EFFECT OF LENGTH ON THE PERFORMANCE OF LEAN NO_X TRAPS

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ABSTRACT: *The effect of monolith length on the NO_x performance of Lean NO_x Traps (LNTs) has been investigated using a bench flow reactor (BFR). The composition of the catalyst samples consists of Pt/K supported on γ-Al_2O_3 washcoat. Samples of 2.22-cm in diameter and three different lengths of 2.54, 5.08 and 7.62 cm were evaluated at a fixed gas hourly space velocity (GHSV) using long and short-cycle experiments with only H_2 as the reductant in the rich phase, and the NO_x performance was compared between samples of different lengths. No significant difference in performance was observed in long and short-cycle experiments with full regeneration. On the other hand, significant difference in performance was observed in short-cycle experiments with partial regeneration: the longer the sample the better the performance. The intra-catalyst concentration of H_2 measured by a Spatially Resolved Capillary Inlet Mass Spectrometer (SpaciMS) at different axial locations in short-cycle experiments with partial regeneration indicated that higher H_2 consumption in shorter samples is responsible for the reduction of NOx performance.*

Keywords: *Exhaust Gas Emissions, Exhaust Gas Aftertreatment, NsOx solution.*

1. INTRODUCTION

Lean NOx Trap (LNT) offers higher NO_x conversion efficiency and wider operating temperature window than Selective Catalytic Reduction (SCR) and Lean NO_x Catalyst (LNC), making LNT an attractive candidate for NO_x abatement in lean-burn engine exhaust. In LNT technology, NO_x reduction is achieved by storing NO_x during normal lean exhaust conditions and reducing the stored NO_x during periodic rich excursions of short duration.

A typical LNT catalyst consists of a honeycomb-like ceramic monolith coated with three primary components: precious metals such as Pt, Pd and Rh, alkali or alkaline earth metals such as Ba and K supported on high surface γ-Al_2O_3 washcoat. During normal lean exhaust conditions, NO is oxidized to NO_2 over the precious metal and stored on alkali/alkaline earth metals in the form of nitrites or nitrates. During periodic rich excursions, NO_x is released from the storage sites and (ideally) reduced to N_2 over the precious metals [1-13].

Even though changing gas hourly space velocity affects NO_x conversion in LNTs, i.e., NO_x conversion increases with decreasing GHSV due to longer residence time [14, 15], NO_x conversion should not be affected by changing the sample length as long as the space velocity or the residence time remains constant. However, significantly different results are often obtained from LNT evaluation experiments performed under the same conditions, i.e., same catalyst formulation, temperature, space velocity, and gas mixture composition [16]. As different sample sizes are often used in LNT evaluation as imposed on by reactor size, sample length is suspected as the culprit of LNT performance disparity.

The main objective of the present investigation is to determine if and how monolith length affects LNT performance. Samples of same diameter of three different lengths were evaluated at a fixed GHSV using a bench-flow reactor. To maintain constant GHSV, irrespective of the length of the sample, the volumetric flow rate or the linear gas velocity in the sample has to be increased with increasing sample length.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

A bench flow reactor illustrated schematically in Figure 1, was used to investigate the effect of monolith length on LNT performance. Individual components of simulated exhaust gases are introduced into the reactor via mass flow controllers. For lean/rich cycling a solenoid-actuated four-way valve with fast switching time (0.2 s) was used to introduce the lean or rich pulse into the reactor. A peristaltic pump was used to deliver liquid water to the water evaporator in which liquid water absorbed onto quartz wool evaporated and was swept by inert carrier gases. Directly downstream of the water evaporator, inert gases and water vapor were combined with lean or rich gases and introduced to the reactor.

