

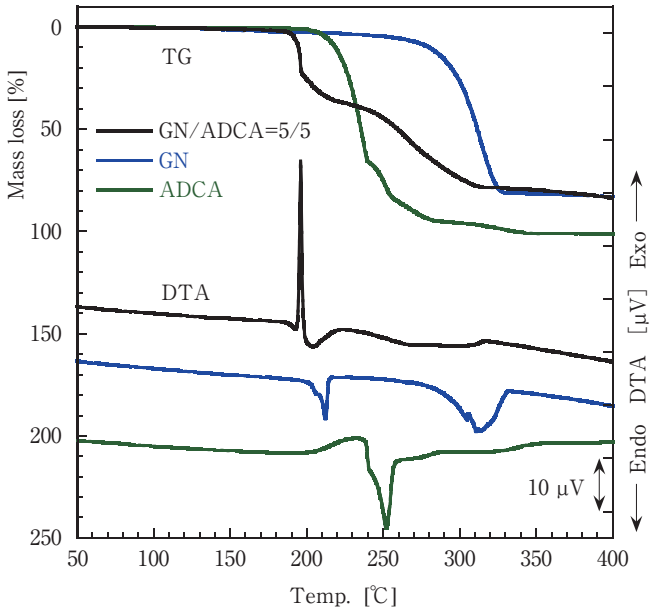

Figure 2 TG-DTA curves of GN, ADCA and ADCA/GN=5/5 composition.

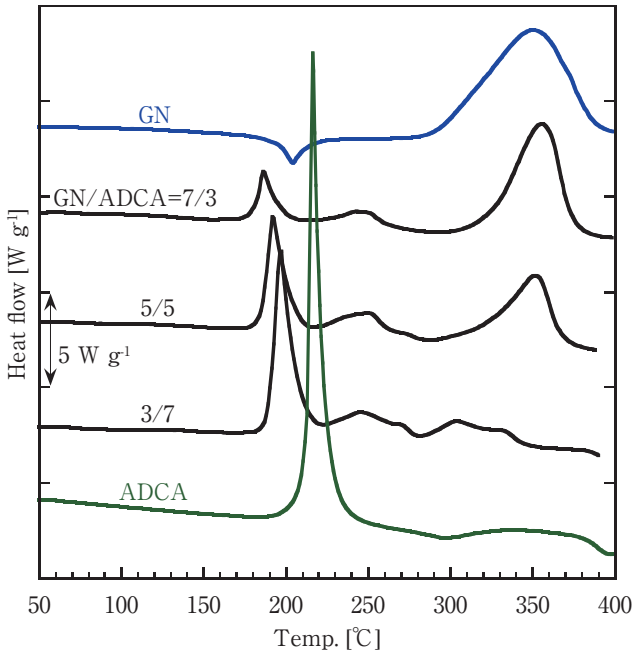

Figure 3 Sealed cell DSC curves of GN, ADCA and ADCA/GN compositions.

Table 1 Sealed cell DSC results for ADCA/GN compositions.

Mixing ratio (GN/ADCA)	Onset temperature [°C]	Heat of reaction [kJ g^{-1}]
10/0	290	1.9
7/3	180	1.2
5/5	184	1.4
3/7	189	1.5
0/10	209	1.9

