Research paper

Influence of metal oxides on the combustion behavior of guanidine nitrate/basic copper nitrate mixture

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Abstract

A guanidine nitrate (GN)/basic copper nitrate (BCN) mixture is used as the main component of gas generators in an automotive airbag system. In this study, in order to search for novel additives that can reduce the amount of toxic combustion gases, we investigated the influence of the addition of metal oxides (ZrO_2, Al_2O_3, MgO, TiO_2, CuO, Cu_2O, SnO_2, V_2O_5, WO_3, and MoO_3) on the combustion behavior of the GN/BCN mixture. Combustion tests carried out using a chimney-type strand burner indicated that the burning rate of GN/BCN containing a metal oxide increased in comparison with that of additive-free GN/BCN. The composition of the combustion gas changed depending on the type of metal oxide added. The amount of CO included in the combustion gas markedly decreased in GN/BCN containing metal oxides having a low boiling point of less than 2300 °C (CuO, Cu_2O, SnO_2, V_2O_5, WO_3, or MoO_3). On the other hand, for GN/BCN containing Al_2O_3 or MgO, the NO_x amount decreased and the CO amount was almost the same as that of additive-free GN/BCN. Analysis of the combustion residue showed that the metal oxide acted as an oxidizer to decrease the CO content, while Al_2O_3 and MgO acted as catalysts for the reduction of NO_x. No significant change in the toxic gas composition was observed between GN/BCN containing TiO_2 or ZrO_2 and additive-free GN/BCN.

Keywords: airbag, gas generator, guanidine nitrate, basic copper nitrate, combustion gas

1. Introduction

Automobile airbags are safety devices used to reduce the shock experienced by the passenger in the event of an accident. It is necessary for the airbags to inflate as soon as the passenger collides with the windshield or steering wheel. For this reason, the airbag is inflated by the combustion gas from gas generators with a high combustion rate[1)−5)]. However, these generators release toxic gases such as CO, NO_x, and NH_3 as the result of incomplete combustion. In recent years, the amount of toxic gases released from gas generators has increased due to the increase in the types and numbers of airbags, such as side airbags and knee airbags, which are used to enhance the safety performance for passengers. Therefore, not only suitable combustion properties such as burning rate and gas transformation rate, but also reduced toxicity of combustion gases, have recently been identified to be critical for the performance of gas generators.

Nowadays, many kinds of metal oxides are employed as catalysts for the purification of combustion exhaust gases in diverse industrial fields[6),7)]. Previous studies have reported that the addition of SiO_2 or $Al(OH)_3$ into gas generators reduces the amount of toxic combustion gases[8),9)]. A mixture of guanidine nitrate (GN) as the fuel and basic copper nitrate (BCN) as the oxidizer is generally used as the main component of gas generators[10)–21)]. Therefore, the amount of toxic combustion gases released from the gas generator can be reduced more effectively if optimal metal oxides for combustion gas purification can be found.

In this study, in order to investigate suitable additives to mitigate the generation of toxic gases (CO, NO_x, and NH_3), we prepared GN/BCN mixtures containing various metal oxides (ZrO_2, Al_2O_3, MgO, TiO_2, CuO, Cu_2O, SnO_2, V_2O_5, WO_3, and MoO) as additives and investigated the influence of these additives on the burning rate and combustion gas composition of the GN/BCN mixture.

2. Experimental

2.1 Samples

GN (Wako Pure Chemical Industries, Ltd., 100–212 μm) as the fuel and BCN (Nihon Kagaku Sangyo Co., Ltd., under 10 μm) as the oxidizer were mixed in a 9:4 molar ratio, with a total weight of 3.0 g, in accordance with the chemical formula for complete combustion shown in Equation (1).

$$9\ CN_4H_6O_3+4\ Cu_2(OH)_3NO_3 \rightarrow 9\ CO_2+20\ N_2+33\ H_2O+8\ Cu \quad (1)$$

ZrO_2 (Wako Pure Chemical Industries, Ltd., 0.4–3 μm), MgO (Wako Pure Chemical Industries, Ltd., 0.1–5 μm), Al_2O_3 (Showa Denko, Ltd., 0.5–20 μm), TiO_2 (Wako Pure Chemical Industries, Ltd., 0.07–0.5 μm), CuO (Wako Pure Chemical Industries, Ltd., 30–300 μm), Cu_2O (Wako Pure Chemical Industries, Ltd., 0.2–10 μm), SnO_2 (Wako Pure Chemical Industries, Ltd., 0.5–20 μm), V_2O_5 (Wako Pure Chemical Industries, Ltd., 1–100 μm), WO_3 (Wako Pure Chemical Industries, Ltd., 10–110 μm), and MoO_3 (Wako Pure Chemical Industries, Ltd., 0.1–5 μm) were used as additives. These metal oxides were mixed with GN/BCN in the ratio 6.5–20 mass%. The mixed samples were compressed and cylindrically molded (diameter: 9.6 mm, length: 23–26 mm, bulk density: approximately 1.8–1.9 g cm^{-3}) for use in the combustion test described below.

