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Synthesis and catalytic properties of the electrochemical NO_x reduction system

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Catalytic and electrical properties of an electrochemical NO_x reduction system were investigated. This system had a laminated structure composed of $BaCo(Al,Ga)_{11}O_{19}$-based catalyst layer on a Pt/YSZ/Pt sheet. The stacked catalyst system can directly reduce more than 65% of NO_x to N_2 under an external bias above 2.5 V at 650 °C. In this system, oxygen existing around the catalyst layer was removed by O^{2-} transportation through the YSZ layer.

KEY WORDS: electrochemical NO_x reduction; hexaaluminate catalyst; excess oxygen condition.

1. Introduction

Nitrogen oxide (NO_x) produced by high-temperature combustion is an important environmental issue, since it is a cause of acid rain, the greenhouse effect, and air pollution. Direct NO_x decomposition is the simplest and yet the most challenging removal process. However, to date, there is no effective powder catalyst that can directly decompose NO_x into N_2 and O_2 in the presence of oxygen without undesirable reactions. That is because this process is easily inhibited by the adsorption of released oxygen generated by the reduction of the NO_x [1,2]. The selective catalytic reduction of NO_x with reductant gases, such as hydrocarbons and urea, has attracted much attention as an alternative process, because the NO_x can be reduced to N_2, even in the presence of excess oxygen [1,3,4].

Several NO_x selective catalytic reduction systems have been practically used and showed potential for future applications in different systems for exhaust gases [5–7]. However, these reduction systems still need further improvements before their adaptation in exhaust generators. Three-way catalysts remove NO_x, CO, and HC simultaneously and also lose significant activities due to the presence of excess oxygen. Therefore, accurate control for lowering the concentration of coexisting O_2 can be achieved by combining catalysts with an exhaust gas recirculation system or an electronically controlled fuel injection system. In contrast, NO_x reduction with NH_3 has an advantage because nothing is lost in the presence of excess oxygen. However, that system is difficult to apply because of chemical risks.

Huggins *et al.* [8,9] and Hibino *et al.* [10,11] have reported the electrochemical reduction of NO_x using the oxygen-pumping function of a zirconia-based electrolyte. Oxygen was electrolytically pumped away from a platinum cathode, resulting in the cleaning of the platinum surfaces. NO was able to decompose to N_2 at the cathode when the O^{2-} was transported from the cathode to the anode using a direct current to the reactor. The main advantage of this reactor is that the current efficiency for removing NO is unaffected even in the presence of excess H_2O and O_2 [10,11]. However, this electrochemical NO_x reduction still has some problems to be solved, such as the undesirable N_2O production [12,13] and the low current efficiency due to the simultaneous reduction of oxygen at the cathode side [14].

The objective of the present study was to develop an improved electrochemical NO_x reduction system with high NO_x removal efficiency, as illustrated in figure 1. This system is characterized by a stacked structure composed of a catalyst layer to reduce NO_x effectively even in the presence of excess oxygen, a cathode layer, a solid electrolyte layer with oxide-ionic conductivity, and an anode layer. A hexaaluminate compound and 8 mol% Y_2O_3-stabilized ZrO_2 (YSZ) were selected as the catalyst and electrolyte, respectively, in this study. Hexaaluminate ($M^{2+}Al_{12}O_{19}$) compounds, members of the β-alumina family, are hexagonally symmetric and have an anisotropic plate-like shape [15]. Various metal ions can be introduced to their aluminum sites to create unique catalytic activities [16–18] Along with the new catalytic abilities for the NO_x reduction, what happens when the synthesis of hexaaluminate is substituted with gallium and transition metals has been reported elsewhere [19–21].

This study focused on the synthesis and catalytic properties of the novel catalyst system with a laminated structure between $BaCo(Al,Ga)_{11}O_{19}$ layer and Pt/YSZ/Pt. The YSZ-$BaCo(Al,Ga)_{11}O_{19}$ mixed catalyst layer

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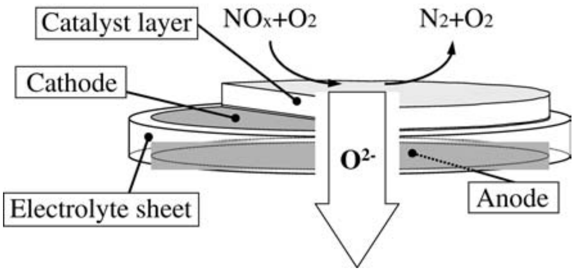

Figure 1. Schematic of an improved electrochemical NO_x reduction system with catalyst/Pt/YSZ/Pt laminated structure.

was deposited onto a Pt/YSZ/Pt sheet by a screen-printing method. The NO_x removal abilities of the catalyst system were evaluated for the NO/O_2 reaction under an external bias.

