Synthesis of hexaaluminogallate catalysts for NO_x reduction

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$BaCo(Al,Ga)_{11}O_{19}$ with β-alumina structure was found to be an effective catalyst for NO_x reduction and successfully synthesized by the coprecipitation method using metal nitrates and ammonium carbonate. Anisotropic $BaCo(Al,Ga)_{11}O_{19}$ particles crystallized at 1100 °C for 2 h through the coprecipitation method. $BaCo(Al,Ga)_{11}O_{19}$ supported on a cordierite honeycomb had the NO_x removal activity with methane over 500 °C in the presence of excess oxygen.

KEY WORDS: NO_x reduction; coprecipitation; hexaaluminogallate and cobalt addition.

1. Introduction

One of the most effective approaches for the improvement of the energy efficiency is the combustion system operated at higher temperatures and under lean conditions. However, nitrogen oxides (NO_x), which damage the environments by causing air pollution, are produced in such systems. Hydrocarbon-selective catalytic reduction over Cu-exchanged zeolite was developed to reduce NO_x in the presence of excess oxygen [1,2]. The activity of these catalysts, however, decreases at high temperatures [3] or in the presence of water vapor [2,4] On the other hand, alumina-based catalysts were found to have higher thermal stability but lower NO_x removal activity than zeolite catalysts [5]. Various metal ions supported on alumina are reported to improve the activity at lower temperatures, Co-supported Al_2O_3 catalysts have especially been studied extensively because of the high removal activity of NO_x in the presence of excess oxygen.Barium hexaaluminogallate ($Ba(Al,Ga)_{12}O_{19}$) and barium hexaaluminate ($BaAl_{12}O_{19}$) have β-alumina structure with hexagonal symmetry of space group P6$_3$/mmc. They have the characteristic layered structure consisting of alternative stacking of closed packed spinel blocks and mirror planes containing large cations, such as Ba or La, along the *c* axis. The packing density of the mirror plane is only a quarter that of spinel block, therefore, oxide ions diffuse preferentially in the mirror plane [6,7]. This anisotropic O^{2-} diffusion in the mirror plane leads to the inhibition of grain growth along the *c*-axis and the excellent thermal stability. Hexaaluminogallate compounds show high melting point and can be doped with various transition metals for aluminum (or gallium) sites in their structures, and have a tendency to grow as characteristic plate-like particles [8–10]. Therefore, this compound is expected to be one of the promising high temperature catalysts.

In this study, the chemical processing of Co-substituted barium hexaaluminogallate was investigated. Anisotropic $BaCo(Al,Ga)_{11}O_{19}$ particles were synthesized from aqueous solutions of metal nitrates by coprecipitation method. The selective reduction of NO_x by methane in the presence of excess oxygen was also evaluated for $BaCo(Al,Ga)_{11}O_{19}$ supported on a cordierite honeycomb.

2. Experimental procedure

2.1. *Synthesis of hexaaluminogallate compounds*

Solid state reaction method, which was based on the conventional mixing of oxide and carbonate, was investigated for the decision of the composition of hexaaluminogallate. Starting powders used for the solid state reaction were as follows:$BaCO_3$ (Ko-Jundo Chemical Co.), CoO (Ko-Jundo Chemical Co.), α-Al_2O_3 (Sumitomo Chemical Industries Co., AKP-30), Ga_2O_3 (Ko-Jundo Chemical Co.)

Hexaaluminogallate powders were synthesized via the precursor powders prepared by the coprecipitation method [11]. $Ba(NO_3)_2$ (Kishida Chemical Co.), $Al(NO_3)_3 \cdot 9H_2O$ (Kishida Chemical Co.), $Ga(NO_3)_3 \cdot 6H_2O$ (Ko-Jundo Chemical Co.) and $Co(NO_3)_2 \cdot 6H_2O$ (Kishida Chemical Co.) were used as metal sources for the hexaaluminogallate. Appropriate amounts of starting nitrates were dissolved in distilled water to prepare 0.02 mol/L aqueous solution with $BaCo(Al,Ga)_{11}O_{19}$ (Al/Ga = 9/3) compositions. In order to coprecipitate metal ions, an aqueous $(NH_4)_2CO_3$ solution (2.0 mol/L) was utilized for yielding the suspension dispersed with hexaaluminogallate precursor powders. The precipitates were collected from the suspension using ultrafiltration and then washed with ethanol. A membrane filter

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(Advantec, Ultrafilter UK-50) to pass the species with a molecular weight below 50,000 was used for ultrafiltration. Co-substituted hexaaluminogallate precursor powders were heat-treated at 1100 °C for 2 h in air.

