 

# Direct Decomposition of NO into $N_2$ and $O_2$ on $SrFe_{0.7}Mg_{0.3}O_3$ Perovskite Oxide

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NO direct decomposition on doped $SrFeO_3$ perovskite oxide was investigated. The ability of $SrFeO_3$ for direct decomposition of NO is strongly affected by the dopant in Fe sites. Among the examined dopants and compositions, the highest yield of $N_2$ was achieved on $SrFe_{0.7}Mg_{0.3}O_3$. When $SrFe_{0.7}Mg_{0.3}O_3$ was loaded with Pt, the $N_2$ yield further improved, and the light-off temperature fell by 100 K. On this catalyst, the yields of $N_2$ and $O_2$ were 56 and 35%, respectively, at 1123 K. On the Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ catalyst, the NO decomposition rate increased with increase in the NO partial pressure with $P_{NO}{}^{1.31}$. The presence of oxygen slightly decreased the $N_2$ yield with $P_{O_2}{}^{-0.12}$. Therefore, the effect of oxygen poisoning on NO decomposition upon Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ is small. From the result of $O_2$-TPD, Pt loading possibly weakens the adsorption strength of surface oxygen and enhances NO adsorption. In summary, this study shows that the substitution of Fe with lower valence cation in $SrFeO_3$ and also loading a small amount of Pt are highly effective for increasing the NO decomposition activity.

Nitrogen oxides ($NO_x$), which mainly form in lean combustion engines, such as diesel engines, are extremely toxic to the human body and also harmful to environment, because they are one of the main sources of both acid rain and photochemical smog. At present, because of the increase in the number of the diesel engine cars, the amount of $NO_x$ emission in urban area has increased significantly. Several methods have been proposed for $NO_x$ removal.[1–3] Among them, the selective reduction of $NO_x$ by hydrocarbons has been studied extensively, and various catalysts,[4–14] in particular, Cu-ZSM-5, have been proposed as an active catalyst for this reaction.[15–19] However, due to the low selectivity of the reductant, this method is not practical. Instead of hydrocarbon reduction, selective reduction of $NO_x$ with urea is now considered the most promising method for the removal of $NO_x$ under oxygen containing atmosphere. However, for this method, a slight excess of urea to $NO_x$ is required and so, environmental problems from urea or ammonia formed are also possible. On the other hand, direct decomposition of NO into $N_2$ and $O_2$ ($2NO = N_2 + O_2$) is the most ideal reaction for $NO_x$ removal, because the process is quite simple.[20,21] However, it is well known that the formed oxygen adsorbs strongly on the catalyst, resulting in the deactivation of the catalyst. Some catalysts, such as Cu-ZSM-5,[22] Co-ZSM-5 (which contains Co in the framework[23]), $La_2O_3$,[24] Ba/MgO,[25] and $LaCoO_3$[26] based perovskite oxides, are active toward the direct decomposition of NO. In particular, Teraoka et al. have reported that $La_{0.8}Sr_{0.2}CoO_3$ is highly active toward NO decomposition and that the $N_2$ yield is 40% at 1073 K.[27] Although the reaction temperature is higher, high NO decomposition activity is expected on perovskite oxides. High reaction temperatures are sometimes better from the viewpoint of practical applications, because the negative effects of oxygen, water, and sulfur compounds seem to decrease with an increase in the temperature.

In our previous study, NO direct decomposition over $LaMnO_3$ perovskite oxide doped with Ba for the La site and In for the Mn site has been investigated, and it has been found that $La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O_3$ perovskite oxide exhibits high activity toward NO direct decomposition over 1073 K.[28] On the other hand, NO direct decomposition with $Fe^{4+}$, which is an anomalous valence number of Fe at high temperature, has hardly been studied. Shin et al. have reported that brownmillerite-like compound of $Sr_2Fe_2O_5$ exhibits rather high NO decomposition activity in the range of 973–1173 K.[29–31] In addition, they have also shown that an oxygen-deficient perovskite of composition $SrFeO_{3-x}$ selectively absorbs NO gas above approximately 373 K, and analysis of the infrared spectrum of the system $^{14}NO$–$^{15}NO$–$SrFeO_{3-x}$ has shown that the absorbed species in $SrFeO_{3-x}$ is possibly the nitrosyl ion ($NO^-$) bound to the iron ion accommodate in some oxygen vacancies.[32] However, except for their IR study on NO adsorption species on $SrFeO_3$, the number of studies on the NO decomposition activity of oxides consisting of $Fe^{IV}$ is limited. Perovskite oxide, which contains $Fe^{4+}$, is expected to be a new NO direct decomposition catalyst, since reduction of $Fe^{4+}$ to $Fe^{3+}$ proceeds easily and the removal of the surface oxygen can be easily achieved at reasonably low temperature. In this study, effects of various dopants at the Fe site in $SrFeO_3$ on NO decomposition activity were investigated. NO decomposition activity was greatly improved by a small amount of dopant in case of $LaMnO_3$ or $BaMnO_3$ catalyst.

