

Impact of Rh Oxidation State on NO_x Reduction Performance of Multi-Component Lean NO_x Trap (LNT) Catalyst

Junhui Li, Neal Currier, and Aleksey Yezerets
Cummins Inc.

Hai-Ying Chen, Howard Hess, and Shadab Mulla
Johnson Matthey Inc.

ABSTRACT

Typical Lean NO_x Trap (LNT) catalyst composition includes precious metal components (Pt, Pd, and/or Rh), responsible for NO oxidation during lean operation and NO_x reduction during rich operation. It was found that redox history of commercial LNT catalyst plays a significant role on deciding its NO_x conversion under Lean/Rich cyclic condition. Further test had shown that fully formulated LNT catalyst being pre-reduced had shown much better NO reduction activity during the temperature-programmed reduction (TPRx) of NO than the same LNT catalyst being oxidized. The following study with Rh-only and Pt-only catalyst had demonstrated that Rh plays a key role on the large variation of the NO reduction function due to oxidation state change over LNT catalyst.

Kinetic analysis of the NO reduction was performed in an attempt to elucidate the underlying mechanistic relationship, where it was found that NO reduction over reduced Rh can be well described by an Arrhenius equation with first-order dependence on NO concentration while the oxidized catalyst had been changing its surface redox state during NO reduction. The activation energy of the NO reduction process over reduced fully formulated LNT catalyst was found to be $\sim 180 \pm 14$ kJ/mol, which is consistent with Rh-only catalyst but very different from Pt-only catalyst. The observed apparent activation energy of NO reduction on LNT catalyst was independent of the reductant used or the degree of hydrothermal aging either from field-aging or lab aging. These findings are consistent with NO dissociation being the rate-limiting step in the NO reduction process. The hydrothermal aging, redox state as well as the reductant type would only change the total number of sites available, active sites accessible as well as the surface coverage, respectively.

CITATION: Li, J., Currier, N., Yezerets, A., Chen, H. et al., "Impact of Rh Oxidation State on NO_x Reduction Performance of Multi-Component Lean NO_x Trap (LNT) Catalyst," *SAE Int. J. Engines* 9(3):2016, doi:10.4271/2016-01-0947.

INTRODUCTION

Compression ignition (diesel) engines are utilized due to their desirable torque characteristics and high fuel economy. Over the last decade, the environmental regulations for NO_x emissions from internal combustion engines have become increasingly stringent, which presents major challenges to catalytic reduction of NO_x for lean burn engines.

Lean NO_x traps (LNT or NO_x storage and release catalyst or NSR; NO_x absorber catalyst, NAC), represents one of the technologies, capable of meeting increasing emissions challenges as shown in multiple commercialized diesel aftertreatment systems [1]. The NO_x reduction on a LNT occurs through a cyclic process achieved transition from fuel-lean (excess oxygen) operation to fuel-rich (excess reductant) operation. During the typical lean conditions, the NO is oxidized to NO₂ at the catalyst surface and trapped as nitrate or nitrite. During rich operation, the nitrite and nitrate are released and reduced to N₂ or other products.

In a practical application, an LNT catalyst is typically operated under three different types of conditions, including deNO_x (lean/rich cycling in the temperature range of 150–450°C), desoot (extended lean exposure in the temperature range of 500–700°C) and desulfation (lean/rich cycle in the temperature range of 500–700°C). Therefore, the redox state of an LNT catalyst is highly dynamic according to its specific operation history. Significant efforts have been made to explore multiple functions of the LNT catalyst, such as NO oxidation, NO_x storage, NO_x release and NO_x reduction [1, 3]. Nevertheless, limited attention has been paid to the understanding of the effect of the oxidation state of catalyst surface, and specifically of the precious metal components, on the performance of an LNT catalyst although a lot of study had been done for TWC previously [4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,].

In this study it had been observed that the oxidation of LNT catalyst can severely decrease its NO reduction activity. In particular, it had demonstrated that the oxidation of Rh plays the key role for this type

of reversible deactivation. Detailed kinetics study for the reaction of NO reduction to N_2 with different aging stages and oxidation states specifically of Rh, has been further performed to elucidate the underlying process and its significance to the overall cyclic operation.

