NO Decomposition on Ruddlesden–Popper-Type Oxide, Sr₃Fe₂O₇, Doped with Ba and Zr

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Study of the NO decomposition activity of the Ruddlesden– Popper-type oxide $Sr_3Fe_2O_7$ doped with Ba and Zr revealed that $Sr_3Fe_2O_7$ exhibits a high NO decomposition activity. Doping Ba and Zr for the Sr and Fe sites, respectively, is highly effective for improving NO decomposition activity. A high N₂ yield of 72% is achieved at 1123 K and a N₂ yield of 32% is sustained under a 2.5% oxygen cofeeding condition.

The diesel engine is an ideal lean combustion engine that exhibits high fuel efficiency. However, it produces a high concentration of nitrogen oxides (NO_X) , which are extremely toxic to the human body and are also harmful to the environment being principal causes of both acid rain and photochemical smog. At present, because of the increase in the number of diesel engine cars, the amount of NO emission in urban areas has been markedly increasing. Several methods of NO_X removal have been proposed.^{1–7} Among them, the selective reduction of NO_X by hydrocarbons has been studied extensively, and various catalysts, particularly Cu-ZSM-5, have been proposed for this reaction.⁸ In contrast to NO_X removal by selective reduction, the direct decomposition of NO into N_2 and O_2 (2NO = $N_2 + O_2$) is the ideal reaction owing to its simplicity.^{9,10} However, because of strong oxygen adsorption, the NO decomposition activity of conventional catalysts decreases significantly under an oxygen cofeeding condition.¹¹ We have found that the perovskite oxide Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O₃ (BLMMg), containing Mn^{VI}, is highly active for direct NO decomposition.¹² In the presence of this compound as a catalyst, the NO decomposition activity of non-La- and non-Mg-doped BaMnO3 is low; however, it markedly increases in BaMnO₃ doped with a low-valence cation. Therefore, the use of dopants is highly effective for achieving high NO decomposition activity, which may be the result of the introduction of oxygen vacancies into lattice. Although BaMnO₃ has a high NO decomposition activity, its Mn component makes it not preferable from the viewpoint of toxicity. We have also found that SrFeO3 perovskite oxide shows a rather high NO decomposition activity.¹³ In this study, the NO decomposition activity of Sr₃Fe₂O₇ oxide with a Ruddlesden-Popper structure, a perovskite-related structure that contains a much higher number of oxygen vacancies, was investigated.

Doped $Sr_3Fe_2O_7$ was prepared by conventional solidstate reaction. $Sr(CH_3COO)_2 \cdot 0.5H_2O$ (Wako Pure Chem.), $Fe(NO_3)_3 \cdot 3H_2O$ (Kishida Chem.), and nitrie acid were used as starting materials. The formation of single-phase $Sr_3Fe_2O_7$ was confirmed by XRD analysis. The direct decomposition of NO was performed with a conventional fixed-bed gas-flow reactor with a quartz glass tube of 12-mm diameter. NO_2 formation was observed by the reaction of NO and O_2 produced by NO decomposition; thus, the yield of N_2 was always higher than that of O_2 . The activity of each catalyst for NO decomposition is discussed mainly in terms of N_2 yield. It is noted that no N_2O formation was observed in this study.

Table 1 summarizes the NO decompositions in the presence of Sr₃Fe₂O₇ doped with various cations for the Fe site. As in the case of SrFeO₃ perovskite oxide,¹³ NO decomposition activity of Sr₃Fe₂O₇ was markedly improved by the use of a dopant. In particular, a high N₂ yield was generally obtained by doping tetravalent cations, i.e., Zr, Ti, Ce, and Sn, for the Fe site. The highest N₂ yield is obtained by doping Zr for the Fe site. For SrFeO₃, the most pronounced effect was obtained by doping Mg, which has a lower valence number than Fe resulting in the formation of oxygen vacancies. However, despite their similar structures, the optimum dopant is different between them, which may be explained by the difference in the number of oxygen vacancies. The crystal structure of Sr₃Fe₂O₇ consists of two blocks: a dual perovskite layer (SrFeO₃) and a single rock salt (SrO). Since a large number of oxygen vacancies originally exist in the rock salt, the introduction of oxygen vacancies into the perovskite layer by doping with a low-valence cation is not effective, but the introduction of excess oxygen by doping with a high-valence cation is effective for increasing NO decomposition activity in the case of Sr₃Fe₂O₇. Since the most pronounced effects on NO decomposition were obtained using Zr as a dopant, the effects of Zr were further studied.

