

Effects of Rapid High Temperature Cyclic Aging on a Fully-Formulated Lean NO_x Trap Catalyst

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ABSTRACT

In this study, high-temperature deactivation of a fully-formulated lean NO_x trap (LNT) is investigated with an accelerated aging protocol where accelerated aging is accomplished by rapid temperature cycling and by higher temperatures. Thermal aging is carried out in a bench-flow reactor at nominal temperatures of 700, 800, 900, and 1000°C using an aging cycle consisting of a 130s lean-phase and a 50s rich-phase. After a prescribed number of lean/rich aging cycles, the NO_x conversion of the aged LNT is evaluated at 200, 300, and 400°C. The NO_x performance is obtained at a GHSV of 30,000 h⁻¹ using an evaluation cycle consisting of a 60s lean-phase and 5s rich-phase. The effects of aging on the LNT washcoat are determined with EPMA, XRD, STEM/EDS, and BET. Aging at 700 and 800°C has a minimal effect on LNT performance and material properties. However, at aging temperatures of 900 and 1000°C reduction in surface area and sintering of PGM particles are observed and result in a drastic reduction in NO_x conversion. Additionally, after aging at 900°C and 1000°C the NO_x storage medium, BaCO₃, is no longer visible in the XRD patterns, even though a Ba-phase identified by EPMA still exists in all aged samples. BaAl₂O₄ is not identified at any aging temperatures; possibly due to stabilization effects provided by washcoat additives present in this particular LNT.

INTRODUCTION

As fuel prices rise and consumers begin demanding more efficient automobiles, lean-burn diesel and gasoline engines are receiving more attention. Since lean-burn engines are more efficient, they also emit less CO₂, a green house gas that is one of the major sources of global warming [1]. However, a major challenge with lean-burn engines is the reduction of NO_x in an oxidizing environment.

Several NO_x reduction technologies are currently being investigated, and one of the most promising solutions is lean NO_x traps (LNTs)—also referred to as NO_x storage/reduction (NSR) catalysts. LNTs are typically formulated with an alkali or alkaline earth metal storage component, a high surface area support, and one or more precious metal components. During the lean phase, NO_x is oxidized by the precious metal and trapped on the storage component. Before NO_x slip becomes significant the LNT is subjected to a brief rich excursion, during which stored NO_x is released and reduced to N₂ over the precious metal sites.

LNTs are capable of achieving NO_x conversion efficiencies of greater than 90% [2-4]. However, their low sulfur tolerance is a major hurdle that must be addressed before they can be commercially viable. Like NO_x, sulfur is “trapped” on the storage component and can significantly diminish the storage capacity and performance of LNTs. For this reason, LNTs have to undergo periodic desulfurization at temperatures exceeding 650°C [2-10]. These high-temperature

excursions during repeated regeneration and desulfurization treatments are responsible for thermal aging and performance loss of LNTs. A number of studies have been conducted in order to elucidate the thermal deactivation mechanisms of LNTs [10-26]. From these studies, several deactivation mechanisms have been identified: sintering of the precious metals and the NO_x storage component, interaction between barium and $\gamma\text{-Al}_2\text{O}_3$ washcoat to form less efficient storage media, and loss of washcoat surface area.

In the present study, a bench-flow reactor is used to perform both accelerated lean/rich thermal aging and NO_x performance evaluation on a fully-formulated LNT using simulated diesel exhaust gases. The aged samples are then characterized for changes in the material properties using a number of techniques. Degradations in NO_x performance are then compared to precious metal sintering and reduction in surface area in order to determine which deactivation mechanisms are most detrimental under various aging and operating conditions. By characterizing the deactivation of LNTs under a variety of conditions the results of this study can provide further insights into the loss of NO_x performance due to thermal aging.

EXPERIMENTAL APPARATUS AND PROCEDURE

BENCH-FLOW REACTOR AGING AND EVALUATING - Thermal aging of the LNTs is performed in a bench-flow reactor (BFR), shown schematically in Figure 1. The bench-flow reactor has been described in detail elsewhere [11], and only a brief description is given here. The simulated exhaust gas stream with a composition similar to the exhaust gases from lean-burn diesel engines is introduced into the bench-flow reactor by means of mass flow controllers.