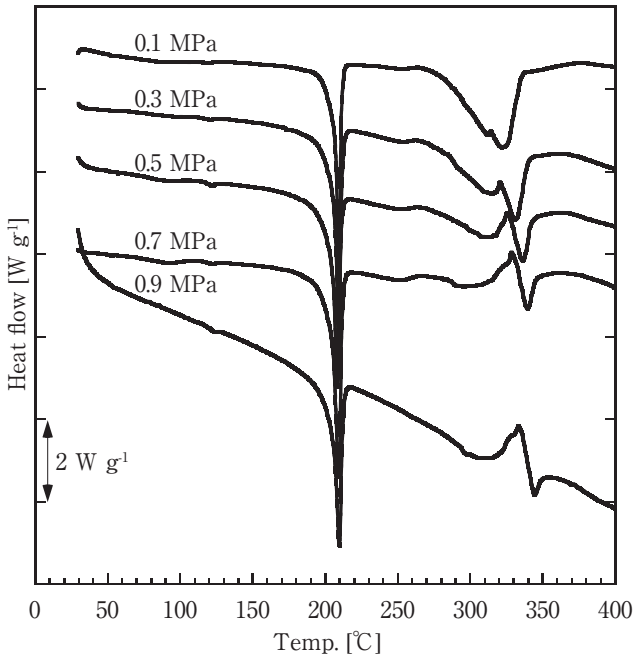

Figure 4 Influence of ambient pressure on DSC profiles of GN.

of GN. Concerning the DSC curves at above 260 °C, both of endothermic and exothermic peaks were observed. Figure 5 shows plots of exothermic heat of reaction at around 310 °C and ambient pressure values. The apparent

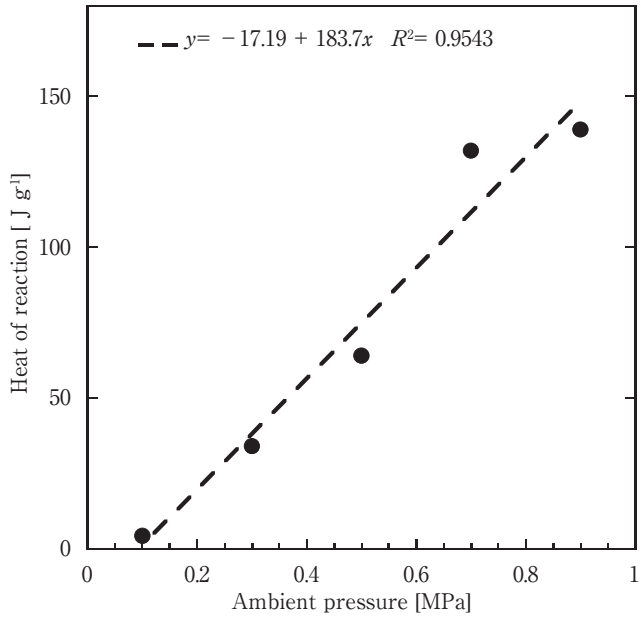

Figure 5 Plots of heat of reaction vs. ambient pressure of GN.

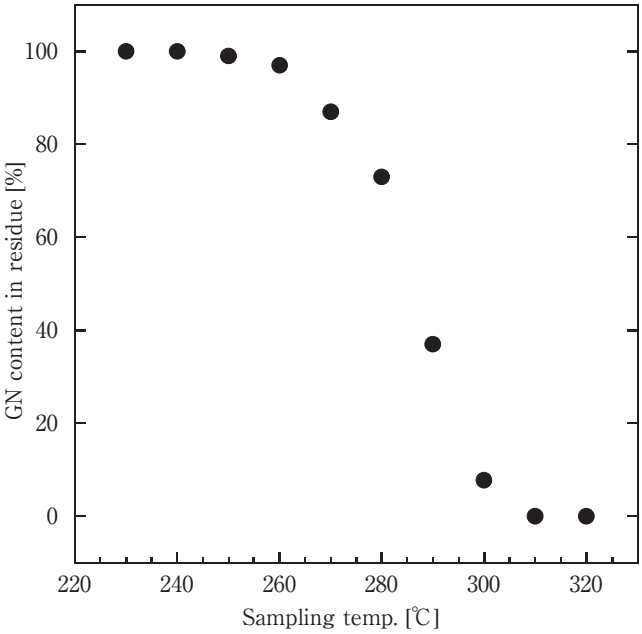

Figure 6 Ratio of GN remained in GN decomposition residue at sampling temperatures.

exothermic heat of reaction increased linearly with an increase in ambient pressure.