2.2. Preparation of barium hexaaluminogallate catalyst

Cordierite honeycomb was used as a support material for $BaCo(Al,Ga)_{11}O_{19}$ layer in order to evaluate the activity of nitrogen oxides removal. The size of cordierite honeycomb support (mesh 25) was 32 mm in diameter and 10 mm in length. The cordierite honeycomb was dipped into the suspension dispersed with hexaaluminogallate precursor powder as shown in the section (2.1). After drying, the honeycomb coated with catalyst was heat-treated at 1100 °C for 6 h in air. To show the effectiveness of the coprecipitation method, the honeycomb catalyst was also coated with the polyethylene glycol (PEG, Kishida Chemical Co.) suspension dispersed with the $BaCo(Al,Ga)_{11}O_{19}$ (Al/Ga = 9/3) powders produced by the solid state reaction. In addition, the cordierite honeycomb coated with $Ba(Al,Ga)_{12}O_{19}$(Al/Ga = 9/3) was synthesized by the same coprecipitation method as mentioned above.

2.3. 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 and honeycomb catalysts were examined by a scanning electron microscope (SEM; JEOL, JSM-6100) with an energy dispersive X-ray (EDX) analyzer (JEOL, JED-2001). The compositions of the hexaaluminogallate powders were investigated by ICP-AES (Jarrell Ash, Plasma AtomComp MK II). Catalytic properties of the honeycomb catalysts were measured for the selective catalytic reduction of NO by methane. The composition of mixture gas used for the catalytic measurement was 10% O_2, 250 ppm NO, 500 ppm CH_4 in N_2 balance gas at a space velocity (S.V.) of 3500 h^{-1}. The NO_x concentration was analyzed by gas chromatography and NO_x analyzer (PG-250, HORIBA).

3. Results and discussion

3.1. Determination of the composition of hexaaluminogallate

Cobalt is one of the effective ions for NO_x reduction in alumina-based catalysts [5], therefore, the incorporation of Co to $Ba(Al,Ga)_{12}O_{19}$ was attempted. The synthesis of $BaCoAl_{11}O_{19}$ single phase is quite difficult because of the larger ionic radius of Co^{2+} (0.8 Å) than that of Al^{3+} (0.5 Å). However, the substitution of Ga^{3+} (ionic radius: 0.6 Å) for the Al^{3+} sites in the hexaaluminate framework is expected to modify the lattice parameters, resulting in facilitating Co-substitution of Co ions for Al or Ga ions in the lattice framework [12–15].

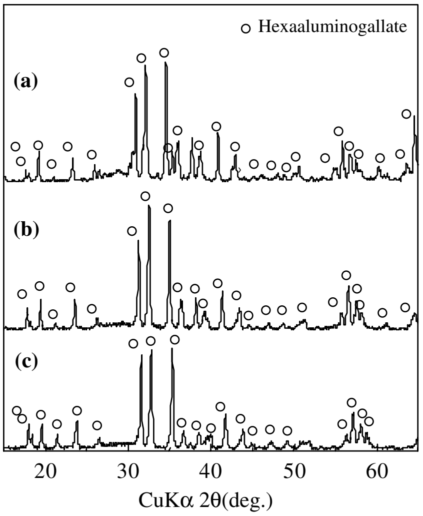

Figure 1. XRD profiles of $Ba(Al,Ga)_{12}O_{19}$ powders heat-treated at 1400 °C for 6 h at various Al/Ga ratios: Al/Ga = (a) 3/9, (b) 6/6, (c) 9/3.

