

Enhanced Low-Temperature NO_x Conversion by High-Frequency Hydrocarbon Pulsing on a Dual Layer LNT-SCR Catalyst

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ABSTRACT

Current NO_x emission reduction systems, selective catalytic reduction (SCR) and NO_x storage and reduction (NSR), function well after achieving their operation temperature (typically ca. 250 °C) but have unsatisfactory NO_x conversion at lower exhaust temperatures encountered during cold start and low load operation. The reduced exhaust temperature of advanced diesel engines with higher fuel efficiency challenges the low-T NO_x reduction. We report here a new concept of high low-T deNO_x efficiency of up to 80% at a feed temperature of ca. 200 °C at relevant space velocities (70k h⁻¹). It utilizes high-frequency hydrocarbon pulsing on a dual-layer LNT-SCR monolithic catalyst under lean conditions. This system has the potential to expand the operating temperature window of the conventional deNO_x devices.

Inspired by Toyota's Di-Air ("Diesel NO_x aftertreatment by Adsorbed Intermediate Reductants) process [1], the proposed dual-layer LNT-SCR operation utilizes rapid short-cycle injection of hydrocarbons to increase the NO_x conversion at low temperatures (< 250 °C). The new operation exploits the reported Di-Air mechanism which involves generation of short-lived intermediates in the LNT base layer that can be captured and utilized by a top layer SCR-zeolite catalyst for incremental NO_x conversion.

Our experiments consisted of rapid short cyclic injection of propene into a lean NO_x stream fed to an aged LNT-SCR dual-layer catalyst. High frequency HC pulsing on the dual-layer reduced the light-off temperature by ca. 50 °C below that of an LNT catalyst subjected to conventional NSR cycling. The enhanced low-T performance can be attributed to both chemical and thermal effects. Under high frequency operation the deposited SCR layer enables utilization of intermediate species (C_xH_yO_z and C_xH_yO_zN_l) and appreciable storage of heat both generated from oxidation of the hydrocarbon by O₂/NO_x in the underlying LNT layer. Under fast cycling the low-T NO_x conversion of the dual-layer catalyst exceeds that of either the LNT alone or of LNT-SCR dual-brick catalysts. Increased PGM loading of the dual-layer catalyst to 120 g/ft³ decreases the light-off temperature to a feed temperature of around 175 °C.

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INTRODUCTION

Diesel passenger vehicles, having higher fuel economy than conventional gasoline vehicles, offer an effective solution for automakers to satisfy the upcoming 2017-2025 US EPA greenhouse gas and NHTSA fuel economy standards [2]. A key challenge facing the diesel engine today is the upcoming LEV III or Tier 3 emission regulations that tightens the fleet-averaged NMOG+NO_x emission limit by ~80% from current LEV or Tier 2 Bin 5 level. Leading NO_x aftertreatment systems, selective catalytic reduction (SCR) and NO_x storage and reduction (NSR), achieve high deNO_x efficiency after the catalysts reach their operation temperatures, which are typically ca. 250 °C. Their performance, however, are inferior under low-temperature operating conditions of the vehicle, as encountered during the cold startup or low load operation. Reducing low-temperature NO_x emission is critical to meet the stringent regulation

requirements. Satisfying this regulation is becoming more difficult due to the reduced exhaust gas temperature of advanced engine and powertrain technologies having higher fuel economy [3].

An effective approach to increase low temperature NO_x conversion is a combined LNT+SCR system, in the form of either zoned or layered configurations [4, 5, 6, 7, 8, 9]. For example, to reduce the cold start NO_x emissions when the exhaust temperature is too low for urea dosing, a urea-SCR system can be coupled with an LNT. Upon reaching its operation temperature, the urea SCR provides high deNO_x efficiency at minimal fuel consumption. The active SCR-based combined system is able to meet the LEV III requirements, as reported by Cummins [10], SwRI [11] and Hyundai [7]. But it faces packaging, cost and control complexity issues, especially for light duty applications [8].