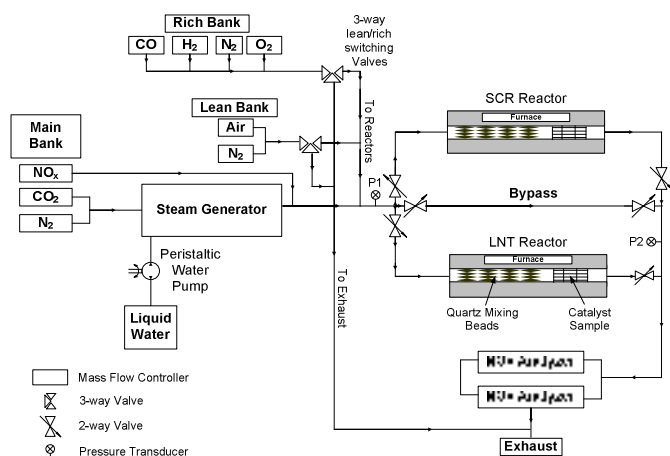


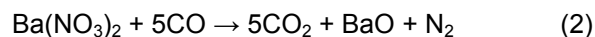
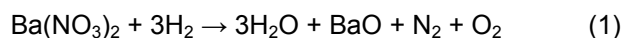
Figure 1: Schematic of bench-flow reactor.

Water vapor is introduced into the system via the steam generator using N_2 and CO_2 as carrier gases. Three

different banks of mass flow controllers are used to control the flow of gases. The main bank, in which the gases flow continuously, consists of CO_2 , NO_x , and N_2 . The other two banks are the rich and lean banks; the rich bank consists of N_2 , CO , H_2 , and O_2 , while only air and N_2 make up the lean bank. By activating the two three-way solenoid valves, lean and rich pulses of any duration can be achieved.

The LNT reactor is a 43 cm long quartz tube with a 25 mm outside diameter placed inside a Lindberg Minimate furnace. The upstream section of the quartz tube is filled with quartz beads of 5 mm diameter to ensure good mixing and uniform heating of the incoming gas. A 400 cpsi (cells per square inch), fully-formulated LNT catalyst sample with a diameter of 2.2 cm and a length of 7.6 cm wrapped in FiberFlax fiber strands to prevent gas bypass is placed in the downstream section of the quartz tube. Six type-K thermocouples are used to measure the axial temperature variation across the LNT. Two of the thermocouples positioned approximately 5 mm from the LNT's inlet and exit, are used to measure the inlet and exit gas temperatures. The remaining four thermocouples located at 5, 19, 38, and 57 mm from the LNT's inlet are used to measure the intra-catalyst temperature. The inlet and exit concentrations of NO and NO_x are measured with two chemiluminescent NO_x analyzers. Upstream of the two NO_x analyzers, an ammonia scrubber is installed to prevent NH_3 from interfering with NO_x measurements.

The catalyst activity of fresh LNT samples is first stabilized by degreening in the BFR at 450°C and a gas hourly space velocity (GHSV) of $30,000\text{ hr}^{-1}$ for 4 hours in an environment consisting of 10% O_2 , 10% H_2O and 80% N_2 . The NO_x conversion of the degreened LNT is then evaluated at 200, 300, and 400°C —these temperatures are chosen to represent typical LNT operating temperatures. NO_x conversion of fresh and aged LNTs is evaluated at a GHSV of $30,000\text{ h}^{-1}$ using a short evaluation cycle of 60s lean and 5s rich. Table 1 lists the composition of the lean and rich gases used in the evaluation cycle; note that NO is present in both the lean and the rich phases. A H_2 to CO ratio of 3:5 is used in the rich phase since 3 moles of H_2 and 5 moles of CO are required for the stoichiometric reduction of 1 mole of NO_x stored in the form of $\text{Ba}(\text{NO}_3)_2$ as shown in Equations 1 and 2.



The evaluation cycles are repeated at each temperature until the cycle-to-cycle variation is minimized. This “steady-state” cycle is used to determine the NO_x conversion for the fresh and aged catalysts.

LNTs are aged at nominal aging temperatures of 700, 800, 900 and 1000°C at a GHSV of $57,000\text{ h}^{-1}$ using a slow aging cycle consisting of 130s lean and 50s rich. The aging temperatures of 700 and 800°C are chosen

to replicate the occasional desulfurization treatment (de-SO_x) required with LNTs, whereas aging temperatures exceeding 800°C were chosen to determine if a rapid aging protocol utilizing these higher temperatures would result in similar but more rapid material degradation as at lower temperatures. For an aging cycle the lean phase is comprised of N₂, O₂, CO₂, and H₂O, while the rich phase is made up of H₂, CO, O₂, N₂, CO₂ and H₂O. Aging temperatures are induced solely by exotherms under net rich conditions resulting from the periodic introduction of H₂, CO, and O₂ into the LNT. By varying the concentration of these three gases in the rich phase of the aging cycle, it is possible to achieve the desired aging temperature inside the LNT. Table 2 lists the concentration of H₂, CO, and O₂ in the rich phase of the aging cycle at different nominal aging temperatures. To study the effect of aging cycles at a given nominal aging temperature on the degradation of LNT performance the aging cycle is repeated until the desired number of aging cycles is achieved.