2.2 Combustion test

The combustion tests were conducted under a N_2 gas flow (1 MPa) using a chimney-type strand combustion apparatus[22)]. The sample was installed on the sample stand and ignited by an electrically energized coiled nichrome wire, and the burning rate was measured by the break wire method[19)–22)]. The combustion gases were collected with the N_2 flow into a sampling bag (220 L) to measure the concentrations of CO, NO_x, and NH_3 using gas detector tubes (GASTEC Corp., 1La, 3L, 11S). The observed concentration values were converted into the volume of CO, NH_3, and NO_x per unit mass of GN/BCN using Equation (2).

$$\text{Gas amount} = \frac{CV}{M} \quad (2)$$

where C indicates the detected concentrations of CO, NO_x, and NH_3; V is the total volume of the combustion gas and flow gas; and M is the mass of the GN/BCN mixture.

The combustion residues of the samples were analyzed using an X-ray diffractometer (SHIMADZU Corp., LabX XRD-6100). The XRD measurements were conducted at a rotational speed of 2° min^{-1} in the rotation range 10–80°, with CuK$_\alpha$ radiation and at a voltage of 40.0 kV and electric current of 30.0 mA.

3. Results and discussion

3.1 Influence of the type of metal oxide

Table 1 lists the burning rates of GN/BCN and its mixtures with metal oxides (10 mass%) in a N_2 atmosphere of 1 MPa. The burning rate of additive-free GN/BCN was 2.9 mm·s^{-1}. On the other hand, when metal oxides (ZrO_2, MgO, Al_2O_3, TiO_2, CuO, Cu_2O, V_2O_5, and MoO_3) were added to GN/BCN, the burning rates increased to a maximum of 4.7 mm·s^{-1}. It was considered that some metal oxides promoted the oxidative combustion of GN/BCN.

Figure 1 shows the amounts of CO, NO_x, and NH_3 included in the combustion gas generated from GN/BCN and GN/BCN mixtures with metal oxides (10 mass%) in an atmosphere of 1 MPa. The CO amount in GN/BCN mixed with CuO, Cu_2O, SnO_2, V_2O_5, WO_3, or MoO_3 was markedly lower than that in additive-free GN/BCN, although the NO_x amount was almost the same or higher. On the other hand, the NO_x amount in GN/BCN mixed with Al_2O_3 or MgO decreased to a greater extent than that in additive-free GN/BCN, whereas the amounts of CO and NH_3 were almost equivalent in both cases. No significant change in the combustion gas composition was observed between GN/BCN mixed with TiO_2 or ZrO_2 and additive-free GN/BCN. From these results, it was clear that the composition of the combustion gas changed depending on the type of metal oxide added, and that some metal oxides could reduce the toxic combustion gas released by GN/BCN.

The XRD patterns of the combustion residues of GN/BCN/Al_2O_3 and GN/BCN/MoO_3 mixtures are shown in Figures 2(a) and (b). The main components of the combustion residue for all the samples, estimated based on the XRD results and the appearances, are summarized in Table 1. The components of the combustion residues of

Table 1 Burning rates and combustion residues of the GN/BCN mixture and GN/BCN/metal oxide (10 mass%) mixtures.