For small-size vehicles, use of an LNT + passive SCR system which avoids urea dosing is favored due to smaller packaging space and lower system cost [6, 12]. The SCR traps and utilizes reductants for incremental NO_x conversion, primarily NH₃ generated by the LNT during rich regeneration, as well as unreacted hydrocarbons slipping from the LNT. The overall NO_x reduction is still dominated by the LNT performance that is relatively low at both low and high temperatures. The low-temperature LNT performance suffers from an inefficient utilization of reductants like CO and hydrocarbons (HCs) during the rich regeneration, as well as limited NO oxidation during the lean phase. On the other hand its high-temperature performance (>350 °C) is limited by decreased NO_x storage capacity and NH₃ yield limit. Thus, the combined LNT + passive SCR require further improvements to achieve high NO_x conversion over a wide operating temperature window.

Toyota researchers recently developed a high-performance deNO_x system named Di-Air (diesel NO_x aftertreatment by adsorbed intermediate reductants) [1]. It utilizes rapid short-cycle injection of hydrocarbons into a lean exhaust stream fed to an LNT catalyst. It significantly enhances NO_x reduction over that of a conventional NSR under high-temperature and high-SV operation. (Typically 30-60s fuel-lean feed followed by 3-10s fuel-rich feed) The enhanced performance is primarily attributed to adsorbed intermediates containing H, C, N, and O generated during the high-frequency HC pulsing, by a reaction between adsorbed NO_x and partially oxidized hydrocarbons [13]. These short-lived intermediates are then selectively converted through reaction with surface and gas phase NO_x species to N₂ during the lean part of the cycle. They pointed out that in contrast to conversional NSR, the high-temperature NO_x conversion of the Di-Air injecting a HC reductant was superior to injecting either H₂ or CO [14]. A recent study of our group found that high frequency pulsing of propylene enhanced somewhat deNO_x activity of LNT catalysts even at low temperatures, but to a smaller extent than at high temperatures [15].

The reaction mechanism of Di-Air is somewhat similar to the so-called “non-NH₃” pathway in the LNT-SCR system proposed and generated by Ford researchers [16, 17]. This pathway involves the formation of organic intermediates (C_xH_yO_z, C_xH_yO_zN_l) via the reaction of adsorbed NO_x with HCs over the LNT catalyst during the rich feed of the NSR, followed by the capture and utilization of these non-NH₃ reductants by the SCR catalyst for incremental NO_x conversion. A recent report by our group verified that this non-NH₃ pathway played an important role in the low-T NO_x conversion enhancement of combined LNT-SCR dual-layer catalysts [12]. Thus, we decided to check if high-frequency HC pulsing can benefit a combined LNT+ passive SCR system at low temperatures. The main goal of this study is to determine if and how a high-frequency HC pulsing can effectively improve low-T NO_x conversion of dual-layer LNT-SCR catalysts over that of conventional NSR. We investigated the chemical and thermal impact on the working mechanism of the low-T enhancement. We also discuss how variations of the catalyst configuration, PGM loading and zoning may enhance this new deNO_x system.

EXPERIMENTAL

Catalysts

The monolithic LNT catalyst provided by BASF (Iselin, NJ) has a cell density of 400 cpsi and washcoat loading of 4.6 g/in³, corresponding to a thickness of ~80 μm. It contains Pt/Rh/BaO/CeO₂/Al₂O₃ with a PGM loading of 90 g/ft³, 15 wt.% BaO and 34 wt.% CeO₂ on a γ-alumina support. In some cases, LNT with higher PGM loading of 120 g/ft³ was used and also from BASF. Small cylindrical catalyst samples (~55 channels, D = 0.42 in, L = 1 in) were drilled out of a large brick. The in-house synthesized small-pore Cu-SAPO-34 SCR catalyst powder was prepared via a method described elsewhere [18]. The as-prepared SCR powder was washcoated onto the LNT monoliths by a dip-coating technique described elsewhere [19]. A uniform SCR layer of 0.8 g/in³ was deposited on top of the LNT layer creating an LNT-SCR dual-layer catalyst. All catalysts were aged at 700 °C for 33 hours in air only, equivalent to 160,000-km aging, prior to bench reactor experiments (following the protocol of Bisaiji et al. [1]).

