

The Effects of Sulfur Poisoning and Desulfation Temperature on the NO_x Conversion of LNT+SCR Systems for Diesel Applications

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ABSTRACT

A laboratory study was performed to assess the effects of sulfur poisoning and desulfation temperature on the NO_x conversion of a LNT+(Cu/SCR) in-situ system. Four LNT+(Cu/SCR) systems were aged for 4.5 hours without sulfur at 600, 700, 750, and 800°C using A/F ratio modulations to represent 23K miles of desulfations at different temperatures. NO_x conversion tests were performed on the LNT alone and on the LNT+SCR system using a 60 s lean/5 s rich cycle. The catalysts were then sulfur poisoned at 400°C and desulfated four times and re-evaluated on the 60/5 tests. This test sequence was repeated 3 more times to represent 100K miles of desulfations. After simulating 23K miles of desulfations, the Cu-based SCR catalysts improved the NO_x conversion of the LNT at low temperatures (e.g., 300°C), although the benefit decreased as the desulfation temperature increased from 600°C to 800°C. During the poisonings and desulfations, the SCR catalyst was effective at converting H₂S and COS produced by the LNT back into SO₂. After simulating 47K miles of desulfations, the benefit of the SCR catalyst for NO_x conversion on the 60/5 test was minimal, regardless of the aging temperature. However, the rich purge time was increased to 6 seconds after simulating 73K and 100K miles, and the benefit of the SCR catalyst for low temperature NO_x conversion was observed again for all four desulfation temperatures. These results suggested that, as the LNT+SCR system ages on a vehicle, the rich purge time may need to be increased to maintain the benefit of the SCR catalyst for low temperature NO_x conversion. This can be attributed to a decrease in the purge kinetics of the LNT with thermal aging. The optimal desulfation temperature for this LNT+SCR system was 750°C, as lower temperatures resulted in incomplete desulfations and consequently lower NO_x

conversions at high temperatures, while 800°C desulfations resulted in thermal degradation.

INTRODUCTION

A lean NO_x trap (LNT) can be used to treat the NO_x emissions from diesel engines and lean-burn gasoline engines. NO_x traps function by storing NO_x during lean periods which can last on the order of 30 to 300 seconds, depending on the flow rate, NO_x concentration, and exhaust temperature. The traps then reduce the stored NO_x to N₂ during periodic rich periods which typically last on the order of 2 to 5 seconds [1]. The LNT contains relatively high loadings of precious metal [i.e., platinum (Pt) and rhodium (Rh), optionally palladium (Pd)] and also contains high concentrations of alkaline-earth metals (e.g., barium, magnesium) and/or alkali metals (e.g., cesium, potassium, sodium); these materials serve as NO_x storage materials by reacting with NO_x under lean conditions to form stable nitrates. NO_x traps can also contain high concentrations of oxygen storage (OSC) materials such as cerium oxide, which can provide several benefits including improved thermal durability, improved sulfur tolerance, and better NO_x conversion at low temperatures but at the expense of requiring longer purges [2].

NO_x traps function best in a range or “window” of temperature that varies with the composition, precious metal loading, and aging condition but is typically between 300 and 500°C. Below 300°C, the kinetics of NO oxidation and incomplete purging limit how much NO_x can be stored. Also, during the rich purges at low temperatures (e.g., 250°C), some of the stored NO_x can be released from the LNT without being reduced to N₂ due to slow rates of NO_x

reduction; this phenomenon is referred to as “purge NO_x release” [3]. Another issue at low temperatures is that some of the stored NO_x can be released from the LNT as ammonia (NH₃). At temperatures above 500°C, the decreasing stability of the nitrates limits how much NO_x can be stored. In addition, purge NO_x release can be observed at temperatures above 400°C, largely because of the exotherm generated during the lean-to-rich transition; this exotherm results from the reductants (H₂, CO, HC) in the rich exhaust reacting with the oxygen from any oxygen storage materials that are present [3].

