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De-NO_x characteristics of a combined system of LNT and SCR catalysts according to hydrothermal aging and sulfur poisoning

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ABSTRACT

This paper aims to evaluate the de-NO_x performance of a combined system of LNT + SCR catalysts according to the durability of hydrothermal aging and sulfur poisoning. NO_x conversion, NH_3 production, and N_2O emission from the LNT and the combined system of LNT and SCR were evaluated according to the conditions of hydrothermal aging (750–900 °C) and sulfur poisoning (1.0–1.48 g/L). Regarding the NO_x-TPD characteristics, it was found that the amount of NO_x desorption decreased due to hydrothermal aging and sulfur poisoning. The NO_x conversion of the combined system of LNT and SCR (aged at 750 °C and 900 °C) was 10–30% higher than that of the LNT system. During this time, the maximum $(NH_3)_{produced}/(H_2)_{inlet}$ ratio of the LNT catalyst was 0.81%, which the produced NH_3 reacted with NO_x as a reductant at the downstream SCR catalyst. These characteristics are some merits that compensate the reduction in catalyst activity due to hydrothermal aging. The NO_x conversion of the 1.48 g/L sulfur-poisoned LNT + SCR system was 20% lower after poisoning than before poisoning, and the NO_x conversion of the LNT + SCR system did not recover due to excessive sulfur poisoning even after desulfation. The N_2O emission of the hydrothermally aged catalyst was small because the NO_x quantity stored on the LNT was reduced. The combined system of LNT and SCR catalysts had the merit of compensating the de-NO_x performance, and reducing the NH_3 slip and the N_2O emission, even though the catalysts were aged hydrothermally.

1. Introduction

Regulations on both mobile and stationary sources of exhaust emissions have become progressively stringent in recent years as the problems of environmental pollution are considerably worsening due to rapid industrialization. Exhaust emission standards for vehicles have become particularly stricter. Recently, the European Union (EU) published the EuroVI regulation, setting the limit of 10 ppm of ammonia for the European Transient and European Steady-State Cycles [1]. As diesel engines have good fuel economy with low CO_2 emissions, their market shares of commercial vehicles as well as passenger cars are increasing [2]. However, because of the intrinsic nature of diesel combustion, nitrogen oxides (NO_x) are generated in the localized high-temperature reaction zones, and particulate matters (PM) are formed in the diffusive combustion zones.

In order to reduce these harmful emissions, several technologies are being implemented. Currently, there are two main aftertreatment technologies under consideration that potentially comply with such strict limits: NH_3/urea-SCR (Selective Catalytic Reduction) for lager diesel engines [3], and the LNT (Lena NO_x Trap), which is used with direct injection gasoline and small diesel engines [4,5].

Urea-SCR is the most effective among these techniques, and is employed mainly to reduce NO_x in the case of heavy-duty diesel (HDD) engines [5–7]. The aqueous urea solution that is injected in the hot exhaust stream generates NH_3 through the reactions of H_2O decomposition, thermal urea decomposition, and hydrolysis. Nitrate, sulfate, and solid cyanic acid ($HNCO_3$) are often generated in this process [4,5,7]. The SCR system, which uses ion-exchanged Fe or Cu-zeolite without precious metal, faces some critical barriers to its catalytic performance such as poor NO_x conversion at low temperatures and ammonia slip. LNT, based on a three-way catalyst for gasoline engines, has emerged as a solution to reduce NO_x from lean-burn gasoline engines. Since diesel engines are operated only under lean conditions, the NO_x emitted under these conditions has to be adsorbed on the adsorbent (Ba, K) [2,8] before being reduced by the reductants (CO, HC, and H_2) that are generated during short rich operations of the engine [9–11]. Several groups have already evaluated the performance of a combined system of LNT + SCR with light-duty diesel engines [12–16]. In these studies, the LNT

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Table 1
Specifications of the LNT and SCR catalysts.

Catalyst	Components	Relative weights (wt%)	BET (m^2/g)	Mean pore size (nm)
LNT	Pt/Pd/Rh/Ba/Ce/Zr	3.3/0.72/0.31/12.58/7.97/4.49	36.15	11.824
SCR	Fe-(Si/Ai)zeolite	1.82-(11)	121.00	2.23

catalyst was reported to not only remove NO_x but also produce some NH_3 during rich operation [13,16]. The NH_3 formed by the LNT was then utilized by the downstream SCR catalyst to reduce NO_x in the exhaust gas [13,16]. Although the system is somewhat complicated, it may provide a way of lowering NO_x emissions with negligible NH_3 slip. The system cost potentially can be lowered by reducing the amount of precious metals in the LNT, thereby eliminating the NH_3 oxidation catalysts. In order to overcome the regulation of 10 ppm of NH_3, the combined system of LNT and SCR has to be actively researched much more. While the combined system of LNT and SCR can provide improved de-NO_x performance relative to the LNT alone, the system is still sensitive to thermal aging and sulfur poisoning [4,5]. Previous studies focused on the effects of the running mileage on the de-NO_x performance of either the LNT catalyst or the SCR catalyst [12,14]. However, in these studies, the temperature of the catalysts was under 800 °C, even though the exhaust temperature reaches 900 °C in severe engine operating condition. Further, some researchers have reported the effects of sulfur poisoning and the desulfation temperature on the de-NO_x performance of the combined system of LNT and SCR [12,14–16]. However, they have not examined the characteristics of extreme sulfur concentrations and by-products such as nitrous oxide (N_2O) in the combined system. N_2O is known to have a global warming potential that is 310 times that of CO_2. Therefore, not only the study of the NH_3 slip but that of the N_2O slip also is very important in the combined system of LNT and SCR catalysts.