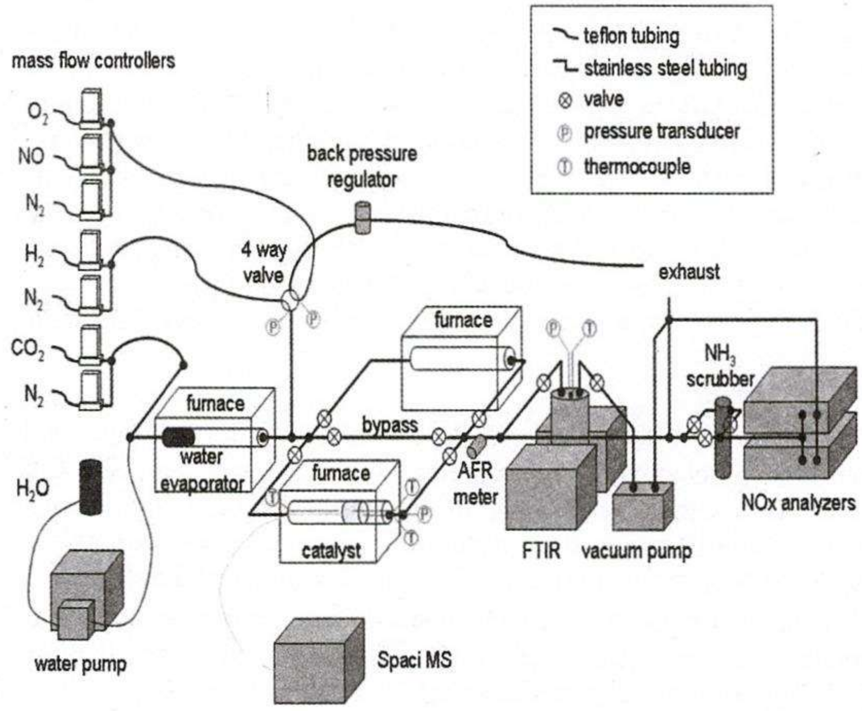

Figure 1. Schematic of the bench flow reactor

LNT catalyst sample of 2.22 cm in diameter was wrapped in Zetex ceramic fiber strips to prevent gas bypass and then inserted in a 2.54-cm OD quartz tube, which in turn is placed inside a tubular furnace. The catalyst sample was typically positioned 25.4 cm from the quartz tube inlet. The section upstream of the catalyst sample was filled with glass beads to promote mixing and uniform heating of the incoming gases. Intra-channel gas phase speciation was performed by Spatially Resolved Capillary Inlet Mass Spectrometer (SpaciMS), which was developed at the Oak Ridge National Laboratory (ORNL) for application to the BFR and other types of emissions and engine measurements where extractive sampling is possible [17]. The SpaciMS used 185 µm OD capillary probes to transport gas mixtures from the reactor to the mass spectrometer. The sampling ends of the capillary probes were inserted through the front end fitting of the reactor and positioned in the radial center at different locations along the catalyst length. The other ends of the probes were connected to a multiple-port valve leading to spectrometer's ionization chamber

Exiting gases were analyzed with a MIDAC Fourier Transform Infrared Spectrometer (FTIR) and two California Analytical Instruments NO_x chemiluminescence analyzers. The FTIR equipped with 375 mL and 3-m path length gas absorption cell was used for measuring the concentration of NO_2, N_2O, NH_3, CO, CO_2 and H_2O. Upstream of the NO_x analyzers, an NH_3 scrubber was used to prevent NH_3 from interfering with NO_x measurements.

A full-size $Pt/K/\gamma\text{-}Al_2O_3$ LNT monolith of cordierite substrate with a cell density of 31 cells per square centimeter supplied by EmeraChem under the trade name of $SCONO_x$ was used in the present study. Samples of 2.22-cm in diameter and length of 2.54, 5.08 and 7.62-cm were cored from full-size monolith and evaluated with two sets of cycling experiments: long and short-cycle experiments. Short-cycle experiments were intended to approximate the catalyst operation in engine exhaust applications while long cycling were performed to explore processes which are not, otherwise, observed in short-cycle experiments. Both sets of cycling experiments were performed at three different temperatures of 200, 300 and 400°C and a fixed GHSV of 30,000 h^{-1}. In the present investigation H_2 was used as the sole reductant in all of the experiments. Two different H_2 concentrations were used in short-cycle experiments: one to simulate partial regeneration and the other full regeneration. The H_2 concentration for partial regeneration experiments represents the concentration of the reductant that is below the theoretical amount needed to reduce the integral amount of NO_x that enters during the trapping part of the cycle. Full regeneration uses significantly higher reductant concentration than theoretical one to ensure that regeneration of the catalyst is not limited by the amount of reductant. The theoretical amount of reductant is calculated based on the assumption that all of the NO_x entering the reactor is stored as KNO_3 during the lean phase, and reduced to N_2 during the rich phase. Typical operating conditions for long and short-cycle experiments are given in Tables 1 and 2, respectively.

Table 1. Long cycling operating conditions

Mode	Time	Gas Composition
Lean	15 min	300 ppm NO, 10% O_2, 5% H_2O, 5% CO_2, balance N_2
Rich	10 min	0.2% H_2, 5% H_2O, 5% CO_2, balance N_2
Lean	15 min	300 ppm NO, 10% O_2, 5% H_2O, 5% CO_2, balance N_2
Rich	10 min	0.5% H_2, 5% H_2O, 5% CO_2, balance N_2

Table 2. Short cycling operating conditions

Mode	Time	Gas Composition
Lean	56 s	300 ppm NO, 10% O_2, 5% H_2O, 5% CO_2, balance N_2
Rich	4 s	1% H_2, 5% H_2O, 5% CO_2, balance N_2
Lean	56 s	300 ppm NO, 10% O_2, 5% H_2O, 5% CO_2, balance N_2
Rich	4 s	2% H_2, 5% H_2O, 5% CO_2, balance N_2

Before each cycling experiment, the catalyst was heated to 500°C and subjected to the regeneration condition consisting of 1% H_2, 5% H_20, 5% CO_2 and a balance of N_2 for 15 minutes for cleansing off adsorbed NO_x from catalyst surface. The catalyst was then cooled down to the desired operating temperature.