Another challenge for lean NO_x traps is their high sensitivity to sulfur poisoning [4,5,6,7,8,9,10,11,12,13]. Sulfur dioxide (SO₂) is present in the exhaust from diesel and gasoline engines, resulting from the combustion of sulfur-containing compounds present in the fuel and oil. This SO₂ reacts with the NO_x storage materials to form sulfates, which are very stable and effectively poison the NO_x storage sites. To recover the NO_x storage capacity, the LNT must be desulfated periodically by exposing the catalyst to several minutes of rich operation at temperatures on the order of 600 to 800°C [14]. However, care must be taken to minimize the release of hydrogen sulfide (H₂S) into the environment to avoid customer dissatisfaction during the desulfation. This is often accomplished by modulating the A/F ratio between a lean condition and a rich condition during the desulfation [15]. Also, the high temperature desulfations can promote sintering of the precious metals and/or NO_x storage materials; this can degrade the performance of the LNT, particularly at low temperatures. Thus, low sulfur fuels are beneficial for minimizing the frequency of the desulfations and consequently the thermal degradation of the LNT.

The limited NO_x conversion of the LNT at low temperatures is an issue for many diesel applications or for turbocharged lean-burn gasoline engines, where the exhaust temperatures can fall below 300°C over a significant portion of the speed/load range. To improve the performance at these lower temperatures, high platinum loadings are needed to increase the NO oxidation capability of the LNT during lean operation [16], while high loadings of rhodium are needed to improve the NO_x reduction capability during the rich purges [17]. However, the high Pt and Rh loadings can result in a costly aftertreatment system. A more cost-effective way to improve the low temperature performance of the LNT can be achieved by placing a selective catalytic reduction (SCR) catalyst downstream of the LNT. The SCR catalyst can store NH₃ produced by the LNT during the rich purges and then use this stored NH₃ to reduce some of the NO_x that slips past the LNT during the lean periods. The stored NH₃ can also be used to reduce some of the NO_x released from the LNT during the rich purges. So the SCR catalyst can improve the

low temperature NO_x conversion of the LNT while simultaneously lowering the NH₃ emissions. This LNT+SCR system has been studied by several other researchers [18,19,20,21,22,23,24,25,26,27], and Daimler put a LNT+SCR system into production on the diesel-powered E320 in 2007, although in that system a particulate filter was placed between the LNT and SCR catalysts. Enderle [25] suggested that the rear SCR catalyst was used to improve the NO_x conversion of the LNT and to deal with the sulfur emissions during desulfations of the LNT. Xu [26] showed that copper (Cu) SCR catalysts are more effective than iron (Fe) SCR catalysts for improving the low temperature NO_x performance of the LNT.

While the LNT+SCR system can provide improved NO_x performance relative to the LNT alone, the system is still sensitive to the effects of sulfur poisoning. McCarthy [24] evaluated a fuel-reformer+LNT+DPF+SCR system on a diesel engine while the system was exposed to 150 poisoning and desulfation events. The performance of the LNT did decrease due to the repeated poisonings and desulfations. However, the SCR catalyst continued to provide some additional NO_x conversion, and the LNT+SCR system provided respectable (~70%) NO_x conversion at the end of the experiment. Hu [20] suggested that the SCR catalyst can help maintain the NO_x conversion as the LNT degrades due to sulfur poisoning, allowing the frequency of the desulfations to be decreased and thereby minimizing the thermal degradation of the LNT.

In this study, the effects of sulfur poisoning and desulfation temperature on the NO_x conversion performance of the LNT+SCR in-situ system were further analyzed. This was accomplished by aging four identical LNT+SCR systems without SO₂ at 600, 700, 750, or 800°C with A/F modulations to simulate desulfations on a vehicle. Periodically, the samples were removed from the aging reactor, evaluated for NO_x performance, sulfur poisoned and desulfated multiple times, and then re-evaluated for NO_x performance. This test sequence was repeated multiple times to simulate 100K miles of desulfations on a vehicle.

EXPERIMENTAL

Catalysts

Several core samples with a diameter of 17.5 mm were drilled from a cordierite brick coated with a LNT washcoat containing 110 gpcf of precious metal. Some of the cores were cut with a diamond saw to produce samples 2.54 cm in length. In a similar fashion, core samples were extracted from a cordierite brick coated with a copper/zeolite SCR washcoat. Small holes were drilled axially through the core samples to allow a 1.6 mm thermocouple to be inserted through the

samples for measuring the inlet temperature during the agings and evaluations.