This paper aims to evaluate the de-NO_x performance of the combined system of LNT and SCR catalysts according to the durability of hydrothermal aging and sulfur poisoning. The basic characteristics of NO_x adsorption and desorption according to the thermal or sulfur aging of the LNT catalyst are evaluated. NO_x conversion, NH_3 production, and N_2O emission from the LNT catalyst and the combined system of LNT and SCR catalysts also are evaluated according to the conditions of hydrothermal aging (750–900 °C) and sulfur poisoning (1.0–1.48 g/L).

2. Experimental details

2.1. Catalysts and characterization

The catalysts (LNT and SCR) used in this experiment are fully formulated monolithic catalysts for automobiles. The suppliers cannot be identified for protecting their confidentiality. The Brunauer–Emmett–Teller (BET) surface area and mean pore size of the catalysts were measured by N_2 adsorption at 77 K through a BET analyzer (Micromeritics, ASAP-2020). The precious metals and alumina molar ratios of the catalysts were determined by an X-ray microanalyzer with a 15 kV electron beam (Shimadzu, EPMA-1600). Table 1 shows the analytical results for the catalysts. The LNT catalyst (600 cpsi), which was a precious-metal combination of Pt/Pd/Rh (3.3/0.7/0.3) (wt%), was supported over Ba-γ-Al_2O_3. Fe-zeolite was used as the SCR catalyst (400 cpsi); the Fe content was 1.8 wt% and that of Si/Al was 11:1.

2.2. Experimental apparatus

Catalytic tests of the combined system of LNT and SCR catalysts were performed using the monolithic type in a fixed-bed-flow reactor system [2]. It was composed of a gas-supply component, a catalyst reaction component, an NH_3/urea injection component, an analyzer, and a control device, as shown in Fig. 1. The total flow rate of the model gas was 2 L/min. The water content was adjusted to 1.5% by the saturated water vapor pressure. The range of H_2O emissions of a diesel engine is about 1.4–7%. However, the H_2O band of an FTIR-analyzer easily overlaps with NO, NO_2, H_2S and COS, therefore, the H_2O concentration was reduced to 1.5 vol.%. The temperatures of the LNT and SCR catalysts were controlled through an electric furnace that was installed separately. A quartz reaction tube with an inner diameter of 19 mm and length of 350 mm was used as the catalyst reactor. The catalyst temperature was measured by fixing a K-type thermocouple ($\varphi = 0.5$ mm) at the center of the catalyst bed. The gas composition after the catalytic reaction was measured at intervals of 4.5 s using an FTIR (Midac, I2000) that was equipped with a gas cell with a path length of 4 m.

2.3. Measurement of the NO_x adsorption and desorption

The LNT catalyst was treated for 30 min under 10% H_2 at a flow rate for 500 mL/min at 500 °C. Subsequently, after refreshing for 30 min under a nitrogen atmosphere at 500 °C, reaction experiments were carried out. The experimental conditions for NO_x adsorption were carried out at a catalyst temperature of 300 °C, NO of 500 ppm, and O_2 of 10% concentration with N_2 balance. NO_x-TPD (Temperature Programmed Desorption) experiments were conducted under a heating rate of 4 °C/min after NO_x was sufficiently adsorbed at the temperature of 300 °C, and the catalyst was flushed under the nitrogen atmosphere. NO_x for TPD test was measured by FTIR analyzer in real time interval of 4.5 s. The capacity of NO_x adsorption was calculated by the capacity of NO_x adsorbed per unit geometric volume of the catalyst (mol/L).

2.4. Evaluation of the de-NO_x performance

The NO_x conversion of the combined system of LNT and SCR (catalyst temperature of 150–600 °C; transient mode; heating rate of 4 °C/min) was investigated under the situation where the lean condition was maintained for 55 s. Then, the reductant (CO 3% + H_2 1.3%) was spiked for 5 s. The NO_x conversion was calculated by Eq. (1).

$$NO_x\,\text{conversion} = \left[1 - \frac{\int (NO_x)_{\text{out}}\,dt}{\int (NO_x)_{\text{in}}\,dt}\right] \times 100\,(\%) \tag{1}$$

In Eq. (1), $(NO_x)_{\text{in}}$ is NO_x concentration at the inlet of the catalyst and $(NO_x)_{\text{out}}$ is NO_x concentration at the outlet of the catalyst. Table 2 shows the basic components of the model gas for the combined system of LNT + SCR catalysts. From the evaluation of de-NO_x performance, the NH_3 ratio was represented by the percentage of produced NH_3 on the basis of supplied hydrogen concentration to the LNT as in Eq. (2).

$$NH_3\,\text{ratio} = \frac{(NH_3)_{\text{produced}}}{(H_2)_{\text{inlet}}} \times 100\,(\%) \tag{2}$$

In Eq. (2), $(NH_3)_{\text{produced}}$ is the concentration of NH_3 from the outlet of the LNT or SCR and $(H_2)_{\text{inlet}}$ is the concentration of supplied hydrogen to the LNT.

