NO\textsubscript{x} oxidation and storage reaction over Sr-Fe mixed oxides

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Abstract: SrFeO\textsubscript{3−δ} and Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7−δ} perovskite catalysts were investigated as a Pt-free NO\textsubscript{x} trapping catalyst. Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7−δ} having a layered perovskite structure of a Ruddlesden-Popper-type showed higher NO\textsubscript{x} storage capacity than SrFeO\textsubscript{3−δ} due to the superior NO\textsubscript{2} trapping ability on the catalyst. The activity was higher than that of Pt/Ba/Al\textsubscript{2}O\textsubscript{3} when the catalysts were calcined at 1273 K. Temperature-programmed reaction with NO revealed that SrFeO\textsubscript{3−δ} and Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7−δ} can oxidize NO to NO\textsubscript{2} by utilizing their lattice oxygens. Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7−δ} worked as a Pt-free NO\textsubscript{x} trapping catalyst having high NO\textsubscript{x} storage capacity and thermal tolerance.

Keywords: NO oxidation, NO\textsubscript{x} trap, perovskite catalyst

1. Introduction

Nitrogen oxides (NO\textsubscript{x}) trapping catalysts are used to remove NO\textsubscript{x} from automobile exhaust gas in a fuel lean or cold start condition, in which catalytic reduction of NO\textsubscript{x} to N\textsubscript{2} is difficult. Pt/Ba/Al\textsubscript{2}O\textsubscript{3} is a typical NO\textsubscript{x} trapping catalyst known as a NO\textsubscript{x} storage and reduction catalyst. In a fuel lean condition, the catalyst removes NO\textsubscript{x} by oxidizing NO to NO\textsubscript{2} and trapping NO\textsubscript{2} on BaO as nitrate. However, the NO\textsubscript{x} trapping efficiency significantly decreases below 473 K because oxidation of NO is kinetically hindered at low temperatures. Pt-based catalysts also have the problem of deactivation by sintering of Pt species at high temperatures. Then, perovskite catalysts have been recently paid attention to Pt-free NO\textsubscript{x} trapping catalysts.\textsuperscript{1}

We have also reported that Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7−δ} having a layered perovskite structure of a Ruddlesden-Popper-type shows high oxygen storage capacity (OSC) and can be used as a support of three-way catalyst.\textsuperscript{2,3} Therefore, this study investigated the NO\textsubscript{x} storage capacity of SrFeO\textsubscript{3−δ} and Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7−δ} from the viewpoint of NO oxidation ability and NO\textsubscript{2} trapping ability.

2. Experimental

SrFeO\textsubscript{3−δ} and Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7−δ} were synthetized by a polymerized complex method. Iron nitrate nonahydrate (Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O) and strontium carbonate (SrCO\textsubscript{3}) were added into citric acid aqueous solution and stirred for 2 h at 353 K to obtain the solution containing metal oxide complexes. After ethylene glycol was added into the solution, it was stirred at 403 K for 4 h to obtain a gelatinous solution. The gel was pyrolyzed in a mantle heater at 623 K for 3 h, and thus-obtained brown powder was calcined at 1273 K for 2 h. Conventional NO\textsubscript{x} trapping catalyst, Pt/Ba/Al\textsubscript{2}O\textsubscript{3} (Pt, 1wt%; Ba, 7wt%), was synthesized by an impregnation method and calcined at 1273 K for 2 h.

NO\textsubscript{x} storage reaction was performed in a fixed bed flow system. Catalyst was added into a quartz reactor and then pretreated at 773 K under 10% O\textsubscript{2}/He gas flow for 1 h. After decreasing the temperature to 573 K, reaction gas (NO, 200ppm; O\textsubscript{2}, 3%; He, balance; GHSV, 50,000 h\textsuperscript{-1}) was flowed at 100 mL min\textsuperscript{-1}. The outlet concentration of NO\textsubscript{x} (= NO + NO\textsubscript{2}) was measured by an on-line chemiluminescence NO\textsubscript{x} analyzer. The reactivity of lattice oxygen in perovskite catalysts with NO was evaluated by temperature-programmed reaction (NO-TPR). The catalyst was heated (5 K min\textsuperscript{-1}) under 0.6% NO/He flow, and the consumption of NO was analyzed. NO\textsubscript{x}-TPD was measured by heating (5 K min\textsuperscript{-1}) under He flow after saturating the sample with NO\textsubscript{2} at 573 K.