Aging Procedure

The highest exhaust temperatures on a diesel engine are typically encountered during the desulfations of the LNT. Therefore, to simulate 25K miles on a vehicle, each set of the LNT+SCR catalysts needed to be aged for the cumulative desulfation time that the catalysts would experience in 25K miles. Assuming a desulfation every 600 miles and 7.5 minutes per desulfation, this resulted in approximately 300 minutes or 5 hours at the desulfation temperature. Therefore, each LNT+SCR set was to be aged for four periods of five hours each to represent 25K, 50K, 75K, and 100K miles of desulfations on the vehicle. During the aging, the A/F ratio was alternated between 10 seconds of lean operation (with 1% O₂) and 20 seconds of rich operation (with 3% CO + 1% H₂, or a lambda of 0.89) to simulate the A/F modulations (a.k.a. A/F “wobbles”) typically used during desulfations on a vehicle to minimize H₂S formation. Finally, in order to assess the effect of the desulfation temperature on the NO_x performance of the catalysts, separate LNT+SCR systems were aged at inlet temperatures of 600, 700, 750, and 800°C.

However, to simulate sulfur poisoning conditions on a vehicle, the samples also needed to be exposed to SO₂ at low to moderate temperatures using an A/F ratio cycle that included extended time (e.g., 60 seconds) at a lean A/F ratio. Therefore, rather than age the catalysts for 300 minutes at the desulfation temperature continuously, the catalysts were aged without SO₂ at the desulfation temperature for 270 minutes to expose the catalysts to the majority of the thermal exposure experienced during 25K miles of desulfations. After the LNT and the LNT+SCR system were evaluated for NO_x conversion performance on the 60/5 test, the LNT was then subjected to a 60 minute rapid poisoning at 400°C with 90 ppm SO₂, followed by a 7.5-minute desulfation at the same temperature as the thermal aging temperature (e.g., the sample thermally aged at 600°C was also desulfated at 600°C). Then the SCR catalyst was placed behind the LNT, and the LNT+SCR system was similarly exposed to three more poisonings and desulfations. By testing only the LNT during the first poisoning/desulfation and the LNT+SCR system during the next 3 poisoning/desulfations, the effect of the SCR catalyst on the sulfur emissions during the poisonings and desulfations could be assessed using a mass spectrometer.

The four 7.5-minute desulfations provided the remaining 30 minutes needed to complete a total of 300 minutes at the desulfation temperature in order to simulate 25K miles of desulfations on a vehicle while simultaneously achieving a steady-state poisoning level on the catalyst that depended on the thermal aging condition of the catalyst and the desulfation

temperature. After the poisonings and desulfations, the LNT and LNT+SCR system were re-evaluated on the 60/5 test. This entire test sequence (i.e., thermal aging without SO₂, 60/5 tests, sulfur poisoning + desulfations, and 60/5 tests) was repeated 3 more times to simulate 50K, 75K, and 100K miles of desulfations on a vehicle.

Performance Evaluations

After each 270-minute thermal aging period and after each set of 4 poisonings + desulfations, the LNT was evaluated by itself for NO_x conversion on the 60/5 test at different temperatures and a space velocity of 25K hr⁻¹. Then the SCR catalyst was placed behind the LNT, and the 60/5 test was repeated on the LNT+SCR system using the same exhaust flow conditions, so the space velocity was reduced to 12,500 hr⁻¹. [Table I](#) displays the gas concentrations during the lean and rich periods of the test. At each temperature, testing was continued until the catalyst performance stabilized. The average NO_x conversion was determined by averaging the stabilized NO_x emissions over the lean and rich periods and dividing by the feedgas NO level according to

$$\text{Ave \% conversion} = 100 * [1 - (\text{ave NO}_x \text{ concentration}) / (\text{FG NO level})] \quad (1)$$

Table I. Gas Concentrations during 60/5 test

Component	Concentration
CO ₂	10%
H ₂ O	10%
NO	500 ppm
CO (rich)	5.0%
H ₂ (rich)	1.7%
O ₂ (lean)	5.0%
Bulk N ₂	Balance

At the time this work was performed, a FTIR analyzer was not available on this reactor, so the NO_x emissions were measured with a chemiluminescence NO_x analyzer.

