NO_x oxidation and storage reaction over Sr-Fe mixed oxides

Kazuki TAMAI,[a] **Saburo HOSOKAWA,**[a,b,*] **Hiroyuki ASAKURA,**[a,b]
Kentaro TERAMURA,[a,b] **and Tsunehiro TANAKA**[a,b]
[a]*Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto, 615-8510, Japan*
[b]*Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Kyoto, 615-8245, Japan*
**Corresponding author: +81-75-383-2561, hosokawa@moleng.kyoto-u.ac.jp*

Abstract: $SrFeO_{3-\delta}$ and $Sr_3Fe_2O_{7-\delta}$ perovskite catalysts were investigated as a Pt-free NO_x trapping catalyst. $Sr_3Fe_2O_{7-\delta}$ having a layered perovskite structure of a Ruddlesden-Popper-type showed higher NO_x storage capacity than $SrFeO_{3-\delta}$ due to the superior NO_2 trapping ability on the catalyst. The activity was higher than that of $Pt/Ba/Al_2O_3$ when the catalysts were calcined at 1273 K. Temperature-programmed reaction with NO revealed that $SrFeO_{3-\delta}$ and $Sr_3Fe_2O_{7-\delta}$ can oxidize NO to NO_2 by utilizing their lattice oxygens. $Sr_3Fe_2O_{7-\delta}$ worked as a Pt-free NO_x trapping catalyst having high NO_x storage capacity and thermal tolerance.
Keywords: NO oxidation, NO_x trap, perovskite catalyst

1. Introduction

Nitrogen oxides (NO_x) trapping catalysts are used to remove NO_x from automobile exhaust gas in a fuel lean or cold start condition, in which catalytic reduction of NO_x to N_2 is difficult. $Pt/Ba/Al_2O_3$ is a typical NO_x trapping catalyst known as a NO_x storage and reduction catalyst. In a fuel lean condition, the catalyst removes NO_x by oxidizing NO to NO_2 and trapping NO_x on BaO as nitrate. However, the NO_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_x trapping catalysts.[1] We have also reported that $Sr_3Fe_2O_{7-\delta}$ 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.[2,3] Therefore, this study investigated the NO_x storage capacity of $SrFeO_{3-\delta}$ and $Sr_3Fe_2O_{7-\delta}$ from the viewpoint of NO oxidation ability and NO_2 trapping ability.

2. Experimental

$SrFeO_{3-\delta}$ and $Sr_3Fe_2O_{7-\delta}$ were synthesized by a polymerized complex method. Iron nitrate nonahydrate ($Fe(NO_3)_3\cdot 9H_2O$) and strontium carbonate ($SrCO_3$) 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_x trapping catalyst, $Pt/Ba/Al_2O_3$ (Pt, 1wt%; Ba, 7wt%), was synthesized by an impregnation method and calcined at 1273 K for 2 h.

NO_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_2/He gas flow for 1 h. After decreasing the temperature to 573 K, reaction gas (NO, 200ppm; O_2, 3%; He, balance; GHSV, 50,000 h^{-1}) was flowed at 100 mL min^{-1}. The outlet concentration of NO_x (= NO + NO_2) was measured by an on-line chemiluminescence NO_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^{-1}) under 0.6% NO/He flow, and the consumption of NO was analyzed. NO_2-TPD was measured by heating (5 K min^{-1}) under He flow after saturating the sample with NO_2 at 573 K.

3. Results and discussion

Figure 1 shows the results of NO_x storage reaction at 573 K on each catalyst. In the absence of catalysts, the outlet NO_x concentration immediately reached 200ppm after introducing NO. On the other hand, when the catalysts were used, the NO_x concentration maintained 0ppm for a certain period and then gradually increased to 200ppm. These behaviors indicate that the catalysts store NO_x. Comparing with $SrFeO_{3-\delta}$ and $Pt/Ba/Al_2O_3$, $Sr_3Fe_2O_{7-\delta}$ stored NO_x for a long time even after calcining at the high temperature. Evaluating the NO_x storage capacity by using the density of trapped NO_x on the catalyst surface (Table 1), the density on perovskite catalysts were much greater than that on $Pt/Ba/Al_2O_3$, especially on $Sr_3Fe_2O_{7-\delta}$. NO_2-TPD revealed $Sr_3Fe_2O_{7-\delta}$ having a layered perovskite structure showed higher NO_2 trapping ability than $SrFeO_{3-\delta}$.

