

# Effects of Transition-Metal Substitution on the Catalytic Properties of Barium Hexaaluminogallate

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The effects of the substitution of transition-metal ions and/or reductant gases on the catalytic properties of barium hexaaluminogallate were investigated. Transition-metal-substituted hexaaluminogallates ( $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$ ,  $\text{M}$  = transition metal,  $\text{Al/Ga} = 9/3$ ) were synthesized from aqueous metal nitrates and ammonium carbonate by the coprecipitation followed by crystallization at  $1100^\circ\text{C}$ . The direct  $\text{NO}_x$  reduction was observed over  $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$  to be around 10%. The  $\text{NO}_x$  removal activity of  $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$  powders was improved by addition of  $\text{C}_3\text{H}_6$  as a reductant gas. Co-, Ni- and Cu-substituted  $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$  catalysts exhibited about 40%  $\text{NO}_x$  reduction with  $\text{C}_3\text{H}_6$  in excess oxygen at a high space velocity of  $10\,000\text{ h}^{-1}$ . The  $\text{NO}_x$  reduction on Mn- and Fe-substituted  $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$  catalysts was less than 10% even in the presence of  $\text{C}_3\text{H}_6$ . The temperature of the effective  $\text{NO}_x$  reduction on  $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$  catalysts could be adjusted from  $350^\circ$  to  $500^\circ\text{C}$  by the selection of the transition-metal substitution in the catalysts. The catalysts hold high activities for  $\text{NO}_x$  reduction even at  $500^\circ\text{C}$  in water vapor produced in the combustion system of reductant gases.

## I. Introduction

THE combustion system at higher temperatures and under lean conditions is one of the most effective approaches for the improvement of the energy efficiency. However, nitrogen oxides ( $\text{NO}_x$ ), which damage the environment by causing acid rain, the greenhouse effect, and air pollution, are produced in such systems. Selective catalytic reduction (SCR) of  $\text{NO}_x$  by hydrocarbons has attracted much attention, because of the potential for  $\text{NO}_x$  reduction even in an exhaust system with excess oxygen. Cu-exchanged zeolite was reported to show high  $\text{NO}_x$  reduction with alkenes.<sup>1,2</sup> However, Cu-exchanged zeolite has poor thermal stability in the presence of water vapor.<sup>2–4</sup> In contrast, alumina-supported metal catalysts were found to have higher heat resistance but lower catalytic activity than zeolite catalysts in the presence of water vapor at high temperatures. For instance, alumina-supported cobalt and alumina-supported copper are reported to improve  $\text{NO}_x$  removal activity.<sup>5</sup> Moreover, the addition of alkaline-earth or rare-earth metal ions to alumina catalysts was also attempted to maintain high surface areas under severe conditions.<sup>6,7</sup>

Hexaaluminogallates ( $\text{M}^{2+}(\text{Al,Ga})_{12}\text{O}_{19}$ ) are solid solutions between hexaaluminate ( $\text{M}^{2+}\text{Al}_{12}\text{O}_{19}$ ) and hexagallate ( $\text{M}^{2+}\text{Ga}_{12}\text{O}_{19}$ ), and their crystal structures are related to  $\beta$ -alumina or magnetoplumbite with hexagonal symmetry of space group  $P6_3/mmc$ .<sup>8,9</sup> Similar to hexaaluminate, hexaaluminogallates have a characteristic layered structure consisting of alternative

stacking of closed-packed spinel blocks and mirror planes containing large cations (Ba or La, etc.) along the  $c$ -axis. The inhibition of grain growth along the  $c$ -axis due to the diffusion anisotropy of oxide ions in the mirror plane results in excellent thermal resistance.<sup>10</sup> In addition, the Al or Ga sites in the hexaaluminogallate structures can be substituted for various transition metals, resulting in reduction/oxidation catalytic functions.<sup>11</sup> Ga ions located at the tetragonal Al sites in the spinel block of hexaaluminate structure are also reported to be able to modify the spinel block framework.<sup>8,9</sup> Therefore, hexaaluminogallate is expected to be a promising high-temperature catalyst, because of its high melting point, its capacities for incorporating various transition metals, and the tendency to grow as characteristic platelike particles. The authors have reported the synthesis of Co-substituted barium hexaaluminogallate and its catalytic properties.<sup>12</sup>  $\text{BaCo}(\text{Al,Ga})_{11}\text{O}_{19}$  supported on cordierite honeycombs showed  $\text{NO}_x$  reduction with  $\text{CH}_4$  in the presence of excess oxygen.

This paper describes the synthesis and catalytic properties of barium hexaaluminogallates incorporated with various transition metals ( $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$ ,  $\text{M}$  = Mn, Fe, Co, Ni, Cu).  $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$  powders were synthesized by the coprecipitation method from aqueous solutions of metal salts. Direct  $\text{NO}_x$  reduction and SCR of  $\text{NO}_x$  with methane and propylene in the presence of excess oxygen were also evaluated for hexaaluminogallate powders with and without the substitution of transition-metal ions.