Sulfur Poisonings and Desulfations

For the sulfur poisonings, the LNT was placed in a flow reactor and rapidly poisoned with 90 ppm SO₂ for 1 hour at a space velocity of 30K hr⁻¹. During the poisoning, the A/F ratio alternated between a lean condition (5% O₂) and a rich condition (1.2% CO + 0.4% H₂) every 60 seconds; the concentrations of H₂O, CO₂, and NO were the same as those listed in [Table I](#). This poisoning was followed by a 7.5-minute desulfation performed at the same temperature as the thermal aging periods. During the desulfation, the A/F ratio was modulated between a 10 second lean condition (2% O₂) and a 20 second rich period (1.2% CO + 0.4% H₂). Then the

SCR catalyst was placed behind the LNT, and three more rapid poisonings and desulfations were performed on the LNT+SCR system. The feedgas SO_2 was turned off during the desulfations so that any SO_2 , H_2S , or COS (carbonyl sulfide) emissions could be attributed to sulfur that was stored on the catalysts. The SO_2 , H_2S , and COS emissions were measured with a V&F mass spectrometer during some of the poisonings and desulfations to assess the effect of the SCR catalyst on the sulfur emissions.

SCR Performance Tests

Periodically, the SCR catalysts were evaluated independently (i.e., without the LNTs) for NO_x conversion performance as the temperature was increased slowly from approximately 150°C to at least 600°C (typically at 3.5 or $4.0^\circ\text{C}/\text{min}$). Here the catalyst was exposed to continuously lean exhaust ($5\% \text{O}_2$) that contained 500 ppm NO and NH_3 along with $10\% \text{CO}_2$, $10\% \text{H}_2\text{O}$, and the balance N_2 . The total exhaust flow rate was 2.5 L/min, resulting in a space velocity of approximately $25,000 \text{ hr}^{-1}$ for a 2.54 cm long sample. To determine the concentration of NH_3 in the exhaust, a portion of the exhaust was directed over a platinum catalyst heated to 500°C , which oxidized any NH_3 to NO. The NH_3 concentration was then calculated by subtracting the NO_x concentration in the untreated exhaust from the NO concentration in this treated exhaust.

RESULTS

Figure 1 shows the average NO_x conversions for the LNT alone (at 25 K hr^{-1}) and for the LNT+SCR system (at 12.5 K hr^{-1}) after aging for 4.5 hours at 600 , 700 , 750 , and 800°C to simulate the thermal aging experienced by the catalysts during approximately 23K miles of desulfations (note: these tests were performed before the four poisonings and desulfations). For all four aging temperatures, the NO_x conversion of the LNT+SCR system was higher than that of the LNT alone over a range of temperature that generally fell below 350°C .

<figure 1 here>

Even though the NH_3 was produced by the LNT only during the rich purges, the improved NO_x control provided by the SCR catalyst was not limited to the duration of these purge periods. For the catalysts aged for 4.5 hours at 700°C , Figure 2 shows the NO_x emissions from the LNT and from the LNT+SCR system during the 60/5 tests at 250°C . The SCR catalyst reduced the NO_x emissions not only during the 5-second rich purges but also during the 60-second lean periods. The improvement is attributed to the SCR catalyst storing some of the NH_3 that was produced by the LNT during the purges and using that stored NH_3 to reduce NO_x

that slips past the LNT during the lean periods. The SCR catalyst can also use previously stored NH_3 to reduce some of the NO_x released from the LNT during the rich purges.