2. Experimental procedure

2.1. Synthesis of catalyst system for NO_x reduction

The starting powder of $BaCo(Al,Ga)_{11}O_{19}$ (Al/Ga = 9/3), which was selected as the composition of the catalyst, was prepared by the coprecipitation method, with $Ba(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ (Kishida Chemical Co.), $Ga(NO_3)_3 \cdot 6H_2O$ (Ko-Jundo Chemical Co.), and ammonium carbonate ($(NH_4)_2CO_3$ Kishida) as the precipitant [19–21]. The composite powder of YSZ-$BaCo(Al,Ga)_{11}O_{19}$ was prepared by mixing the YSZ powder (8 mol% Y_2O_3-ZrO_2, Tosoh Co., TZ8Y) with a precursor powder of $BaCo(Al,Ga)_{11}O_{19}$ in ethanol for 1 h. Pastes with various volume ratios of YSZ-$BaCo(Al,Ga)_{11}O_{19}$ were prepared by mixing the polyethylene glycol (M.W. = 300; Kishida Chemical Co.) and the YSZ-$BaCo(Al,Ga)_{11}O_{19}$ precursor powder in a 0.4–1.0 g ratio.

A cross-sectional view of the catalyst system is given in figure 2. A platinum cathode layer with a diameter of 16 mm was deposited using screen-printing and fired at 1200 °C onto both sides of a YSZ disk (18 mm in diameter and 0.5 mm thick) for 20 min. A 70 vol% YSZ layer with a diameter of 17 mm was then screen-printed onto the platinum cathode and heated at 1100 °C for 2 h. In addition, a 30 vol% YSZ composite layer with a diameter of 17 mm was deposited onto the 70 vol% YSZ composite layer and heated at 1100 °C for 2 h. In order to investigate the microstructure and connectivity of each interface between the composite layers, the sectional microstructure of the synthesized catalyst system was then observed by scanning electron microscopy (SEM; Model JSM-6100, JEOL, Tokyo, Japan).

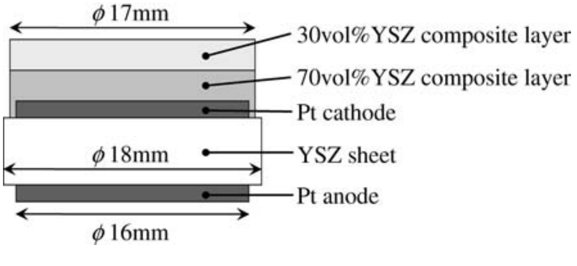

Figure 2. Sectional view of the catalyst/Pt/YSZ/Pt system.

2.2. Evaluation of NO_x removal activity in the catalyst system

The catalyst system was placed in a quartz glass tube (21 mm in diameter), and two platinum wires from the two electrodes were connected to a galvano-potentiostat (Electrochemical Interface Model SI 1287, Solatron). In the experiments, the gas mixtures passed at a flow rate of 50 ml/min (S.V. $\approx$25,000 h^{-1}) and temperatures of 500–650 °C with an applied external voltage of 0–3.0 V. The gas mixture used in the catalytic measurement was 500 ppm NO and 3% O_2 in a helium-balanced gas. The NO_x concentration (the sum of the NO and NO_2) was analyzed with a NO_x analyzer (Analyzer unit BCL-100uH, sampling unit BSU-100uH, Best-sokki). The amounts of O_2, N_2, and N_2O were analyzed by gas chromatography (GC; MicroGC CP-2002, Chrompack,) using a 13× molecular sieve and Porapack Q (GL Sciences) columns. To show the effectiveness of cathode-coating with hexaaluminate-based catalyst layer, the NO_x removal activity of a Pt/YSZ/Pt, which is a conventional system for the electrochemical NO_x reduction, was also evaluated by the same method as mentioned above.