To investigate the mechanism for reductant consumption due to the catalytic reaction between H_2 and O_2 at the interface between the lean and rich phases; the extent of which depends on the degree of mixing at the lean/rich interface, a N_2 purge of 10 s between lean and rich pulse – referred to as back-mixing experiments – was introduced into the BFR. With a N_2 purge an inert environment between the lean and rich front was created, which should eliminate H_2 consumption due to lean/rich front back-mixing.

Prior to the catalyst evaluation, the catalyst samples were "degreened" to achieve stable and reproducible levels of their activity, by performing short storage-reduction cycles for 8 hours at 550°C, which is 150°C higher than the highest operating temperature used in the present study.

3. RESULTS AND DISCUSSION

Long-cycle experiments were performed on 2.54-cm, 5.08-cm and 7.62-cm-long samples at temperatures of 200, 300 and 400°C using two different reductant concentrations of 0.2 and 0.5% in the rich phase. Figure 2 shows typical catalyst outlet gas concentrations and temperature profiles for 2.54, 5.08 and 7.62 cm-long samples with 0.2% H_2 in the rich phase of the cycle at 300°C. Three cycles were run and the results are shown only for the third cycle. No significant difference in the catalyst outlet gas concentrations and temperatures is observed between 2.54, 5.08 and 7.62-cm-long samples with 0.2% H_2 as the reductant. Similar results were also obtained at 200 and 400°C. The cycle average NO_x conversion efficiencies for 2.54, 5.08 and 7.62-cm-long samples closely match each other at any given temperature. Table 3 lists the cycle average NO_x conversion efficiencies for experiments performed at 300°C. The differences in NO_x/NO_2 profiles and NO_x conversion efficiencies between samples of three different lengths seem to indicate that the longer the sample the better the performance. However, the differences in NO_x conversion efficiencies fall within the experimental uncertainty, which makes it difficult to conclude whether these differences result from length variation or experimental limitations.

A second set of long-cycle experiments was performed with 0.5% H_2 concentration in the rich phase (results are not shown).Except for one major difference – NH_3 and N_2O are produced in larger quantities – the trends for these cycles are similar to those with 0.2% H_2. As in the case of long-cycle experiments with 0.2% H_2 in the rich phase, no significant difference is observed between 2.54, 5.08 and 7.62-cm-long samples with temperature. Thus, in long cycle experiments the LNT's performance is not affected by sample length at a given temperature and reductant concentration.