Samples	Burning rates [mm·s^{-1}]	Combustion residues
GN/BCN	2.9±0.02	Cu
+ZrO_2	3.3±0.46	Cu, ZrO_2
+MgO	4.7	Cu, MgO
+Al_2O_3	4.2±0.01	Cu, Cu_2O, Al_2O_3
+TiO_2	3.7±0.38	Cu, TiO_2
+CuO	3.9	Cu, Cu_2O
+Cu_2O	3.7	Cu
+SnO_2	2.5±0.02	Cu_2O, Cu5.6Sn, SnO_2
+V_2O_5	3.9±0.29	Cu, VO_2
+WO_3	2.6±0.27	Cu, WO_2, WO_3
+MoO_3	4.1±0.08	Cu, MoO_2

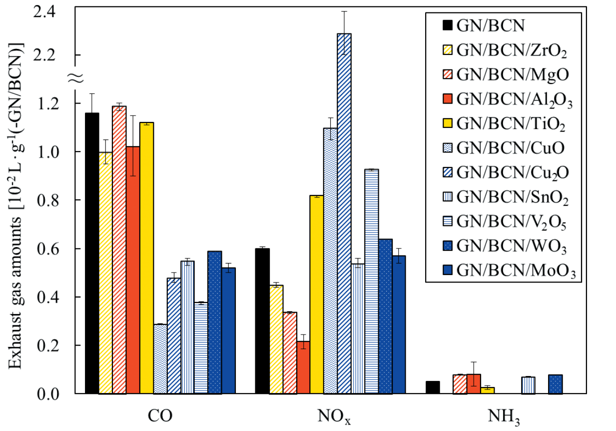
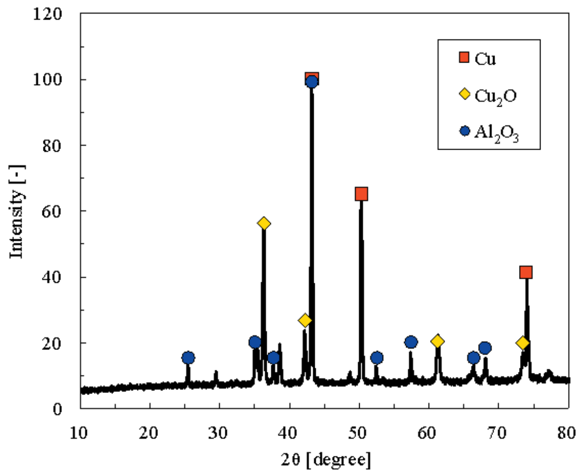
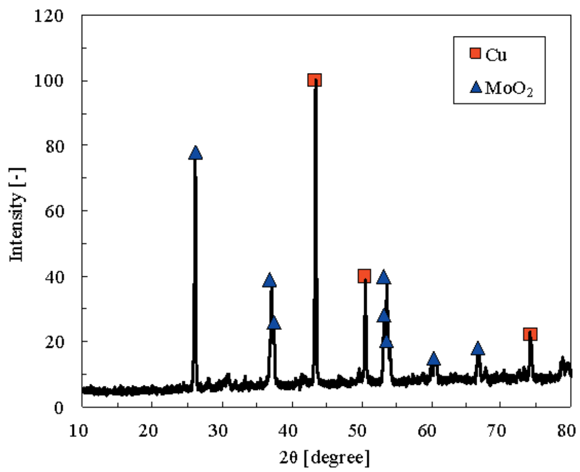


Figure 1 Amounts of CO, NO_x, and NH_3 in GN/BCN mixture and GN/BCN/metal oxide (10 mass%) mixtures.



(a) XRD result for GN/BCN/Al_2O_3 mixture.



(b) XRD result for GN/BCN/MoO_3 mixture.

Figure 2 XRD results for GN/BCN/Al_2O_3 mixture and GN/BCN/MoO_3 mixtures.

GN/BCN mixed with Al_2O_3, MgO, TiO_2, or ZrO_2 were metallic Cu, Cu_2O, and unreacted additives which were the same as those before combustion. Since Al_2O_3 and MgO reduced the NO_x generation amount and promoted the oxidative combustion of GN/BCN, as described above, it is possible that Al_2O_3 and MgO contributed to the combustion as both denitration and combustion catalysts.

In the XRD results of GN/BCN mixed with CuO, Cu_2O, SnO_2, V_2O_5, WO_3, or MoO_3, where the CO generation amount was lower than that of the additive-free GN/BCN, reduced metal oxides originating from the additives as well as metallic Cu were included in the combustion residue. The common property of these added metal oxides is that they have a boiling point of less than 2300 °C, which is lower than the combustion temperature (approximately 2100 °C) of GN/BCN, as estimated from equilibrium calculations by NASA CEA[23]. Therefore, the results indicated that these metal oxides vaporized in combustion flame and were reduced to oxidize CO to CO_2.

