Characteristics of Adsorption, Desorption of Exhaust Gases and Deactivation of LNT and SCR Catalysts for Diesel Vehicles
디젤 자동차용 LNT, SCR 촉매의 배출가스 흡착, 탈리 및 열화 특성

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요약 : 이 논문에서는 디젤자동차용 LNT와 SCR 촉매의 NO, NH₃ 흡착 및 탈리의 기본 특성과 수열화 온도와 시간 및 정량화된 황피독 농도에 대한 de-NOx 촉매의 내구성을 평가하였다. LNT 촉매는 열적으로 열화됨에 따라 Pt 및 Ba의 소결 및 응집으로 활성이 떨어져 NOx 전환율은 감소하였다. 반면에 Pt의 비활성화로 중간생성물인 NH₃ 생성량은 증가하였으며, 이때 생성된 NH₃는 LNT+SCR 복합시스템의 SCR 촉매의 환원제 역할을 담당한다. 1.0 g/L 이상의 황이 피독된 LNT 촉매는 탈황을 하여도 질소 산화물 흡장물질(Ba)의 성능이 회복이 되지 않아 NOx 전환율은 회복되지 않았으며, 탈황 후 Pt 재활성화로 인해 NO2 및 SCR 환원제인 NH₃ 생성량은 증가하였다. SCR 촉매의 NOx 전환율은 700℃ 36h, 800℃ 24h로 수열화 시킨 촉매는 전이금속 입자 성장 및 zeolite 구조 파괴로 인하여 급격하게 떨어졌으며, 0.36 g/L 황 피독된 촉매는 zeolite가 가지는 강산성 특징으로 내피독성이 강하여 탈황시 NOx 전환율은 회복되었다.

1. Introduction

Regulations on mobile and stationary sources of the exhaust emissions have become progressively stringent in the recent years as consequential problems of the environment pollution are considerably worsening due to the rapid industrialization. The exhaust emissions standards for vehicles have become particularly stricter. As diesel engines have high power and good fuel economy with low CO_2 emissions, their market share is increasing in the sectors of commercial vehicle as well as passenger cars[1].

Because of the intrinsic nature of the diesel combustion, however, 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.

Typical ways of reducing NO_x emissions are urea-SCR, which dispenses urea as reducing agent; Lean NO_x Catalyst(LNC), which uses hydrocarbon(HC) as reductant; and LNT(Lean NO_x Trap[2,3]. The urea-SCR is the most effective one among these techniques, and it is employed mainly to reduce NO_x on heavy-duty diesel(HDD) engines. The SCR[4] techique, which uses ion-exchanged non-precious metal(Fe, Cu)[5,6]as such problems as poor NO_x conversion at low temperatures, ammonia slip, need for urea refill, and the urea freezing in cold water. LNT based on the three-way catalyst for gasoline engines, has emerged as a solution to reduce NO_x from

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the lean-burn gasoline engines. Since diesel operates only under lean conditions, NO_x emission under these conditions have to be adsorbed on the adsorbent(Ba, K)[2] before being reduced by reductants(CO, HC, H_2, etc) that are generated during short rich operation of the engine. These studies were carried out on engine test benches, where it is difficult to investigate the detailed mechanism of NH_3 production and the parameters influential to the NH_3 production and/or to the subsequent NO_x reduction.

The present study was carried out to investigate characteristics of the adsorption, desorption and hydrothermal aging, and sulfur poisoning of LNT and SCR catalysts for diesel vehicles.

2. Experimental Setup and Method

To identify the fundamental characteristics of NO_x in the combined system of LNT and SCR, a model gas catalytic reactor system was used. It was composed of a gas-supply 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 temperature of the LNT and SCR catalysts were controlled through an electric furnace that was separately installed. A quartz reaction tube with an inner diameter of 19mm and length of 350mm was used as the catalyst reactor. The catalyst temperature was measured by fixing a K-type thermocouple($\Phi=0.5$mm) at the center of the catalyst system. The gas composition after the catalytic reaction was measured both quantitatively and qualitatively every 4.5 seconds using an FTIR(Midac, I2000) that was equipped with a gas shell that had a path length of 4m. Table 1 shows the analytical results for the catalysts. The characterization of the catalysts were analyzed by a transmission electron microscopy (TEM, JEM-2000FX2, Jeol).
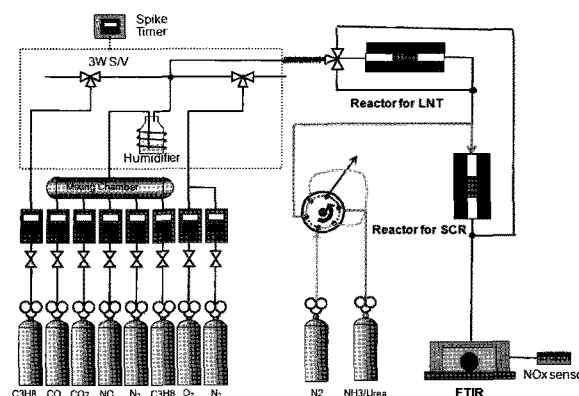