As a preliminary experiment, $Ba(Al,Ga)_{12}O_{19}$ was prepared from a powder mixture of $BaCO_3, \alpha\text{-}Al_2O_3$ and Ga_2O_3. Figure 1 shows the XRD profiles of $Ba(Al,Ga)_{12}O_{19}$ powders with various Al/Ga ratios after heat treatment at 1400 °C for 6 h. Each powder crystallized in β-alumina single phase. With increasing the amount of Ga ion with a larger ionic radius than Al ion, all diffractions shifted to lower diffraction angle, resulting in the increase of the hexaaluminogallate lattice parameters. Below 1300 °C, the powders crystallized in β-alumina as a main phase with a small amount of spinel phase. The $Ba(Al,Ga)_{12}O_{19}$ powders had high crystallinity and consisted of the most small particles at

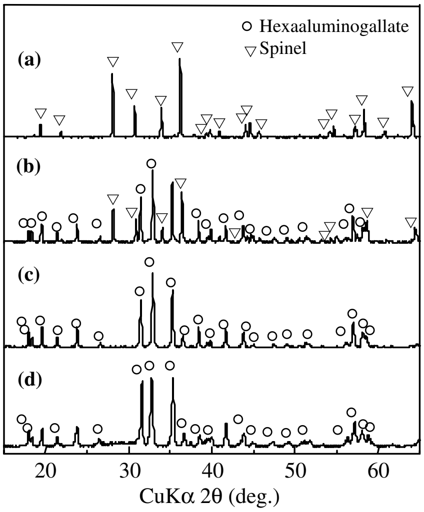

Figure 2. XRD profiles of $BaCo_x(Al, Ga)_{12-x}O_{19}$ powders heat-treated at 1400 °C for 6 h: Co/(Al + Ga) = (a) 4/8, (b) 2/10, (c) 1/11, (d) 0/12.

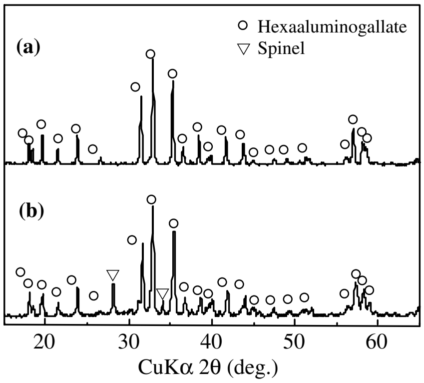

Figure 3. Effect of Co addition on crystallization of powders heat-treated at 1200°C for 6 h: (a) $BaCo(Al,Ga)_{11}O_{19}$, (b) $Ba(Al,Ga)_{12}O_{19}$.

the Al/Ga = 9/3 ratio, therefore, the investigation for hexaaluminogallate with Al/Ga = 9/3 ratio had been advanced.

Figure 2 shows the XRD profiles of $BaCo_x(Al,Ga)_{12-x}O_{19}$ (Al/Ga = 9/3) powders heat-treated at 1400 °C for 6 h with various Co contents. The powders with $Ba(Al,Ga)_{12}O_{19}$ and $BaCo(Al,Ga)_{11}O_{19}$ composition crystallized in β-alumina single phase as shown in figures 2(c) and (d). With the increase of the Co substitution, spinel phase turned to be a main phase (figures 2(a) and (b)). From this results, the solubility limit of Co into $Ba(Al,Ga)_{12}O_{19}$ was found to be Co/(Al+Ga) = 1/11.

Figure 3 shows the effect of Co addition on the crystallization temperature of hexaaluminogallate single phase. At 1200 °C, the powders crystallized in $Ba(Al,Ga)_{12}O_{19}$ of β-alumina phase with a small amount of the spinel phase (figures 3(b)). On the other hand, single-phase $BaCo(Al,Ga)_{11}O_{19}$ was formed at 1200 °C as shown in figure 3(a). This result reveals that the cosubstitution decreases the crystallization temperature of the barium hexaaluminogallate by 200 °C.