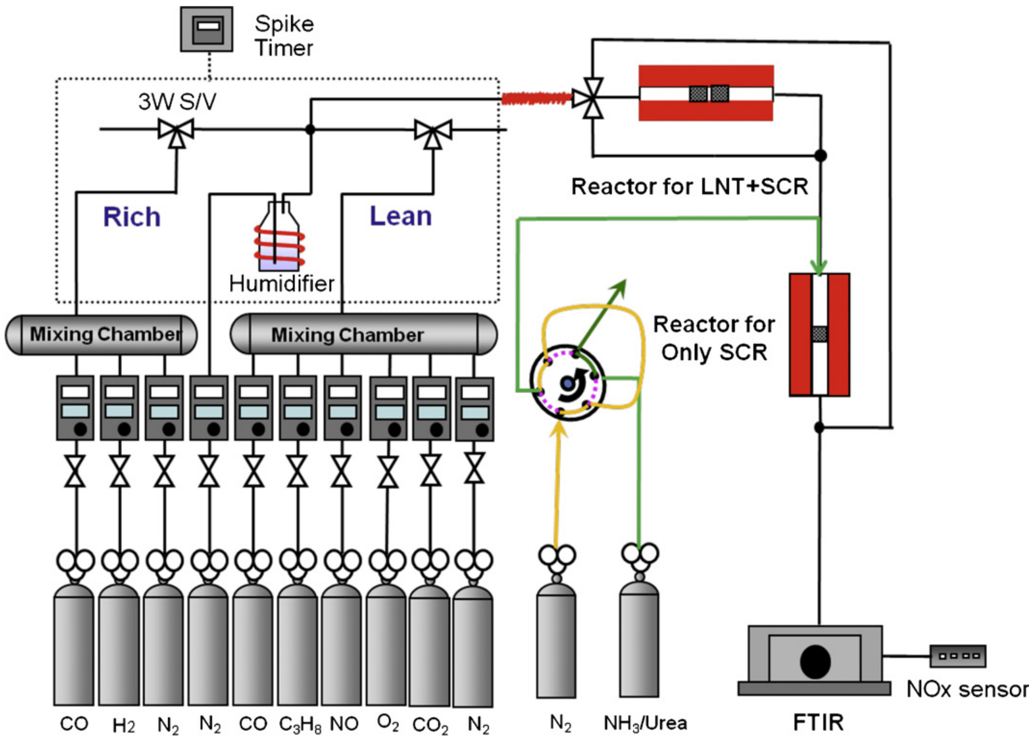

Fig. 1. Schematic diagram of the combined system of LNT and SCR.

2.5. *Hydrothermal aging and sulfur poisoning*

The combined system of LNT and SCR catalysts was conducted the hydrothermal aging supplying air (2 L/min) passing through a humidifier with 10% saturated vapor pressure into an electric furnace at 750 °C or 900 °C mode during some cycles as shown in Fig. 2.

In the sulfur-aging test, the LNT catalyst was exposed to the conditions of SO_2 of 56 ppm, O_2 of 10%, and N_2 balance at 350 °C for 30 min [1.0 g (sulfur weight)/L (catalyst volume)] and 60 min (1.48 g/L), respectively. During the desulfation, a reductant of 1% H_2 at a flow rate of 2 L/min was continuously supplied for 30 min for maintaining the temperature of the reaction tube at 700 °C.

3. Results and discussion

3.1. *NO_x adsorption and desorption on the LNT catalyst*

The LNT catalyst typically contains precious metals (Pt and Rh) and an alkali or alkaline earth metal source component (BaO) that is supported on a high surface area metal oxide. Under lean exhaust conditions, NO is oxidized to NO_2 over the precious metal sites in the catalyst and reversibly stored as nitrates or nitrites on the storage material. The stored NO_x species are subsequently released and reduced to N_2 during short periodic excursion to rich (i.e., net reducing) conditions [10,17,18].

Table 2
Model gas components for evaluating the combined system of LNT and SCR.

Gas components	Lean	Rich
O_2 (%)	10	0
C_3H_8 (ppmC_1)	450	0
CO (ppm)	500	30,000
NO (ppm)	500	0
CO_2 (ppm)	50,000	0
H_2 (%)	0	13,000
H_2O (%)	1.5	1.5
N_2	Balance	Balance
λ	1.5	0.89
SV (1/h)	28,000	28,000

Fig. 3 shows the adsorption characteristics of the LNT catalyst that is aged hydrothermally and sulfur-poisoned at the conditions of NO 500 ppm, O_2 10%, and N_2 balance (SV = 28,000 1/h). For a fresh catalyst, the saturation condition was reached at 1620 s; at this time, the adsorption capacity was 0.0689 mol/L. Hydrothermally aged catalysts, aged at 750 °C or 900 °C mode for 2 cycles, reached saturation after 535 and 345 s, respectively. This is because of changes in the structure of the Pt catalyst and washcoat sintering due to hydrothermal aging, as a result of which the fine catalyst crystallites are unstable and grow bigger. As shown in Fig. 4, under excessive hydrothermal ageing of the catalyst at 900 °C, prominent agglomeration of Ba sites as well as Pt agglomeration could be observed. During this time, the BET surfaces of (a) the fresh catalyst, (b) aged catalyst (2 cycles at 750 °C mode) and (c) aged

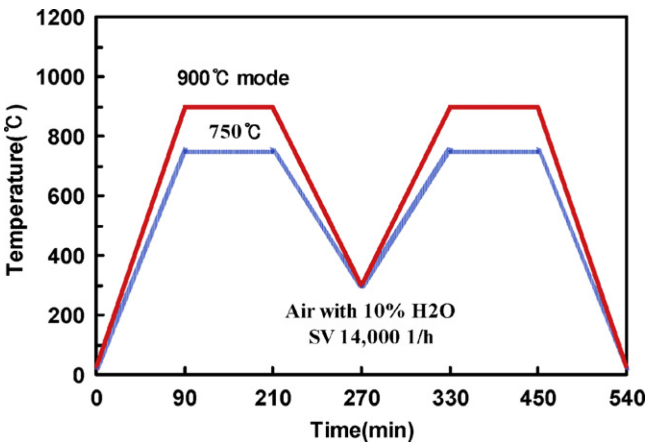

Fig. 2. Hydrothermal aging mode of the combined system of LNT and SCR.

