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# High-temperature structural change of catalytic MnOx-LaOx-$Al_2O_3$ powder for lean-exhaust NO*x* removal treatment

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Solid-state reaction between compositions and sintering behavior of powders at 600–1100°C were examined by x-ray diffraction, electron spin resonance and surface area measurement. Manganese-alumina catalyst, which was even subjected to heat treatment at 1000°C in air, had the NO removal conversion efficiency of 22% at 350–400°C Structural change and chemical state of alumina-supported manganese catalytic powders were studied for the purpose of the improvement of performance in automotive lean-burn NO*x* removal treatment for a model lean exhaust with high space velocity of 100,000 $h^{-1}$. La-modification of support was effective to maintain high surface area of powder, however it did not lead to the improvement of NO removal activity for manganese-based catalyst.

## 1. Introduction

The exhaust emission of automobile is the serious source of nitrogen oxides (NO*x*) resulting in environmental problem. Among many attempts to reduce NO and other NO*x* species from the exhaust, lean-burn engine is an effective system in recent practical automobiles on both problems of NO*x* removal and the reduction of $CO_2$. However, ordinary three-way catalysts using precious metals are not active enough for NO*x* removal under deep and steady-state lean-burn conditions. Recent lean-burn catalyst has complex composition of elements as well as precise management of engine, which results in high cost of such systems. Many workers and companies have studied alternative catalysts in recent years [1–13]. For example, copper ion-exchanged ZSM-5 zeolite was found by Iwamoto *et al.*, and tried to the application to diesel NO*x* removal [2, 6]. Alumina-based catalyst for NO*x* removal in an excess of oxygen is also a potential material that has first examined by Hamada and coworkers [2–5]. In the development of automotive catalysts, the heat-durability should be essential for practical application to automotive engine systems. The structural stability for active state in solid materials is also an important problem in the developments. In the previous work [14, 15], the performance of Cu-$Al_2O_3$ catalyst was well improved by La-modification of alumina support even after the heat-treatment at 1000°C. In this work, we focus on the alumina-supported manganese (Mn) catalysts for lean-burn NO*x* reduction with respect of high-temperature structural change of materials. We have followed the research of NO*x* removal catalysts using various transition metals, and found that Mn has a unique property of the stabilized redox state between 2+ and 3+. The high-temperature solid-state reaction and the change of Mn species are investigated for heat-treated catalysts. The effect of La-addition for structural stabilization is studied.

## 2. Experimental

For the preparation of Mn-$Al_2O_3$ catalyst, $\gamma$-$Al_2O_3$ powder (surface area 135 $m^2/g$ and purity 99.9%) was impregnated with aqueous manganese nitrate, followed by agitation of the suspension. Powders were dried at 110°C for 8 hours and heated at 500°C for 3 hours in air, and then ground. For Mn-La-$Al_2O_3$, $\gamma$-$Al_2O_3$ powder was impregnated with aqueous lanthanum nitrate, dried and heated at 500°C before the impregnation of manganese that was the same process as for Mn-$Al_2O_3$. The prepared powders (catalysts) were heated at various temperatures up to 1100°C in air in order to examine solid-state reactions. In this study, the fraction of added La and Mn in $Al_2O_3$ was with the molar ratio for $Al_2O_3$ : La : Mn = 100 : 0–10 : 0–10. For the phase analysis of samples after heat treatment at various temperatures, powder X-ray diffraction (XRD) apparatus (Rigaku, Rint2000, Japan) with Cu-K$\alpha$ source (20 kV–30 mA) was used. The surface areas of powders were measured by BET method using nitrogen adsorption at 77 K. Samples were pelletized and pre-heated at 200°C for 3 h in flowing nitrogen before the BET measurement.

Steady-state catalytic performance was tested using gas mixtures with a large space velocity, simulating

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automotive exhaust at fuel-lean condition when air-fuel ratio (A/F) is 18. The typical gas-composition is CO 1000 ppm, $C_3H_6$ 800 ppm, NO 700 ppm, $O_2$ 4%, $CO_2$ 12.7%, $H_2O$ 10% and $N_2$ balance. The samples were pressed into pellets of diameter of ca.1 mm, and set in a quartz tube reactor. 3.5 g catalyst sample was used with total gas flow rate of 7 l/min. Space velocity (S.V.) was ca. 100,000 $h^{-1}$. The analyses of NO and $C_3H_6$ at both the inlet and outlet of a catalyst sample bed were performed using chemiluminescence and flame ionization detectors, respectively. Conversion efficiencies were plotted as a function of inlet-gas temperature measured by a thermocouple.