Fig. 1 Schematic of the combined system of LNT+SCR

Table 1 Specification of the LNT and SCR catalysts

Catalyst	Components(wt%)
LNT	Ba/γ-Al$_2$O$_3$, Pt/Pd/Rh(3.3/0.72/0.31)
SCR	Fe- [Si/Ai]zeolite(1.85-[ratio:11])

3. Experimental results and discussion

3.1 Adsorption and desorption characteristics of LNT and SCR catalysts

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[7~9]. The basic characteristics of the adsorption and desorption of the LNT catalyst were investigated.

Fig. 2 shows the NO-adsorption characteristics of the catalyst under a lean condition(NO 500ppm+O_2 10%+N_2 bal, SV 28,000 1/h). Most of the initial NO was adsorbed on the LNT catalyst and the NO_x adsorption almost saturated at 1200 sec. By this time, the conversion of NO to NO_2 was about 25%. The oxidized NO_2 was gradually

stored on the Ba in the form of $Ba(NO_3)_2$ through the Pt catalyst. NO_x storage capacity of the LNT catalyst at 200℃ reached saturation(0.099 mol/L) in about 1200s.

Fig. 3 displays the results of the NO_x-TPD experiments. The NO_2 desorbed below 300℃. This is the adsorbed nitrates on the Al_2O_3 surface of the LNT catalyst decomposed and desorbed. The NO desorption peaks appeared at 330℃ and 480℃. NO peaks desorbed at catalyst temperature 330℃ is to physical adsorption by Van-der-Walls force between BaO and nitrates gas[10]. The chemically adsorbed nitrates on the BaO site (bulk) as an ion state were decomposed, and NO was desorbed at a peak of about 480℃[11].

The SCR catalyst adsorbs NH_3 as a reductant on the acid sites of the surface, and then distribution of the catalyst acid sites can determine the reduction reactivity of NO_x.

Fig. 4 and Fig. 5 show the adsorption and desorption characteristics of NH_3 on the SCR catalyst according to the catalyst temperature. From Fig 4, it is clear that as the catalyst temperature increases, the capacity for NH_3 adsorption decreases. Fig. 5 shows the results of NH_3 desorption according to the catalyst temperature. In the case fo NH_3-TPD at 120℃, desorption peaks of NH_3 appeared at 170℃ and 330℃, showing that NH_3 tends to be strongly adsorbed on the catalyst by physical or chemical adsorption. The desorption capacity of NH_3 at 120℃ was much greater than those at 200℃ and 350℃.
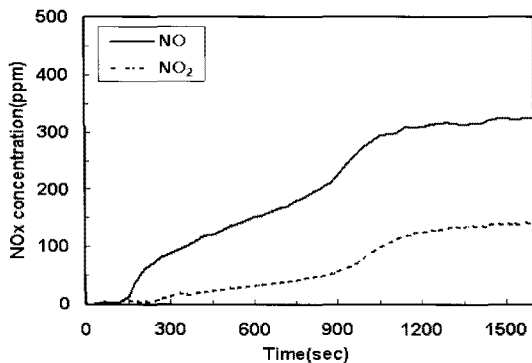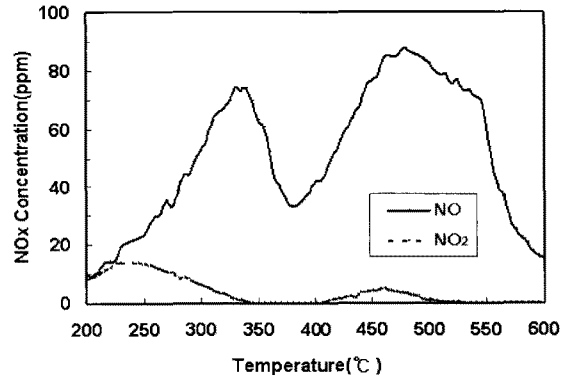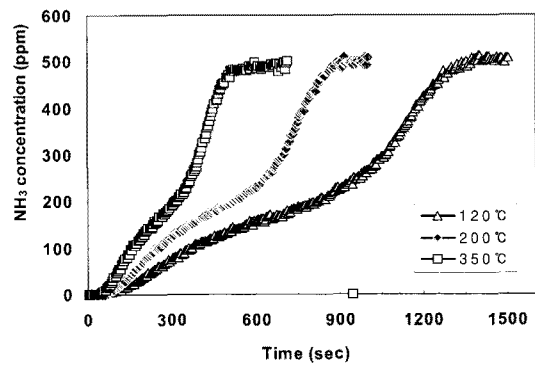