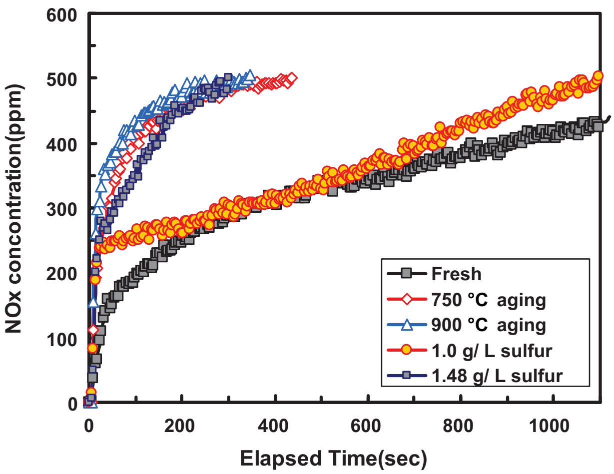

Fig. 3. NO_x adsorption characteristics of the LNT catalyst according to hydrothermal aging and sulfur poisoning (catalyst temperature of 300 °C, NO of 500 ppm, and O_2 of 10%).

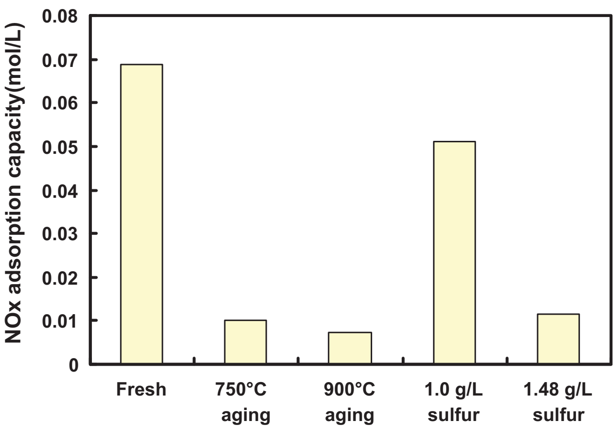

Fig. 5. NO_x adsorption capacity of the LNT catalyst according to hydrothermal aging and sulfur poisoning.

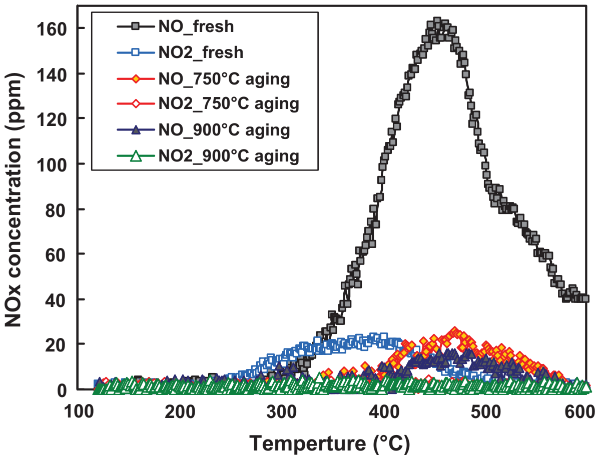

Fig. 6. NO_x-TPD of the LNT catalyst according to hydrothermal aging (under heating rate of 4 °C/min).

catalyst (2 cycles at 900 °C mode) were 38, 32, and 21 m^2/g, respectively. The 1.0 g/L sulfur-poisoned catalyst reached saturation after 1102 s, showing a NO_x adsorption capacity of 0.0510 mol/L. Besides, the 1.48 g/L sulfur-poisoned catalyst reached saturation after 365 s (0.0098 mol/L adsorption). Ba is a metallic alkaline earth metal, having large adsorption stability for sulfates, which are more acidic than nitrates. Nonetheless, the 1.48 g/L sulfur-poisoned catalyst formed barium sulfate ($BaSO_4$) with the adsorption sites; thus, the NO_x adsorption capacity was reduced.

Fig. 5 shows the NO_x adsorption capacity according to the hydrothermally aged and sulfur-poisoned LNT catalysts. The NO_x adsorption capacities of the hydrothermally aged catalysts, aged at 750 °C or 900 °C mode for 2 cycles, represented 14.8% and 10.6%, respectively, of the fresh catalyst. The NO_x conversions of the 1.0 g/L and 1.48 g/L sulfur-poisoned LNT catalysts were 74.1% and 16.7%, respectively, of the fresh catalyst. The NO_x adsorption capacities were sharply decreased by the hydrothermal aging or sulfur poisoning, which would affect the NO_x conversion over the LNT catalyst.

Fig. 6 illustrates the NO_x-TPD results of the LNT catalyst according to hydrothermal aging. For the fresh catalysts, NO_2 that is formed by NO oxidation over the Pt sites adsorbs onto the BaO sites of the catalyst [10,20]. It was found that NO was desorbed at a peak of about 460 °C. Also, about 20 ppm of NO_2 was desorbed at 400 °C starting from about 260 °C (The quantity of the desorbed NO_x is 0.0347 mol/L). That is, the adsorbed nitrates on the Al_2O_3 surface of the LNT catalyst decomposed and desorbed. The NO_2 in the hydrothermally aged catalysts, aged 2 cycles at 750 °C or 900 °C