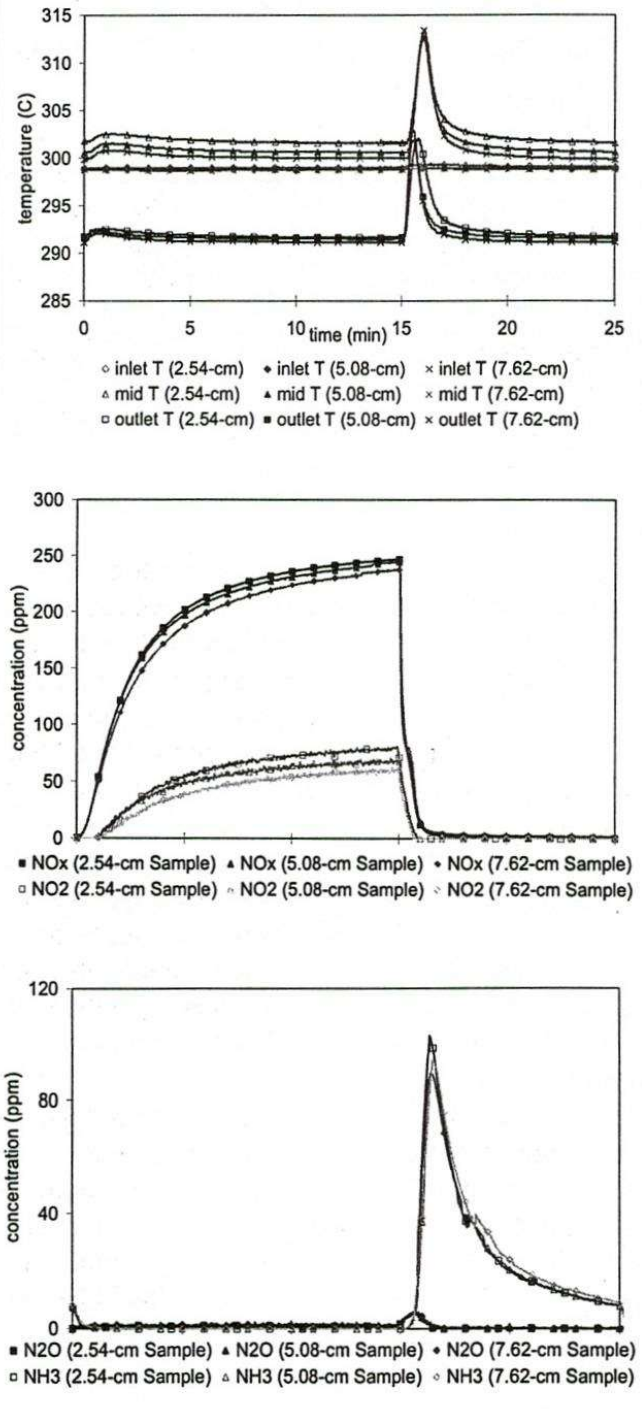

Figure 2. Outlet gas concentrations and temperature profiles for 2.54, 5.08 and 7.62-cm-long samples in long-cycle experiments with 0.2% H_2 in rich phase at 300°C

Table 3. NO_x conversion efficiencies in long-cycle experiments with 0.2% H_2 in rich phase

Temp. Length	300°C
2.54-cm	25.4%
5.08-cm	26.4%
7.62-cm	29.1%

Figure 3 shows the catalyst outlet gas concentrations and temperature profile for short-cycle experiments with 1% H_2 in the regeneration period, whereas Table 4 lists the cycle average NO_x conversion efficiencies. Results for 2% H_2 at 300°C are shown in Figure 4 and Table 5.

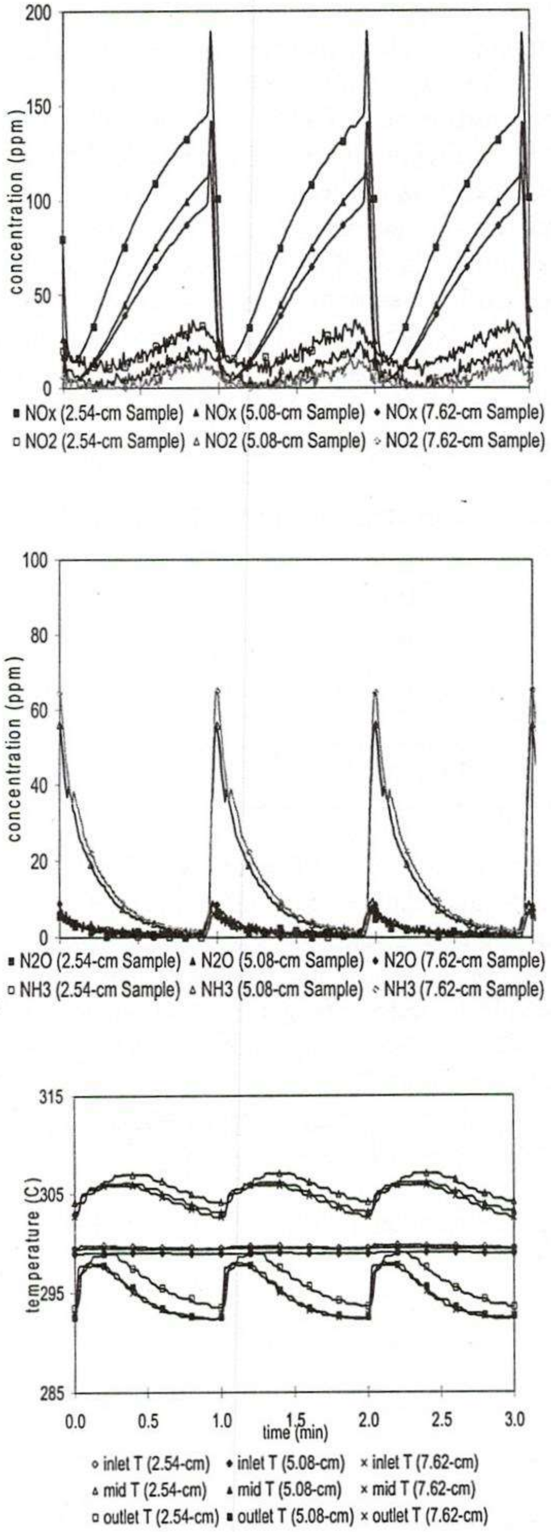

Figure 3. Outlet gas concentrations and temperature profiles for 2.54, 5.08 and 7.62-cm-long samples in short-cycle experiments with 1.0% H_2 in rich phase at 300°C