Fig. 3 NO_x-TPD profile

Fig. 4 NH_3 adsorption characteristics of the SCR catalyst under various catalyst temperatures
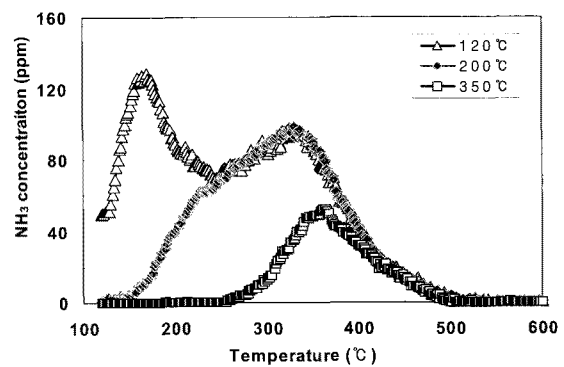

Fig. 5 Variation of the NH_3 desorption characteristics with the temperature which increase at 4℃/min

3.2 Hydrothermal aging and sulfur poisoning

There are many ways in which catalysts deactivate; of those, thermal degradation and sulfur poisoning were considered in this study.

Fig. 6 shows the dependence of the NO_x

Fig. 2 NO_x adsorption on the LNT catalyst at 200℃

conversion and NH_3 formation on the H_2 concentration of the reductant and hydrothermal aging temperature under NO 500ppm+O_2 10%+CO 500ppm+C_3H_8 150ppm+CO_2 5%+H_2O 1.5%. The NO_x conversions under H_2 2% as the reductant were higher than those under H_2 1%. Even though the reductant H_2 concentrations vary, as the hydrothermal aging temperature increase, the NO_x conversion decrease. In contrast, NH_3 formation increases as the hydrothermal aging temperature increases. 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. 7, under excessive hydrothermal aging of the catalyst at 900°C, the prominent agglomeration of Ba sites as well as Pt agglomeration could be observed.

Fig. 8 shows the NO_x conversion of the LNT catalyst with 0.5 g/L and 1 g/L of sulfur poisoning under a fast reaction(NO 250ppm+NO_2 250ppm+O_2 10%+CO 500ppm+C_3H_8 150ppm+CO_2 5%+H_2O 1.5%). The NO_x conversion of the 0.5 g/L sulfur-poisoned catalyst recovered to the state of the fresh catalyst through desulfation (maked in the figure as D/S). Even though the 1.0 g/L sulfur-poisoning catalyst was treated by desulfation, it did not recover.
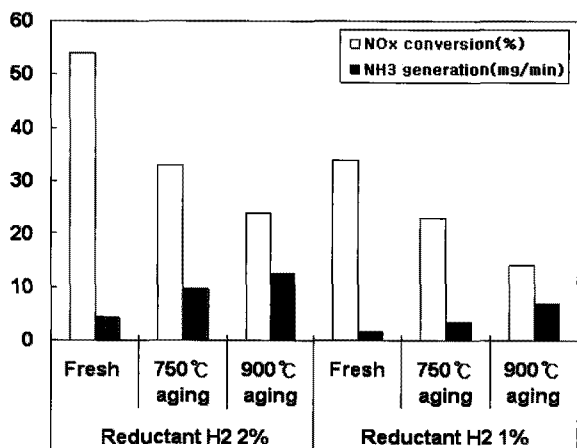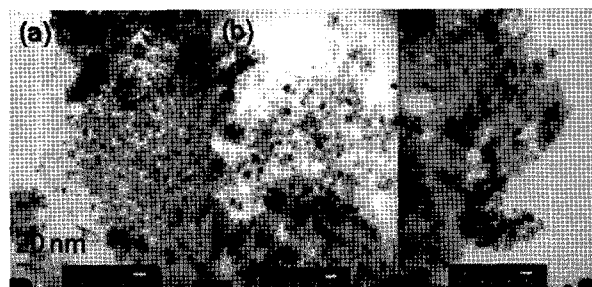