Figure 6 shows the mass loss ratio of GN at each final temperature against the fully decomposed mass loss. Thermal decomposition behaviour of GN changed at around 260 °C and both of vaporization and decomposition proceeded above 260 °C.

FT-IR spectra of pre-heated residue are shown in Figure 7. Although FT-IR spectra of residue, which was pre-heated to 280 °C, was similar to that of GN, IR spectra of residues at 300 °C and 320 °C appeared different. When final temperature was higher, peaks at 1578, 1672 and 3204 cm^{-1} disappeared and instead, peaks at 1432, 1502 and 1640 cm^{-1} appeared. FT-IR analysis supported the discussion that GN vaporizes after melting from 230 °C at 0.1 MPa air atmosphere and decomposes with vaporization from 270 -

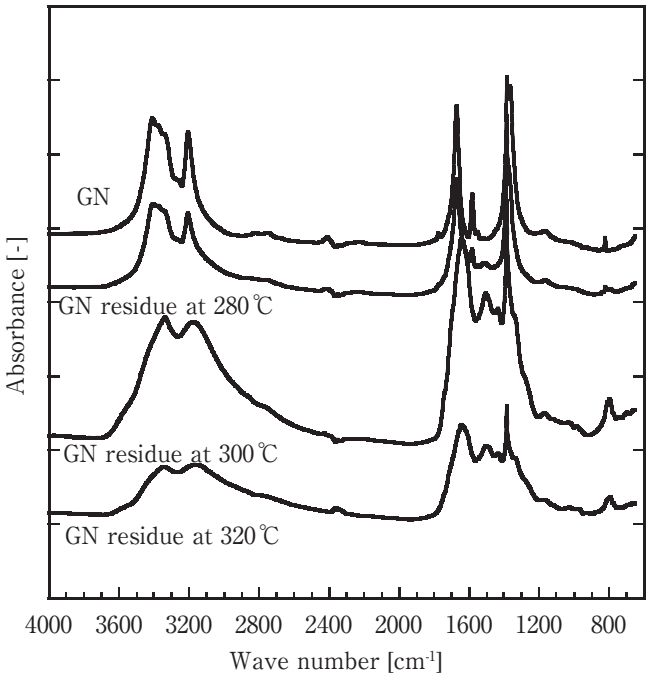

Figure 7 FT−IR spectra of GN and its decomposition residue at 280 °C, 300 °C and 320 °C.

280 °C[15]. From these results, it was found that the vaporization of GN was suppressed under pressurized conditions, and the exothermic reaction of GN was facilitated with increase ambient pressure.

4.3 Evolved gas analysis of GN/ADCA compositions

Evolved gas analysis of GN, ADCA and GN/ADCA compositions were performed with TG-DTA-IR and TG-DTA-MS. IR spectra of gasses evolved is shown in Figure 8. The signals observed were νCO_2 : 2300 - 2400 cm^{-1}, νHNCO : 2250 - 2275 cm^{-1}, νN_2O : 2150 - 2225 cm^{-1}, νCO : 2000 - 2200, and δNH_3 : 950 cm^{-1}. The averaged MS spectra