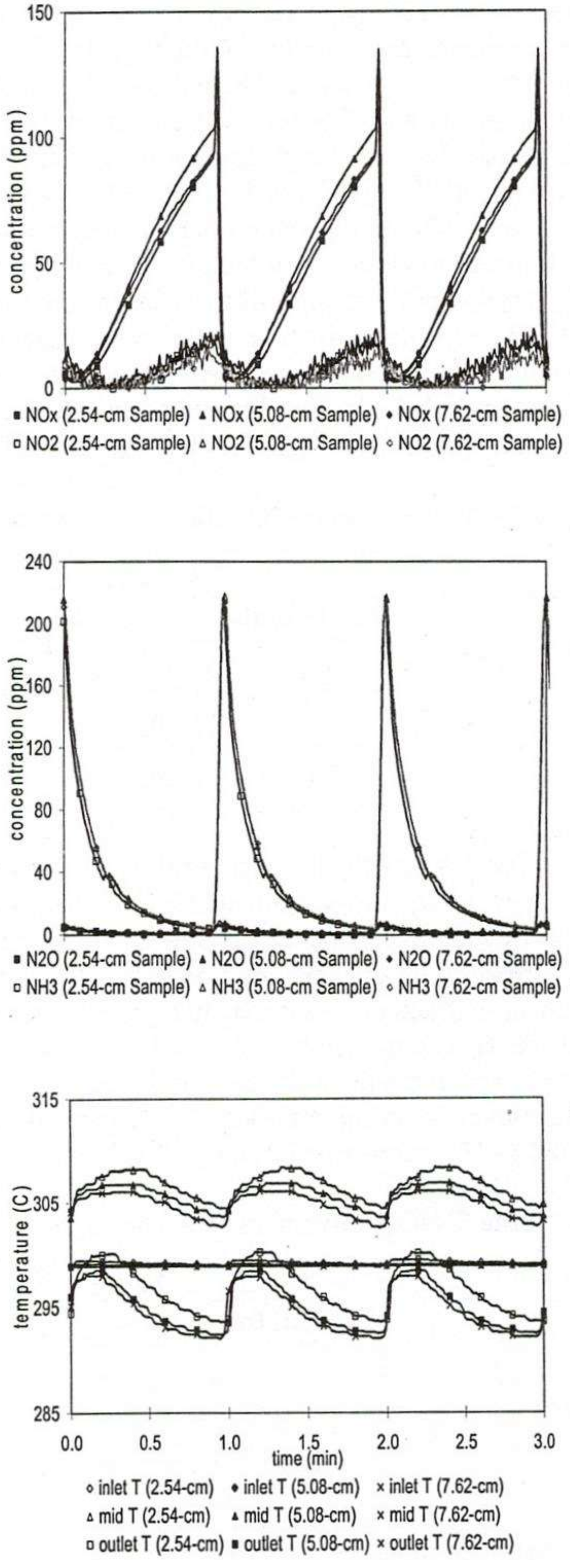

Figure 4. Outlet gas concentrations and temperature profiles for 2.54, 5.08 and 7.62-cm-long samples in short-cycle experiments with 2.0% H_2 in rich phase at 300°C

A total of 120 cycles were performed but only 3 representative cycles acquired toward the end of the 120-cycle run are shown in the figures. The general trends for the short-cycle experiments are similar to those obtained in the long-cycle experiments. No significant difference is observed between 2.54, 5.08 and 7.62-cm-long samples in short-cycle experiments with 2% H_2 in regeneration phase, and a difference of 15% is observed between 2.54 and 7.62-cm-long samples using 1% H_2 (partial regeneration). On the other hand a difference of only 3.4% is observed between 5.08 and 7.62-cm-long samples with 1% H_2, which is within the experimental uncertainty; and thus it is inconclusive to attribute this difference to variation in length. Amount of NH_3 produced in 5.08 and 7.62-cm-long samples is very similar and significantly larger than in 2.54-cm-long sample in experiments with 1% H_2. Results of short-cycle experiments show that catalyst's performance is affected by sample length during short - cycle experiments when regeneration is limited by the amount of reductant available. On the other hand, increasing the catalyst's length from 5.08 to 7.62 cm appears not to cause significant change in performance regardless of reductant concentration.