EXPERIMENTAL PROCEDURE AND MATERIALS

Experimental set up used in this work is a bench-flow reactor which allows the catalyst to be exposed to different temperatures and different gas compositions, including rapid and well-defined gas composition transients, in a controlled manner. A micro-core (~ 6 mm x 25 mm) of a catalyst is placed into a horizontal quartz reactor tube with 1/4" inner diameter. The required gas species are blended from research grade gases using MKS mass flow controllers to form the desired gas composition. Two thermocouples, in 0.3mm-walled glass wells are placed at the inlet and outlet of the catalyst monolith. The inlet flow of the gaseous species is controlled by the flow rates of the mass flow controllers. The micro-reactor is equipped with a chemiluminescent NOx analyzer (California Instrument, 400HCLD, modified for full flow of the sample gas) to measure the outlet NOx concentrations and a Mass Spectrometer (Agilent, 5973N) to measure outlet propylene concentration. More detailed description about the system could be found in our previous work [30].

The catalysts used for our study were two fully formulated LNTs manufactured by Johnson Matthey. Both catalysts were received in the form of cylindrical, washcoated, honeycomb monoliths, 9 inches in diameter and 5 inches long. Total precious metal loadings on these two commercial LNT catalysts were 60 and 72 g/ft³, both with the Pt/Rh ratio of 4:1. The total surface area of the degreened catalyst/monolith combination was measured to be about 30–40 m²/g by N_2 adsorption using BET method. There was no palladium in these samples.

Additionally, two model catalysts were provided by Johnson Matthey, and used to help interpret the behavior of the fully-formulated LNTs. The first is Rh coated on the ceria/zirconia/alumina (12g Rh/ft³) and the second catalyst is the Pt coated on alumina (48g Pt/ft³) to specifically decouple the effect of oxidation state of Rh and Pt on the NO reduction function over the commercial LNT catalyst.

In Table 1 we listed all the gas mixtures being used during the lean, rich or cyclic operation being reported in the following study. Since engine out gas composition during rich operation always includes hydrocarbons, CO and H_2 , the reductant mixture containing CO, H_2 and C_3H_6 with different ratios were explored in which 4% CO, 1.25% H_2 and 0.2% propylene (Rich2) was used as the standard rich mixture, unless otherwise stated. The 5% H_2O and 5% CO_2 were also always present in both lean and rich mixtures, to ensure practical relevance of the test results. In the following discussion, the composition of the rich mixture being used is reported as the concentrations of $H_2/CO/C_3H_6$. For example, Rich2 is reported as 1.25/4/0.2, corresponding to the molar composition of 1.25% H_2 , 4.0% CO and 0.2% C_3H_6 .

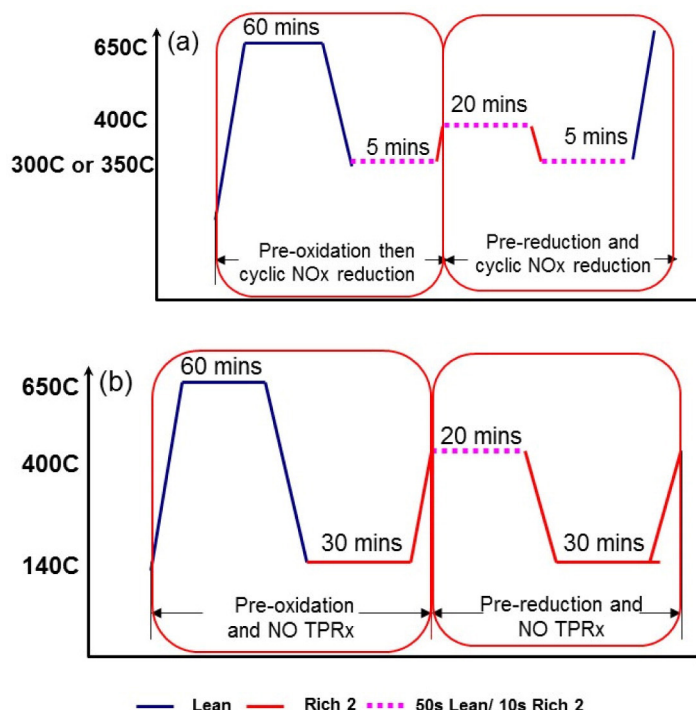


Figure 1. Test Procedure for Reduced or Oxidized Catalyst (a) Cyclic NOx reduction at 300°C and 350°C (5 cycles with 50sLean/10s Rich (rich2) (b) NO TPRx from 140°C to 400°C (rich 2)

