

Direct Decomposition of NO on Cu-Doped La(Ba)Mn(In)O₃ Perovskite Oxide under Coexistence of O₂, H₂O, and SO₂

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It was found that the substitution of Mn with Cu in La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O₃ is effective for increasing activity to NO direct decomposition. NO direct decomposition proceeds on the perovskite oxide of La_{0.7}Ba_{0.3}Mn_{0.6}In_{0.2}Cu_{0.2}O₃ under coexistence of O₂, H₂O, and SO₂ at high temperature.

Nitrogen oxides (NO_x), which are mainly formed by an internal combustion engine, are extremely toxic for human body and harmful for environment as a main source of acid rain. At present, several methods have been proposed for NO_x removal.¹⁻⁴ Among them, direct decomposition of NO to N₂ and O₂ (2NO = N₂ + O₂) is the most ideal method for the NO removal, since the process is simple and of high efficiency. However, it is well-known that the formed oxygen adsorbs strongly on the catalyst resulting in a deactivation of catalyst. It was reported that Cu-ZSM-5,⁵ LaNiO₃,⁶ and Sr/La₂O₃-based perovskite oxide⁷ are active for the direct decomposition of NO. In particular, Teraoka et al. reported that La_{0.8}Sr_{0.2}CoO₃ is highly active for the NO decomposition.⁸ The high activity for NO decomposition under a practical exhaust gas condition is expected on perovskite oxide catalyst. In our previous study, it was found that La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O₃ (LBMI) perovskite oxide exhibits the high activity to NO direct decomposition.⁹ In the present study, effects of transition cation substitution for Mn in LBMI were studied for further increasing the NO decomposition activity. In particular, effects of coexistence of H₂O, O₂, and SO₂, which are generally contained in exhaust gas from internal combustion engines, on NO decomposition were also studied.

Doped LaMnO₃ was prepared by a conventional solid solution method. The precursor of LaMnO₃-based perovskite oxide was obtained by using the aqueous suspension of a calculated amount of La(NO₃)₃, Ba(NO₃)₂, Mn(CH₃COO)₂, In₂O₃, and metal nitrate. Obtained mixtures were calcined in air at 1273 K for 3 h. From X-ray diffraction measurement, it was confirmed that the obtained sample was consisted of a single phase of LaMnO₃-based perovskite oxide. Direct decomposition of NO was performed with a conventional fixed bed gas flow reactor and a gaseous mixture of 1% NO diluted with He was fed to the catalyst bed at $W/F = 3.0 \text{ g} \cdot \text{min}/\text{cm}^3$, where W and F mean the catalyst weight and the gas flow rate. Here, for the accelerated deactivation by oxygen formed in NO decomposition, we generally used the concentration of NO at 1%, which is much higher than that in the actual exhaust gas. Produced N₂, O₂, and fed NO were analyzed with an on-lined gas chromatography with thermal conductivity detector (TCD). Formation rate of NO₂ was estimated by N₂ and O₂ material balance. Addition of H₂O was performed by using micro pump and fed H₂O was

evaporated at the ahead of reactor.

Table 1 summarized the NO decomposition activity on La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.1}M_{0.1}O₃ (M = Ti, Cr, V, Ni, Co, Fe, or Cu) at 1073 K. Since no additional phase was observed on XRD patterns in all doped LBMI oxides and shift in diffraction angle of peaks was also observed, doped metal cation is considered to substitute the lattice position of Mn in LaMnO₃ oxide. It is seen that N₂ or O₂ yield was strongly affected by the dopant for Mn. Activity to NO decomposition on LBMI greatly decreased by doping Ti, Cr, and V. On the other hand, it is seen that N₂ yield greatly improved by doping Fe, Co, Ni, and Cu. In particular, N₂ yield becomes 1.5 times higher than that of nondoped one by doping Cu. Therefore, it is clear that the partial substitution of Mn with Cu is effective for increasing NO decomposition activity. In this study, we investigated the NO decomposition activity on Cu added LBMI.