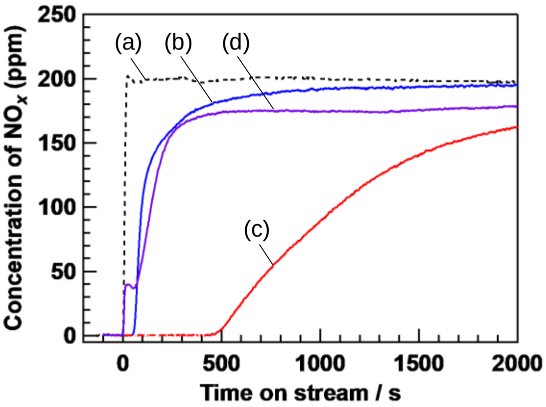

Figure 1. Time course of the NO_x storage reaction at 573 K. (a) without catalyst, (b) $SrFeO_{3-\delta}$, (c) $Sr_3Fe_2O_{7-\delta}$, and (d) $Pt/Ba/Al_2O_3$.

Figure 2 shows the NO-TPR profiles of $SrFeO_{3-\delta}$ and $Sr_3Fe_2O_{7-\delta}$. NO consumption was observed in both catalysts above 400 K. The consumption was mainly derived from the oxidation of NO to NO_2. The formation of NO_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 $Pt/Ba/Al_2O_3$. These results suggest that OSC of the catalysts play an important role for NO oxidation to NO_2.

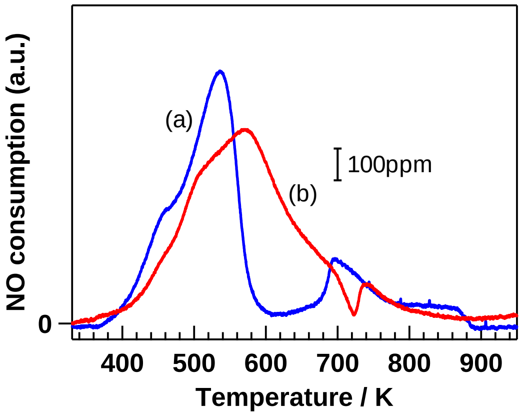

Figure 2. NO-TPR profiles of (a) $SrFeO_{3-\delta}$ and (b) $Sr_3Fe_2O_{7-\delta}$.

4. Conclusions

$SrFeO_{3-\delta}$ and $Sr_3Fe_2O_{7-\delta}$ perovskites having OSC showed higher NO_x storage capacity than the Pt-based NO_x trapping catalyst, $Pt/Ba/Al_2O_3$. $Sr_3Fe_2O_{7-\delta}$ having a layered perovskite structure exhibited superior NO_2 adsorption ability to $SrFeO_{3-\delta}$. NO-TPR and XRD revealed that $SrFeO_{3-\delta}$ and $Sr_3Fe_2O_{7-\delta}$ can oxidized NO to NO_2 below 473 K by using the lattice oxygen.

Table 1. Amount of trapped NO_x on each catalyst.

	Amount of trapped NO_x^a / µmol g^{-1}	Specific surface area / m^2 g^{-1}	Density of trapped NO_x^a / molecules nm^{-2}
$SrFeO_{3-\delta}$	9.9	1.3	4.6
$Sr_3Fe_2O_{7-\delta}$	85.9	2.8	18.5
$Pt/Ba/Al_2O_3$	84.8	108	0.5

a) Total amount of the trapped NO_x until the outlet concentration of NO_x reached 180ppm (90% of introduced NO).

References

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