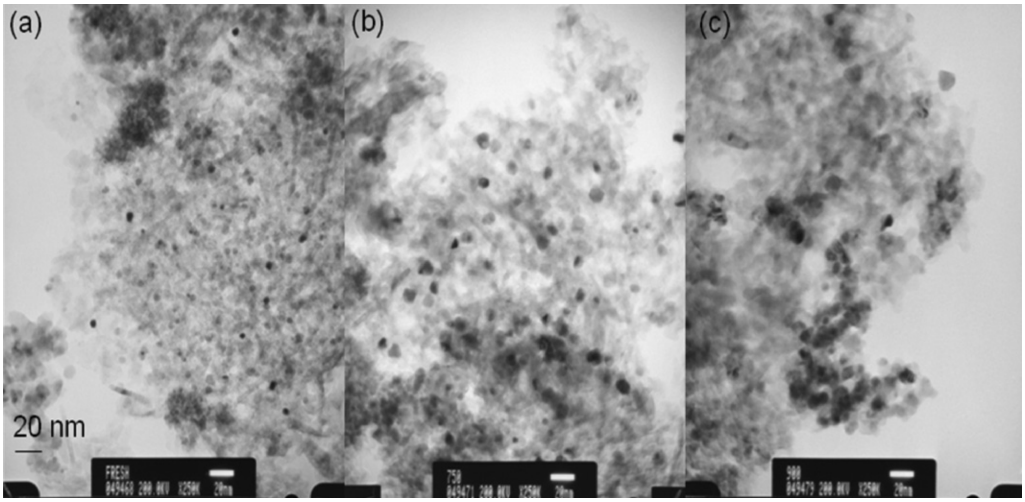

Fig. 4. TEM image for fresh and aged catalysts ((a) fresh (b) 750 °C aging(c) 900 °C aging (×250 K)).

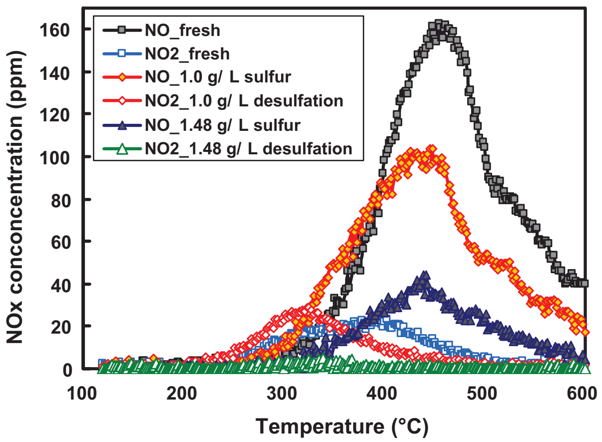

Fig. 7. NO_x-TPD of the LNT catalyst according to sulfur poisoning (under heating rate of 4 °C/min).

mode, was not desorbed because of the low storage capacity of the NO_x (see Fig. 5) and the sintering of the BaO, γ-Al_2O_3 [22]. For the catalyst aged 2 cycles at 900 °C mode, NO was desorbed slightly at 460 °C, because the storage capacity of NO_x was reduced by the particle growth of the Ba sites.

Fig. 7 represents the NO_x-TPD of the LNT catalyst with sulfur poisoning. The conditions of sulfur poisoning were 1.0 g/L and 1.48 g/L. NO desorption over the sulfur-poisoned catalyst commenced from a lower temperature than that for the fresh catalyst, and the desorption peak appeared at around 450 °C. For the 1.0 g/L sulfur-poisoned catalyst, the peak regarding NO desorption appeared at 105 ppm at 450 °C. NO_2 desorption commenced from 240 °C, which was lower than that for the fresh catalyst; the peak of the desorbed NO_2 appeared at 310 °C, and the concentration was 24 ppm. For the 1.48 g/L sulfur-poisoned catalyst, the quantity of NO desorption decreased compared with the case of 1.0 g/L sulfur poisoning or fresh catalyst. Also, NO_2 did not appear due to excessive sulfur poisoning. That was because aluminum sulfate $(Al_2SO_4)_3$ was generated on the γ-Al_2O_3 surface of the LNT catalyst due to sulfur poisoning, plugging the micro-pores that were able to absorb NO_x [21].

3.2. NH_3 generation on the LNT catalyst

The limited NO_x conversion of the LNT catalyst at low temperatures is an issue for many diesel-engine applications. A more cost-effective way to improve the low-temperature performance of the LNT can be achieved by placing an SCR catalyst downstream of the LNT catalyst. In this case, the generative mechanism of NH_3 on the LNT catalyst is very important for understanding the combined system of LNT and SCR. We will illustrate the effect of the hydrothermal aging and sulfur poisoning of the LNT catalyst on the production of NH_3, that appears by the percentage of the produced-NH_3 on the basis of hydrogen concentration at the inlet of the LNT catalyst.

Fig. 8 shows the effect of the sulfur poisoning of the LNT catalyst on the production of NH_3. The LNT catalyst under 1.0 g/L sulfur poisoning produced NH_3 that the NH_3 ratio was 0.05% or less. And in case of desulfated this LNT catalyst, the NH_3 ratio was 0.37% at 250 °C. The deactivation of Pt because of sulfur poisoning reduced the NH_3 selectivity, but the NH_3 generation was promoted by the reactivation of Pt. The NH_3 emission from the desulfated LNT will be useful to improve the NO_x conversion at the downstream SCR catalyst.

Fig. 9 shows the mechanism of generating NH_3 as an intermediate product during the reduction reaction of the nitrate $(NO_3)_2$ stored in the Ba site on the LNT catalyst when H_2 is supplied as the reductant. The low dispersion of the Pt catalyst with the growth of particles exhibited low activity, and the NO_x conversion reduced, during this time, much more NH_3 was generated. The intermediate product of NH_3 is formed due to the reduction of the adsorbed NO_x species, according to the stoichiometry of the following global reaction of Eq. (3). Also, the formed NH_3 reacts with the adsorbed NO_x to yield N_2, as shown in Eq. (4) [4,8,16,19].