Electron spin resonance (ESR) spectra of Cu cation (2+) in samples were measured using an ESR spectrometer (JEOL,3MX, Japan) at room temperature in X-band with a modulation frequency of 100 kHz. Pelletized samples were positioned in a quartz tube with 4 mm o.d. −3 mm i.d., and microwave power levels were kept as low as 1mV enough to avoid saturation and distortion of resonance. The g-values were estimated with a DPPH tube near a sample.

## 3. Result and discussion

### 3.1. Solid-state reaction, phase transformation and sintering in Mn-$Al_2O_3$ and Mn-La-$Al_2O_3$

Fig. 1 shows the change of the XRD patterns for Mn(10 mol%)-$Al_2O_3$ heated at temperatures up to 1100°C. For $Al_2O_3$, the initial $\gamma$-type structure gradually transformed to $\delta$-type, further to $\theta$-type, and then $\alpha$-type with increasing temperature. The sequence of structural change of powders via heat treatment at temperatures up to 1100°C (XRD observation) is summarized as following,

$$\begin{aligned}&\gamma\text{-}Al_2O_3 + \beta\text{-}MnO_2\ (500^\circ C)\\&\to \gamma\text{-}Al_2O_3\ (800^\circ C)\\&\to \gamma\text{-}Al_2O_3 + \alpha\text{-}Al_2O_3\ (900^\circ C)\\&\to \alpha\text{-}Al_2O_3\ (1000^\circ C)\\&\to \alpha\text{-}Al_2O_3 + Mn_3O_4\ (1100^\circ C)\end{aligned}$$

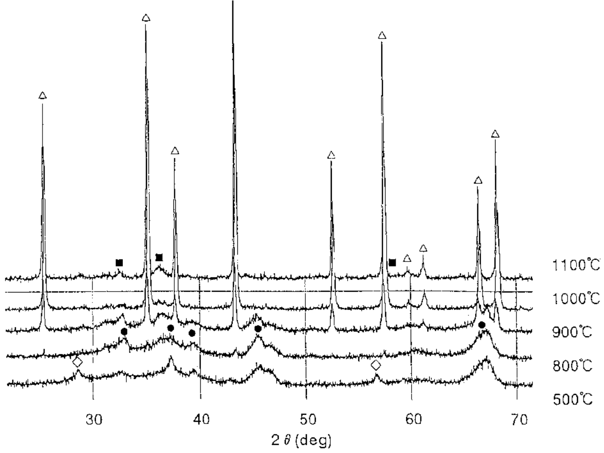

*Figure 1* XRD patterns of 10mol%Mn-$Al_2O_3$ heated at 500–1100°C. ●; $\gamma$-$Al_2O_3$, △; $\theta$-$Al_2O_3$, △; $\alpha$-$Al_2O_3$ ◇; $\beta$-$MnO_2$, ■; $Mn_3O_4$.

The XRD indicates that the solid-state reaction between MnO$x$ (that first phase is $\beta$-$MnO_2$) and $Al_2O_3$ results in a single phase solid solution of $\gamma$-$Al_2O_3$ (with MnO$x$) after heat-treatment below 900°C. The samples heated at 900–1000°C consist of major $\alpha$-$Al_2O_3$ and additional $\gamma$-$Al_2O_3$. They seem to contain a small amount of amorphous MnO$x$ species or MnO$x$-doped $\gamma$-$Al_2O_3$ which is not clearly detected by XRD. At 1100°C, the grown $Mn_3O_4$ particles appear with ca.100nm in crystallite-size.

The effect of La-addition on the stabilization of alumina support itself was examined. As reported by several workers [16–19], La-modification resulted in the prevention of $\alpha$-transformation below 1100°C and the formation of $LaAlO_3$ above 850°C. The surface area of alumina powder after heat-treatment at 1000°C for 3 h in air was improved to be high as 50 $m^2$/g for 5 mol%La-added, 46 $m^2$/g for 10 mol%La-added than 14 $m^2$/g for unmodified aluminas. We selected a support for the catalyst of Mn-La-$Al_2O_3$, because 5 mol%La-alumina was the best with aspect of surface area at 900–1000°C.