## II. Experimental Procedure

### (I) Synthesis of Hexaaluminogallate Powders

Hexaaluminogallate precursor powders were prepared by the coprecipitation method.<sup>12</sup>  $\text{Ba}(\text{NO}_3)_2$  (Kishida Chemical Co.),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Kishida Chemical Co.), and  $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Ko-Jundo Chemical Co.) were used as metal sources for the hexaaluminogallate framework.  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Kishida Chemical Co.),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Kishida Chemical Co.),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Kishida Chemical Co.),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Kishida Chemical Co.), and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Kishida Chemical Co.) were used as the sources of transition metals. Appropriate amounts of starting nitrates were dissolved in distilled water to form 0.02 mol/L aqueous solutions with  $\text{BaM}_x(\text{Al,Ga})_{12-x}\text{O}_{19}$  ( $\text{Al/Ga} = 9/3$ ,  $x = 0$  or  $1$ ) compositions. Aqueous  $(\text{NH}_4)_2\text{CO}_3$  solution (2.0 mol/L) was found to be a proper agent for coprecipitating metal nitrates homogeneously, which results in producing the suspension dispersed with hexaaluminogallate precursor powders.<sup>12</sup> The pH of the suspension was about 7.5 to 8.0. The precipitates were collected from the suspension using ultrafiltration and then washed with ethanol to avoid the aggregation of precipitates. A membrane filter (Advantec, Ultrafilter UK-50 (MW cutoff, 50 000)) was used for ultrafiltration. Hexaaluminogallate precursor powder substituted with transition-metal ion was heat-treated at  $1100^\circ\text{C}$  for 2 h in air.  $\text{Ba}(\text{Al}_9\text{Ga}_3)\text{O}_{19}$  powder was used as a standard of the powder characteristics, such as the crystallinity, BET surface area, and the particle size, and synthesized by heat treatment at  $1200^\circ\text{C}$  for 2 h to make these powder characteristics consistent with that of  $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$  powder.

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### (2) Evaluation of NO and NO<sub>x</sub> Removal Capabilities of Hexaaluminogallate Powders

The NO and NO<sub>x</sub> removal capabilities were investigated for 0.5 g of each hexaaluminogallate powder at temperatures between 350° and 650°C. The gas mixtures of three compositions were used for the catalytic measurements: (1) direct reduction of NO<sub>x</sub>—500 ppm NO, 8% O<sub>2</sub> in He balance gas; (2) selective reduction of NO<sub>x</sub> with methane—500 ppm NO, 1000 ppm CH<sub>4</sub>, 8% O<sub>2</sub> in He balance gas; (3) selective reduction of NO<sub>x</sub> with propylene—500 ppm NO, 1000 ppm C<sub>3</sub>H<sub>6</sub>, 8% O<sub>2</sub> in He balance gas, at a flow rate 150 mL/min. The hexaaluminogallate powder was placed in a quartz glass tube with 1 cm diameter. The gas mixtures were passed through the catalytic powder layer at a flow rate of 150 mL/min (space velocity = 10 000 h<sup>-1</sup>). Then, a part of the reacted gases was sucked by the pump introducing a NO<sub>x</sub> analyzer. Both NO and NO<sub>2</sub> compositions were measured using the NO<sub>x</sub> analyzer. The NO<sub>x</sub> concentration was analyzed with a NO<sub>x</sub> analyzer (Best-sokki, Analyzer unit BCL-100uH, Sampling unit BSU-100uH).

### (3) Characterization

The crystalline phases were identified by X-ray diffractometry (XRD; Rigaku RAD-2X) using CuKα radiation with a monochromator. The microstructures of the synthesized powders were examined by scanning electron microscopy (SEM; JEOL, JSM-6100). The BET surface area was measured with an automatic surface area analyzer (Model 4200, Leeds and Northrup Co., North Wales, PA).

## III. Results

### (1) Preparation of Hexaaluminogallate Powders by the Coprecipitation Method

The coprecipitation method was selected to prepare fine hexaaluminogallate precursor powders with high reactivity. The coprecipitation method was found to be superior in terms of the low-temperature synthesis of barium hexaaluminogallate to the conventional solid-state reaction.<sup>12</sup>

Figure 1 shows the XRD profiles of BaM(Al,Ga)<sub>11</sub>O<sub>19</sub> (Al/Ga = 9/3) powders obtained from the precipitates after heat treatment at 1100°C for 2 h. At 1100°C, all powders except BaNi(Al,Ga)<sub>11</sub>O<sub>19</sub> crystallized well in hexaaluminogallate single phase with β-alumina structure.<sup>12</sup> As shown in Fig. 1(f), for nonsubstituted Ba(Al,Ga)<sub>12</sub>O<sub>19</sub> (Al/Ga = 9/3), heat treatment at 1200°C for 2 h was necessary for achieving crystallinity as good as that of BaM(Al,Ga)<sub>11</sub>O<sub>19</sub>. The incorporation of transition metals was, therefore, found to enhance the crystallization of barium hexaaluminogallate at lower temperature. However, as shown in Fig. 1(d), broad diffractions were observed from 2θ = 20° to 40° with several diffractions of unknown phases in the XRD profile of BaNi(Al,Ga)<sub>11</sub>O<sub>19</sub>. After heat treatment at 1200°C for 2 h, the broad diffractions disappeared, and single-phase BaNi(Al,Ga)<sub>11</sub>O<sub>19</sub> was formed. The diffraction pattern of BaNi(Al,Ga)<sub>11</sub>O<sub>19</sub> crystallized at 1200°C was the same as those of other BaM(Al,Ga)<sub>11</sub>O<sub>19</sub>, as shown in Fig. 1(g).