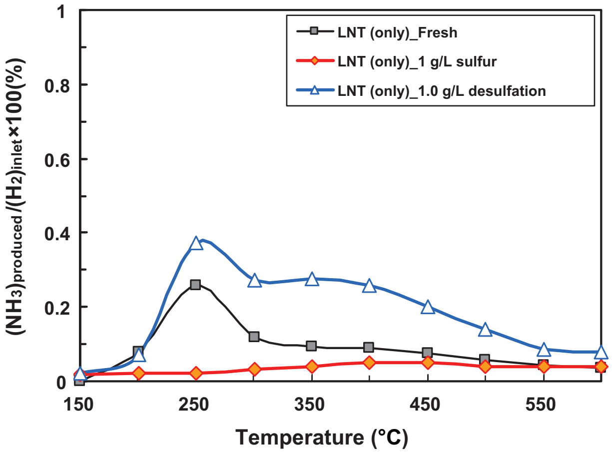

Fig. 8. The effect of the sulfur poisoning of the LNT catalyst on the production of NH_3 (transient mode: under heating rate of 4 °C/min).

$$Ba(NO_3)_2 + 8H_2 \rightarrow 2NH_3 + BaO + 5H_2O \quad (3)$$

$$Ba(NO_3)_2 + 10NH_3 \rightarrow 8N_2 + 3BaO + 15H_2O \quad (4)$$

3.3. Effect of hydrothermal aging on the de-NO_x performance of the combined system of LNT + SCR

The combined system of LNT and SCR was simultaneously hydrothermally aged at the condition of H_2O 5% at the temperatures of 750 °C and 900 °C in order to investigate its activity and durability. The overall space velocity (SV) of the combined system of LNT and SCR catalysts was 14,000 1/h. The temperature of 900 °C is an extreme exposure condition in realistic diesel-engine operating conditions. Fig. 10(a) shows the NO_x conversion according to the temperature of the hydrothermally aged LNT catalyst and the combined system of LNT + SCR. Regarding the fresh catalyst, the NO_x conversion of the combined system was about 15% higher than that of the LNT catalyst alone at temperatures below 450 °C. As shown in Fig. 10(b), NH_3 could form on the LNT catalyst; therefore, the NH_3 ratio of the fresh LNT catalyst was 0.27%. The NH_3 emitted from

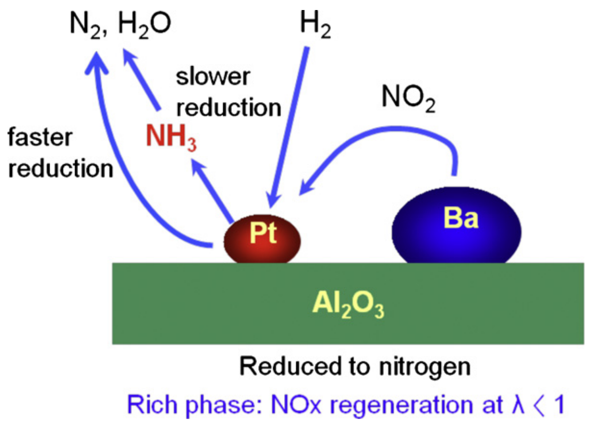

Fig. 9. Mechanism of NH_3 generation of the LNT catalyst.