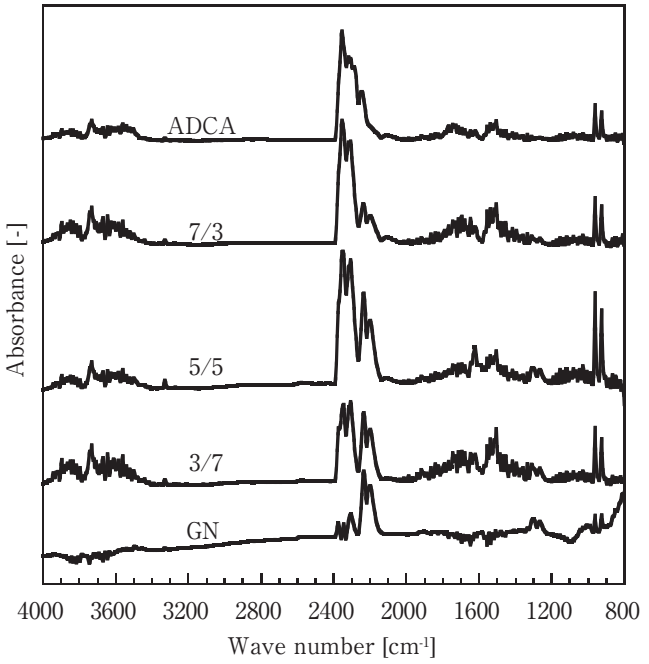

Figure 8 FT−IR spectra of gases evolved from GN, ADCA and GN/ADCA compositions.

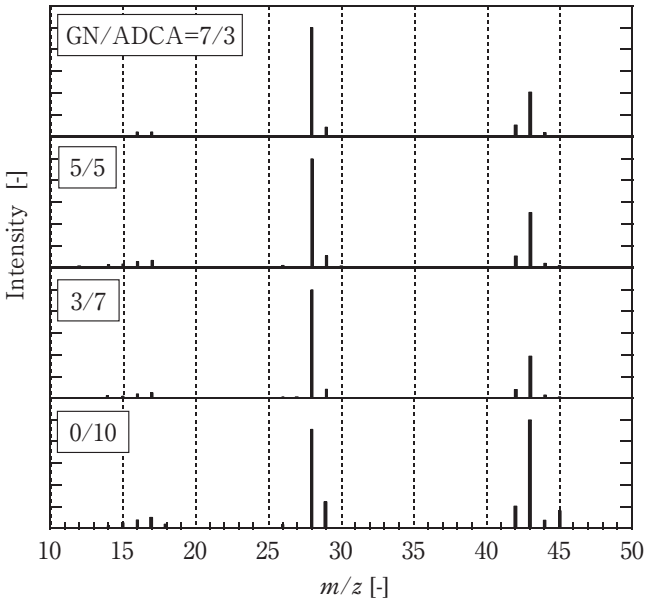

Figure 9 Mass spectra of gases evolved from ADCA and GN/ADCA compositions at around 200 °C.

of gasses evolved from ADCA and GN/ADCA compositions (7/3, 5/5, 3, 7, and ADCA) at around 200 °C are shown in Figure 9. The peaks in the mass spectrum correspond to mass-to-charge ratio (m/z) of 17 (NH_3 etc.), 28 (N_2 and CO), 42 (NCO), 43 (HNCO)[12], 44 (CO_2, N_2O)[18]. These results are summarized in Table 2. As GN is stable and does not show physical or chemical changes below 200 °C, no spectrum signal from GN was observed at 200 °C. Major products of GN/ADCA compositions are estimated to be NH_3, N_2, CO, CO_2, HNCO and N_2O. It was found that the evolved gases from GN/ADCA compositions showed larger amount of N_2, since the $m/z = 28$ peaks due to N_2 exhibited higher intensity. N_2 is very important for gas generants, but a small amount of N_2 was identified from the decomposition gas products of GN. Therefore, it is suggested that the mixture with suitable composition of ADCA shall be necessary when GN is used.

The MS spectra at 200 °C showed a similar pattern, and it is reasonable to speculate that exothermic decompositions would result from the similar reaction, regardless of the mixing ratios.

Figure 10 shows mass spectra of gases evolved from GN/ADCA compositions at above 260 °C. From the figure, gas products of each composition were affected by the mixing ratio at above 260 °C. The peak of $m/z = 44$ became larger with an increase in the amount of GN. Taking into account fragment peaks, the substance of $m/z = 44$ is mainly

Table 2 Gas products of each composition determined with TG−DTA−IR and TG−DTA−MS.

