

## NO Decomposition on Ruddlesden–Popper-Type Oxide, $\text{Sr}_3\text{Fe}_2\text{O}_7$ , Doped with Ba and Zr

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Study of the NO decomposition activity of the Ruddlesden–Popper-type oxide  $\text{Sr}_3\text{Fe}_2\text{O}_7$  doped with Ba and Zr revealed that  $\text{Sr}_3\text{Fe}_2\text{O}_7$  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  $\text{N}_2$  yield of 72% is achieved at 1123 K and a  $\text{N}_2$  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 ( $\text{NO}_x$ ), 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  $\text{NO}_x$  removal have been proposed.<sup>1–7</sup> Among them, the selective reduction of  $\text{NO}_x$  by hydrocarbons has been studied extensively, and various catalysts, particularly Cu-ZSM-5, have been proposed for this reaction.<sup>8</sup> In contrast to  $\text{NO}_x$  removal by selective reduction, the direct decomposition of NO into  $\text{N}_2$  and  $\text{O}_2$  ( $2\text{NO} = \text{N}_2 + \text{O}_2$ ) is the ideal reaction owing to its simplicity.<sup>9,10</sup> However, because of strong oxygen adsorption, the NO decomposition activity of conventional catalysts decreases significantly under an oxygen cofeeding condition.<sup>11</sup> We have found that the perovskite oxide  $\text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$  (BLMMg), containing  $\text{Mn}^{\text{VI}}$ , is highly active for direct NO decomposition.<sup>12</sup> In the presence of this compound as a catalyst, the NO decomposition activity of non-La- and non-Mg-doped  $\text{BaMnO}_3$  is low; however, it markedly increases in  $\text{BaMnO}_3$  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  $\text{BaMnO}_3$  has a high NO decomposition activity, its Mn component makes it not preferable from the viewpoint of toxicity. We have also found that  $\text{SrFeO}_3$  perovskite oxide shows a rather high NO decomposition activity.<sup>13</sup> In this study, the NO decomposition activity of  $\text{Sr}_3\text{Fe}_2\text{O}_7$  oxide with a Ruddlesden–Popper structure, a perovskite-related structure that contains a much higher number of oxygen vacancies, was investigated.

Doped  $\text{Sr}_3\text{Fe}_2\text{O}_7$  was prepared by conventional solid-state reaction.  $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 0.5\text{H}_2\text{O}$  (Wako Pure Chem.),  $\text{Fe}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  (Kishida Chem.), and nitric acid were used as starting materials. The formation of single-phase  $\text{Sr}_3\text{Fe}_2\text{O}_7$  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.  $\text{NO}_2$  formation was observed by the reaction of NO and  $\text{O}_2$  produced by NO decomposition; thus, the yield of  $\text{N}_2$  was always higher than that of  $\text{O}_2$ . The activity of each catalyst for NO decomposition

is discussed mainly in terms of  $\text{N}_2$  yield. It is noted that no  $\text{N}_2\text{O}$  formation was observed in this study.

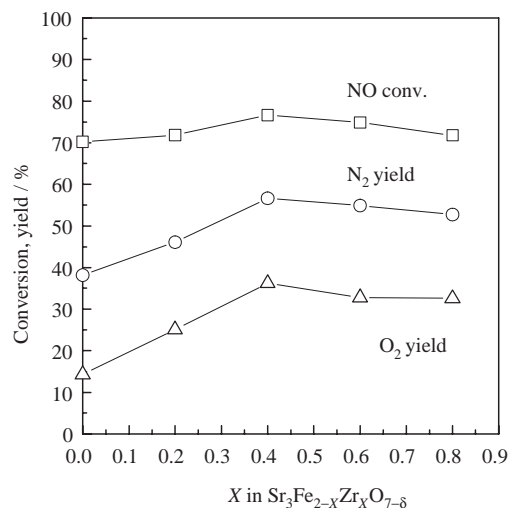
Table 1 summarizes the NO decompositions in the presence of  $\text{Sr}_3\text{Fe}_2\text{O}_7$  doped with various cations for the Fe site. As in the case of  $\text{SrFeO}_3$  perovskite oxide,<sup>13</sup> NO decomposition activity of  $\text{Sr}_3\text{Fe}_2\text{O}_7$  was markedly improved by the use of a dopant. In particular, a high  $\text{N}_2$  yield was generally obtained by doping tetravalent cations, i.e., Zr, Ti, Ce, and Sn, for the Fe site. The highest  $\text{N}_2$  yield is obtained by doping Zr for the Fe site. For  $\text{SrFeO}_3$ , 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  $\text{Sr}_3\text{Fe}_2\text{O}_7$  consists of two blocks: a dual perovskite layer ( $\text{SrFeO}_3$ ) and a single rock salt ( $\text{SrO}$ ). 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  $\text{Sr}_3\text{Fe}_2\text{O}_7$ . 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  $\text{N}_2$  and  $\text{O}_2$  yields at 1123 K as functions of the Zr content ( $X$ ) of the  $\text{Sr}_3\text{Fe}_2\text{O}_7$