3. Results and discussion
Figure 1 shows the results of NO\textsubscript{x} storage reaction at 573 K on each catalyst. In the absence of catalysts, the outlet NO\textsubscript{x} concentration immediately reached 200ppm after introducing NO. On the other hand, when the catalysts were used, the NO\textsubscript{x} concentration maintained 0ppm for a certain period and then gradually increased to 200ppm. These behaviors indicate that the catalysts store NO\textsubscript{x}. Comparing with SrFeO\textsubscript{3-δ} and Pt/Ba/Al\textsubscript{2}O\textsubscript{3}, Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7-δ} stored NO\textsubscript{x} for a long time even after calcining at the high temperature. Evaluating the NO\textsubscript{x} storage capacity by using the density of trapped NO\textsubscript{x} on the catalyst surface (Table 1), the density on perovskite catalysts were much greater than that on Pt/Ba/Al\textsubscript{2}O\textsubscript{3}, especially on Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7-δ}. NO\textsubscript{x}-TPD revealed Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7-δ} having a layered perovskite structure showed higher NO\textsubscript{x} trapping ability than SrFeO\textsubscript{3-δ}.

Figure 2 shows the NO-TPR profiles of SrFeO\textsubscript{3-δ} and Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7-δ}. NO consumption was observed in both catalysts above 400 K. The consumption was mainly derived from the oxidation of NO to NO\textsubscript{2}. The formation of NO\textsubscript{2} in the absence of oxygen in the feed gas indicates that NO molecules can be oxidized by lattice oxygen in the catalysts. XRD patterns of the catalysts after NO-TPR showed structure changes due to the topotactic transition, in which the original perovskite framework is preserved even by the release of lattice oxygen. In contrast, such NO consumption and structure change were not observed in the case of Pt/Ba/Al\textsubscript{2}O\textsubscript{3}. These results suggest that OSC of the catalysts play an important role for NO oxidation to NO\textsubscript{2}.

### 4. Conclusions

SrFeO\textsubscript{3-δ} and Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7-δ} perovskites having OSC showed higher NO\textsubscript{x} storage capacity than the Pt-based NO\textsubscript{x} trapping catalyst, Pt/Ba/Al\textsubscript{2}O\textsubscript{3}. Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7-δ} having a layered perovskite structure exhibited superior NO\textsubscript{2} adsorption ability to SrFeO\textsubscript{3-δ}. NO-TPR and XRD revealed that SrFeO\textsubscript{3-δ} and Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7-δ} can oxidized NO to NO\textsubscript{2} below 473 K by using the lattice oxygen.

### Table 1. Amount of trapped NO\textsubscript{x} on each catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Amount of trapped NO\textsubscript{x} / μmol g\textsuperscript{-1}</th>
<th>Specific surface area / m\textsuperscript{2} g\textsuperscript{-1}</th>
<th>Density of trapped NO\textsubscript{x} / molecules nm\textsuperscript{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrFeO\textsubscript{3-δ}</td>
<td>9.9</td>
<td>1.3</td>
<td>4.6</td>
</tr>
<tr>
<td>Sr\textsubscript{3}Fe\textsubscript{2}O\textsubscript{7-δ}</td>
<td>85.9</td>
<td>2.8</td>
<td>18.5</td>
</tr>
<tr>
<td>Pt/Ba/Al\textsubscript{2}O\textsubscript{3}</td>
<td>84.8</td>
<td>108</td>
<td>0.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Total amount of the trapped NO\textsubscript{x} until the outlet concentration of NO\textsubscript{x} reached 180ppm (90% of introduced NO).

### References