Fig. 2 shows the change of the XRD patterns for Mn(10 mol%)-La(5 mol%)-$Al_2O_3$ heated at temperatures up to 1100°C. In Mn-La-$Al_2O_3$, the crystallites of $LaAlO_3$ and $LaMnAl_{11}O_{19}$ formed at elevated temperatures. The sequence of structural change is as following,

$$\begin{aligned}&\gamma\text{-}Al_2O_3\ (500^\circ C) \to \gamma\text{-}Al_2O_3 + LaAlO_3\ (800\text{-}900^\circ C)\\&\to \gamma\text{-}Al_2O_3 + \theta\text{-}Al_2O_3 + LaMnAl_{11}O_{19}\\&\quad + \alpha\text{-}Al_2O_3\ (1000^\circ C)\\&\to LaMnAl_{11}O_{19} + LaAlO_3 + Mn_3O_4\ (1100^\circ C)\end{aligned}$$

The BET surface area was 62 $m^2$/g (heated at 900°C) and 15 $m^2$/g (1000°C) for Mn-$Al_2O_3$, and 81 $m^2$/g (900°C) and 48 $m^2$/g (1000°C) for Mn-La-$Al_2O_3$, respectively. The data indicate the inhibition effect of La-modification on sintering of powder in the temperature range of 900–1000°C. The phenomenon is believed to result from the inhibition of sintering of alumina support itself with La-related oxide layer on the surface or as bulk state [15, 17].

Our previous electron spin resonance study indicated the effect of La-modification on the stabilization of clusters such as MnO$x$($H_2O$)$y$ species in samples

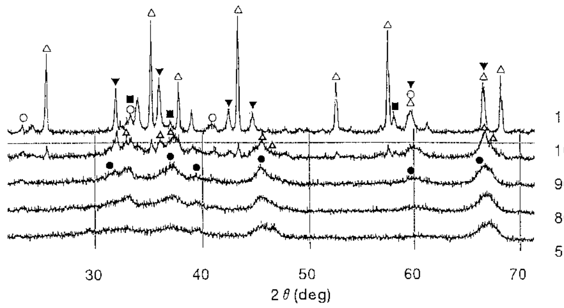

*Figure 2* XRD patterns of 10mol%Mn-5mol%La-$Al_2O_3$ heated at 500–1100°C. ●; $\gamma$-$Al_2O_3$, △; $\theta$-$Al_2O_3$, △; $\alpha$-$Al_2O_3$, ◇; $\beta$-$MnO_2$, ■; $Mn_3O_4$, ○; $LaAlO_3$, ▼; $LaMnAl_{11}O_{19}$.

heated at 600 °C [17]. Crystalline Mn-containing compound was not found after the impregnation followed by heat-treatment at 500°C. After heat-teatment at 800°C, $LaAlO_3$ formed through the reaction between $Al_2O_3$ and LaO$x$ impregrated on the surface. Thus, the initial surface structure (with MnO$x$($H_2O$)$y$ on support) seems to be differently destroyed by the reactions at 800–900°C. In the Mn-$Al_2O_3$ sample, formation of solid solution is supposed. In the La-modified catalyst, LaOx layer should induce complex surface solid-state reaction and compounds resulting in the different property for catalysis from pure MnO$x$-$Al_2O_3$ system. Above 1000°C, the solid state reaction was more complicated, as magnetplumbite-type $LaMnAl_{11}O_{19}$ and $\alpha$-$Al_2O_3$ formed. $LaMnAl_{11}O_{19}$ results from the reaction between $LaAlO_3$, $\gamma$-$Al_2O_3$ and MnO$x$ during heat treatment. This difference on stable Mn-related compounds at 1000°C is evident for the two catalyst powders.

## 3.2. NO removal activity and characterization

Figs 3 and 4 compare the removal conversion efficiencies of NO, CO and $C_3H_6$ at $A/F = 18$ and $S.V. = 100{,}000\ h^{-1}$ for 10 mol% Mn-$Al_2O_3$ and 10 mol% Mn-5 mol% La-$Al_2O_3$ heated at 1000°C in air. The NO removal conversion efficiencies were 22% at 350–400°C for Mn-$Al_2O_3$, whereas below 8% for Mn-La-$Al_2O_3$. The Mn-$Al_2O_3$ catalyst appears to has the nominal selectivity of NO to $C_3H_6$ at the NO removal efficiency of 0-to-25% (in a plot of removal efficiencies of NO vs. $C_3H_6$). The NO removal efficiency has the maximum at 350–400°C and then decreases with increasing temperature. This phenomenon has been observed before previously for copper-zeolite catalysts and others [1–13]. The present activity for the Mn-$Al_2O_3$ catalyst subjected to heat treatment at 1000 °C is comparable to 0.1–0.5 wt%Pt-alumina catalysts prepared at low temperature heat treatment [9], and that of Cu-ZSM-5 subjected to heat condition at 800°C [10]. The relation of NO and $C_3H_6$ conversions vs. temperature for Mn-La-$Al_2O_3$ was different from that for Mn-$Al_2O_3$. The cause for this difference is due to the chemical state of Mn, not to the physical dispersion of the same Mn species. Here we discuss Mn species using electron spin resonance (ESR).