Mixing ratio (GN/ADCA)	Gas products determined
10/0	NH_3, H_2O, N_2, CO, CO_2, N_2O
7/3	NH_3, H_2O, N_2, CO, HNCO, CO_2, N_2
5/5	NH_3, N_2, CO, HNCO, CO_2
3/7	NH_3, N_2, CO, HNCO, CO_2
0/10	NH_3, N_2, CO, HNCO, CO_2

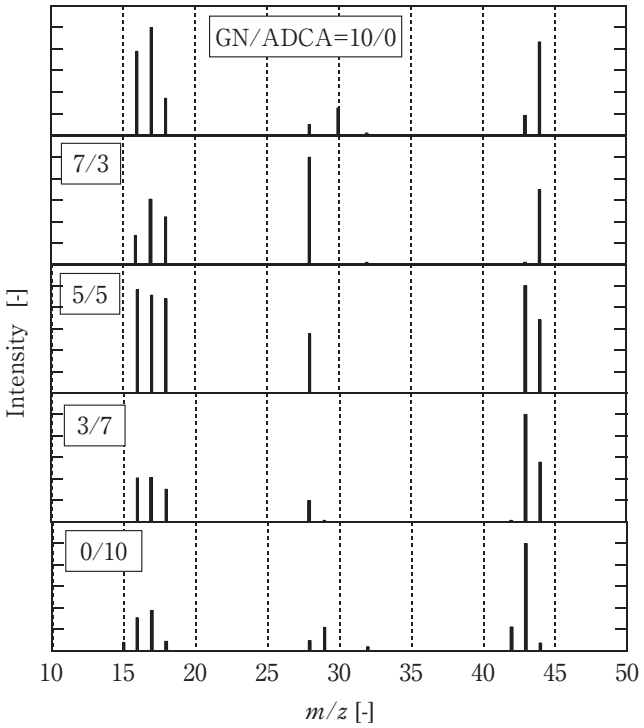

Figure10 Mass spectra of gases evolved from GN, ADCA and GN/ADCA compositions at above 260 °C.

considered to be CO_2, but a small amount of N_2O is also possible for GN/ADCA=7/3 composition. The peak of $m/z = 43$, which is considered to be HNCO (isocyanate), became smaller with an increase in the amount of GN. Meanwhile, NO_2 was not identified from any composition including GN.

From the evolved gas analyses of GN/ADCA compositions, it is concluded that evolved gas of GN/ADCA compositions shows larger amount of HNCO when ADCA is larger in amount, and N_2 or CO_2 increase with an increase in the amount of GN. As the most appropriate mixing ratio of GN/ADCA composition should be determined from physical and chemical risk, quantitative analyses will be needed as the further work for detailed discussion.

5. Conclusions

From experimental investigation of thermal and evolved gas analyses of GN/ADCA compositions, following conclusions can be drawn.

(1) Onset temperatures of exothermic reaction of GN/ADCA compositions were lower than individual compounds of GN and ADCA.

(2) Thermal decomposition of GN takes place with the balance between vaporization and decomposition, and it is strongly influenced by the ambient pressure.

(3) Evolved gas of GN/ADCA compositions shows larger amount of HNCO when ADCA is larger in amount, and N_2 or CO_2 increases with an increase in the amount of GN.

Acknowledement

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硝酸グアニジン／アゾジカルボンアミド組成物の熱分解特性

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硝酸グアニジン（GN）とアゾジカルボンアミド（ADCA）よりなる組成物の熱分解特性を検討するため，示差走査熱量測定（DSC），熱重量示差熱-赤外分光分析同時測定（TG-DTA-IR）および熱重量示差熱-質量分析同時測定（TG-DTA-MS）を用いて熱分解時の発熱開始温度，発熱量ならびに生成ガスの分析を行った。さらに，各測定条件における熱分解残留物をフーリエ変換赤外分光分析により同定した。これらの結果から，GNの熱分解過程はある温度以上において気化と分解の割合に依存し，GN/ADCA組成物の熱分解生成ガスは組成比に大きく影響を受け，変化することが明らかとなった。

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