Table 4 NO_x conversion efficiencies in short-cycle experiments with 1.0% H_2 in rich phase

Temp. / Length	300°C
2.54-cm	65.7%
5.08-cm	77.1%
7.62-cm	80.5%

The intra-catalyst concentration of H_2 was measured at three different axial locations – catalyst inlet, mid-section and exit – with SpaciMS, and the H_2 concentration profiles for short-cycle experiments at 300°C are shown in Figures 5 and 6. From these profiles, information on the consumption of H_2 along the length of 2.54, 5.08 and 7.62-cm-long samples can be extracted. As seen in Figure 5, in short-cycle experiments with 1% H_2 in the rich phase, H_2 is completely consumed in the front half of the 2.54-cm-long sample; whereas about 25% of H_2 remains in the 5.08 and 7.62-cm long samples. With 2% H_2 in the rich phase of the short-cycle experiments, 80% is consumed in 2.54-cm-long sample, whereas approximately 60% of H_2 is consumed in the entire length of 5.08 and 7.62-cm-long samples (see Figure 6).

Table 5 NO_x conversion efficiencies in short-cycle experiments with 2.0% H_2 in rich phase

Temp. / Length	300°C
2.54-cm	82.1%
5.08-cm	79.5%
7.62-cm	81.7%

Higher consumption of H_2 in 2.54-cm-long sample should result in higher NO_x conversion, however the opposite is observed: 2.54-cm-long sample has lower NO_x conversion efficiency than longer samples in short-cycle experiments with partial regeneration, and no difference is observed with full regeneration.

Different H_2 consumption in 2.54, 5.08 and 7.62-cm-long samples seems to indicate that the consumption of H_2 might possibly occur via the catalytic reaction between H_2 and O_2 at the interface between the lean and rich phases. The extent of H_2 consumption depends on the degree of mixing at the lean/rich interface. Higher degree of back-mixing would result in higher H_2 consumption and lesser amount of H_2 available for reducing stored NO_x, thereby lowering catalyst's NO_x conversion. The extent of lean/rich front back-mixing can be seen in Figure 7, in which a N_2 purge of 10s is introduced between the lean and rich front, seems to eliminate H_2 consumption due to mixing at the lean/rich interface. As seen in the figure, N_2 purge decreases H_2 consumption in the front half of the 2.54-cm-long sample by 35% in experiment with 1% H_2 in rich phase and by about 10% in both 5.08 and 7.62-cm-long samples. Similar results are obtained in back-mixing experiments with 2% H_2 (not shown).

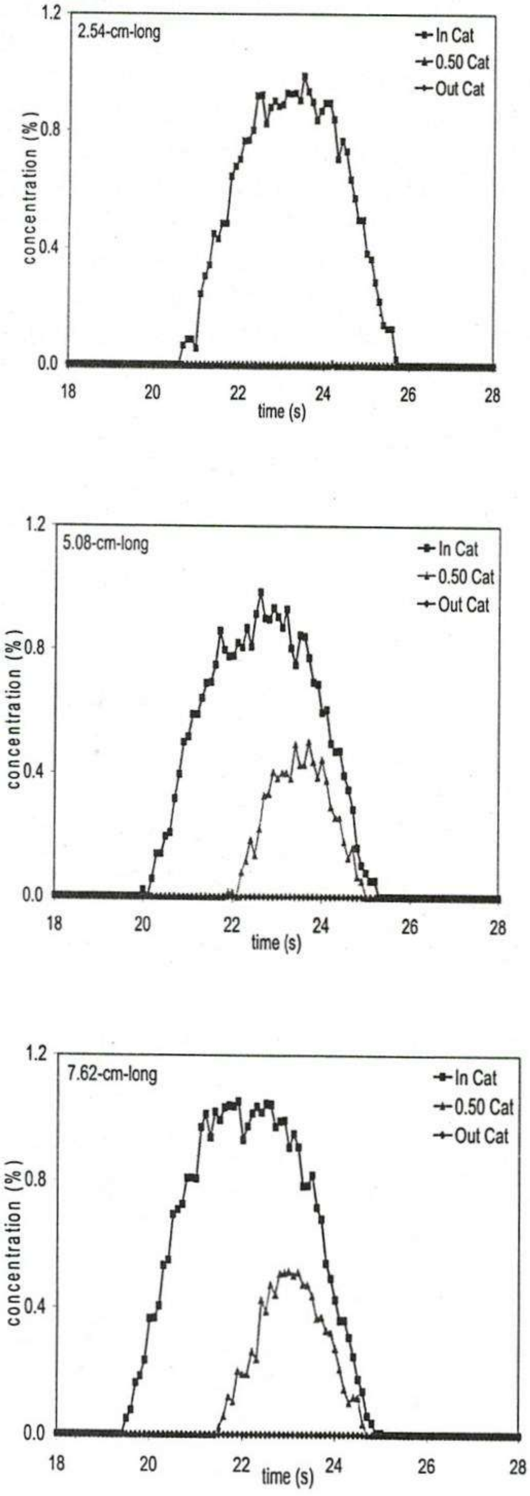

Figure 5. H_2 consumption trends in 2.54, 5.08 and 7.62-cm-long samples in short-cycle experiments with 1.0% H_2 in rich phase at 300°C