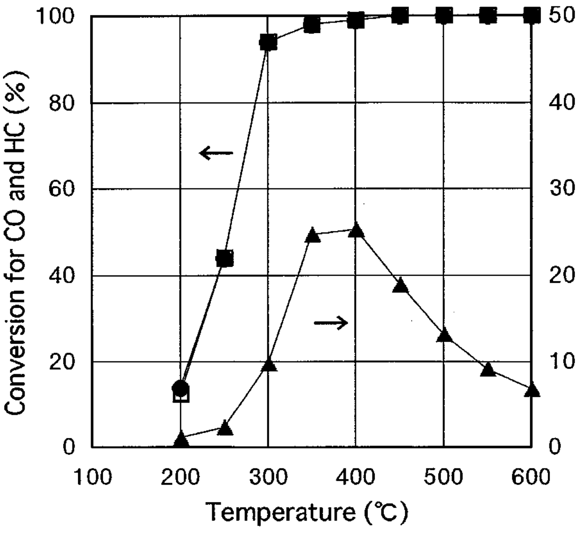

*Figure 3* Removal efficiencies of NO (▲), CO (●) and $C_3H_6$ (□) at A/F = 18 and S.V. = 100,000 $h^{-1}$ over 10 mol%Mn-$Al_2O_3$ heat-treated at 1000°C for 3 h in air.

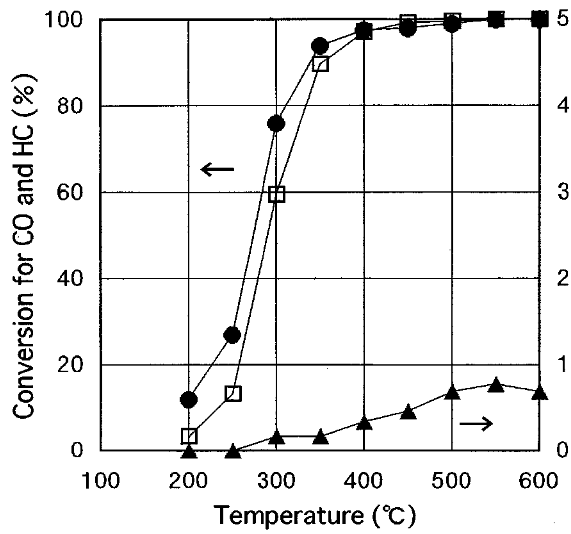

*Figure 4* Removal efficiencies of NO (▲), CO (●) and $C_3H_6$ (□) at A/F = 18 and S.V. = 100,000 $h^{-1}$ over 10 mol%Mn-5mol%La-$Al_2O_3$ heated at 1000°C for 3 h in air.