Figure 2 shows the microstructures of Ba(Al<sub>9</sub>Ga<sub>3</sub>)O<sub>19</sub> powder and hexaaluminogallate powders substituted for transition-metal ions. The former was synthesized at 1200°C for 2 h, the latter at 1100°C for 2 h. The morphology of the hexaaluminogallate powders without and with transition-metal ions except for Fe ion were mixtures of isotropic particles and platelets with submicrometer size. However, the BaFe(Al,Ga)<sub>11</sub>O<sub>19</sub> powder consisted only of platelike particles with larger grain sizes above 1 μm.

The BET surface areas of hexaaluminogallate powders are summarized in Table I. BaNi(Al,Ga)<sub>11</sub>O<sub>19</sub> with lower crystallinity had the largest surface area among them. BaFe(Al,Ga)<sub>11</sub>O<sub>19</sub> with large grain size (Fig. 2(b)) had the smallest surface area. Other powders had surface areas from 15 to 20 m<sup>2</sup>/g, which reflects the growth tendency of particles shown in Fig. 2. The powder characteristics, such as crystallinity, BET surface area, shape, and

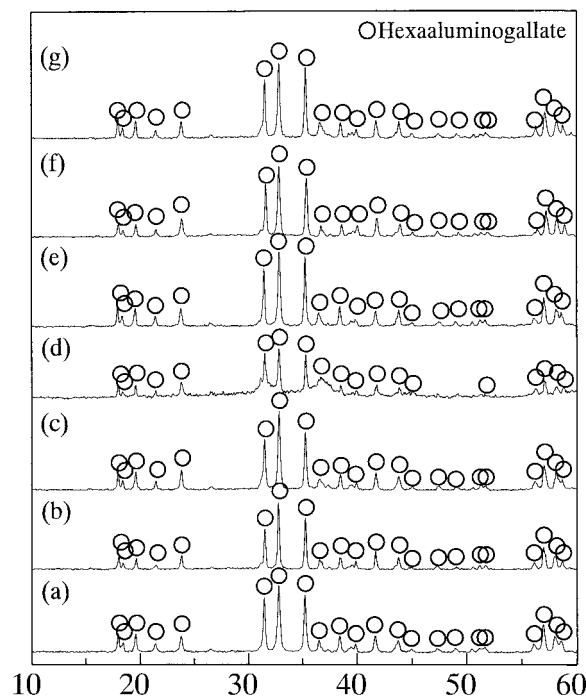


Fig. 1. XRD profiles of barium hexaaluminogallate powders substituted with (a) Mn, (b) Fe, (c) Co, (d) Ni, and (e) Cu synthesized by heat treatment at 1100°C for 2 h, (f) Ba(Al,Ga)<sub>12</sub>O<sub>19</sub> synthesized by heat treatment at 1200°C for 2 h, and (g) BaNi(Al,Ga)<sub>11</sub>O<sub>19</sub> synthesized by heat treatment at 1200°C for 2 h.

size of BaM(Al,Ga)<sub>11</sub>O<sub>19</sub> except for Fe and Ni, were almost the same as those of Ba(Al,Ga)<sub>12</sub>O<sub>19</sub> powder.

### (2) NO and NO<sub>x</sub> Removal Capability of BaM(Al,Ga)<sub>11</sub>O<sub>19</sub>

The NO and NO<sub>x</sub> removal capabilities of the barium hexaaluminogallate powders were evaluated for three kinds of gas mixtures: (1) direct reduction of NO<sub>x</sub> gas, (2) selective reduction of NO<sub>x</sub> gas with methane (CH<sub>4</sub>), and (3) selective reduction of NO<sub>x</sub> gas with propylene (C<sub>3</sub>H<sub>6</sub>). The differences in catalytic behavior reflect the different nature of transition-metal ions because hexaaluminogallates have almost the same powder characteristics. The NO conversion is the sum of the conversion of NO to N<sub>2</sub> and NO<sub>2</sub> generated by desorption of activated NO<sub>3</sub><sup>\*</sup> without being decomposed to N and O. In other words, the NO conversion includes not only the reduction to N<sub>2</sub> but also the conversion to NO<sub>2</sub>, as shown schematically in Eq. (1). The reduction of NO + NO<sub>2</sub>, corresponding to NO<sub>x</sub>, is the conversion of activated NO<sub>3</sub><sup>\*</sup> to N<sub>2</sub>, as shown in Eq. (2).

NO conversion:



NO<sub>x</sub> reduction:

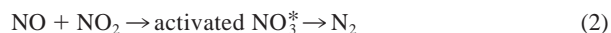
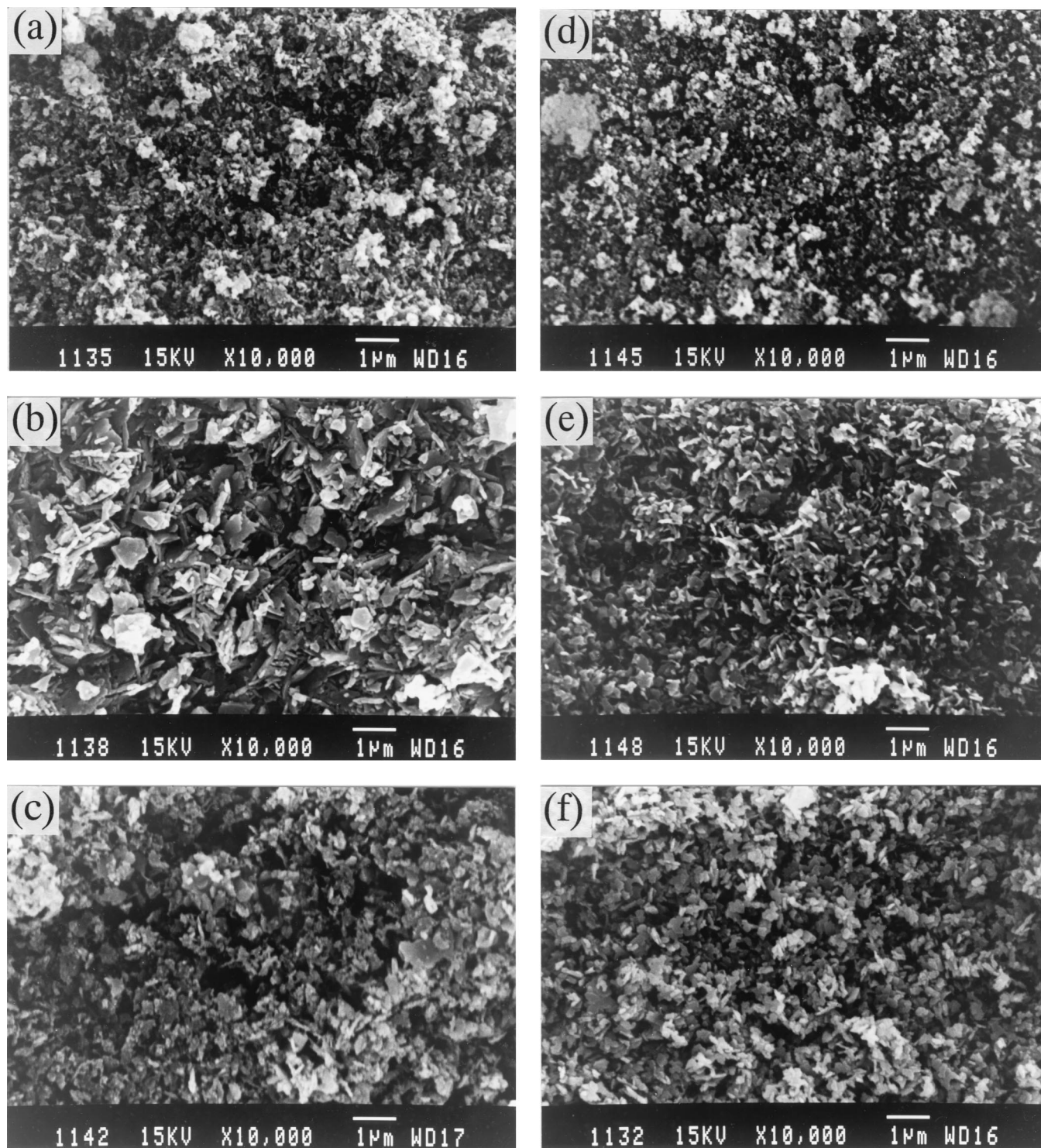


Figure 3 shows the direct NO<sub>x</sub> reduction to N<sub>2</sub> of various BaM(Al,Ga)<sub>11</sub>O<sub>19</sub> without reductant gases. The catalysts had direct NO<sub>x</sub> reduction capabilities of around 10% as the maximum value from 400° to 600°C. The temperature indicating the maximum catalytic activity for Cu- and Mn-substituted hexaaluminogallate was lower by about 100°C than those for other specimens. Figure 4 shows NO conversion to N<sub>2</sub> and NO<sub>2</sub> by hexaaluminogallate powders without reductant gases. The NO conversion behavior except for Cu and Mn ions was almost the same, and the highest values of NO conversion were about 20%. On the other hand, Cu- and Mn-substituted hexaaluminogallate





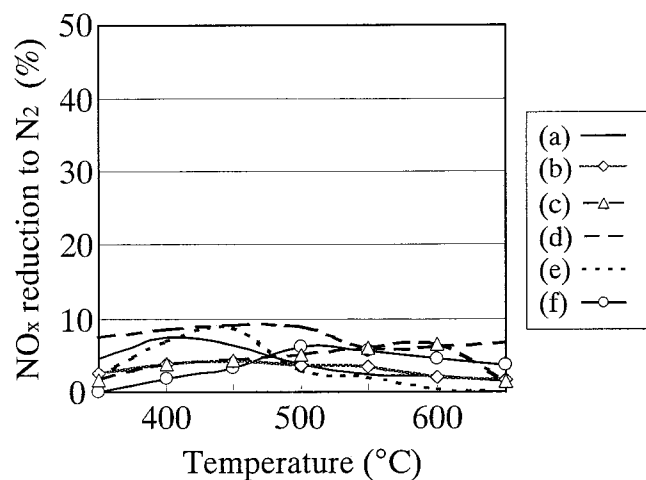
**Fig. 2.** Microstructures of barium hexaaluminogallate powders substituted with (a) Mn, (b) Fe, (c) Co, (d) Ni, and (e) Cu synthesized by heat treatment at 1100°C for 2 h and (f) Ba(Al,Ga)<sub>12</sub>O<sub>19</sub> synthesized by heat treatment at 1200°C for 2 h.

had higher NO conversion capabilities of about 35–40% without reductant gas.