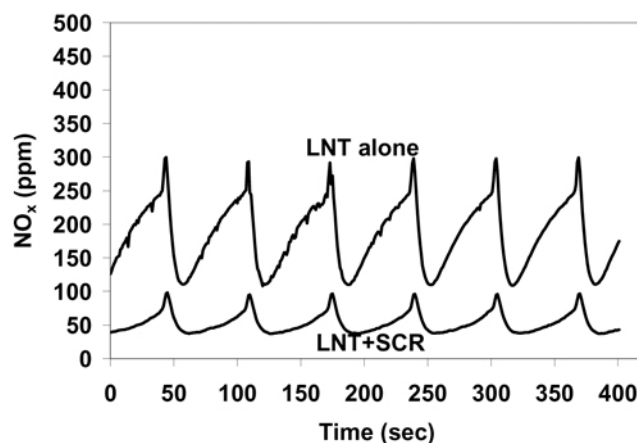


Fig. 2. NO_x emissions of LNT+SCR system and LNT after aging without SO_2 for 4.5 hrs using A/F modulations at inlet temperature of 700°C , evaluated on 60/5 cycle at 250°C .

Figure 1 indicated that the SCR catalyst improved the NO_x conversion of the LNT after all aging temperatures. However, the improvement decreased as the aging temperature increased. For the samples aged at 600 , 700 , 750 , and 800°C , the NO_x conversion of the LNT+SCR system at 250°C was higher than that of the LNT alone by approximately 50%, 25%, 10%, and 0%, respectively (the particularly large improvement for the catalysts aged at 600°C was partly due to an unexpectedly low conversion from the LNT alone at 250°C). To investigate if this decreased benefit was due to thermal degradation of the SCR catalysts, the SCR catalysts were tested without the LNT samples with 500 ppm NO and NH_3 in lean exhaust as the temperature was ramped slowly (i.e., 3 to $4^\circ\text{C}/\text{min}$) from approximately 150°C to at least 600°C . Figure 3 shows the NO_x conversion of the samples at 250 , 350 , 450 , and 550°C . The SCR samples aged at different temperatures had similar NO_x conversions when evaluated with this equimolar mixture of NO and NH_3 under continuously lean conditions.

However, the SCR catalyst in the LNT+SCR system stores NH_3 generated by the LNT during the rich purges and uses that stored NH_3 to improve the overall NO_x conversion. Therefore, in addition to good NO_x conversion, it is critical that the SCR catalyst also maintain good NH_3 storage capacity. NH_3 storage tests were not performed during this project, but a relative comparison of the NH_3 storage capacities between samples can be obtained from the NH_3 emissions during the temperature ramps. At the beginning of