Figure 1 shows the NO conversion and N_2 and O_2 yields at 1123 K as functions of the Zr content (X) of the $Sr_3Fe_2O_7$

Table 1. NO decomposition on doped Sr₃Fe₂O₇ catalysts^a

	Conversion/% Yield/%				
	NO	N_2	O ₂	N_2O	NO_2
No dopant	70.2	38.2	14.3	0.0	28.0
$Sr_{3}Fe_{1.8}A_{0.2}O_{7+\delta}$					
A = Zr	70.5	49.6	31.2	0.0	19.7
Ni	70.3	48.8	31.3	0.0	19.5
Ce	69.0	48.1	30.0	0.0	19.5
Mn	66.5	47.9	29.6	0.0	18.5
Ti	71.2	47.0	27.9	0.0	21.7
Sn	71.2	46.2	26.2	0.0	22.5
Mg	65.7	43.8	24.9	0.0	20.4
Co	62.2	43.2	25.1	0.0	18.6
Ru	58.9	38.3	21.0	0.0	18.9
Hf	44.9	28.8	14.1	0.0	15.4
Мо	26.3	15.7	6.9	0.0	9.7
Sr _{2.7} B _{0.3} Fe _{1.8} Zr _{0.2} O _{7+δ}					
B = Ba	79.2	62.2	38.6	0.0	20.3
Pr	73.1	53.2	31.6	0.0	20.8
La	73.5	52.7	29.3	0.0	22.1
Ce	71.7	51.0	28.9	0.0	21.4

^aTemperature: 1123 K, NO: 1%, $W/F = 3.0 \text{ g s cm}^{-3}$.



Figure 1. NO conversion and N₂ and O₂ yields at 1123 K as functions of Zr content of Sr₃Fe₂O₇ catalyst (NO: 1%, $W/F = 3.0 \text{ g s cm}^{-3}$).

catalyst. The NO conversion and N₂ yield monotonically increased with increasing X up to 0.4. For the catalyst with X = 0.4, the N₂ yield is almost 1.5 times higher than that for the nondoped one. Therefore, the optimized Zr amount for doping is approximately X = 0.4. Since XRD analysis suggested that the secondary phases of SrO and SrZrO₃ start to form at approximately X = 0.3, the solubility limit of Zr seems to be between X = 0.3 and 0.4. As a result, an excess of Zr dopant forms the secondary phase of SrZrO₃ resulting in decreased NO decomposition activity. Thus, the optimum amount for Zr doping is X = 0.4, which is slightly higher than the solubility limit.

In our previous study of BaMnO₃, additives into the Ba site of BaMnO₃ were found to be also useful for increasing NO decomposition activity.¹² In Table 1, the effects of dopants for the Sr site of Sr₃Fe_{1.8}Zr_{0.2}O_{7- δ} are also shown. Clearly, a dopant for the Sr site is highly effective for increasing NO decomposition activity. Among the examined dopants, it was found that Ba shows the most pronounced effects of Ba doping could be explained by the enhanced NO adsorption. In the NO decomposition catalyst, NO adsorption and activation are two of the most important steps in NO_X removal, and Ba is generally effective for enhancing NO adsorption.^{13,14} As a result, the optimum dopants are Ba for the Sr site and Zr for the Fe site in Sr₃Fe₂O₇ oxides.

Figure 2 shows the temperature dependences of N_2 and O_2 yields on $Sr_{2.7}Ba_{0.3}Fe_{1.6}Zr_{0.4}O_3$. In Figure 2, the NO decomposition activity of the BLMMg catalyst, which was identified as one of the most active NO decomposition catalysts in our previous study, is also shown.¹² It is seen that NO decomposition proceeds on doped $Sr_3Fe_2O_7$ at approximately 873 K. With increasing temperature, N_2 yield monotonically increased, and at 1123 K, N_2 yield of 75% is obtained, which is similar to the yield obtained with the BLMMg catalyst but much higher than that obtained with $SrFe_{0.7}Mg_{0.3}O_3$ (N_2 yield: 43% at 1073 K).

Since the $Sr_3Fe_2O_7$ catalyst contains Fe, which is more environmentally friendly than Mn, $Sr_3Fe_2O_7$ doped with Ba



Figure 2. Temperature dependences of N₂ and O₂ yields with the use of Sr_{2.7}Ba_{0.3}Fe_{1.6}Zr_{0.4}O₃ and Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O₃. (NO: 1%, $W/F = 3.0 \text{ g s cm}^{-3}$).

and Zr is desirable as a NO decomposition catalyst in terms of environmental impact. The high NO decomposition activity of Sr_{2.7}Ba_{0.3}Fe_{1.6}Zr_{0.4}O₃ is sustained in the presence of O₂, resulting in a N₂ yield of 32% under a 2.5% O₂ cofeeding condition (See Figure S.I.1).¹⁵ Thus, it is clear that the Ruddlesden–Popper-type oxide Sr₃Fe₂O₇ doped with Ba and Zr is a highly active catalyst for direct NO decomposition.

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