The effect of Co-substitution is attributed to the stabilization of the spinel blocks in the $Ba(Al,Ga)_{12}O_{19}$ structure as reported for $BaAl_{12}O_{19}$ [16]. This is because that Co^{2+} ions stabilize the spinel blocks of $Ba(Al,Ga)_{12}O_{19}$ by decreasing the amount of vacancies in the unit cell, resulting in the stabilization of spinel structure of alumina up to higher temperature. In addition, the charge compensation for the substitution of Al^{3+} for Co^{2+} accelerates the incorporation of Ba^{2+} and O^{2-} into the mirror plane, which results in promoting the formation of $Ba(Al,Ga)_{12}O_{19}$ crystals.

3.2. Synthesis of hexaaluminogallate compounds by coprecipitation method

The catalytic activity mainly depends on the composition, the surface area and the crystallinity of the powders. Therefore, $BaCo(Al,Ga)_{11}O_{19}$ was selected as the composition of hexaaluminogallate, because of its lower crystallization temperature associated with the high activity of powder surface. In addition, the coprecipitation method, one of the chemical processings to synthesize the fine powders with high reactivity, was investigated in order to synthesize Co-substituted barium hexaaluminogallate at lower temperatures with high catalytic activity.

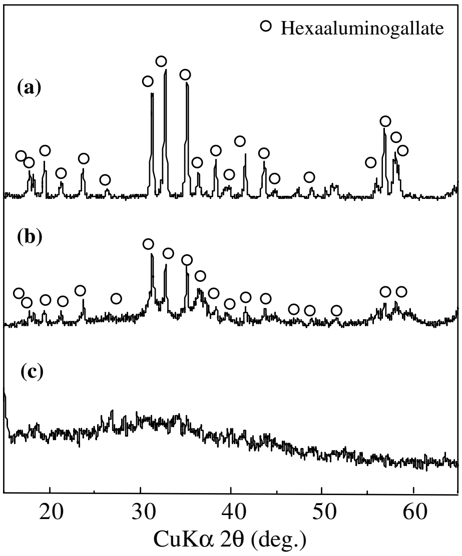

Figure 4. Crystallization behavior of coprecipitated powders with a composition of $BaCo(Al,Ga)_{11}O_{19}$: (a) 1100 °C, 15 min (b) 1050 °C, 15 min, (c) as-precipitated.

Figure 4 shows the crystallization behavior of the as-prepared $BaCo(Al,Ga)_{11}O_{19}$ precursor powder. The as-prepared powder was amorphous state as in figure 4(c), and directly crystallized to $BaCo(Al,Ga)_{11}O_{19}$ at 1050 °C as shown in figure 4(b). The coprecipitated powder was found to crystallize into single-phase of $BaCo(Al,Ga)_{11}O_{19}$ at 1100 °C.

The ICP-AES analysis revealed that the composition of hexaaluminogallate powders synthesized by the coprecipitation method with metal nitrates and ammonium carbonate (Ba/Co/Al/Ga = 1.0/0.9/2.8/8.3) was in agreement with the theoretical one for $BaCo(Al,Ga)_{11}O_{19}$ (Al/Ga = 9/3, Ba/Co/Al/Ga = 1.0/1.0/2.75/8.25). The precursor powders prepared by using the combinations of metal sources such as chlorides and hydroxides, and bases such as ammonia and ammonium oxalate, did not crystallize in β-alumina phase, because some of these sources were stabilized as ionic complexes in the suspension and the compositions of the prepared precursor powders differed from the desired compositions. Only the combination of metal nitrates and ammonium carbonate gave the precursor powders with the theoretical Ba/Co/Al/Ga ratio.

From the SEM observation, the coprecipitated powder had the anisotropic shape at 1100 °C for 2 h. The particles were 0.4 μm in length and 0.1 μm in width (aspect ratio 4). The homogeneous composition in the coprecipitation powder enabled the direct crystallization of β-alumina phase at lower temperature than the solid state reaction. In addition, cobalt-free $Ba(Al,Ga)_{12}O_{19}$($Al/Ga = 9/3$) crystallites were also successfully synthesized at 1200 °C for 2 h from the precursor powder via the same coprecipitation method as stated above.