As for the SnO_2 and WO_3, the effect decreasing CO as well as the effect increasing combustion rate was lower than those of the other additives contributing to decrease in CO. This behavior is thought to mean that SnO_2 and WO_3 are less involved in the combustion of GN/BCN since those have comparatively high boiling point as shown in Table 1. In addition, Cu_2O significantly increased NO_x amount whereas decreasing CO amount by its oxidative effect, which is similar behavior to GN containing rich BCN as mentioned later (Figure 5). Since BCN is considered to release Cu_2O, NO_x amount increases with increase in amount of Cu_2O in the combustion flame regardless of the way addition.

3.2 Influence of the amount of metal oxide additive

In order to investigate the optimal additive amount, combustion tests were conducted on GN/BCN mixtures containing different amounts of Al_2O_3 and MoO_3 (6.5–20 mass%), which increased the burning rate and reduced toxic combustion gases, in a N_2 atmosphere of 1 MPa. The relationship between the burning rate and the amount of metal oxide additive is shown in Figure 3. The burning rates of GN/BCN mixtures containing Al_2O_3 and MoO_3 were similar, regardless of the additive amount.

The amounts of CO, NO_x, and NH_3 generated from GN/BCN containing different amounts of Al_2O_3 or MoO_3 additive (6.5–20 mass%) were observed; the results are shown in Figures 4(a)–(c). The CO amount decreased with an increase the additive amount for both samples, as shown in Figure 4(a). The NO_x amount in the case of GN/BCN/Al_2O_3 decreased with an increase in the additive amount but increased slightly in the case of GN/BCN/MoO_3, as shown in Figure 4(b). The NH_3 amount hardly changed with the additive amount (Figure 4(c)). Thus, the optimal additive amount would be 10–15 mass% because the amount of toxic gas becomes steady at 15–20 mass% of metal oxide addition.

As mentioned in Section 3.1, MoO_3 may reduce the amount of CO by acting as an oxidizer. If MoO_3 simply acts as an oxidizer, the combustion behavior of GN/BCN containing MoO_3 would be identical to that of additive-free GN/BCN with different fuel-oxidizer ratios. Thus, the amounts of toxic gases generated from GN/BCN mixtures with different fuel-oxidizer ratios and GN/BCN containing 6.5–20 mass% MoO_3 were compared. Figures 5(a)–(c) illustrate the relationship between the amounts of toxic gases and the oxygen balance of additive-free GN/BCN[24] and GN/BCN/MoO_3. The oxygen balance for GN/BCN was calculated using Equations(3) and (4), while that for

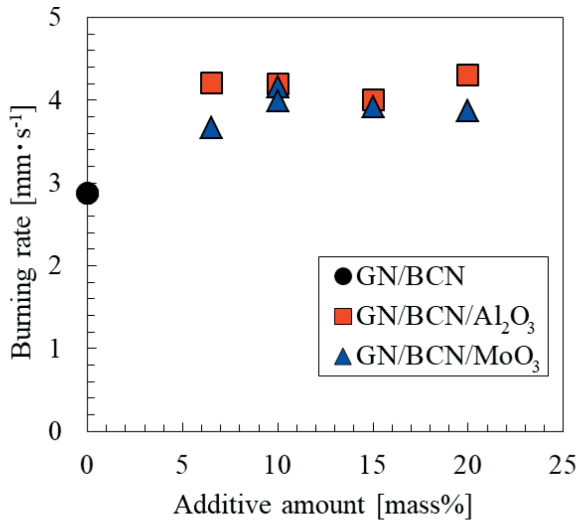


Figure 3 Burning rates of GN/BCN mixture and GN/BCN/metal oxide (6.5–20 mass%) mixtures.

GN/BCN containing different amounts of MoO_3 was calculated using Equations (5) and (6), based on the experimental results (Table 1 and Figure 2(b)).

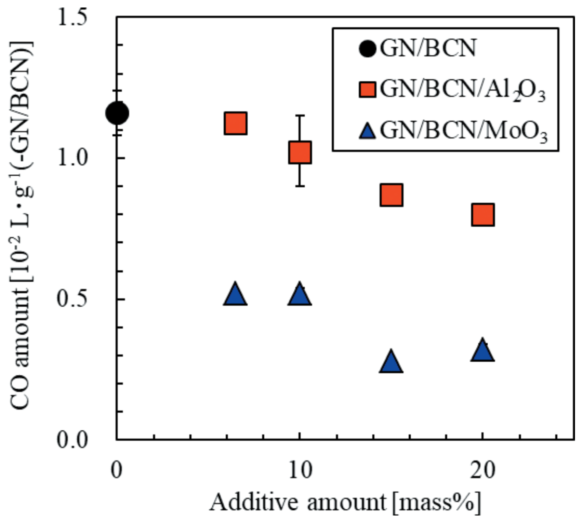
$$a\,C(NH_2)_3NO_3 + b\,Cu_2(OH)_3NO_3 \rightarrow a\,CO_2 + \frac{4a+b}{2}N_2 + \frac{6a+3b}{2}H_2O + 2b\,Cu \pm \frac{4a-9b}{4}O_2 \quad (3)$$