Figure 5 shows the results for the selective NO<sub>x</sub> reduction to N<sub>2</sub> by hexaaluminogallate powders with CH<sub>4</sub> in excess oxygen. All hexaaluminogallate powders showed about 10% NO<sub>x</sub> removal capabilities, similar to the results for the direct NO<sub>x</sub> reduction even if introduced with reductant gas. In comparison with the results shown in Fig. 3, CH<sub>4</sub> did not enhance the NO<sub>x</sub> reduction. The NO conversion to N<sub>2</sub> and NO<sub>2</sub> with CH<sub>4</sub> is shown in Fig. 6. Cu- and Mn-substituted hexaaluminogallate revealed the maximum NO conversions of 23% and 38%, respectively, which were better than

**Table I.** BET Surface Areas of Hexaaluminogallate Powders

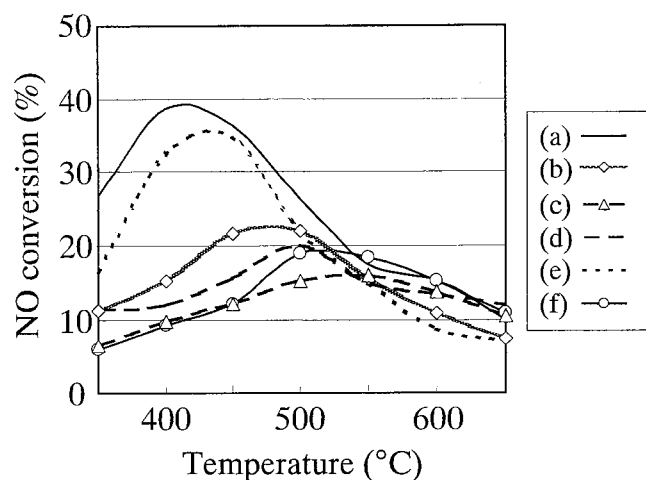
Compositions of hexaaluminogallates	BET surface area (m <sup>2</sup> /g)
Ba(Al,Ga) <sub>12</sub> O <sub>19</sub> (Al/Ga = 9/3)	16.0
BaMn(Al,Ga) <sub>11</sub> O <sub>19</sub> (Al/Ga = 9/3)	20.2
BaFe(Al,Ga) <sub>11</sub> O <sub>19</sub> (Al/Ga = 9/3)	4.2
BaCo(Al,Ga) <sub>11</sub> O <sub>19</sub> (Al/Ga = 9/3)	21.1
BaNi(Al,Ga) <sub>11</sub> O <sub>19</sub> (Al/Ga = 9/3)	43.6
BaCu(Al,Ga) <sub>11</sub> O <sub>19</sub> (Al/Ga = 9/3)	14.2



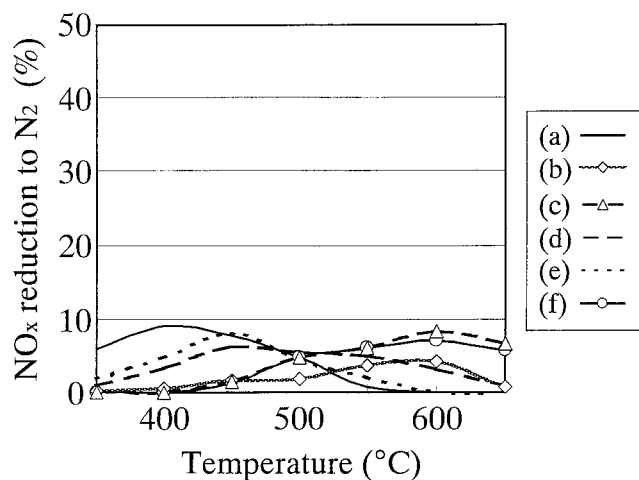
**Fig. 3.** Direct  $\text{NO}_x$  reduction on barium hexaaluminogallate substituted with (a) Mn, (b) Fe, (c) Co, (d) Ni, and (e) Cu and (f)  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$ .

those by other transition metals, such as Fe, Co, and Ni. However, all results for the NO conversions by hexaaluminogallate powders with  $\text{CH}_4$  were lower than those of the direct NO conversion shown in Fig. 4. The maximum NO conversion of 23% with  $\text{CH}_4$  for  $\text{BaCu}(\text{Al,Ga})_{11}\text{O}_{19}$  is still lower than that by direct conversion of 35% (Fig. 4).

Figure 7 shows  $\text{NO}_x$  reduction to  $\text{N}_2$  with  $\text{C}_3\text{H}_6$  for various hexaaluminogallate powders. The  $\text{NO}_x$  removal capabilities except for Fe- and Mn-substituted hexaaluminogallates were improved markedly compared with  $\text{CH}_4$  as reductant gas, and their highest values were over 40% at temperatures from 400° to 500°C.  $\text{NO}_x$  reduction by  $\text{BaFe}(\text{Al,Ga})_{11}\text{O}_{19}$  with  $\text{C}_3\text{H}_6$  was about 11%, which has improved slightly compared with that with  $\text{CH}_4$  (Fig. 5(b)). However,  $\text{NO}_x$  reduction by  $\text{BaMn}(\text{Al,Ga})_{11}\text{O}_{19}$  with  $\text{C}_3\text{H}_6$  was below 5%, which is lower than that of the highest value obtained using  $\text{CH}_4$  (Fig. 5). These results also suggest that  $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$  can act as a gas-sensing catalyst, which recognizes species of  $\text{CH}_4$  or  $\text{C}_3\text{H}_6$ . The NO conversion–temperature curves for Co-, Ni-, and Cu-substituted hexaaluminogallate shown in Figs. 4 and 6 do not correspond to the  $\text{NO}_x$  reduction–temperature curves shown in Figs. 3 and 5, respectively. However, the curves for Co-, Ni-, and Cu-substituted hexaaluminogallate shown in Fig. 8 are almost consistent with those shown in Fig. 7. Parent  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$  had 30% NO and  $\text{NO}_x$  removal capabilities at 550°C, as shown in Figs. 7 and 8.