3.3. Preparation of cordierite honeycomb catalyst coated with hexaaluminogallate powders

The NO_x removal ability of $BaCo(Al,Ga)_{11}O_{19}$ was evaluated by using cordierite honeycomb coated with $BaCo(Al,Ga)_{11}O_{19}$ catalyst. Figure 5 illustrates the relationship between the viscosity and the concentration of the suspension dispersed with the hexaaluminogallate precursor powders prepared from metal nitrates and ammonium carbonate. The suspension with the concentration over 0.03 mol/L had too high viscosity to penetrate to the channel of the cordierite honeycomb, resulting in the heterogeneous coating of the cordierite surface and many residual cracks in the coating layer. Below 0.01 mol/L, the thickness of the coating layer was very thin, and parts of the cordierite surface were exposed. On the other hand, at 0.02 mol/L, the surface of cordierite honeycomb was completely coated with the catalyst layer consisted of the anisotropic particles, whose size was comparable with that of $BaCo(Al,Ga)_{11}O_{19}$ particles described above. The thickness of the catalyst layer was about 10 μ m by SEM observation. From the analysis by EDX, the composition of the coating layer was found to be almost the same Ba/Co/Ga/Al ratio as that of the designed $BaCo(Al,Ga)_{11}O_{19}$ phase.

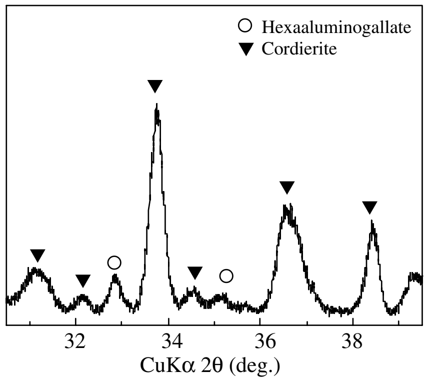

Figure 6. XRD profile of coating layer on cordierite honeycomb.

Figure 6 shows the XRD profile of the $BaCo(Al,Ga)_{11}O_{19}$ catalyst layer on the cordierite honeycomb prepared by heat treatment at 1100 °C for 6 h. The diffractions at $2\theta = 33°$ and 38° were assigned to the two strongest ones of $BaCo(Al,Ga)_{11}O_{19}$. From the results of SEM, EDX and XRD, it was concluded that the cordierite honeycomb coated with $BaCo(Al,Ga)_{11}O_{19}$ catalyst layer was successfully synthesized by optimizing the coprecipitation, coating and heating conditions.

3.4. Evaluation of NO_x removal ability

The catalytic activity of $BaCo(Al,Ga)_{11}O_{19}$ supported on the cordierite honeycomb at the path length of 10mm was evaluated for the selective reduction of nitrogen oxides (NO_x) at the space velocity of 3500 h^{-1}. The NO_x conversion through the $BaCo(Al,Ga)_{11}O_{19}$-coated honeycomb is shown in figure 7. Figure 7 also describes the NO_x reduction of the honeycomb catalyst coated with the $BaCo(Al,Ga)_{11}O_{19}$ produced by the solid state reaction. This sample was synthesized by the heat-treatment at 1100 °C for 6 h of the honeycomb dipped into the PEG suspension dispersed with the $BaCo(Al,Ga)_{11}O_{19}$ powders prepared via the solid state reaction at 1100 °C for 6 h. The NO_x conversion of the catalysts via coprecipitation and solid state reaction methods increases with increasing from 500 °C to 550 °C, and showed a maximum value of 12% and

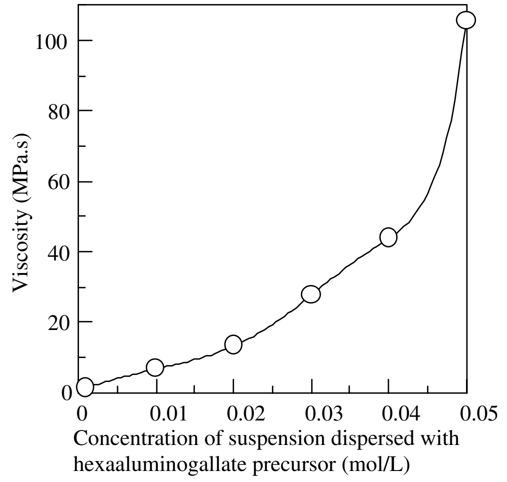

Figure 5. Viscosity of the suspensions dispersed with hexaaluminogallate precursor at various concentration.