3. Results and discussions

3.1. Preparation of catalyst system for NO_x reduction

The platinum cathode layer covered by a 30 vol% YSZ-70 vol% $BaCo(Al,Ga)_{11}O_{19}$/70 vol% YSZ-30 vol% $BaCo(Al,Ga)_{11}O_{19}$ double catalyst layer and a platinum anode layer were deposited onto each side of the YSZ sheet, where $BaCo(Al,Ga)_{11}O_{19}$ (Al/Ga = 9/3) was selected as the composition of the hexaaluminate catalyst, because of its promising catalytic performance for direct NO_x reduction and its high chemical stability in a reducing atmosphere under high temperatures [19–21]. Figure 3 shows XRD profiles of the catalyst/Pt/YSZ/Pt surface at the cathode side. The double catalyst layer consisted of a mixture of hexaaluminate single phase and c-ZrO_2 phase (figure 3(b)), and the mixed phases were stably present after the NO_x removal measurement (figure 3(a)). The 70 vol% YSZ-30 vol% $BaCo(Al,Ga)_{11}O_{19}$ layer played an important role in minimizing the sintering mismatch between the YSZ layer and the 30 vol% YSZ layer, and also in covering the platinum cathode. By inserting a buffer layer of 70 vol% YSZ-30 vol% $BaCo(Al,Ga)_{11}O_{19}$, we effectively adjusted the sintering behaviors of the 100 vol% YSZ and

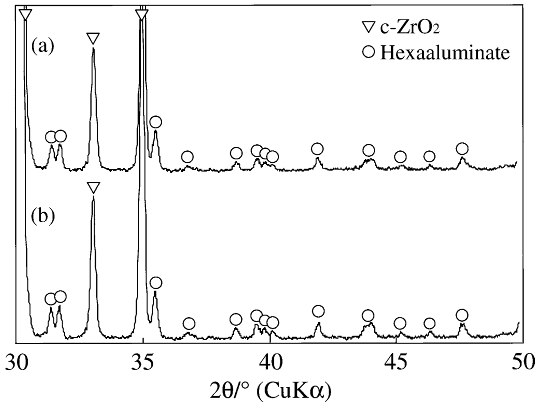

Figure 3. XRD profiles of the catalyst/Pt/YSZ/Pt surfaces at the cathode side; (a) after the NO_x reduction measurement and (b) before the NO_x reduction measurement.

hexaaluminate layers mixed with the 30 vol% YSZ, resulting in a tight connection between the layers with no delamination [22]. In contrast, a buffer layer with YSZ less than 70 vol% led to the delamination of a double catalyst layer. Figure 4(a) shows a cross-sectional view of the cathode side of the synthesized catalyst system, and figure 4(b) shows the surface microstructure of the 30 vol% YSZ-70 vol% $BaCo(Al,Ga)_{11}O_{19}$ layer. The platinum cathode (16 mm in diameter and 10-μm thick) was completely covered by the porous 30 vol% YSZ/ 70 vol% YSZ double catalyst layer (17 mm in diameter and 30-μm thick). Numerous pores ~1 μm in size remained in the catalyst layers, as shown in these figure 4(a) and (b). The porosity of the double catalyst layer at the cathode side was estimated to be above 35%. A porous platinum layer was also successfully deposited onto the YSZ sheet on the anode side. Microstructural observation revealed that very fine hexaaluminate platelets, < 0.5 μm in size, were homogeneously dispersed at the grain boundaries of YSZ particles that were 1–2 μm in size. As shown in figure 4(c), no change was seen in the microstructure of double catalyst layer after the NO_x reduction measurement.

In addition, as stated below, a Pt/YSZ/Pt system reduced the NO_x by less than one-third of that in catalyst/Pt/YSZ/Pt system during the NO/O_2 reaction, because the coexisting O_2 in the gas mixture preferentially decomposed to O^{2-} at the cathode electrode. Among the various combinations of the double catalyst layer, the 30 vol% YSZ/70 vol% YSZ ratio exhibited the highest NO_x reduction with a lower working power.