## Experimental

Doped $SrFeO_3$ were prepared by a conventional solid-state reaction method. The precursor of $SrFeO_3$ was obtained by evaporating an aqueous solution of a calculated amount of $Sr(NO_3)_2$, $Fe(NO_3)_2$, and metal nitrates. The mixtures obtained were precalcined in air at 673 K for 2 h to decompose the metal nitrates,

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Table 1. NO Direct Decomposition into $N_2$ and $O_2$ over $SrFe_{0.7}M_{0.3}O_3$

| Catalyst | Specific surface area/$m^2\,g^{-1}$ | Conversion/% | Yield/% | | | |
|---|---|---|---|---|---|---|
| | | NO | $N_2$ | $O_2$ | $N_2O$ | $NO_2$[a)] |
| $SrFe_{0.7}M_{0.3}O_3$ | | | | | | |
| M = Mg | 1.7 | 86.4 | 47.3 | 23.4 | 0.0 | 31.5 |
| Sn | 0.8 | 79.1 | 42.7 | 19.0 | 0.0 | 30.1 |
| Ni | 1.2 | 76.1 | 41.6 | 17.2 | 0.0 | 29.5 |
| Ce | 1.3 | 77.7 | 41.3 | 14.2 | 0.0 | 31.8 |
| Zr | 1.6 | 78.1 | 37.5 | 11.8 | 0.0 | 33.2 |
| Mn | 0.7 | 62.4 | 27.0 | 5.2 | 0.0 | 28.6 |
| Ga | 0.9 | 60.1 | 25.5 | 4.3 | 0.0 | 27.9 |
| Co | 0.6 | 48.2 | 17.3 | 2.6 | 0.0 | 22.8 |
| Ru | 1.4 | 29.6 | 13.2 | 1.7 | 0.0 | 14.0 |
| Ir | 2.0 | 26.1 | 11.1 | 1.6 | 0.0 | 12.3 |
| Si | 0.6 | 11.1 | 3.8 | 0.5 | 0.0 | 5.3 |
| Ge | 0.9 | 6.8 | 3.9 | 0.4 | 0.0 | 3.2 |
| Cu | 0.8 | 18.6 | 3.3 | 0.9 | 0.0 | 8.8 |
| Ti | 0.6 | 3.9 | 0.8 | 0.4 | 0.0 | 1.8 |

a) Estimated based on material balance of nitrogen. NO = 1%, He balance, $W/F = 3.0\,g\,s\,cm^{-3}$, temperature: 1123 K.

and then calcined in air at 1473 K for 6 h. X-ray diffraction was preformed on this sample using a Cu K$\alpha$ line, and the formation of perovskite phase was confirmed. This catalyst powder was pressed into disks, crushed and sieved into 16 to 32 meshes. Pt (1 wt %) was loaded on $SrFe_{0.7}Mg_{0.3}O_3$ by conventional impregnation with tetraammineplatinum(II) chloride, 1-hydrate ($Pt(NH_3)_4Cl_2 \cdot H_2O$).

Direct decomposition of NO was performed with a conventional fixed-bed gas-flow reactor with a quartz glass tube (12-mm diameter). Gaseous mixture of 1% NO diluted with He was fed to the catalyst bed for NO direct decomposition reactions. The catalyst (1 g) was always set in the reactor by using quartz wool (ca. 0.5 cm in catalyst height), and the feed rate of the reactant was fixed at $W/F = 3.0\,g\,s\,cm^{-3}$, where $W$ and $F$ are the catalyst weight and the gas flow rate, respectively. Reaction was performed at 773–1123 K, and $N_2$, $O_2$, and fed NO were analyzed with online gas chromatography with a 5A molecular sieve column. $N_2O$ was analyzed using a Porapak-Q column with a thermal conductivity detector (TCD). Because $NO_2$ cannot be analyzed with gas chromatography, $NO_2$ formation rate was estimated by the amount of nitrogen and oxygen molar amounts before and after the catalyst bed, namely average of (NO conversion–$N_2$ yield) and ($N_2$ yield–$O_2$ yield) values. In this study, the activity of the catalyst toward NO decomposition is mainly discussed based on the $N_2$ yield. It is also noted that the formation of $N_2O$ was not observed in this study. Effects of the coexistence of $O_2$ were measured by mixing 1–5% $O_2$ diluted with He with the reactant gas. In order to keep the total flow rate of $20\,mL\,min^{-1}$ constant, the feed rate of He was varied as a balance gas.

Temperature-programmed desorption (TPD) of NO and $O_2$ was performed to analyze the adsorption state of $O_2$ and NO. After evacuation of the catalyst at 773 K for 1 h, the catalyst was exposed to 101 kPa NO or $O_2$ for 1 h, followed by cooling to room temperature. After evacuation at room temperature for 30 min, the catalyst was heated at $10\,K\,min^{-1}$, and the desorbed gas was monitored by using a quadrupole mass spectrometer (ANELVA, AQR-100R).

Adsorption state of NO was measured with FT-IR (JASCO type 610) with a diffuse reflection unit equipped with a heating unit and KBr window. The catalyst (ca. 0.15 g) was set into the measurement pan and evacuated at 773 K for 3 h to remove the adsorbed water. After evacuation, a background spectrum was acquired at 773 K, and gaseous NO (ca. 10 kPa) was introduced into the measurement cell at 773 K. NO adsorption was performed at 773 K for 30 min, and the catalyst was cooled to room temperature. IR spectra of adsorbed NO were measured after evacuation of the catalyst at the described temperature for 30 min.