Figure 1 (a) and (b) describes the procedure employed to explore the reactivity of an oxidized catalyst and reduced catalyst in our study. As shown in Figure 1 (a), the catalyst was first heated up to 650°C under lean conditions and the temperature was maintained at 650°C for 1h to oxidize the catalyst. The oxidation temperature, 650°C, was chosen as the representative of on-engine desoot conditions. Samples treated in this manner are referred to as oxidized. In Figure 1(a) the temperature was reduced to 300°C or 350°C under lean environment then 5 cyclic NOx reduction with 50s Lean/10s Rich (rich2) were performed. This type of treatment was used to probe the cyclic performance of the catalyst, relevant to its practical operation. The catalyst was then pre-reduced by performing 20 Lean (50s)/Rich (10s) cycles using rich composition (Rich2) at 400°C. Samples treated in this manner are referred to as reduced. The sample was cooled down to 300°C or 350°C in Figure 1(a) under the net rich condition to avoid any re-oxidation of the catalyst. Then the cyclic performance was quantified again as shown in Figure 1(a).

In Figure 1(b), catalyst was oxidized or reduced with the same manner being specified in Figure 1(a). After the oxidation, the catalyst temperature was reduced to 140°C under lean environment then the system was switched to rich (rich2) condition for 30 mins with 200 ppm flow of NO. The temperature was ramped up from 140 to 400°C to measure the NO light-off performance using TPRx. This type of treatment was used to probe the NO reduction function alone, independently of the other steps in the overall cycle. After the reduction, the sample was again cooled down to 140°C in Figure 1(b) under the net rich condition to avoid any re-oxidation of the catalyst. NO light-off using TPRx was quantified again as shown in Figure 1(b).

Table 1. Gas Composition during Catalyst Performance Test

Gas Species	Rich					Lean
	Red1	Red2	Red3	Red4	Red5	
NO (ppm)	200	200	200	200	200	0/200
H ₂ (%)	0	1.25	1.25	0	1.25	0
CO (%)	0	4.00	1.25	1.25	0	0
C ₃ H ₆ (%)	0.8	0.2	0.2	0.2	0	0
O ₂ (%)	0	0	0	0	0	5
H ₂ O (%)	5	5	5	5	5	5
CO ₂ (%)	5	5	5	5	5	5
H ₂ /CO/C ₃ H ₆	0/0/0.8	1.25/4/0.2	1.25/1.25/0.2	0/1.25/0.2	1.25/0/0.2	-
Lambda	0.86	0.86	0.91	0.93	0.93	1.31