Fig. 7 TEM image for fresh and aged catalysts [(a) fresh (b) 750°C aging (c) 900°C aging (×250K)]
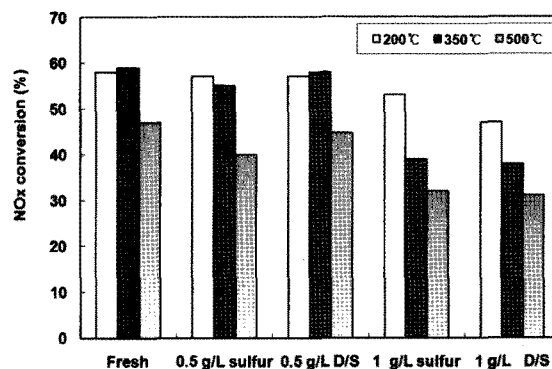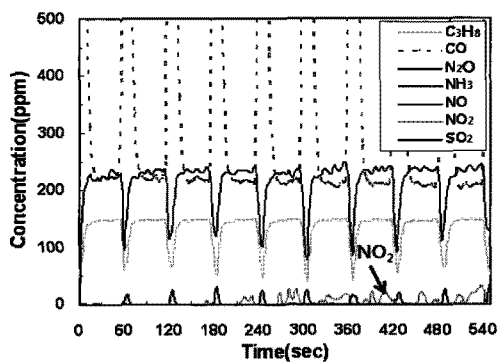

Fig. 8 NO_x conversion of LNT with 0.5 and 1 g/L sulfur poisoning under a fast reaction (CO 2%+H_2 1%)

(a) Sulfated catalyst(1 g/L sulfur)

(b) Desulfated catalyst

Fig. 6 The NO_x conversion and NH_3 formation under a hydrothermally aged LNT catalyst at 350°C under a standard reaction
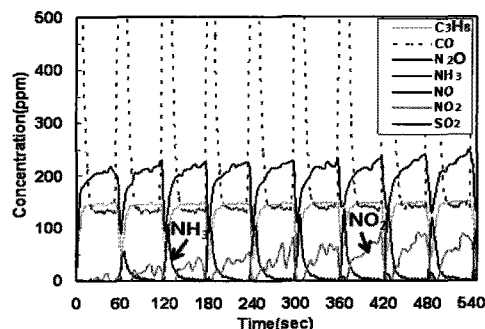
Fig. 9. Reaction behavior of exhaust emission on sulfated and desulfated LNT catalyst at 200°C: reduct(CO 2%+H_2 1%)
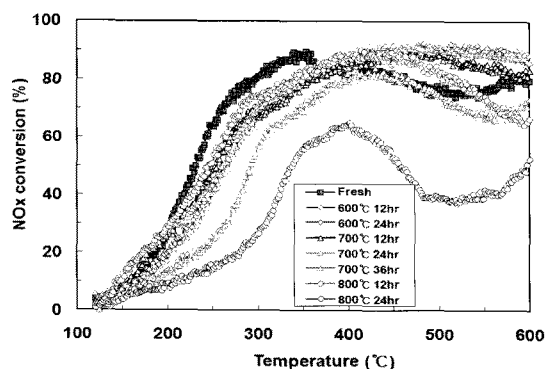
Fig. 10 NO$_x$ conversion of the SCR catalyst for rapid hydrothermal aging

Fig. 9 shows the standard reaction characteristics of exhaust emissions over the LNT catalyst during the condition poisoning under 1 g/L sulfur. Fig 9(a) shows that a small amount of NO$_2$ is produced under the sulfated catalyst due to Pt poisoning. Also, the CO conversion in the lean condition was about 59%. NH$_3$ was not produced over the sulfated catalyst. Fig. 9(b) shows the NO$_2$ concentration increased and CO conversion also increased to 77% in the context of a desulfated catalyst. NH$_3$ of 21 mg/min was produced with Pt reactivity in the rich condition by desulfation. This NH$_3$ was able to act as a reducing agent for the SCR catalyst in the combined system of LNT+SCR.