$$\text{Oxygen balance} = \frac{(-4a+9b)/4 \times 32\frac{g}{mol} \times 100}{\left(a \times 122\frac{g}{mol} + b \times 240\frac{g}{mol}\right)} \quad (4)$$

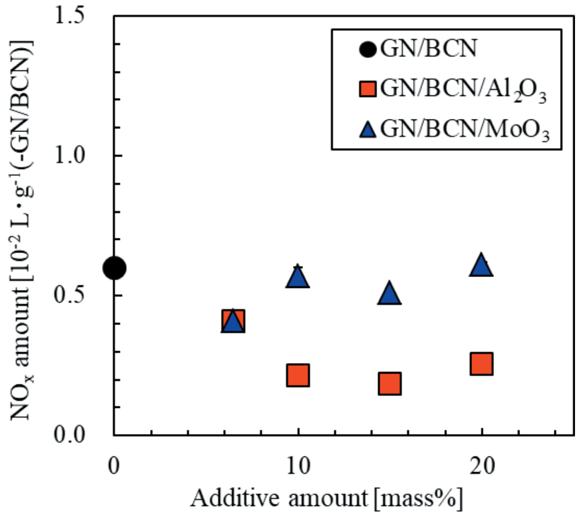
$$9\,C(NH_2)_3NO_3 + 4\,Cu_2(OH)_3NO_3 + c\,MoO_3 \rightarrow 9\,CO_2 + 20\,N_2 + 33\,H_2O + 8\,Cu + c\,MoO_2 + \frac{c}{2}O_2 \quad (5)$$

$$\text{Oxygen balance} = \frac{c/2 \times 32\frac{g}{mol} \times 100}{\left(9 \times 122\frac{g}{mol} + 4 \times 240\frac{g}{mol} + c \times 40.3\frac{g}{mol}\right)} \quad (6)$$

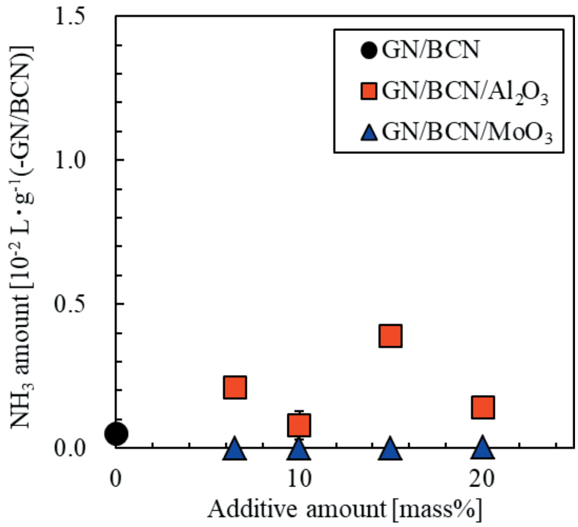
The results are shown in Figures 5(a)–(c). The amounts of CO (Figure 5(a)) and NH_3 (Figure 5(c)) generated from GN/BCN/MoO_3 were almost the same as those in the case of additive-free GN/BCN at identical oxygen balance, which supported the assumption that MoO_3 decreases the amount of CO by acting as an oxidizer. On the other hand, the amount of NO_x generated from GN/BCN/MoO_3 was lower than that in the case of additive-free GN/BCN at identical oxygen balance, and this behavior was unchanged even when the oxygen balance become positive, unlike the BCN-rich conditions. This result may imply that NO_x was mainly released from the reaction related to BCN, and that the release of NO_x was suppressed because of the relatively low BCN content in GN/BCN/MoO_3.



(a) Relationship between CO amount and additive amount.



(b) Relationship between NO_x amount and additive amount.