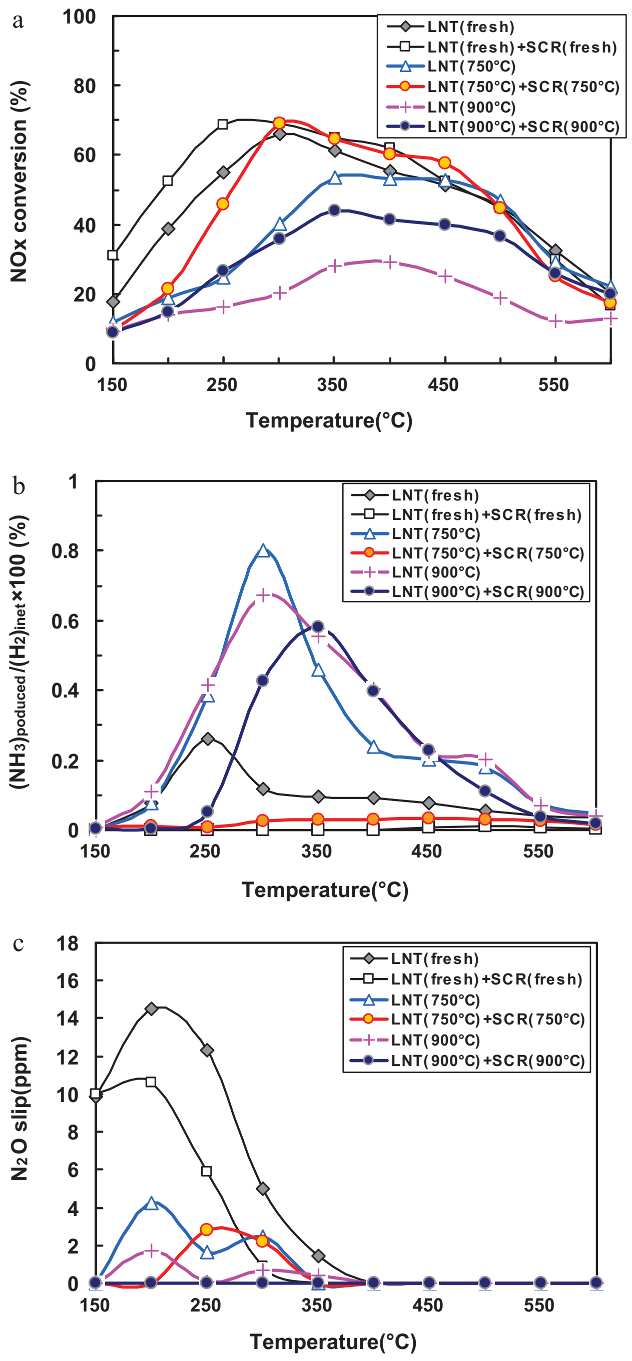

Fig. 10. Effect of hydrothermal aging on the NO_x conversion and NH_3 and N_2O production of the combined system of LNT + SCR (transient mode: under heating rate of 4 °C/min): (a) NO_x conversion, (b) NH_3 ratio, (c) N_2O slip.

the LNT catalyst should serve as a reactant for the downstream SCR catalyst.

As compared to the fresh LNT catalyst, the NO_x conversion of the LNT catalyst aged at 750 °C showed a 10–30% reduction at temperatures of 400 °C or lower due to the decreased adsorption capacity of NO_x (as seen in Fig. 4), and the NO_x conversion window shifted to higher temperatures. The NO_x conversion of the combined system (aged at 750 °C) was 10–30% higher than that of the LNT catalyst (aged at 750 °C). Especially, the NO_x conversion over 300 °C was almost the same as that of the fresh combined system of LNT and SCR catalysts. It can be seen from Fig. 10(b) that the NH_3 ratio of the LNT catalyst (aged at 750 °C) was 0.81%, because the hydrothermally aged catalyst caused a reduction in the adsorption and reaction sites of the LNT catalyst. Further, the generated NH_3, as a reductant, reacted with NO_x at the downstream SCR catalyst.

The aging condition of 900 °C especially should be an extreme condition for the LNT catalyst; therefore, the maximum NO_x conversion reached only 30% at 375 °C. Casapu et al. observed the formation of $BaAl_2O_4$ and $BaCeO_3$ on the LNT catalyst at around 850 °C [24]. However, the combined system (aged at 900 °C) showed the maximum NO_x conversion of 40% at 350 °C. The system contributed to the maximum improvement of 20% in the NO_x conversion as compared to the LNT catalyst (aged at 900 °C). That is, with progressive hydrothermal aging, the precious metal Pt particles grow to reduce the reaction activity of the catalysts. This phenomenon is because the generative capacity of NH_3 increases. From Fig. 10(b), the combined system aged at 900 °C could be seen to emit a maximum 0.6% of the NH_3 ratio at 350 °C. The emitted NH_3 acted as a reductant for the downstream SCR catalyst. This characteristic has the important feature of compensating the reduction in catalyst performance according to hydrothermal aging that causes the deactivation of the de-NO_x catalyst. The range of the temperature for actual use of the combined system of LNT and SCR catalysts should be 750–900 °C.

As shown in Fig. 10(c), the N_2O slip of the fresh LNT catalyst and the combined system of LNT and SCR were maximums of 14 and 11 ppm, respectively, at 200 °C. In the case of the fresh LNT catalyst, the adsorption capacity of NO_x was very large (as seen in Fig. 4); therefore, N_2O of higher concentration formed due to the reaction between the adsorbed NO_x and H_2 on the LNT catalyst. However, the N_2O emissions of the catalysts aged at 750 or 900 °C °C were small due to the reduction in the NO_x capacity stored of the LNT catalysts. The combined system has the advantage of compensating the de-NO_x performance, and reducing the NH_3 slip and the N_2O slip, even though the catalysts are aged hydrothermally.

The characteristics of hydrothermal aging of the SCR catalyst alone have been reported in the literature [23]. According to the results, the NO_x conversion of the SCR catalyst drastically dropped after a hydrothermal aging process during which the catalyst temperature was maintained 2 cycles at 900 °C.

3.4. Effect of sulfur poisoning on the de-NO_x performance of the combined system of LNT + SCR

The durability of the combined system of LNT and SCR catalysts was evaluated against that of the fresh catalyst and against those of the 1.0 g/L and 1.48 g/L sulfur-poisoned and desulfated catalysts. During desulfation, the sulfur might have changed to H_2S or COS [20,22,25–27], which could not have been detected by FTIR analyzer because of the overlapping H_2O band [23].

Fig. 11(a) shows a reduction of 4–20% in the NO_x conversion below 350 °C for the 1.0 g/L sulfur-poisoned catalyst in the combined system of LNT and SCR, and especially shows a prominent reduction in the NO_x conversion at 200 °C. The reasons for the performance degradation of sulfur-poisoned catalysts are a reduction in the NO_x storage capacity (as seen in Figs. 2 and 4) and the deactivation of Pt due to the poisoning of SO_4 at the Ba sites of the LNT catalysts. Following desulfation, the NO_x conversion of the 1.0 g/L sulfur-poisoned catalyst in the combined system of LNT and SCR catalysts reverted to the same value as that before the poisoning. However, the NO_x conversion of the 1.48 g/L sulfur-poisoned catalyst in the combined system of LNT and SCR catalysts was 20% lower after the poisoning than it was before the poisoning, and the NO_x conversion of the combined system of LNT and SCR catalysts did not recover due to excessive sulfur poisoning even after desulfation. The recovery or non-recovery of the NO_x