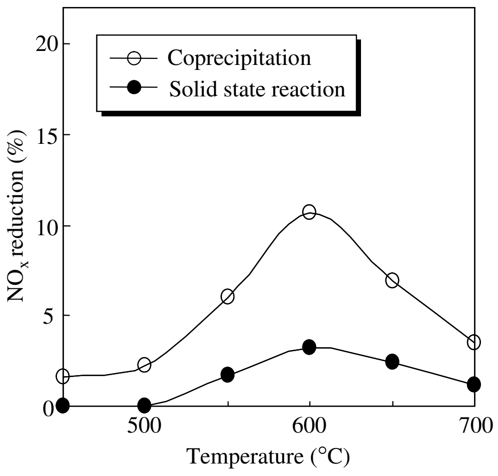

Figure 7. Selective catalytic reduction of NO_x by CH_4 with $BaCo(Al,Ga)_{11}O_{19}$ supported on a cordierite honeycomb.

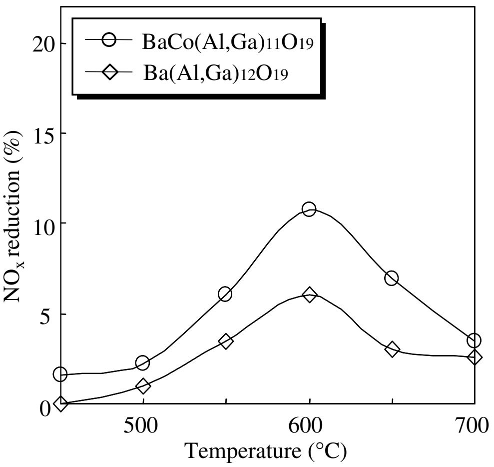

Figure 8. Selective catalytic reduction of NO_x by CH_4 with $BaCo(Al,Ga)_{11}O_{19}$ supported on a cordierite honeycomb.

3%, respectively, at 600 °C. The difference of NO_x removal activities between two honeycombs was mainly depended on their surface areas of $BaCo(Al,Ga)_{11}O_{19}$ crystallites for catalyst layers. The BET surface areas of the $BaCo(Al,Ga)_{11}O_{19}$ powders via coprecipitation and solid state reaction methods were 21.1 and 4.1 m^2/g, respectively, resulting in the higher catalytic activity of the coprecipitation sample rather than the solid state reaction sample.

NO_x reduction by methane with $BaCo(Al,Ga)_{11}O_{19}$ and $Ba(Al,Ga)_{12}O_{19}$ (BET surface area 16.0 m^2/g) supported on a cordierite honeycomb was shown in Figure 8. The catalyst suspensions were prepared by coprecipitation method according to the section (2.2). The $Ba(Al,Ga)_{12}O_{19}$ sample also shows a maximum value of NO_x reduction about 3.5% at 600 °C, while the cobalt-added sample could reduce about 12% of NO_x in the presence of excess oxygen. Substitution with cobalt is effective for the enhancement of NO_x reduction, because of the easy valence change capability of cobalt.

4. Conclusions

Hexaaluminogallate powders with the composition of $BaCo(Al,Ga)_{11}O_{19}$ were synthesized by the coprecipitate method. The crystallization temperature of barium hexaaluminogallate could be lowered by the addition of cobalt with a ratio of $Co/(Al+Ga) = 1/11$. The coprecipitation method was superior to the solid state reaction method to obtain highly active catalyst with a high surface area by the direct formation of plate-like $BaCo(Al,Ga)_{11}O_{19}$ catalyst. The $BaCo(Al,Ga)_{11}O_{19}$ catalyst via the coprecipitation method was found to be effective in reducing NO_x by methane in the excess oxygen above 500 °C.

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