Table 1: Composition of lean and rich phase of the evaluating cycle. Note that NO_x is present in both the lean and rich phases.

	Lean (60s)	Rich (5s)
NO, ppm	300	300
CO ₂ , %	5	5
CO, %	0	1.13
H ₂ , %	0	0.68
Air, %	10	0
H ₂ O, %	5	5
N ₂	balance	balance

Table 2: Reductant and O₂ concentrations in the rich phase of the aging cycle at different aging temperatures.

	H ₂ (%)	CO (%)	O ₂ (%)
700°C	1.25	4.2	3.5
800°C	2.5	4.5	3.5
900°C	3.25	5.1	4
1000°C	4.55	5.9	5

CHARACTERIZATION TECHNIQUES - Fresh and aged LNT catalysts are characterized using electron probe microanalysis (EPMA), powder X-ray diffraction (XRD), scanning transmission electron microscopy/energy dispersive X-ray spectroscopy (STEM/EDS), and BET surface area measurements in order to determine the effect of aging temperature and number of aging cycles on the material properties of the LNT's washcoat. After aging, the LNTs are sectioned into four pieces coinciding with the locations of the four thermocouples. This allows each section to be characterized with a known temperature history. In such a manner the effect of aging temperature on material properties can be determined and correlated with performance.

EPMA is used to obtain qualitative elemental maps of Ce and Ba and quantitative concentration profiles or line-scans of Si, Al, Mg, Ce, Ba, Pt, and Zr in the washcoat. The EPMA instrument, a Cameca SX-52, is equipped with a backscatter detector and four wavelength dispersive spectrometers. Samples of fresh and aged LNTs are potted in epoxy and polished using 1 µm diamond paste prior to analysis.

Powder XRD is used to monitor the physicochemical properties of the washcoat components, including average PGM crystallite size and phase transitions of γ-Al₂O₃ as a result of thermal aging. The sectioned samples are scraped to remove the washcoat from the cordierite. The powder samples are then heated to 350°C in CO₂/Ar mixture in an attempt to convert all of the Ba to BaCO₃. Approximately 0.15 g of this treated washcoat is ground up and mixed with acetone on a zero background tray. A PANalytical® X'Pert PRO diffractometer operating at 40 kV and 40 mA with a 4° anti-scatter slit and an automatic divergence slit maintaining an irradiated length of 7 mm is used for all XRD analyses in this study. Scans are taken between 15 and 85° (2θ) with a step size of 0.0167° (2θ) and a time per step of 61s. Additionally, high intensity scans of the BaAl₂O₄ and BaCO₃ region between 18 and 26° (2θ) are taken with a step size of 0.0167° (2θ) and a time per step of 245s. The diffractograms are analyzed with X'Pert Highscore® and Jade 6.5® using powder diffraction files (PDF) from the International Center for Diffraction Data (ICDD).

TEM is also used to determine average PGM particle size and particle size distributions. This is necessary because the resolution of the XRD instrument and the complexity of the XRD patterns make it impossible to determine the PGM particle sizes in samples aged at lower aging temperatures. LNT samples are dusted onto a lacey carbon film supported on a 200-mesh copper grid for the TEM observation. TEM analysis is carried out using a Hitachi HF-3300 TEM/STEM at 300 kV (1Å resolution) equipped with a Thermo Noran Nano Trace EDS Detector with NORVAR light elements window (4485A-4NESSN). The TEM micrographs are taken at Z-contrast mode as well as second electron mode. Particle size analysis is performed with ImageJ® and Excel®.

RESULTS AND DISCUSSION

TEMPERATURE AND NO_x CONVERSION HISTORIES DURING AGING AND EVALUATION EXPERIMENTS - The presence of H₂, CO, and O₂ in the rich phase of the slow aging cycles results in brief exotherms whose magnitude depends on the axial location within the catalyst. Figure 2 shows a typical axial temperature history for two aging cycles at a nominal aging temperature of 1000°C. The front of the catalyst experiences the highest temperature of 1070°C, while the middle of the catalyst is at the nominal aging temperature of 1000°C, and the rear section experiences a lower temperature of 930°C. The axial temperature

trends for all four nominal aging temperatures—700, 800, 900, and 1000°C—are similar, and for this reason only the profile at 1000°C is presented. Figure 3 shows the maximum aging temperatures achieved during the rich phase at different locations in the LNT for all aging temperatures. As seen in the figure, the 5 mm-location always experiences the highest aging temperature, the 38 mm-location indicates the nominal aging temperature, and the 58 mm-location always experiences the lowest aging temperature. Since the front-half of the aged LNT is subjected to higher temperatures for longer duration than the rear-half, it is expected that characterization studies will reveal more severe degradation of the washcoat at the front locations, i.e., 5 and 19 mm, than the rear locations, i.e., 38 and 57 mm.