3.2. Evaluation of catalytic and electrical properties of catalyst system during NO/O_2 reaction

Figure 5 compares direct NO_x reductions by the two catalyst systems, a Pt/YSZ/Pt system and a catalyst/Pt/YSZ/Pt system, under the application of an external bias without reductant gases at 650 °C. The catalyst/Pt/YSZ/Pt system had NO_x reductions of ~10% and ~65% under the application of a 2.0 V and a 2.5 V bias, respectively, whereas the NO_x was reduced by $< 0.5\%$ under the application of a 1.75 V bias. In addition, simultaneous GC analysis revealed that the N_2 amount produced in the NO/O_2 reaction balanced exactly the amount of decomposed NO_x, indicating direct decom-

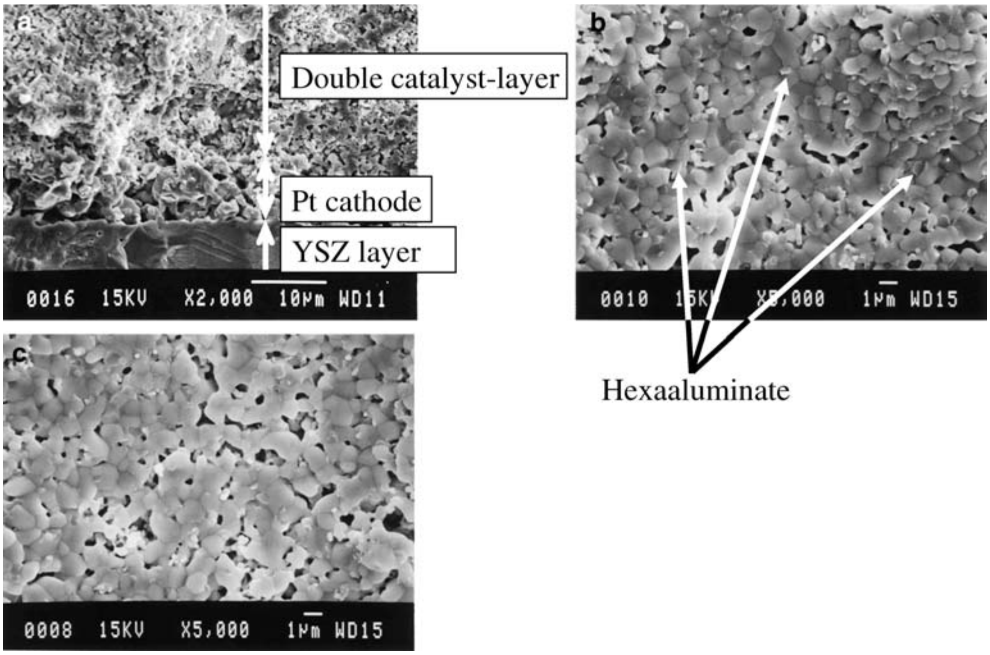

Figure 4. Microstructures of the synthesized catalyst system; (a) sectional view of the cathode side, surfaces of 30 vol% YSZ-70 vol% $BaCo(Al,Ga)_{11}O_{19}$ top-layer, (b) before the NO_x reduction measurement, and (c) after the NO_x reduction measurement.

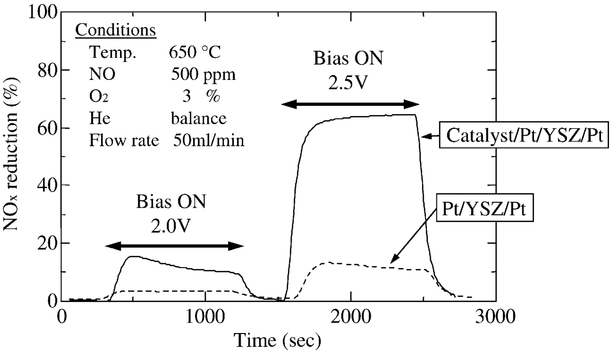

Figure 5. Direct NO_x reductions of the catalyst/Pt/YSZ/Pt and Pt/YSZ/Pt systems under the application of external bias at 650 °C.

position of NO_x to N_2 during the NO/O_2 reaction. However, the Pt/YSZ/Pt system reduced the NO_x by less than one-third of the value achieved by the catalyst/Pt/YSZ/Pt system under the application of an external bias at 650 °C, as shown by the dotted curve in figure 5.