**Fig. 4.** Direct NO conversion on barium hexaaluminogallate substituted with (a) Mn, (b) Fe, (c) Co, (d) Ni, and (e) Cu and (f)  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$ .



**Fig. 5.** Selective  $\text{NO}_x$  reduction with  $\text{CH}_4$  on barium hexaaluminogallate substituted with (a) Mn, (b) Fe, (c) Co, (d) Ni, and (e) Cu and (f)  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$ .

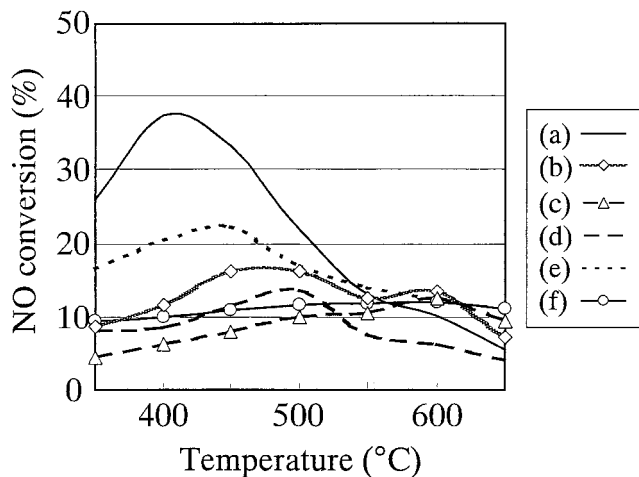
#### IV. Discussion

##### (1) Synthesis and Particle Size of $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$ Powders by the Coprecipitation Method

The hexaaluminogallate crystals could be successfully synthesized at a lower temperature of 1100°C than the solid-state reaction (1300°C).<sup>12</sup> This is because  $\text{Ba}^{2+}$  ions, one of the key cations of the nucleation of hexaaluminogallate phases,<sup>13</sup> were dispersed homogeneously in the precursor powders, resulting in a lowering of the crystallization temperature of hexaaluminogallate phases.

Transition metals are considered to stabilize the spinel blocks in the  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$  structure, as reported for  $\text{BaAl}_{12}\text{O}_{19}$ .<sup>14</sup> The charge compensation in the substitution of  $\text{Al}^{3+}$  for  $\text{M}^{2+}$  accelerates the incorporation of  $\text{Ba}^{2+}$  and  $\text{O}^{2-}$  into the mirror plane, which results in promoting the formation of  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$  crystals. Also, the defective spinel structure of  $\gamma\text{-Al}_2\text{O}_3$  is known to be stabilized by  $\text{M}^{2+}$  ions with a decrease in the number of vacancies. The formation of  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$  phases is considered to proceed in a similar way, where  $\text{M}^{2+}$  ions stabilize the spinel blocks of  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$  via a decrease in the number of vacancies in the unit cell.

Transition-metal-substituted  $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$  powders were submicrometer in size, and mixtures of isotropic and platelet particles, while  $\text{BaFe}(\text{Al,Ga})_{11}\text{O}_{19}$  powders consisted only of a



**Fig. 6.** Selective NO conversion with  $\text{CH}_4$  on barium hexaaluminogallate substituted with (a) Mn, (b) Fe, (c) Co, (d) Ni, and (e) Cu and (f)  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$ .



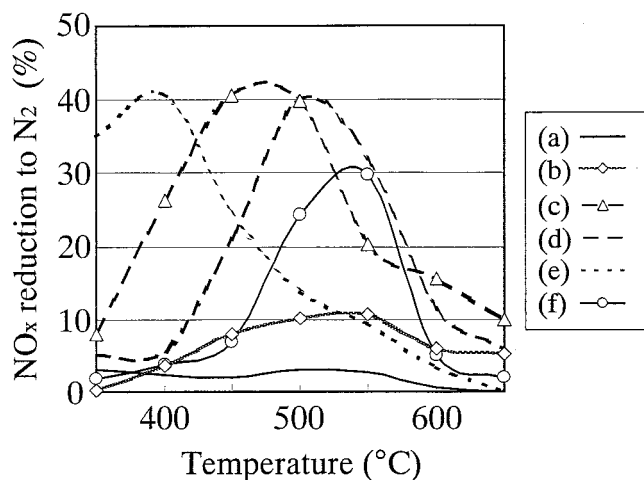


Fig. 7. Selective  $\text{NO}_x$  reduction with  $\text{C}_3\text{H}_6$  on barium hexaaluminogallate substituted with (a) Mn, (b) Fe, (c) Co, (d) Ni, and (e) Cu and (f)  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$ .

platelike morphology of about  $1\ \mu\text{m}$  in size. MP-type  $\text{BaFe}_{12}\text{O}_{19}$  has almost the same crystal structure as those of  $\beta$ -alumina-type  $\text{BaAl}_{12}\text{O}_{19}$  and  $\text{BaGa}_{12}\text{O}_{19}$  except for their mirror plane.<sup>15</sup> Since  $\text{BaFe}_{12}\text{O}_{19}$  is considered to form solid solutions easily with  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$ , and the melting point of  $\text{BaFe}_{12}\text{O}_{19}$  phase is low ( $1565^\circ\text{C}$ ),  $\text{BaFe}(\text{Al,Ga})_{11}\text{O}_{19}$  particles have a tendency to grow larger under the same reaction conditions. In contrast, other transition metals play a role in accelerating the nucleation of hexaaluminogallate crystals by stabilizing the spinel block in the structure, resulting in the formation of fine particles with sizes under  $0.5\ \mu\text{m}$ .