## Results and Discussion

**Effects of Dopant in $SrFeO_3$ on NO Direct Decomposition Activity.** Table 1 shows the NO decomposition activities of $SrFeO_3$ perovskite oxide doped with various cations (Mg, Sn, Ni, Ce, Zr, Mn, Ga, Co, Ru, Ir, Si, Ge, Cu, and Ti). The NO direct decomposition activity of $SrFeO_3$ without dopant was not measured in this study, because it was not stable and its single phase cannot be obtained. Similar to $LaMnO_3$, the NO decomposition activity of the $SrFeO_3$ catalyst was strongly affected by additives. Among the catalysts examined, Mg-doped $SrFeO_3$ catalyst afforded the highest $N_2$ yield. Other catalysts, such as Sn, Ni, Ce, and Zr-doped catalysts, also exhibited fairly high $N_2$ formation rate. On the contrary, $N_2$ formation rates on Si, Ge, Cu, and Ti-doped catalysts were smaller than 4%. Therefore, doping with these cations, which are mainly tetravalent cations, does not enhance the NO decomposition activity. BET surface area of the doped $SrFeO_3$ is also shown in Table 1. Since BET surface area did not significantly change with the dopant, change in NO decomposition activity was assigned to the dopant effects. Since it was found that the Mg-dopant was the most effective for the direct decomposition of NO, Mg-doped $SrFeO_3$ was further studied in the following part.

Figure 1 shows the XRD patterns of $SrFe_{1-x}Mg_xO_3$ catalysts. The X-ray diffraction peaks shifted to a lower angle with an increase in the amount of Mg, suggesting an increase in the lattice constant. Considering the effective ionic radius of 6 coordination of $Mg^{2+}$ is 86.0 pm, which is larger than that of 6-coordinate $Fe^{4+}$ (72.5 pm) and that of 12-coordinate $Sr^{2+}$

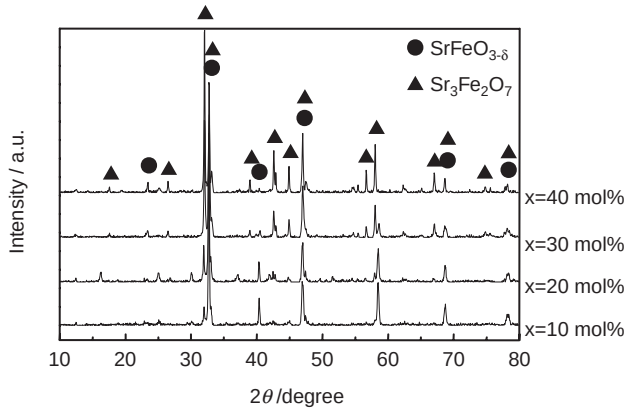


Fig. 1. XRD patterns of $SrFe_{1-x}Mg_xO_3$ prepared.

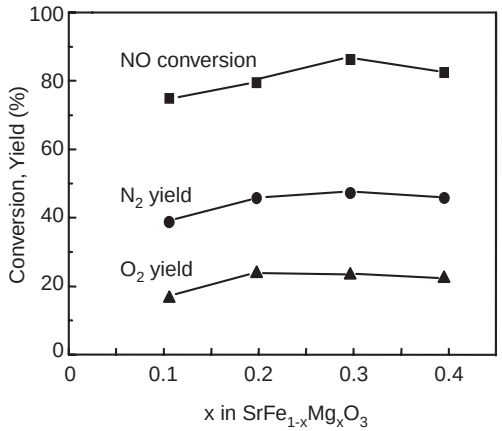


Fig. 2. $N_2$ and $O_2$ yield on NO direct decomposition over $SrFe_{1-x}Mg_xO_3$ at 1123 K as a function of $x$ value ($P_{NO} = 1\%$, $W/F = 3.0\,g\,s\,cm^{-3}$).

(158 pm),[33] it is thought that Mg replaces Fe, but not Sr, in $SrFeO_3$. Although the formation of a small amount of $Sr_3Fe_2O_7$ phase was observed, the main diffraction peaks were assigned to those of $SrFeO_3$. An impurity phase appeared when the $x$ value was higher than 0.3 and became significant with an increase in the amount of Mg. Therefore, it seems likely that the solubility limit of Mg into Fe site of $SrFeO_3$ exists around $x = 0.3$ and Mg replaces Fe in $SrFeO_3$ lattice. Valence number of Fe in $SrFeO_3$ is +4 from the molecular formula, which is an unusual valence number, and by doping lower valence cations of Mg, the number of oxygen vacancies is increased for charge compensation. The $Fe^{4+}$ ion is not stable at high temperatures, and so, the solid solubility of Mg into Fe site is not large due to the low lattice stability. In any case, at $x$ values less than 0.3, the main phase of Mg-doped sample is a perovskite structure of $SrFeO_3$.

Figure 2 shows the $N_2$ and $O_2$ yield on NO direct decomposition over $SrFe_{1-x}Mg_xO_3$ catalyst at 1123 K as a function of $x$ value. It was observed that the $N_2$ yield as well as $O_2$ yield increased with an increase in the amount of Mg and the yields reached a maximum at $x = 0.3$, which is close to the solid solubility limit of Mg. After the $N_2$ and $O_2$ yield became saturated at ca. 47 and 23%, respectively, a further increase in the amount of Mg decreased the $N_2$ and $O_2$ yield. Considering the solubility limit of Mg, it is seen that the optimum amount of Mg into Fe site is at $x = 0.3$. As a result, the optimum amount for Mg doping is 30 mol % of Fe sites in $SrFeO_3$.

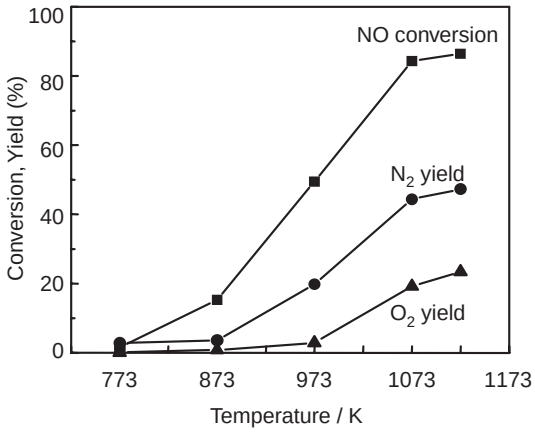


Fig. 3. Temperature dependence of NO decomposition activity upon $SrFe_{0.7}Mg_{0.3}O_3$ in the range of 773–1123 K ($P_{NO} = 1\%$, $W/F = 3.0\,g\,s\,cm^{-3}$).