**Table 1.** NO decomposition on doped  $\text{Sr}_3\text{Fe}_2\text{O}_7$  catalysts<sup>a</sup>

	Conversion/%	Yield/%			
	NO	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub> O	NO <sub>2</sub>
No dopant	70.2	38.2	14.3	0.0	28.0
Sr <sub>3</sub> Fe <sub>1.8</sub> A <sub>0.2</sub> O <sub>7+δ</sub>					
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
Mo	26.3	15.7	6.9	0.0	9.7
Sr <sub>2.7</sub> B <sub>0.3</sub> Fe <sub>1.8</sub> Zr <sub>0.2</sub> O <sub>7+δ</sub>					
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

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



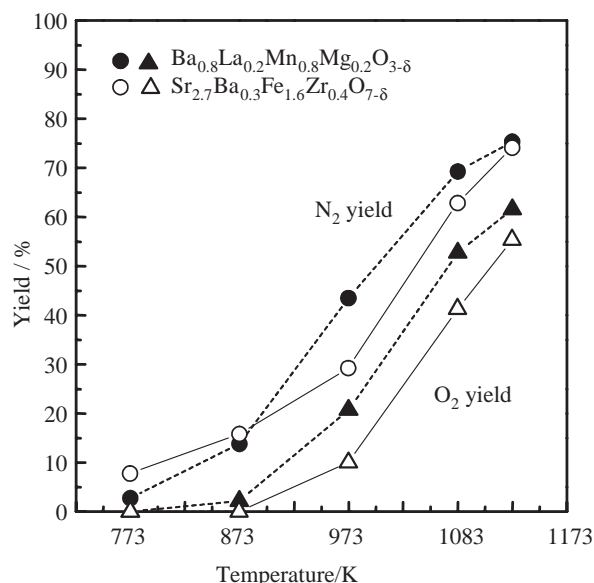
**Figure 1.** NO conversion and N<sub>2</sub> and O<sub>2</sub> yields at 1123 K as functions of Zr content of Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> catalyst (NO: 1%, W/F = 3.0 g s cm<sup>-3</sup>).

catalyst. The NO conversion and N<sub>2</sub> yield monotonically increased with increasing X up to 0.4. For the catalyst with X = 0.4, the N<sub>2</sub> 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 SrZrO<sub>3</sub> 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 SrZrO<sub>3</sub> 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 BaMnO<sub>3</sub>, additives into the Ba site of BaMnO<sub>3</sub> were found to be also useful for increasing NO decomposition activity.<sup>12</sup> In Table 1, the effects of dopants for the Sr site of Sr<sub>3</sub>Fe<sub>1.8</sub>Zr<sub>0.2</sub>O<sub>7-δ</sub> 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 increasing NO decomposition activity. The 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<sub>x</sub> removal, and Ba is generally effective for enhancing NO adsorption.<sup>13,14</sup> As a result, the optimum dopants are Ba for the Sr site and Zr for the Fe site in Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> oxides.

Figure 2 shows the temperature dependences of N<sub>2</sub> and O<sub>2</sub> yields on Sr<sub>2.7</sub>Ba<sub>0.3</sub>Fe<sub>1.6</sub>Zr<sub>0.4</sub>O<sub>3</sub>. 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.<sup>12</sup> It is seen that NO decomposition proceeds on doped Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> at approximately 873 K. With increasing temperature, N<sub>2</sub> yield monotonically increased, and at 1123 K, N<sub>2</sub> yield of 75% is obtained, which is similar to the yield obtained with the BLMMg catalyst but much higher than that obtained with SrFe<sub>0.7</sub>Mg<sub>0.3</sub>O<sub>3</sub> (N<sub>2</sub> yield: 43% at 1073 K).

Since the Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> catalyst contains Fe, which is more environmentally friendly than Mn, Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> doped with Ba



**Figure 2.** Temperature dependences of N<sub>2</sub> and O<sub>2</sub> yields with the use of Sr<sub>2.7</sub>Ba<sub>0.3</sub>Fe<sub>1.6</sub>Zr<sub>0.4</sub>O<sub>3</sub> and Ba<sub>0.8</sub>La<sub>0.2</sub>Mn<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-δ</sub> (NO: 1%, W/F = 3.0 g s cm<sup>-3</sup>).

and Zr is desirable as a NO decomposition catalyst in terms of environmental impact. The high NO decomposition activity of Sr<sub>2.7</sub>Ba<sub>0.3</sub>Fe<sub>1.6</sub>Zr<sub>0.4</sub>O<sub>3</sub> is sustained in the presence of O<sub>2</sub>, resulting in a N<sub>2</sub> yield of 32% under a 2.5% O<sub>2</sub> cofeeding condition (See Figure S.I.1).<sup>15</sup> Thus, it is clear that the Ruddlesden-Popper-type oxide Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7</sub> doped with Ba and Zr is a highly active catalyst for direct NO decomposition.

## References and Notes

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- 15 Supporting Information is available electronically at the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.