## (2) Catalytic $\text{NO}_x$ Reduction over $\text{BaM}(\text{Al,Ga})_{11}\text{O}_{19}$ Powders

It is reported that NO is oxidized (converted) first to  $\text{NO}_3^*$  on the active sites, then converted to N and O adsorbed on the active sites.<sup>16–19</sup> The N ions react to form  $\text{N}_2$  molecules on the active sites, which desorb from the active sites easily. On the other hand, the bond between O ions and active sites is especially strong. Therefore, the  $\text{NO}_x$  removal capability of the catalyst with a large storage capacity for oxygen tends to decrease with time, because of a decrease in the number of active sites on the catalyst surface. However, part of the activated  $\text{NO}_3^*$  is not decomposed to N and O, but converted to  $\text{NO}_2$  or  $\text{N}_2\text{O}$ .  $\text{N}_2\text{O}$  formation from NO is not

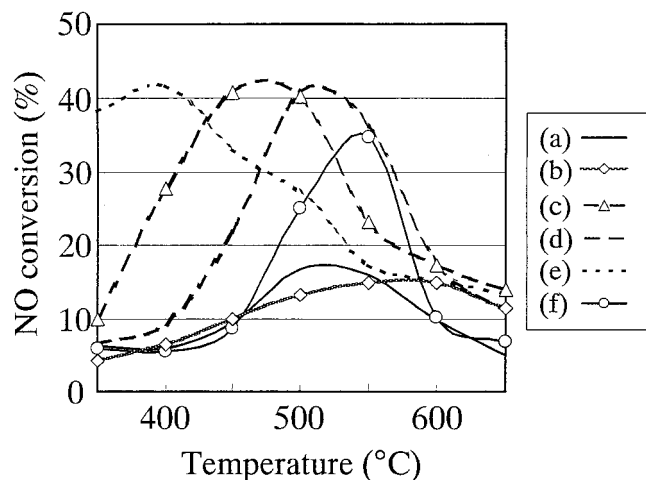


Fig. 8. Selective NO conversion with  $\text{C}_3\text{H}_6$  on barium hexaaluminogallate substituted with (a) Mn, (b) Fe, (c) Co, (d) Ni, and (e) Cu and (f)  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$ .

detected at all in this study; therefore, NO conversion corresponds to the total conversion to  $\text{N}_2$  and  $\text{NO}_2$ , as shown in Eq. (1). The reaction of  $\text{NO}_x^*$ , that is,  $\text{NO} + \text{NO}_2$ , reduction gives  $\text{N}_2$  through activated  $\text{NO}_3^*$ , as shown in Eq. (2). It turns out that catalytic  $\text{NO}_x$  removal depends mainly on the adsorption and activation capabilities of the reactive gases and the desorption capability of oxygen from the active sites.

From the results on the catalytic activities of hexaaluminogallates, there were large differences in removal capabilities between NO and  $\text{NO}_x$  in the case of direct  $\text{NO}_x$  reduction and SCR with  $\text{CH}_4$ . On the other hand, both NO and  $\text{NO}_x$  decompositions for the SCR with  $\text{C}_3\text{H}_6$  had similar tendencies in the decomposition-temperature curves. Also, the catalytic activities of hexaaluminogallate were improved enormously by the addition of  $\text{C}_3\text{H}_6$  as a reductant gas at temperatures from  $350^\circ$  to  $550^\circ\text{C}$ . Transition-metal ions incorporated into Al or Ga sites of hexaaluminogallate distinctly improve NO and  $\text{NO}_x$  removal capabilities with and without reductant gases.

The behaviors of the direct NO conversion (Fig. 4) and the NO conversion with  $\text{CH}_4$  (Fig. 6) in excess oxygen are divided into two groups, Mn-, Cu-substituted hexaaluminogallates and others. Mn and Cu ions have higher interaction and activation capabilities with NO and  $\text{O}_2$ , resulting in the enhancement of NO conversion to  $\text{N}_2$  and  $\text{NO}_2$  over 35% and lowering the temperature of the maximum catalytic activity, as shown in Figs. 4(a,e) and 6(a,e). The large interaction is attributed to the easy valence change capability between M(II) and M(III) for Cu and Mn. Especially the large interaction between  $\text{CH}_4$  and Cu ions suppresses the NO conversion to 23% as in Fig. 6(e). On the other hand, the NO conversion behaviors of Fe-, Co-, and Ni-substituted hexaaluminogallate had tendencies similar to that of  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$  with and without  $\text{CH}_4$ . The effects of Fe, Co, and Ni on NO conversion to  $\text{N}_2$  and  $\text{NO}_2$  were scarcely observed. Also, despite the addition of  $\text{CH}_4$ ,  $\text{NO}_x$  removal capabilities of all hexaaluminogallates were up to 10%, which was similar to the results on direct  $\text{NO}_x$  reduction to  $\text{N}_2$ .