Figure 1 shows the N₂, O₂, NO₂, N₂O yields on Cu-added LBMI at 1223 K as a function of Cu amount. It is seen that formation of N₂O was hardly observed over all compositions examined. N₂ yield increased with increasing Cu amount and the largest N₂ yield was achieved at the composition from $x = 0.2$ to 0.3 in La_{0.7}Ba_{0.3}Mn_{0.8-x}In_{0.2}Cu_xO₃. Considering the O₂ yield, it can be said that the optimum amount for Cu addition seems to exist at La_{0.7}Ba_{0.3}Mn_{0.6}In_{0.2}Cu_{0.2}O₃ (denoted as LBMICu). It is also noted that NO₂ may be formed in a cool zone after the reactor.

It is reported that coexistence of O₂ and H₂O shows significant interference for NO decomposition^{6,10} and so, NO direct decomposition under coexistence of O₂ and H₂O is highly difficult subject. This is because H₂O and O₂ strongly adsorb on the active site resulting in deactivation of the catalyst. Figure 2 shows the term stability of N₂ and N₂O yield on LBMICu catalyst under coexistence of 5% H₂O and 1% O₂. It is seen that under coexistence of H₂O and O₂, N₂ yield of ca. 50% was stably sus-

Table 1. Effects of M cation in La_{0.7}Ba_{0.3}Mn_{0.2}In_{0.2}M_{0.1}O₃ on NO decomposition at 1073 K

Dopant	Yield%			
	N ₂	O ₂	NO ₂	N ₂ O
none	46.8	19.1	27.7	0
Ti	2.2	0.6	1.6	0
Cr	10.7	0.0	10.7	0
V	25.7	2.3	23.4	0
Ni	58.0	34.9	23.1	0
Co	59.0	38.0	21.0	0
Fe	64.5	44.2	20.4	0
Cu	69.4	42.3	27.1	0

$P_{\text{NO}} = 1\%$, $W/F = 3 \text{ g} \cdot \text{cat. min cm}^{-3}$

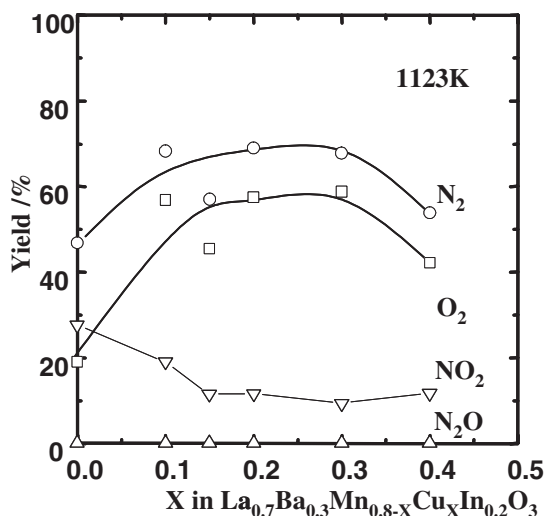


Figure 1. N_2 , O_2 , N_2O yield on Cu added LBMI at 1123 K as a function of Cu amount. ($P_{\text{NO}} = 1\%$, $W/F = 3 \text{ g-cat. min cm}^{-3}$)

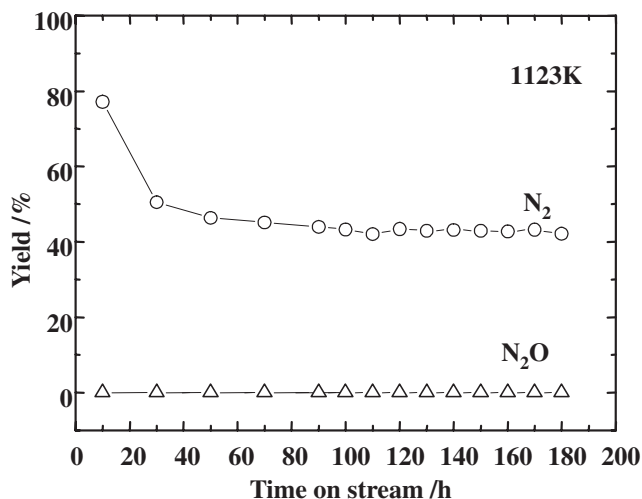


Figure 2. Term stability of N_2 and N_2O yield in NO direct decomposition on LBMICu catalyst under coexistence of H_2O and O_2 . ($P_{\text{NO}} = 1\%$, $P_{\text{O}_2} = 1\%$, $P_{\text{H}_2\text{O}} = 5\%$)