Temperature dependence of NO decomposition activity upon $SrFe_{0.7}Mg_{0.3}O_3$ is shown in Fig. 3. It was observed that NO decomposition started around 873 K, at which $N_2$ and $O_2$ start to form. $N_2$ and $O_2$ yield monotonically increased with the reaction temperature. $N_2$ yield reached a value of 47% at 1123 K. Although the contact time is much longer and the NO concentration is much higher than that of the actual exhaust gas from engines, it was found that fairly high NO conversion could be achieved on $SrFe_{0.7}Mg_{0.3}O_3$ catalyst. Therefore, perovskite oxide of $SrFe_{0.7}Mg_{0.3}O_3$ is an interesting NO decomposition catalyst, although a high reaction temperature is required.

**Effects of Pt Loading on $SrFe_{0.7}O_3$ on NO Direct Decomposition Activity.** In order to improve the NO decomposition activity, loading a small amount of a precious metal is sometimes effective. For example, it has been reported that loading Pt on $TiO_2$, $SiO_2$, and $Al_2O_3$ is effective for increasing NO decomposition activity.[34] It has also been reported that Pt loading is effective for increasing the NO decomposition activity on a $BaO/Al_2O_3$ catalyst.[35] In this study, effects of 1 wt % Pt loading for $SrFe_{0.7}Mg_{0.3}O_3$ on the NO decomposition activity were also studied. Temperature dependence of NO decomposition activity upon Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ is shown in Fig. 4. The NO decomposition activity improved greatly due to Pt-loading. In addition, the $N_2$ yield improved from 47 to 56%, and the $O_2$ yield increased from 23 to 36% at 1123 K by loading Pt. Therefore, it can be said that the loading Pt is quite effective for improving the NO decomposition activity of $SrFe_{0.7}Mg_{0.3}O_3$. At present, a detailed mechanism for the improved NO decomposition activity by Pt loading is not clear; however, loading Pt did not always improve the NO decomposition activity. In fact, loading Pt into $BaMnO_3$ simply decreased the NO decomposition activity. Therefore, improvement in NO decomposition activity is not a simple summation of the activity of Pt and $SrFeO_3$ catalyst. It is considered that there are synergy effects between Pt and $SrFe_{0.7}Mg_{0.3}O_3$. The light-off temperature of NO decomposition activity also shifted by as much as 100 K to a lower temperature. Effects of

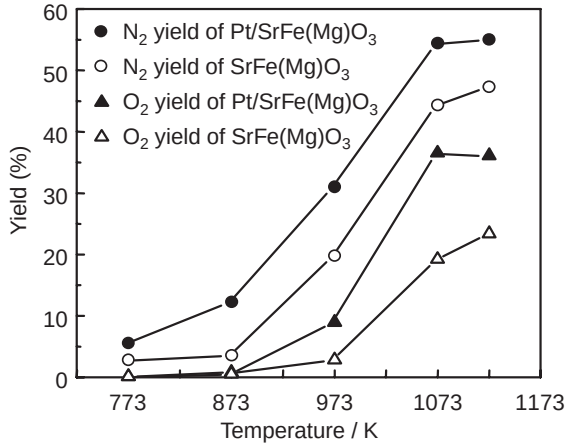


Fig. 4. Temperature dependence of NO decomposition activity upon 1 wt % $Pt/SrFe_{0.7}Mg_{0.3}O_3$ in the range of 773–1123 K ($P_{NO} = 1\%$, $W/F = 3.0\,g\,s\,cm^{-3}$).

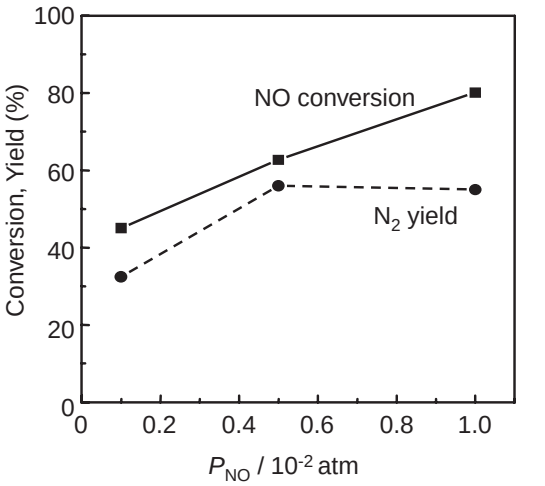


Fig. 5. NO conversion and $N_2$ yield from NO direct decomposition over 1 wt % $Pt/SrFe_{0.7}Mg_{0.3}O_3$ as a function of NO partial pressure at 1123 K ($W/F = 3.0\,g\,s\,cm^{-3}$).