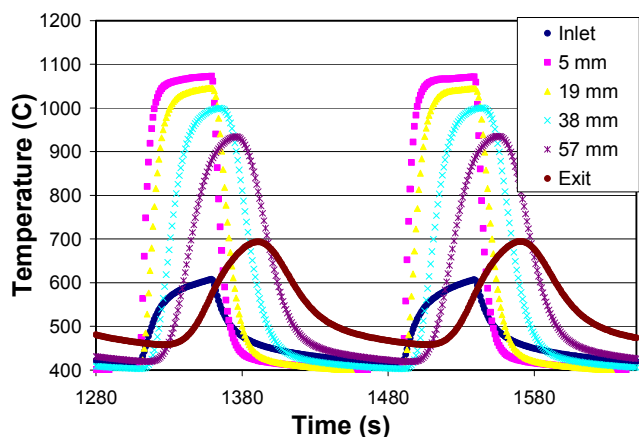


Figure 2: Temperature histories when aging at a nominal aging temperature of 1000°C.

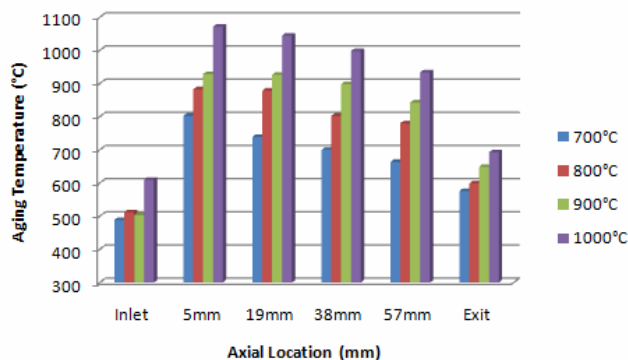


Figure 3: Maximum rich phase aging temperature at each axial location for the various nominal aging temperatures. Target aging temperatures were always achieved at midpoint located at 38 mm from LNT's inlet.

After a predetermined number of aging cycles, the NO_x conversion of the LNTs is evaluated at 200, 300, and 400°C. The NO_x slip profile shown in Figure 4 is obtained at an evaluating temperature of 400°C for an LNT aged at 900°C and is representative of data obtained at other evaluating temperatures. After an initial transient period of approximately 1500 s (23 evaluating cycles), there is minimal cycle-to-cycle variation for the remainder of the

evaluation. The abrupt increase in NO_x slip at 3250s is due to the introduction of span gas into the reactor in order to ensure the accuracy of the NO_x analyzers. Though NO_x slip histories when evaluating at 300°C and 400°C are very similar, NO_x slip histories at 200°C have a notably different profile. At an evaluating temperature of 200°C, the NO_x slip requires a very long time to reach steady state, irrespective of whether the catalyst is fresh or aged. Steady state NO_x slip is defined in the present study when no cycle-to-cycle variation in the NO_x slip is observed for at least five consecutive cycles. Even when experiments are performed at 200°C for up to three hours, both the NO and NO_x outlet concentrations are still slightly increasing. This slow increase is indicative of the high storage capacity at 200°C coupled with incomplete regeneration, i.e., after each cycle a portion of the NO_x stored during the lean-phase remains on the catalyst after the rich-phase. A complication arising from this phenomenon is that it can be difficult to determine when steady-state is achieved, and therefore there will be a higher degree of variability with the conversions at 200°C. For instance, the NO_x conversion of fresh LNTs can vary from 58 to 72% for evaluations at 200°C.

Figures 5, 6 and 7 show the NO_x slips of a fresh LNT during the last five consecutive lean/rich cycles at evaluating temperatures of 200, 300, and 400°C, respectively. The NO_x profiles at these evaluating temperatures show similar trends, except that a higher NO level at the end of the lean phase and a higher NO_x excursion during the rich phase occur at 200 and 400°C compared to 300°C. The high level of NO_x slip at the end of the lean phase indicates lower NO_x storage, whereas the increase in NO_x excursion at the onset of the rich phase indicates the rate of NO_x entering the system combined with the rate of NO_x released from the LNT are higher than the rate of NO_x reduction to N₂. Since the NO_x slip and the NO_x excursion are higher at 200 and 400°C than at 300°C the average NO_x conversion is consequently lower at these two temperatures.

Corresponding temperature histories at various locations in a fresh LNT during evaluations at 200, 300, and 400°C are shown in Figures 8, 9, and 10, respectively. As seen in these figures, it appears that during the rich phase the majority of the reductants are consumed in the front-half of the catalyst at all evaluating temperatures as evidenced by the larger exotherms. In addition, the magnitude of the rich-phase exotherms increases with increasing evaluating temperature with the magnitude of those at 200°C approximately 10°C lower than at 400°C.