tained over 180 h examined after slight decrease in N_2 yield within the initial 20 h. On the other hand, no formation of N_2O was observed over 180 h examined. Comparing the N_2 yield (ca. 55%) without coexistence of H_2O and O_2 , small decrease in N_2 yield is observed by coexistence of H_2O and O_2 ; however, decrease in NO decomposition activity is not significant and returned to an original level after stopping H_2O . Considering the term stability curves of N_2 yield in Figure 2, it is considered that N_2 yield is stably sustained for further longer period. Therefore, NO direct decomposition can proceed over LBMICu perovskite oxide under coexistence of H_2O and O_2 . Up to now, there is only limited number of catalyst on which NO decomposition proceeds under H_2O and O_2 coexisting atmosphere. Therefore, LBMICu is highly attractive as NO removal catalyst based on direct NO decomposition. One reason for small negative influence of H_2O and O_2 on this catalyst is high reaction temperature.

In the exhaust gas from diesel engines, there is small amount of SO_x contained and large part of catalyst is deactivated under

existence of SO_x .¹¹ Figure 3 shows the N_2 yield at 1123 K as a function of time under coexistence of H_2O , O_2 , and SO_2 . Although the period for term stability test is not long, it is evident that the catalyst is tolerant against SO_x and the stable N_2 yield was sustained over 10 h, while the further decrease in N_2 yield was observed by coexistence of SO_2 . N_2 yield decreased from 55 to 33% in the initial 5 h. SO_x is strongly adsorbed on the active site on LBMICu resulting in the decreased N_2 yield. However, after stopping SO_x co-feed, the N_2 yield was recovered to almost the original level. Therefore, deactivation of catalyst is not permanent and it is considered that SO_x adsorption is not strong at 1123 K on this catalyst. This is also supported by no compound containing sulfur formed during reaction by XRD measurement.

Consequently, this study revealed that Cu-added $\text{La}(\text{Ba})\text{Mn}(\text{In})\text{O}_3$ is highly attractive as NO decomposition catalyst under the actual exhaust gas atmosphere.

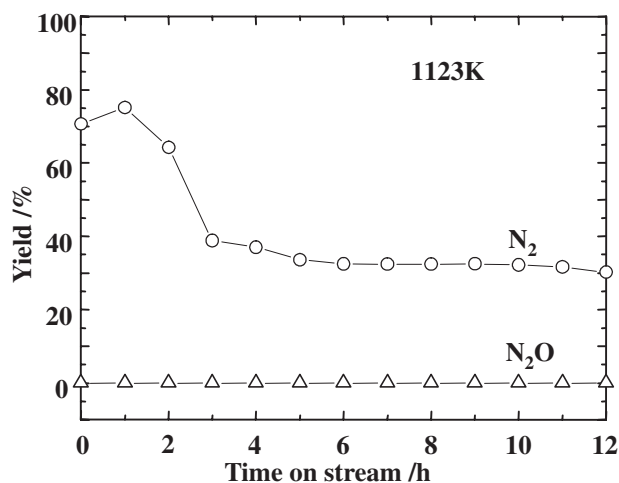


Figure 3. N_2 yield in NO direct decomposition on LBMICu as a function of time under coexistence of H_2O , O_2 , and SO_2 . ($P_{\text{NO}} = 1\%$, $P_{\text{O}_2} = 1\%$, $P_{\text{H}_2\text{O}} = 5\%$, $P_{\text{SO}_2} = 0.0085\%$)

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