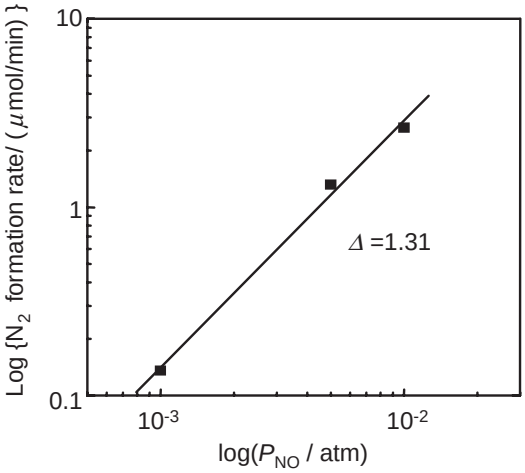


Fig. 6. $N_2$ formation rate from NO direct decomposition over 1 wt % $Pt/SrFe_{0.7}Mg_{0.3}O_3$ as a function of NO partial pressure at 1123 K ($W/F = 3.0\,g\,s\,cm^{-3}$).

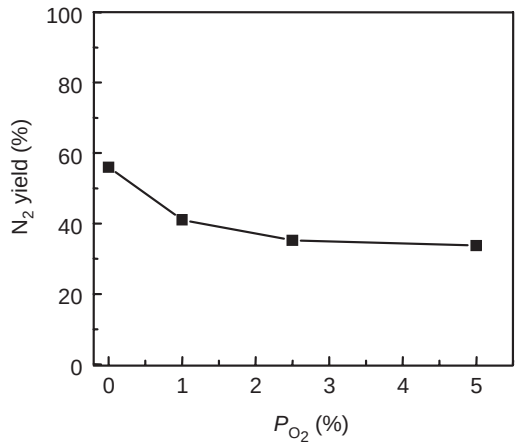


Fig. 7. $N_2$ yield from NO direct decomposition over 1 wt % $Pt/SrFe_{0.7}Mg_{0.3}O_3$ as a function of $O_2$ partial pressure at 1123 K ($P_{NO} = 0.5\%$, $W/F = 3.0\,g\,s\,cm^{-3}$).

reaction conditions on NO decomposition activity are also reported.

Figure 5 shows the $N_2$ formation rate as a function of NO partial pressure. From our previous study, the $N_2$ formation rate increases with an increase in the NO partial pressure, and the rate-determining step might be adsorption or activation of NO.[28] Similar to a Mn-based perovskite oxide, the NO conversion increases with an increase into the NO partial pressure. High NO conversion at low NO partial pressure is an important for a NO decomposition catalyst. However, at 1000 ppm NO, conversion of NO was still reasonably high (ca. 45%). Therefore, this $SrFeO_3$-based catalyst also exhibited high NO decomposition activity in a low $P_{NO}$ range. $N_2$ formation rate is plotted against NO partial pressure in Fig. 6. The $N_2$ formation rate monotonically increased with an increase in the logarithm of NO partial pressure, and the $P_{NO}$ dependence was $P_{NO}^{1.31}$, which is almost the same value with that of La(Ba)-Mn(In)$O_3$ in our previous study. This suggests that the adsorption and activation of NO are also important steps on $Pt/SrFe_{0.7}Mg_{0.3}O_3$ catalyst. Coupling of NO adsorption species is essentially required in some step for the formation of $N_2$ under NO decomposition, and for this, a high concentration of surface NO is needed.

Figure 7 shows the $N_2$ yield as a function of the $O_2$ partial pressure. In the conventional study, the presence of $O_2$ significantly lowered the catalyst activity for NO decomposition, and the number of the catalyst exhibiting a high NO conversion in the presence of $O_2$ was quite small. As shown in Fig. 7, the $N_2$ yield decreased from 56 to 42% in the presence of 1% $O_2$; however, the decrease in the $N_2$ yield was not significant in the $P_{O_2}$ range from 1 to 5%. As a result, even under a $P_{O_2}$ of 5%, a $N_2$ yield of 35% was obtained. Therefore, the negative effects of $O_2$ are not serious, and Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ is highly tolerant against $O_2$. Figure 8 shows the $N_2$ formation rate as a function of oxygen partial pressure. The $N_2$ formation rate slightly decreased with an increase in the $P_{O_2}$, and the $P_{O_2}$ dependency was as small as $P_{O_2}^{-0.12}$, which is much smaller than that of the similar perovskite oxides reported.[28] Therefore, the negative effects of $O_2$ are much smaller than that for other perovskite catalysts, and it is expected that a high

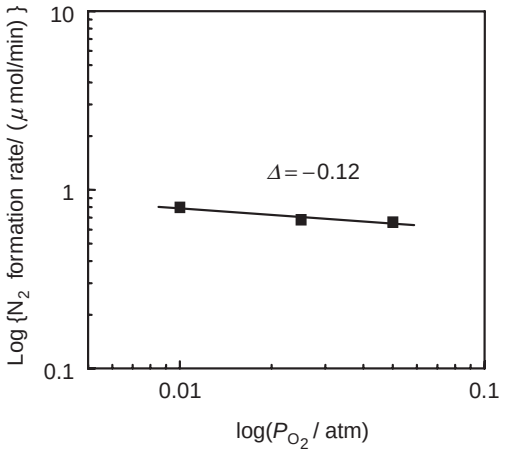


Fig. 8. $N_2$ formation rate from NO direct decomposition over 1 wt % $Pt/SrFe_{0.7}Mg_{0.3}O_3$ as a function of $O_2$ partial pressure at 1123 K ($P_{NO} = 0.5\%$, $W/F = 3.0\,g\,s\,cm^{-3}$).