Figs 5 and 6 show the ESR spectra for the catalysts heated at various temperatures. The ESR for both the samples heated at 500°C showed similar spectra with $g = 2.01$ and hyperfine constant $A = 90$ (spectrum A). It suggests, in the prepared catalysts, the mixture of aggregated and isolated $Mn^{2+}$ cations; the latter is characterized by the open-octahedral coordination with oxygen and hydroxyl group on alumina surface [17]. For the Mn-$Al_2O_3$ system, an initial spectrum A changed to very broad hyperfine structures at 800–900 °C (spectrum B; $g = 2.01$ ; b and c in Fig. 5), and further to another smaller ESR absorption (spectrum C; $g = 2.08$; d in Fig. 5) at 1000°C, and then a very weak spectrum D (e in Fig. 5) at 1100°C. The spectrum B, which has the broad hyperfine structure, is assumed to correspond to $Mn^{2+}$ in defective spinel-type alumina. The spectrum C has a larger g value and smaller amplitude than those of a spectrum B. The XRD indicates only $\alpha$-$Al_2O_3$ in corresponding sample at 1000°C, suggesting no other crystalline phase. The mixed-valent compound $Mn_3O_4$ ($Mn^{2+}Mn_2^{3+}O_4$) forms with $\alpha$-transformation of alumina at 1100°C. Therefore, a part of the ferromagnetic $Mn^{2+}$ may change to ESR-silent $Mn^{3+}$ and form clusters or disordered oxide of Mn at 1000°C. In the other hand, for the Mn-La-$Al_2O_3$ system, the spectrum A changed to broad spectra, E and F ($g = 2.01$; b, c and d in Fig. 6) at 800–1000°C, and G ($g = 2.02$ ; e in Fig. 6) at 1100°C. The peak-to-peak width increased from 380 gauss (b in Fig. 6) to 430 gauss (d in Fig. 6), and was 460 gauss (e in Fig. 6), respectively. These spectra suggest formation of paramagnetic compounds or clustered $Mn^{2+}$-doped in crystalline phase, which are largely different from the initial surface-$Mn^{2+}$ species. The ESR results clearly indicate the different paramagnetic state of Mn cations for the Mn-$Al_2O_3$ and Mn-La-$Al_2O_3$ catalysts heated at 1000°C. After heat treatment at 1000°C,

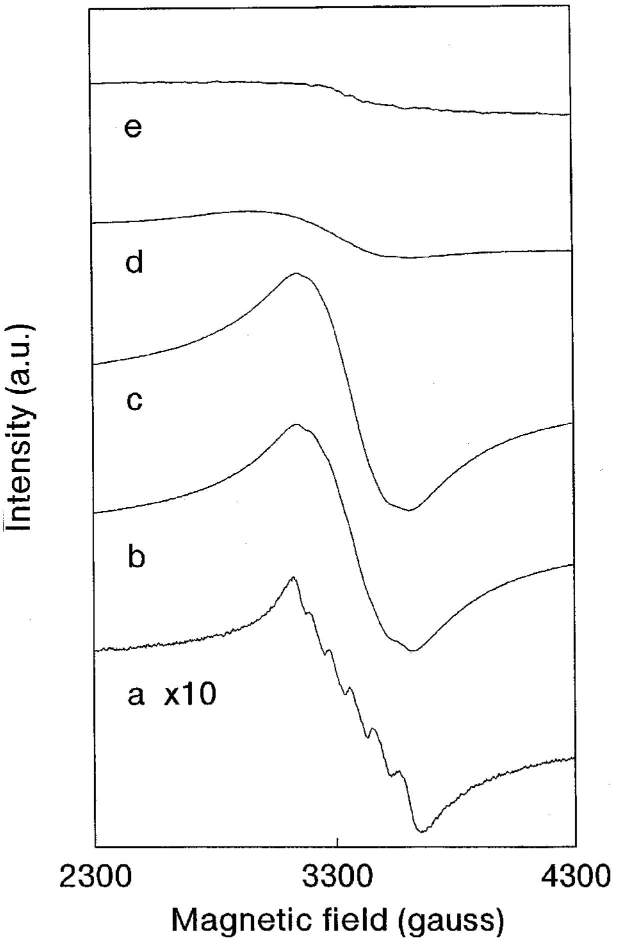

*Figure 5* ESR spectra for 10 mol%Mn-$Al_2O_3$ heated at various temperatures. a; 500°C, b; 800°C, c; 900°C, d; 1000°C, e; 1100°C.