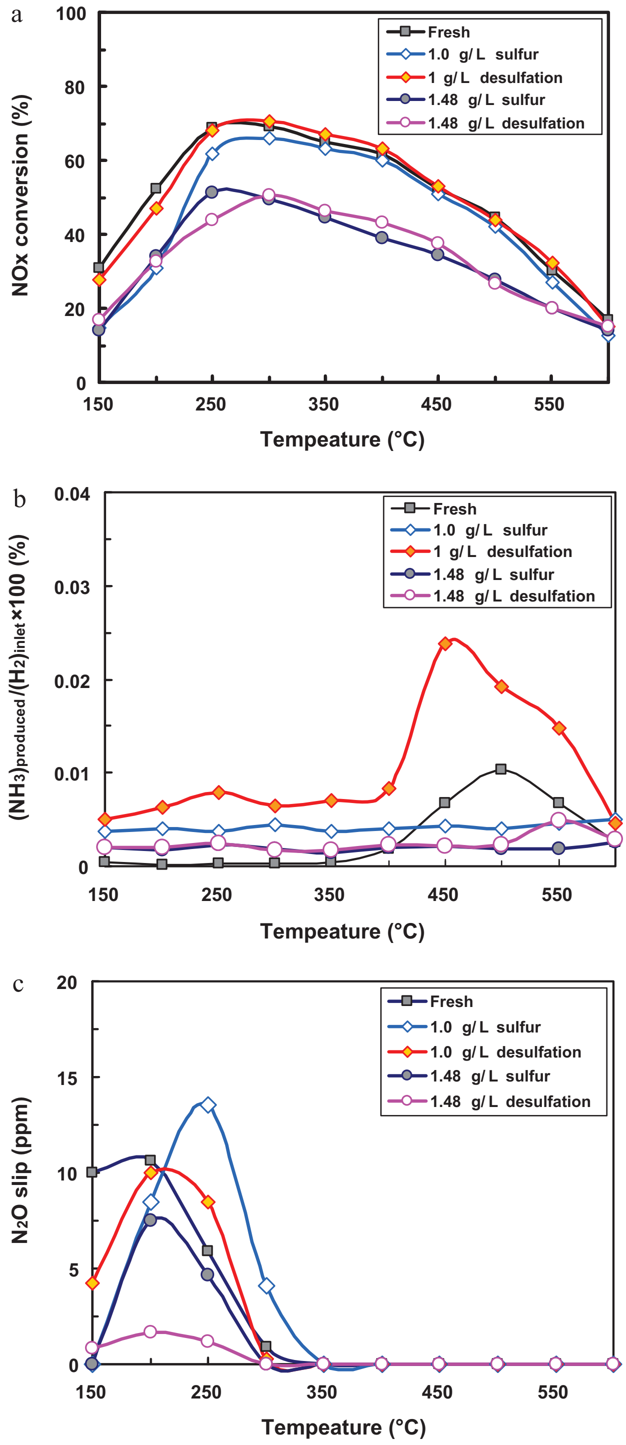

Fig. 11. Effect of the sulfur poisoning of the combined system of LNT + SCR on NO_x conversion, and NH_3 and N_2O production: (transient mode: under heating rate of 4 °C/min): (a) NO_x conversion, (b) NH_3 ratio, (c) N_2O slip.

conversion can be illustrated by the NH_3 generation, as seen in Fig. 7.

Fig. 11(b) shows the NH_3 emission capacities of the sulfur-poisoned catalysts depending on the catalyst temperature. The 1.0 g/L and 1.48 g/L sulfur-poisoned catalysts emitted lower concentrations of NH_3 due to Pt deactivation, and the 1.0 g/L desulfated catalyst emitted NH_3, therefore the NH_3 ratio was below 0.02% at 400 °C or higher temperatures due to Pt reactivity.

Fig. 11(c) shows the N_2O slip of the sulfur-poisoned catalysts. The N_2O slip under the 1.0 g/L sulfur-poisoned catalyst increased during the reduction reactions of nitrates at 250 °C. The 1.48 g/L sulfur-poisoned catalyst generated the least N_2O due to excessive sulfur poisoning. During this time, the surface should have changed from Ba sites to those of $BaSO_4$ [24]. The N_2O slip decreased in the case of excessive sulfur poisoning compared to the case of the fresh catalyst.

4. Conclusions

This research has shown the durability characteristics of hydrothermal aging and sulfur poisoning of the combined system of LNT and SCR. The NO_x adsorption capacity was decreased due to hydrothermal aging and sulfur poisoning. Regarding the NO_x-TPD characteristics, it was found that the quantity of NO_x desorption decreased due to hydrothermal aging and sulfur poisoning. The NO_x conversion over the combined system of LNT and SCR (aged at 750 °C and 900 °C) was 10–30% higher than that of the LNT system; during this time, the maximum $(NH_3)_{produced}/(H_2)_{inlet}$ ratio of the LNT catalyst was 0.81%, which the produced NH_3 reacted with NO_x as a reductant at the downstream SCR catalyst. The characteristics have the important feature of compensating the reduction in the catalyst performance according to hydrothermal aging that causes deactivation of the catalyst. The NO_x conversion of the 1.48 g/L sulfur-poisoned catalyst in the combined system of LNT and SCR was 20% lower after the poisoning than before the poisoning, and the NO_x conversion of the combined system of LNT and SCR did not recover due to excessive sulfur poisoning even after desulfation. The N_2O emissions of the catalysts aged at 750 or 900 °C were small due to the reduction in the stored NO_x capacity of the LNT catalysts. The combined system of LNT and SCR has the merit of compensating the de-NO_x performance, and reducing the NH_3 slip and the N_2O emission, even though the catalysts are aged hydrothermally. The N_2O slip decreased in the case of excessive sulfur poisoning compared to the case of the fresh catalyst.

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