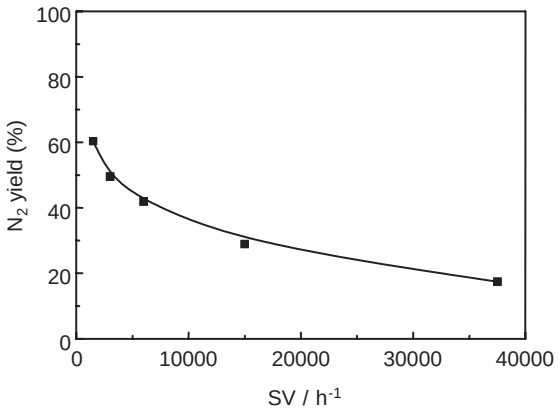


Fig. 9. $N_2$ yield from NO direct decomposition over 1 wt % $Pt/SrFe_{0.7}Mg_{0.3}O_3$ as a function of space velocity at 1123 K ($P_{NO} = 1.0\%$).

NO decomposition activity will be maintained for a longer period on this Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ catalyst in the presence of $O_2$.

In order to use a catalyst in an actual NO removal processes from automobile exhaust gas, a high NO removal rate should be maintained at a high space velocity. Since the NO decomposition reaction is considered a rather slow reaction, compared to the selective reduction of NO, the NO decomposition activity is generally lower at an elevated space velocity. In addition, BET surface area of perovskite oxide is small, that is, a few $m^2\,g^{-1}$, because high-temperature calcination is needed to obtain a single phase. In fact, the BET surface area of $SrFeO_3$-based oxide is less than $4\,m^2\,g^{-1}$ as shown in Table 1. Figure 9 shows the $N_2$ yield as a function of the space velocity of NO. $N_2$ formation rate decreased with an increase in the space velocity; however, a reasonably high $N_2$ formation rate was sustained at a high space velocity of NO, considering the BET surface area was about $1.7\,m^2\,g^{-1}$. In addition, a $N_2$ yield of 20% was still obtained at SV = $40000\,h^{-1}$. Although the high activity is needed even at a few $100000\,h^{-1}$ for a commercial de-$NO_x$ catalyst, the NO decomposition activity of Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ catalyst is reasonably high among

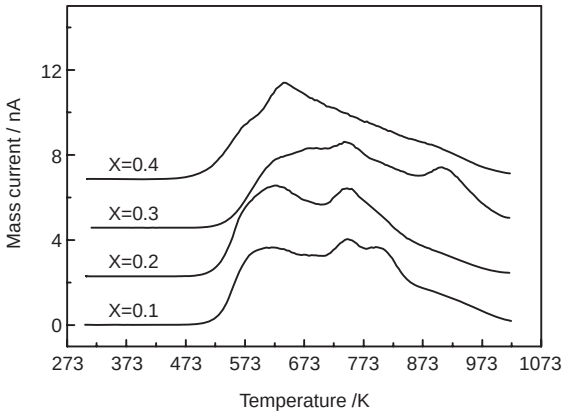


Fig. 10. $O_2$ desorption profiles from $SrFe_{1-x}Mg_xO_3$ ($O_2$ adsorption: 773 K for 1 h).

the conventional NO decomposition catalyst. Considering the BET surface area of the present catalyst, NO decomposition reaction at a large space velocity might be diffusion limited, and so, by increasing the surface area, it is thought that the NO decomposition activity should improve. Long-term stability of the NO decomposition activity over Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ catalyst was also examined, and it was confirmed that the NO decomposition activity decreased negligibly up to 90 h after the reaction started. These results indicate that Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ catalyst is active and good NO decomposition.

**Effects of Mg Dopant and Pt Loading to $O_2$ and NO Adsorption State.** Since the NO decomposition activity was greatly improved by doping Mg for Fe site and Pt loading, effects of the dopant and metal addition on NO and $O_2$ adsorptions were investigated by $O_2$ and NO-TPD. Normally, a higher NO decomposition activity tends to be achieved on a catalyst that weakly absorbs oxygen. In this study, change in oxygen adsorption state was investigated by $O_2$-TPD.

Figure 10 shows the $O_2$-TPD curves on $SrFe_{1-x}Mg_xO_3$. Oxygen desorption was observed at temperature higher than 523 K and desorption peaks at 573, 773, and 973 K, were observed on all catalysts. Comparing the desorption temperature of oxygen from the Mn-based perovskite oxide,[28] $O_2$ desorption temperature from $SrFeO_3$ is much lower, and the amount is also larger. This suggests that the strength of surface oxygen on $SrFeO_3$ is much weaker than that on $LaMnO_3$. The desorption temperature of oxygen around 573 K did not change with an increase in the Mg; however, the amount of total oxygen desorption increased with an increase in the Mg amount and reached a maximum at $x = 0.3$, at which the highest NO decomposition activity is achieved. Although quantitative analysis by mass spectrometry is not precise, it is noted that the peak area of TPD peaks from 323 to 1023 K was ca. 4% larger by addition of 30% Mg to Fe site of $SrFeO_3$. Therefore, the high NO decomposition activity on $SrFe_{0.7}Mg_{0.3}O_3$ can be explained by how easily the surface $O_2$ desorbs. The small $P_{O_2}$ dependence of NO decomposition activity is also in good agreement with these results.