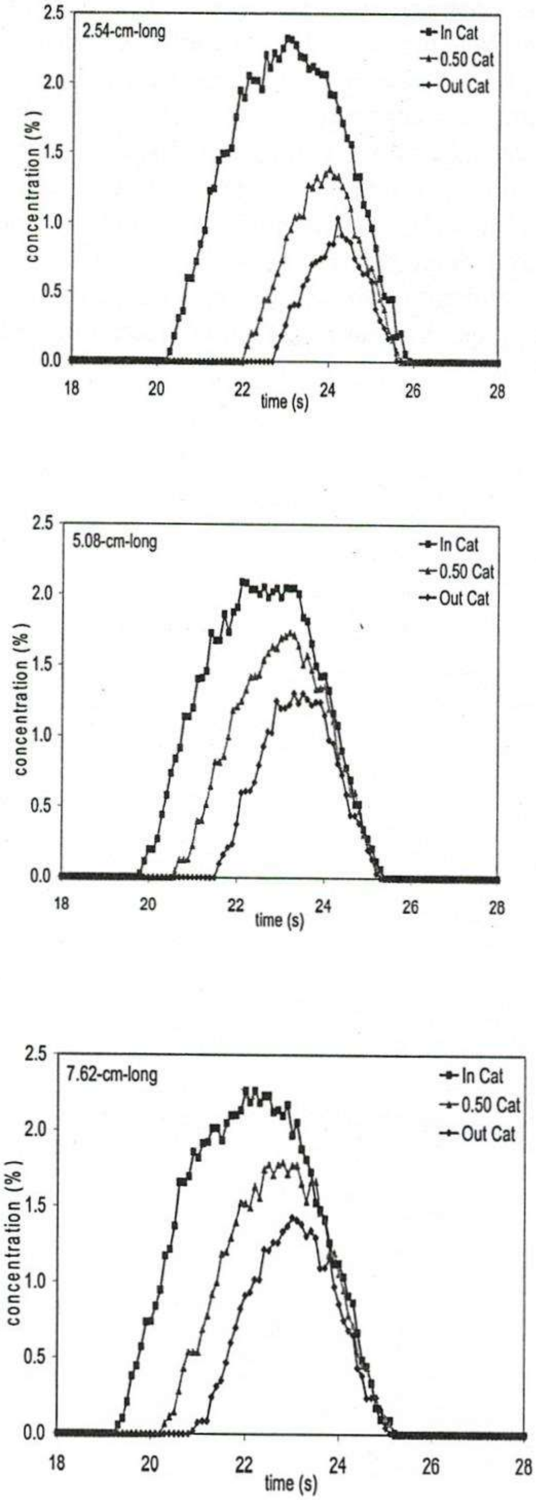

Figure 6. H_2 consumption trends in 2.54, 5.08 and 7.62-cm-long samples in short-cycle experiments with 2.0% H_2 in rich phase at 300°C