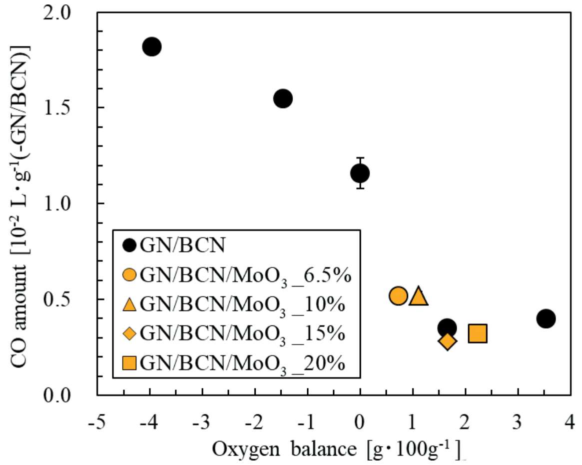


(c) Relationship between NH_3 amount and additive amount.

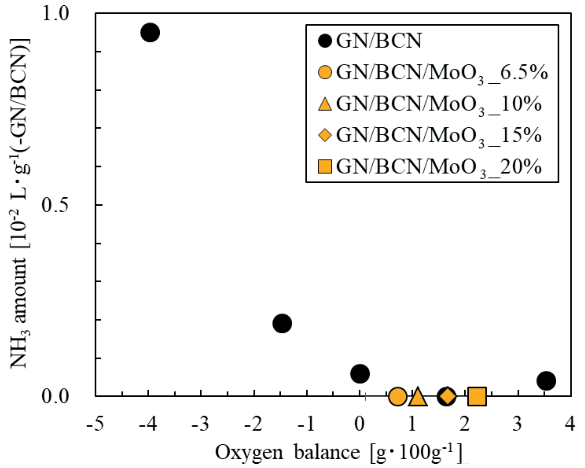
Figure 4 Amounts of CO, NO_x, and NH_3 of GN/BCN/metal oxide (6.5–20 mass%) mixtures.

4. Conclusions

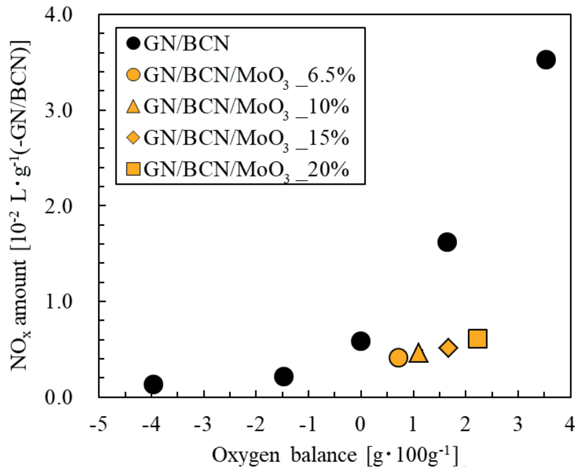
In this study, the combustion behavior of GN/BCN mixtures containing various metal oxides (ZrO_2, MgO, Al_2O_3, TiO_2, CuO, Cu_2O, SnO_2, V_2O_5, WO_3, and MoO_3) was



(a) Relationship between CO amount and oxygen balance.



(b) Relationship between NH_3 amount and oxygen balance.



(c) Relationship between NO_x amount and oxygen balance.

Figure 5 Relationship between the amounts of CO, NO_x, and NH_3 and oxygen balance of GN/BCN mixtures and GN/BCN/MoO_3 (6.5–20 mass%) mixtures.

investigated in order to investigate the role of these additives in reducing the amount of toxic gases (CO, NO_x, and NH_3) included in the combustion gas generated from the gas generator in automotive airbags. The following conclusions could be drawn:

- The addition of metal oxides, regardless of the type, tended to increase the burning rate of GN/BCN, suggesting that certain metal oxides promoted the oxidative combustion of GN/BCN.
- The CO amount in GN/BCN mixed with CuO, Cu_2O, SnO_2, V_2O_5, WO_3, or MoO_3 was remarkably lower than that in additive-free GN/BCN. The common property of these added metal oxides is that they have a low boiling point of less than 2300 °C; thus, reduced metal oxides originating from the additives were detected as the combustion residue. These results indicated that these metal oxides vaporized and underwent reduction to oxidize CO.
- The NO_x amount in GN/BCN mixed with Al_2O_3 or MgO decreased more notably than that in additive-free GN/BCN. The combustion residue contained the same unreacted additives as those before combustion, which indicated that Al_2O_3 and MgO contributed to the combustion as a denitration catalyst.
- GN/BCN mixed with TiO_2 or ZrO_2 showed no significant difference in the combustion gas composition from that of additive-free GN/BCN.

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