In contrast to oxygen desorption, NO desorption was not significantly affected by doping Mg for Fe site in $SrFeO_3$. Figure 11 shows the NO desorption curves from $SrFe_{0.7}Mg_{0.3}O_3$. As shown in Fig. 11, $O_2$ and $N_2$ formation was also

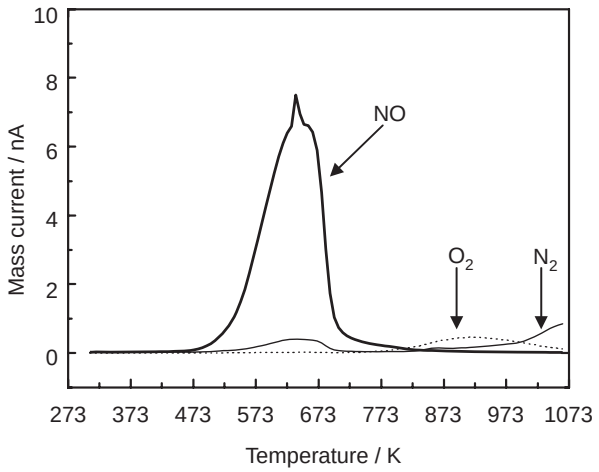


Fig. 11. NO desorption profiles from $SrFe_{0.7}Mg_{0.3}O_3$ (NO adsorption: 773 K for 1 h).

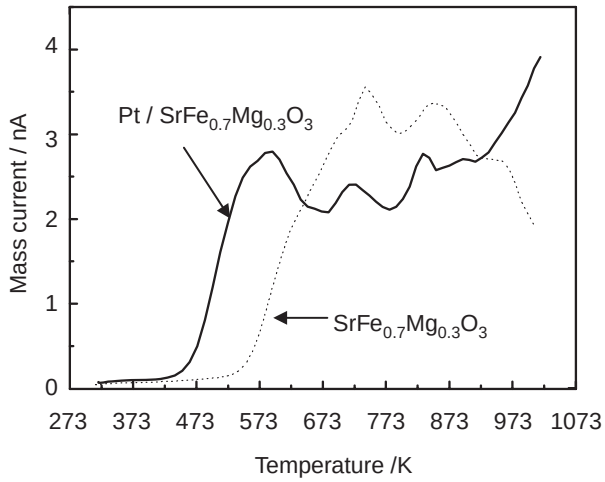


Fig. 12. $O_2$ desorption profiles from 1 wt % Pt/$SrFe_{0.7}Mg_{0.3}O_3$ and $SrFe_{0.7}Mg_{0.3}O_3$ ($O_2$ adsorption: 773 K for 1 h).

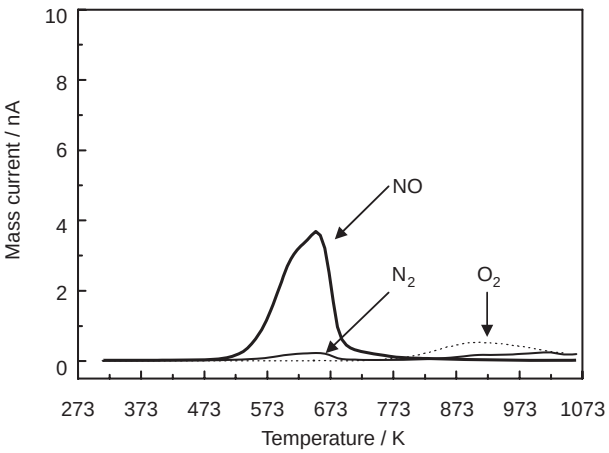


Fig. 13. NO desorption profiles from 1 wt % Pt/$SrFe_{0.7}Mg_{0.3}O_3$ (NO adsorption: 773 K for 1 h).

observed in NO-TPD. It was also observed that the molecular NO desorption occurred around 573 K, at which a fairly large amount of $N_2$ desorption was also observed. However, no oxygen desorbed at this temperature. This suggests that the formed oxygen was trapped on the surface of $SrFeO_3$-based oxide around 573 K. This trapped oxygen started to desorb above 773 K, followed by $N_2$ desorption. Therefore, it is thought that some amount of surface NO decomposed as the temperature increased and adsorption of NO is dissociative. Considering desorption of molecular NO and $N_2$ but not $O_2$, NO disproportionation reaction (for example; $3NO = N_2 + NO_{3ad}$) occurs around 573 K, and the nitrogen oxide surface species may decompose at temperatures higher than 873 K. Therefore, desorption of $O_2$ and $N_2$ is observed at temperatures higher than 873 K. Formation of $NO_3$ surface species has also been observed on $LaMnO_3$ oxide.[28] This means that the surface of $SrFe_{0.7}Mg_{0.3}O_3$ is covered with oxygen formed by the decomposition of NO around 573 K. However, once the surface oxygen is removed, i.e., by decomposition of $NO_3$, NO direct decomposition seems to proceed, because $N_2$ desorption was observed after $O_2$ desorption was observed around 973 K. Therefore, $SrFe_{0.7}Mg_{0.3}O_3$ exhibits high activity toward NO direct decomposition at temperatures higher than 973 K due to desorption oxygen. If the adsorbed oxygen can be removed, then it can be expected that direct decomposition of NO will proceed at a temperature around 773 K. In any case, doping with Mg at the Fe sites of $SrFeO_3$ makes oxygen desorption easier.