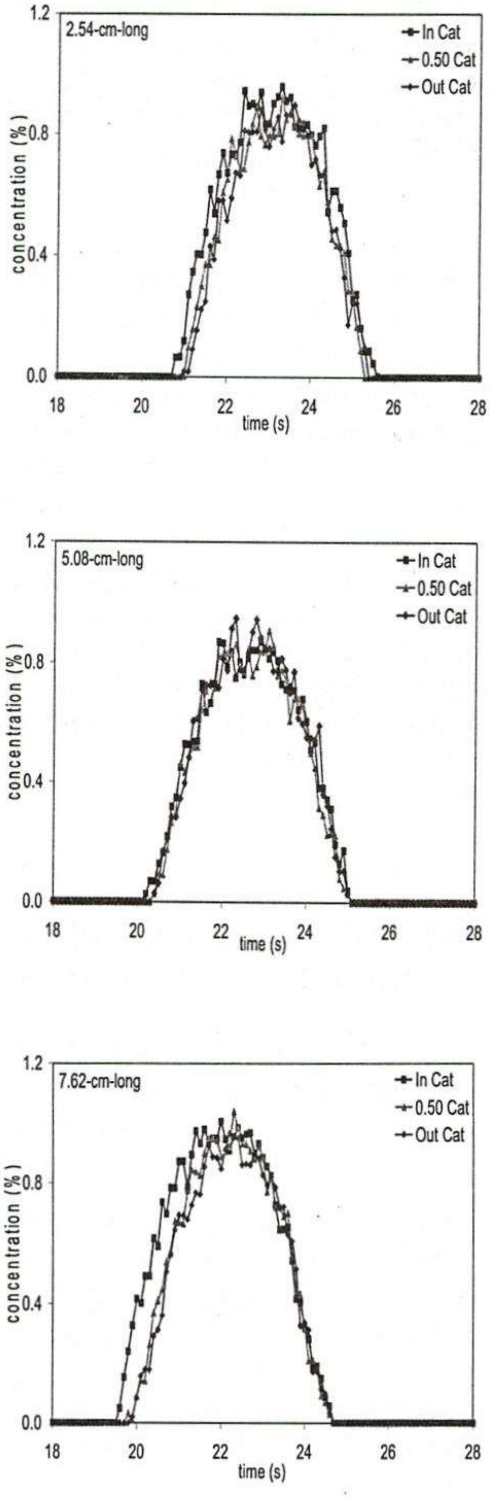

Figure 7. H_2 consumption trends in 2.54, 5.08 and 7.62-cm-long samples in back-mixing short-cycle experiments with 10s N_2 purge and 1.0% H_2 in rich phase at 300°C

Thus, higher consumption of H_2 in 2.54-cm-long sample than in 5.08 and 7.62-cm samples can be attributed to higher degree of back-mixing in the shorter sample. For example, in the 2.54-cm-long sample as much as 35% of H_2 is consumed from the catalytic oxidation at the lean/rich interface – compared to only 10% in the longer sample – resulting in a reduction of 15% in NO_x conversion in short-cycle experiments with 1% H_2. The higher consumption of H_2 in shorter sample is further confirm by smaller quantity of NH_3 formed in 2.54-cm-long sample, since NH_3 production decreases with decreasing H_2 concentration [18].

4. CONCLUSIONS

The effect of monolith length on the NO_x performance of Lean NO_x Traps was investigated in the present study. Samples of three different lengths were evaluated with long and short - cycle experiments at a fixed GHSV.

No significant difference in performance was observed in long and short-cycle experiments with full regeneration. On the other hand, significant difference is observed in short-cycle experiments with partial regeneration: the longer the sample the better the performance. A difference as large as 20% in NO_x conversion efficiency was observed between 2.54 and 7.62-cm-long samples with lower performance in shorter sample.

H_2 consumption trends during short-cycle experiments indicate different degrees of lean and rich front back-mixing for samples of different lengths. Higher back-mixing results in a higher H_2 loss via its oxidation by O_2 and lesser H_2 availability for reducing stored NO_x, which in turn affects catalyst's performance when regeneration is limited by amount of H_2 available. In 2.54-cm-long sample as much as 35% of H_2 is consumed from the catalytic oxidation at the lean/rich interface resulting in a reduction of 15% in NO_x conversion in short-cycle experiments with partial regeneration.

CƠ CHẾ MẤT TÁC DỤNG CỦA BỘ XÚC TÁC NOx ĐÃ BỊ LÃO HÓA NHIỆT

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TÓM TẮT: *Bộ xúc tác làm sạch NO_x (LNTs) có chứa các chất Pt, Pd, Rh, Ba, Ce, Zr, và các chất phụ gia khác trên lớp nền của hợp kim γ-Al_2O_3 được đưa vào khảo sát trong trạng thái lão hóa nhiệt ở các nhiệt độ 750, 880, 930, và 1070°C. Dùng các phương pháp XRD, STEM/EDS, BET phân tích khả năng lưu giữ NO_x, o xy hóa NO, chuyển biến NO_x, và phân tích DRIFTS để xác định các cơ chế mất tác dụng của bộ xúc tác ở nhiệt độ lão hóa cao. Khi sự phân tán PGM giảm, sự oxy hóa theo mol bề mặt PGM giảm ở các nhiệt độ đánh giá 200, 300, và 400°C. Sự lưu giữ NO_x và nhiệt độ tách hấp thu theo chương trình (TPD) thí nghiệm thực hiện với DRIFTS ở 200, 300, và 400°C chỉ ra rằng một lượng đáng kể NO_x được lưu giữ trên nền γ-Al_2O_3 dưới dạng các nitrates ở 200 và 300°C trước lão hóa. Tuy nhiên, hầu như không có chất nitrate nào trên nền alumina sau khi lão hóa ở 900 và 1000°C, kết quả là có sự giảm đáng kể khả năng lưu giữ NO_x. Không có sự tạo thành các nitrates.*

Từ khóa: *Độ phát thải, Xử lý khí thải, Giải pháp Nox.*

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