The activation (oxidation) rate of NO into  $\text{NO}_3^*$ , which is the first step of  $\text{NO}_x$  reduction, was presumed to be accelerated on the transition-metal sites.<sup>18</sup> Since NO is activated and converted into  $\text{NO}_3^*$  on the active sites, especially on Cu and Mn sites, therefore the low  $\text{NO}_x$  reduction activities are due to the low decomposition rate of activated  $\text{NO}_3^*$  adsorbed on the active sites, which is the second step of  $\text{NO}_x$  reduction, and the desorption rate of adsorbed oxygen on the active sites, which is the third step of  $\text{NO}_x$  reduction, leading to the rate-determining process on hexaaluminogallate catalysts. The combustion temperature of  $\text{CH}_4$  was reported to be over  $600^\circ\text{C}$  on barium hexaaluminate.<sup>10</sup> Similarly, barium hexaaluminogallate compounds are considered to combust  $\text{CH}_4$  over  $600^\circ\text{C}$ .  $\text{CH}_4$  was inactive with oxygen in the reacting gas mixture or with that produced by decomposition of activated  $\text{NO}_3^*$  below  $550^\circ\text{C}$ .  $\text{CH}_4$ , therefore, did not act for the  $\text{NO}_x$  reductive reaction to  $\text{N}_2$ , even if barium hexaaluminogallate compounds had the potential to reduce  $\text{NO}_x$  gas.

$\text{C}_3\text{H}_6$  has a  $\text{C}=\text{C}$  double bond in the molecular structure, and  $\pi$  electrons in the double bond tend to interact with the  $d$ -orbitals of a transition metal more efficiently than  $\text{CH}_4$  with  $\sigma$  bonds alone in its structure. Therefore,  $\text{C}_3\text{H}_6$  is expected to be combusted and remove the oxygen adsorbed on the catalytic active sites of hexaaluminogallate surfaces at lower temperatures, which results in enhancement of NO and  $\text{NO}_x$  removal activities of hexaaluminogallate catalysts by accelerating the rate-determining step of  $\text{NO}_3^*$  decomposition. As shown in Figs. 7 and 8, there was little difference in the removal behaviors between NO and  $\text{NO}_x$ , which is attributable to the fact that most  $\text{NO}_3^*$  generated from the activation of NO reacted with  $\text{C}_3\text{H}_6$  in the reactive gas mixtures at the active sites, and then these  $\text{NO}_x$  molecules adsorbed on the active sites were decomposed into  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{CO}_2$ . Co, Ni, and Cu ions activated the NO and  $\text{NO}_x$  removal reactions with  $\text{C}_3\text{H}_6$ , compared with  $\text{Ba}(\text{Al,Ga})_{12}\text{O}_{19}$ . The lowest surface area of  $\text{BaFe}(\text{Al,Ga})_{11}\text{O}_{19}$  resulted in a low value of 10%  $\text{NO}_x$  reduction, as shown in Fig. 7(b). On the other hand,  $\text{BaMn}(\text{Al,Ga})_{11}\text{O}_{19}$  had a  $\text{NO}_x$  removal capability below 5%, as in Fig. 7(a).

BaMn(Al,Ga)<sub>11</sub>O<sub>19</sub> converted 40% of NO into NO<sub>3</sub><sup>\*</sup> without reductant gases (Fig. 4(a)). This fact reveals that BaMn(Al,Ga)<sub>11</sub>O<sub>19</sub> has a potential to catalyze the reduction of NO<sub>x</sub>. However, the large interaction between Mn and C<sub>3</sub>H<sub>6</sub> might result in the stabilization of C<sub>3</sub>H<sub>6</sub> on Mn, leading to a depression of NO<sub>x</sub> reduction to N<sub>2</sub> of less than 5%. The temperature of maximum NO<sub>x</sub> reduction of nonsubstituted Ba(Al<sub>9</sub>Ga<sub>3</sub>)O<sub>19</sub> was 550°C and depended on the kind of transition metal (Fig. 7). Co-, Ni-, and Cu-substituted BaM(Al,Ga)<sub>11</sub>O<sub>19</sub> showed a maximum at lower temperatures from 350° to 500°C. These results indicate that the working temperature of catalysts can be controlled by selection of the transition metal, M, in BaM(Al,Ga)<sub>11</sub>O<sub>19</sub>.

## V. Conclusions

Transition-metal-substituted barium hexaaluminogallates were found to be an important catalyst for NO<sub>x</sub> reduction to N<sub>2</sub>, which could successfully be synthesized at 1100°C from precursor powders prepared by the coprecipitation method. The hexaaluminogallate powders were mixtures of isotropic and anisotropic particles with submicrometer sizes. The direct NO<sub>x</sub> reduction was around 10% for all BaM(Al,Ga)<sub>11</sub>O<sub>19</sub> powders, although the NO conversions by Mn- and Cu-substituted BaM(Al,Ga)<sub>11</sub>O<sub>19</sub> were 35%–40% at a higher space velocity of 10 000 h<sup>-1</sup>. The selective NO<sub>x</sub> reduction by CH<sub>4</sub> exhibited tendencies similar to those as in the direct reduction without CH<sub>4</sub>. Co-, Ni-, and Cu-substituted BaM(Al,Ga)<sub>11</sub>O<sub>19</sub> showed the capability of reducing NO<sub>x</sub> by about 40% with C<sub>3</sub>H<sub>6</sub> from 380° to 520°C in excess oxygen gas. C<sub>3</sub>H<sub>6</sub> accelerated not only NO conversion but also NO<sub>x</sub> reduction over Co-, Ni-, and Cu-substituted BaM(Al,Ga)<sub>11</sub>O<sub>19</sub> powders. The temperature of the maximum activity was found to be controlled by the selection of the transition metal and reductant.

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