Figure 6 displays NO_x reductions of the catalyst/Pt/YSZ/Pt and Pt/YSZ/Pt systems under the application of various external voltages. The two systems exhibit NO_x reduction above 1.75 V bias, and the catalyst/Pt/YSZ/Pt system has superior NO_x removal activities to the Pt/YSZ/Pt system. This result indicates that the $BaCo(Al,Ga)_{11}O_{19}$ catalyst layer mixed with YSZ played an important role in decomposing NO_x directly to N_2. In the catalyst/Pt/YSZ/Pt system, the applied bias causes oxygen to be eliminated from the cathode side to the anode side through the YSZ layer, led to the acceleration of the direct NO_x reduction over the hexaaluminate catalyst layer mixed with YSZ. On the other hand, the Pt/YSZ/Pt system can only reduce 10% of NO_x to N_2, while the oxygen was removed from the gas mixture as well as the catalyst/Pt/YSZ/Pt system. The difference of the NO_x removal activity between the two systems is mainly dependant on the selectivity of the NO/O_2 decomposition reactions at the cathode side. The preferential decomposition of O_2 to O^{2-} at the cathode of the Pt/YSZ/Pt system inhibited the NO_x decomposition reaction, resulting in low NO_x removal activity. On the other hand, in the case of the catalyst/Pt/YSZ/Pt, the suppression of the preferential O_2 decomposition by covering the Pt cathode with a double catalyst layer led to a superior NO_x removal activity to Pt/YSZ/Pt system.

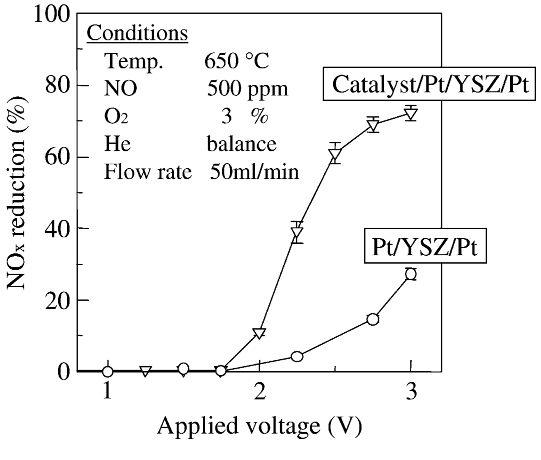

Figure 6. Relations between the applied voltages and NO_x reductions of catalyst/Pt/YSZ/Pt and Pt/YSZ/Pt systems.

3.3. *Effect of measurement temperature on catalytic properties of the catalyst system*

Table 1 summarizes the NO_x reductions during the NO/O_2 reaction, under the application of an external voltage, at various temperatures. NO_x reduction was greatly affected by the measurement temperature. The catalyst system showed a NO_x reduction of $<1\%$ at 550 °C under a bias voltage of 2.5 V. At 600 °C, ~10% of the NO_x was reduced to N_2 under a 2.5 V bias, whereas only a small percent of NO_x was reduced at a 2.0 V bias. These results indicate that the operating temperature must be higher than 600 °C in order to decompose NO_x directly to N_2 without reductant gases.

Table 1

Relation between applied voltage and NO reduction at various temperatures

Temperature (°C)	Applied voltage	NO_x reduction (%)
650	2.5	64.6
	2.0	9.4
	1.5	<0.1
600	2.5	10.0
	2.0	0.5
	1.5	<0.1

4. Conclusions

A catalyst/Pt/YSZ/Pt system was successfully synthesized using a screen-printing method. NO_x reduction in the catalyst system depended on the operating temperature and electric field. The catalyst/Pt/YSZ/Pt system exhibited a direct NO_x removal of ~70% under the application of a 3.0 V bias at 650 °C, whereas a Pt/YSZ/Pt system had a NO_x reduction of $<27\%$. This is because the control of the oxygen decomposition reaction at a Pt cathode by covering it with a double catalyst layer promoted the NO_x reduction. The composite laminate developed in this study exhibited excellent synergistic interaction between NO_x reduction and oxide-ion conduction.

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