EXPERIMENTAL RESULTS AND DISCUSSION

1. Effect of the Redox History on Cyclic Performance

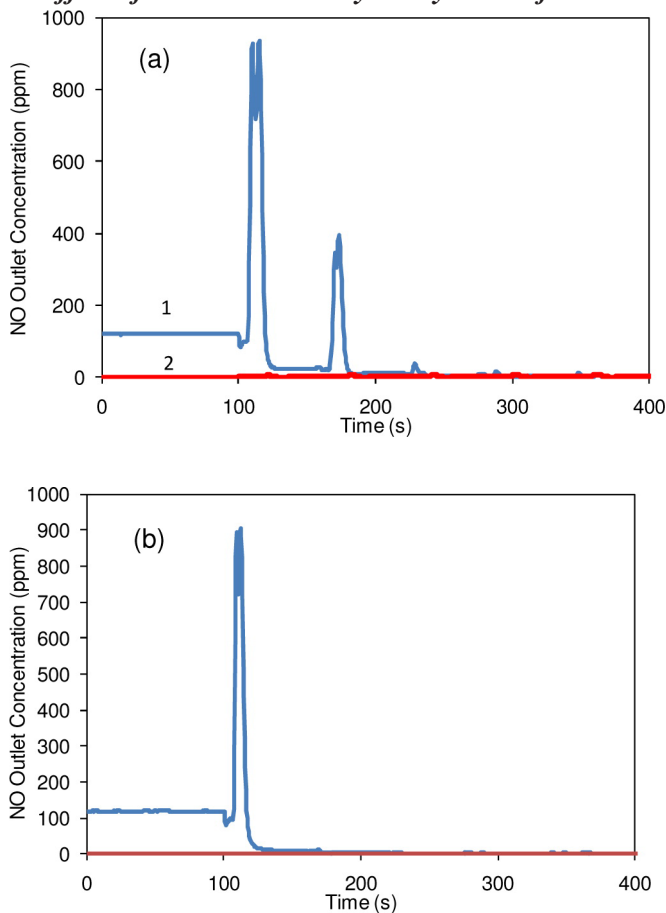


Figure 2. Effect of redox history of fully formulated LNT catalyst on its NO_x performance at (a) 300°C (b) 350°C. Blue line marked as “1” corresponds to the oxidized LNT catalyst, while red line marked as “2” - reduced LNT catalyst (Pt: 48g/ft³, Rh:12g/ft³)

Figure 2 shows the effect of the redox history of a fully formulated LNT catalyst with 48g/ft³ Pt and 12g/ft³ Rh on its deNO_x performance, using the test procedure described in Figure 1(a). As one can see, cyclic operation of a pre-reduced catalyst at the employed conditions produced no measurable slip of unconverted

NO_x, resulting in the cycle-average NO_x conversion above 99%. In contrast, pre-oxidized catalyst produced large spikes of unconverted NO_x at both 300°C and 350°C, resulting in cycle-average NO_x conversion values of 76% and 87%, respectively. These spikes abated after several cycles, likely due to the catalyst changing its oxidation state. At 350°C, it only took one cycle to overcome the effect of the oxidative pretreatment, while at 300°C three cycles were required to accomplish that.

2. Effect of Redox History on NO Reduction under TPRx Conditions

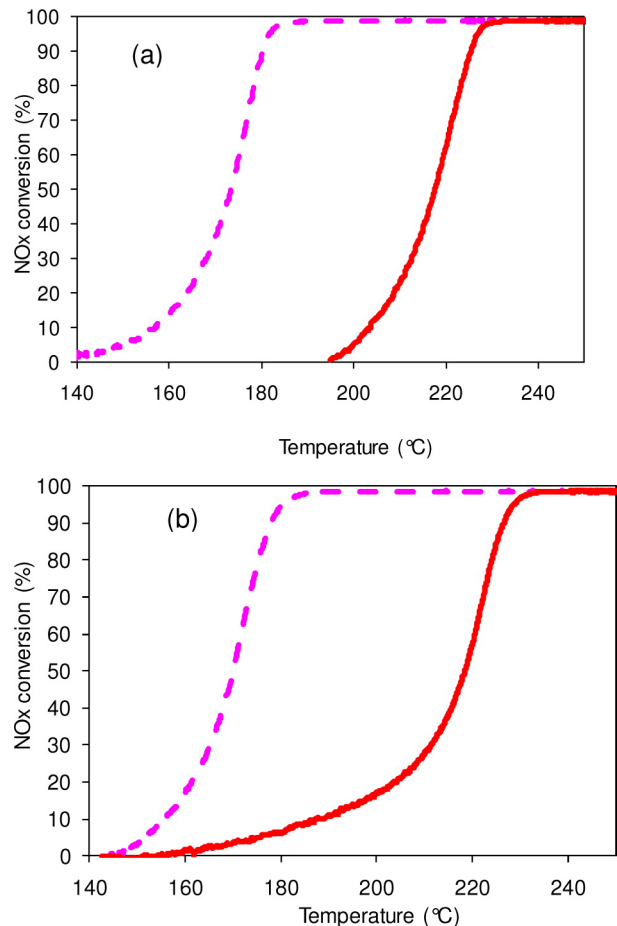


Figure 3. NO Light-Off over reduced and oxidized fully formulated LNT (a) (Pt: 48g/ft³, Rh: 12g/ft³) (b) (Pt: 58g/ft³, Rh: 14g/ft³) dashed line- reduced catalyst; solid line- oxidized catalyst