Fig. 10 shows the NO$_x$ conversion of a SCR catalyst according to the transient mode after treating by the fast hydrothermal mode(NO 500ppm+NH$_3$ 500ppm+O$_2$ 10%+H$_2$O 1.5%). For hydrothermal conditions of 600℃ and 700℃ for 12 h and 24 h, the NO$_x$ conversion decreased more than for fresh catalyst at temperatures below 35 0℃. On the contrary, at high temperatures of more than 350℃, the NO$_x$ reduction rate was higher than for the fresh catalyst. It is well known that mildly dealuminated SCR catalyst can result in a slight increase in the volume of micro-pores and accessibility to strong acid sites[12~13]. However, the NO$_x$ conversion of the SCR catalyst drastically dropped after a hydrothermal aging process during which the catalyst temperature was maintained at 700℃ for

36 h and at 800℃ for 24 h.

Fig. 11 shows the TEM images of fresh and aged SCR catalysts. For fresh SCR catalyst, the zeolite particles show a prototype phases, and the small amount of Fe existing as Fe$_2$O$_3$ is well dispersed to be difficult to identify.

Fig. 11 TEM image for fresh and aged catalysts [(a) fresh (b) 700℃ 36 h aging (c) 800℃ 24 h aging (×100K)]
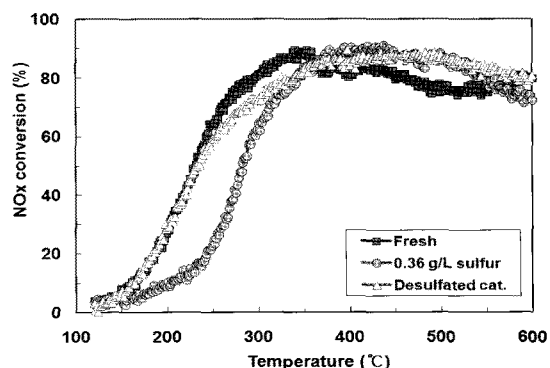

Fig. 12 NO$_x$ conversion of SCR catalyst with 0.36 g/L sulfur poisoning under a standard reaction

The particle growth and shape change of zeolite appear as it is aged for 24h at 800℃. Especially, the black particles observed on the edge of zeolite are judged to be Fe$_2$O$_3$ generated through the growth of small particles. Particle growth leads to the deactivation of catalysts eventually, so the performance in NO$_x$ conversion rate reduces.

Fig. 12 depicts the NO$_x$ conversion regarding sulfur poisoning of the SCR catalyst. In this case, the SCR catalyst was poisoned by about 0.36 g/L sulfur. The NO$_x$ conversion decreased by about 40% at temperature below 350℃ compared to the case of fresh catalyst. The deactivation due to

sulfur poisoning could be attributed to the blocking and/or filling of catalyst pores by deactivating agent[14]. The SCR catalysts was desulfated by 1% of H_2 at a flow rate of 2 liters for 30 minutes at 700℃. After desulfation, the NO_x conversion recovered to close to the values under fresh catalyst because of the strong acid sites of the SCR catalyst.

5. Conclusions

The present study was carried out to investigate the characteristics of the adsorption, desorption and hydrothermal aging, sulfur poisoning of LNT and SCR catalyst. NO_x storage capacity of the LNT catalyst at 200℃ reached saturation(0.099 mol/L) in about 1200s. NH_3 storage capacity of SCR catalyst decreases as the catalyst temperature increases. As the LNT gets deactivated through thermal aging, NH_3 formation increases as the hydrothermal aging temperature increases. Sulfur poisoning over 1.0 g/L was not recovered to values under fresh catalyst. NO_2 and NH_3 as a reducing agent for SCR catalyst of the combined system of LNT+SCR increased due to Pt activity after desulfurization. The NO_x conversion of the SCR catalyst drastically dropped after a hydrothemal aging process during the temperature maintaining period of 36 hours at 700 degC and 24 hours at 800 degC. After desulfurization over 0.36 g/L sulfur poisoning of SCR catalyst, the NO_x conversion recovered to close to the values under fresh catalyst.

Acknowledgement

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