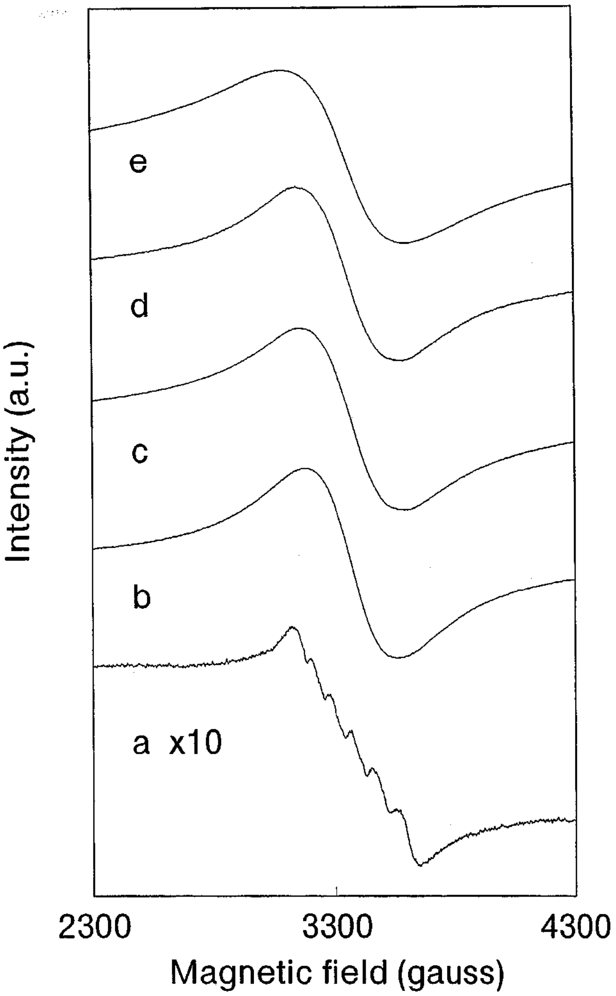

*Figure 6* ESR spectra for 10 mol%Mn-5mol%La-$Al_2O_3$ heated at various temperatures. a; 500°C, b; 800°C, c; 900°C, d; 1000°C, e; 1100°C.

the spectra of Mn-$Al_2O_3$ suggest the formation of ESR-silent Mn species such as $Mn^{3+}$ or precipitation of oxide cluster. It is reported that the addition of $Mn_2O_3$ to ZSM-5 accelerates the conversion of NO to $NO_2$ which should be selectively reduced with hydrocarbons [20]. Thus, new species of Mn, formed at 1000°C, is important for NO removal catalysis over Mn-$Al_2O_3$. Although Vannie *et al.* [21] have discussed the NO adsorption on $Mn_2O_3$ and $Mn_3O_4$ below 650 K, unfortunately we have no data of adsorption comparable to heir discussion.

Other factor is the dispersed LaO*x* itself as a base on solid surface that influences the adsorption of NO at moderate temperatures. It has been reported [22–25] that performance of $La_2O_3/\gamma$ -$Al_2O_3$ for selective reduction of NO*x* is better than Co-ZSM zeolite catalyst that at higher temperature, for example at 700°C. If $La_2O_3$ remained in samples after heat treatment, the tendency for removal efficiency versus temperature below 600°C should be explained by the effect of LaO*x* itself. However, actually major Mn-La-related compound at 1000°C was crystalline $LaMnAl_{11}O_{19}$. Thus, the possible catalytic compound in the Mn-La-$Al_2O_3$ sample is $LaMnAl_{11}O_{19}$ or $LaAlO_3$ (doped with Mn). Here, increasing efficiency for NO with increasing temperature is a feature that was found in perovskite-type oxide catalyst such as $LaMnO_3$ [15, 16]. The solid state reaction should result in the different catalytic performance which relation is shown in a plot of the NO conversion vs. temperature; one of them (without La) has a maximum, and the other one (with La) does the increasing conversion with increasing temperature. Those oxides show an interesting feature for NO*x* reduction, as oxygen defect in lattice is evolved with reaction of gaseous species. However, this effect should result in relatively lower reaction-rate for catalysis than that of reaction between gases absorbed on surface of catalyst, because the diffusion of oxygen controls whole rate of reaction. Since lean burn catalysts have often been used under the condition of as high space velocity as 100,000 $h^{-1}$, well-dispersed metal cations seem to be better for de-NO*x* catalysis as shown in this case. Despite the inhibition of surface area loss at elevated temperatures, La-addition to Mn-$Al_2O_3$ system forms complex oxides between MnO*x*, LaO*x*, and $Al_2O_3$ after heat treatment, resulting in lower activity for NO removal for high velocity lean-burn exhaust. Thus, our results suggest that simply Mn-modified alumina has better potential as NO*x* removal catalyst with heat durability, if it is used under heat environment below 1000°C.

## 4. Summary

Alumina-supported manganese oxides were studied for the purpose of heat-stable automotive lean-burn NO*x* removal catalyst. Mn-$Al_2O_3$ catalyst, which was heat-treated at 1000°C in air, showed the NO removal conversion efficiency of 22% at 350–400°C for a model exhaust with S.V. $= 100{,}000$ $h^{-1}$. The result suggests that Mn-modified alumina is a potential NO$x$ removal catalyst having heat durability. The La-modification to alumina was not effective to the improvement of activities, although surface-area decrease was inhibited.

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