Pt loading was also studied by $O_2$ and NO-TPD. Figure 12 shows the comparison of oxygen desorption profiles on $SrFe_{0.7}Mg_{0.3}O_3$ with and without Pt loading. Obviously, the desorption temperature of oxygen shifted to a lower temperature, and oxygen desorption was observed at temperatures as low as 473 K. In addition, large oxygen desorption peaks were also observed above 873 K, which were not observed on the catalyst without Pt. The total area of $O_2$-TPD peak on Pt loading one was 1.13 times larger than that of non Pt-loading catalyst. Therefore, it is clear that Pt loading is effective for decreasing oxygen desorption temperature and also enlarging the desorption amount. Since Pt is well-known reduction catalyst, small amount of surface Pt may work as the reduction catalyst and is effective for removing the surface oxygen. This means that the surface Pt might be active to break the metal–oxygen bonds on the surface of $SrFeO_3$. Figure 13 shows the NO desorption profiles from Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ catalyst. Similar to the profile for Mg doping, there were no significant changes in NO desorption profiles of Pt-loaded samples, except for a decrease in NO desorption amount and slight increase in oxygen desorption amount. Since the amount of desorbed $N_2$ and $O_2$ is slightly improved by loading Pt, the decrease in the amount of NO desorption (the peak area is almost half of non Pt-loaded one) suggests that Pt causes the NO dissociation on the surface and the amount of molecular NO adsorption decreases. However, amount of surface activated NO seems to increase with Pt loading. Therefore, it seems that the loaded Pt is effective for improving the surface active NO concentration. As discussed earlier, NO adsorption and activation seems to be important factors for NO decomposition activity on this catalyst, and so, Pt has a positive effect on the NO decomposition activity, because oxygen desorbs more readily and thus active sites are recovered.

NO adsorption state on Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ catalyst

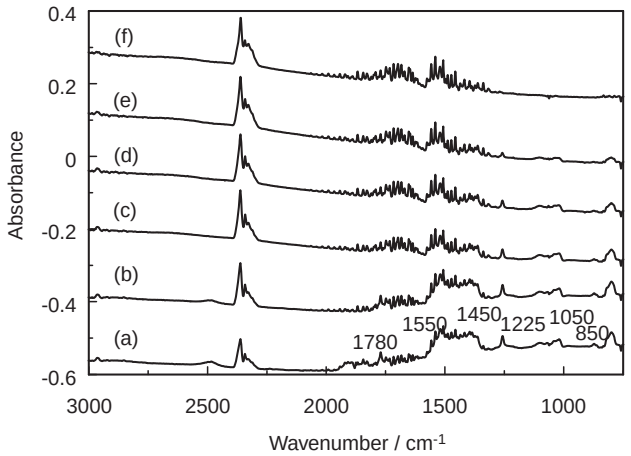


Fig. 14. IR spectra of adsorbed NO on 1 wt % $Pt/SrFe_{0.7}Mg_{0.3}O_3$: (a) NO adsorption at 773 K, (b) evacuation at room temperature, (c) evacuation at 473 K, (d) evacuation at 573 K, (e) evacuation at 673 K, (f) evacuation at 773 K.

was studied. Figure 14 shows the IR spectra of NO after adsorption at 773 K. After adsorption of NO at 773 K, absorption peaks at 1780, 1550, 1450, 1225, 1050, and 850 $cm^{-1}$ were observed. In comparison to the reported values,[28] the peak at 1780 and those around 1500 $cm^{-1}$ were assigned to bent-type NO ($NO^+$) and nitrate oxides, such as $NO_3$ species. Therefore, adsorption of NO seems to be electron donative, i.e., the catalyst is reduced by adsorption of NO, and this is reasonable considering that $Fe^{4+}$ is easily reduced to $Fe^{3+}$, which is a more stable oxidation state. Since the absorption peak at 1780 $cm^{-1}$ disappeared after the sample was placed under a vacuum at 473 K for 30 min, the desorption peak of NO in NO-TPD around 623 K was assigned to that of bent-type NO adsorption species. On the other hand, absorption peaks around 1500 and 1000 $cm^{-1}$ remained after evacuation at 673 K, but disappeared after evacuation at 773 K evacuation, for 30 min. Therefore, $O_2$ and $N_2$ desorption peaks observed in NO-TPD at temperatures higher than 773 K were assigned to the decomposition products of nitrate spices. Since nitrate species strongly cover the active sites for NO decomposition, removal of nitrate species from the surface is highly important to achieve high NO decomposition activity. Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ catalyst needs a relatively low temperature for desorption of nitrate-like surface species resulting in the high NO decomposition activity in an intermediate temperature range. In any case, the decomposition of nitrate species, which forms by disproportionation of NO, is important step for NO decomposition reaction on $SrFeO_3$-based catalyst, and this seems to be accelerated by addition of small amount of Pt.

## Conclusion

The NO decomposition activity increased in the order of Mg > Sn > Ni > Ce > Zr after doping the Fe site in $SrFeO_3$ perovskite oxide. Among the investigated dopants and compositions, the highest $N_2$ yield was achieved with $SrFe_{0.7}Mg_{0.3}O_3$. On this catalyst, NO conversion increased with an increase in the reaction temperature, and conversion of NO into $N_2$ and $O_2$ at 1123 K was 47 and 23%, respectively. The NO decomposition activity improved greatly by loading a small amount of Pt. The $N_2$ yield increased from 47 to 56% and the light-off temperature of NO decomposition activity shifted by as much as 100 K to a lower temperature.

On Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ catalyst, the NO decomposition rate increased with an increase in the NO partial pressure with $P_{NO}^{1.31}$. Therefore, the key step for NO decomposition on Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ seems to be related with the adsorption or activation of NO. The presence of oxygen decreased the $N_2$ yield with $P_{O_2}^{-0.12}$; however, a $N_2$ yield of 35% was afforded even in the presence of 5% $O_2$ at 1123 K. Therefore, oxygen scarcely affects the decomposition reaction, and the effect of oxygen poisoning on NO decomposition upon Pt-loaded $SrFe_{0.7}Mg_{0.3}O_3$ is small. From the $O_2$-TPD results, Pt loading is thought to weaken the adsorption strength of the surface oxygen and to increase the decomposition of nitrate surface species. In summary, this study shows that substituting some of the Fe with a cation in a lower valence state in $SrFeO_3$ and also loading a small amount of Pt are highly effective for increasing the NO decomposition activity.

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