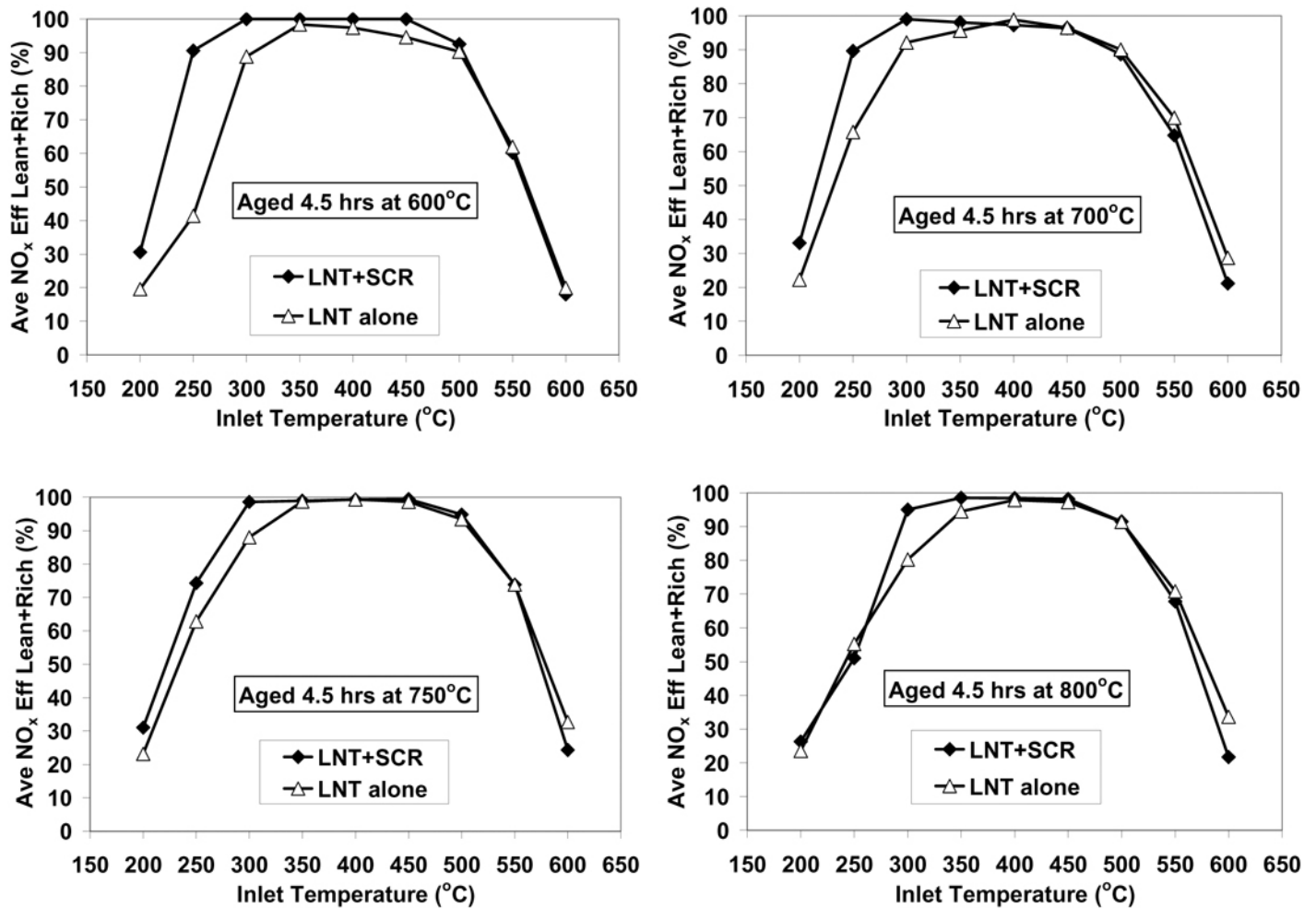


Fig. 1. NO_x conversion of LNT+SCR system and LNT after aging without SO₂ for 4.5 hrs using A/F modulations at inlet temperatures of 600, 700, 750, and 800°C to simulate 23K miles of desulfations.

the ramps, where the NO_x conversions are low, the SCR catalyst will adsorb unreacted NH₃ until the sample is saturated. As the temperature continues to increase, this stored NH₃ will begin to desorb from the catalyst. At temperatures where the NO_x conversion is high (resulting in low slip of the feedgas NH₃) but the ability of the catalyst to oxidize NH₃ to N₂ is low, the measured NH₃ slip that results from desorption can provide a relative comparison

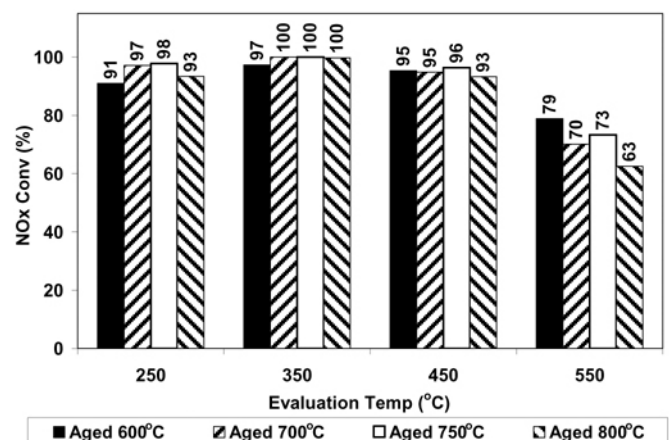


Fig. 3. NO_x conversion of SCR catalysts aged 4.5 hrs with A/F modulations at different inlet temperatures, evaluated under continuously lean conditions at 25K hr⁻¹ as temperature increased at 3 to 4°C/min.