Reactor System

A schematic of the bench-scale reactor system is shown in Fig. 1. The set-up comprised four major components: gas supply, tubular reactor, analytical and data acquisition systems. The flow reactor utilized synthetic exhaust gas mixtures from cylinder-supplied gases (Praxair). Gas flow rates were controlled by mass flow controllers (MKS Instruments). Water was fed by a syringe pump (ISCO Model 500D) and vaporized in a heated line. In all experiments, the total gas flow was 3000 cm³/min, corresponding to a gas hourly space velocity (GHSV) of ca. 74,000 h⁻¹ at standard conditions. The gases were pre-mixed in three separate lines: one of inert species (CO₂, H₂O, Ar), one of lean feed (NO, O₂, Ar) and one of rich feed (NO, O₂, C₃H₆, Ar). The monolith catalyst core sample was wrapped with Fiberfrax® ceramic paper and inserted into a quartz tube (OD = 0.75 in.) positioned inside a Thermocraft™ tube furnace. Localized feed gas and catalyst temperatures were measured using two K-Type thermocouples (Omega Engineering Inc.). One thermocouple was placed 0.5 in. upstream of the catalyst to monitor the feed temperature (T_f), while the other was positioned at the midpoint of the monolith (radial and axial) to measure the temperature at the center of the catalyst (T_c). The outlet gas stream flowed through a heated line at ca. 190 °C to the MultiGas 2030 FTIR (MKS Instruments), which measured concentrations of NO, NO₂, N₂O, C₃H₆, NH₃, HCHO, HNCO, CO, CO₂ and H₂O. We cannot rule out the formation of other product species such as C₂ and C₃ aldehydes, carboxylic acids, and amines. The FTIR was not calibrated for detecting these species. A nitrogen balance could not be done because N₂ cannot be measured by a mass spectrometer due to overlap at m/e = 28 of both CO and C₂H₄. Neither was a carbon balance done since the CO₂ feed concentration of 5% greatly exceeded that of any propylene-derived species. A more detailed study of the byproduct formation is currently underway and will be reported elsewhere.

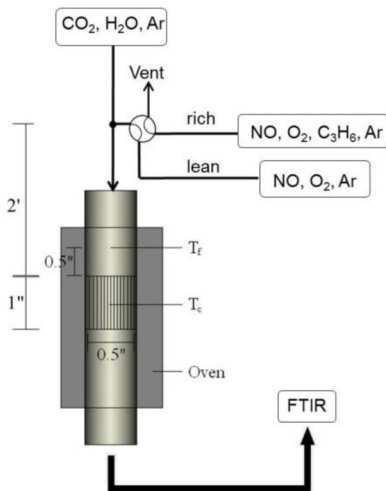


Figure 1. Schematic of the reactor system.

A solenoid actuated four-way valve (Valco Inc., Micro-electric two position valve) generated the high-frequency HC pulsing via fast switching between lean and rich feeds. The two reactive feeds were connected to the inlets of the switching valve, while one outlet of the valve was connected to the main gas line just upstream of the catalyst sample and the other to the vent. The flow rate of inert gas in the main line was kept at 800 cm³/min, lower than 2200 cm³/min of the lean or rich reactive feed. The main purpose was to guarantee that the correct amount of reactive feed was injected during the fast switching. HC premixed in the rich line helps avoid flow mal distribution. This was important as recently pointed out by Toyota researchers that high radial uniformity of HC concentration was essential for Di-Air performance [20]. In order to minimize upstream axial mixing of lean and rich streams, the switching valve was placed in close proximity to the monolithic catalyst (~2 ft. upstream), but sufficiently far to allow preheating of the feed stream. A long distance between the injection point and the catalyst resulted in a well-premixed feed during high frequency operation, thereby decreasing the NOx conversion (We did not investigate in detail this design variable in the current study and 2-ft may not be the optimal distance.). The injection valve, thermocouples and MFCs were all controlled/monitored using LABVIEW™ software. Time delays between the feed point, reactor and the analytical equipment were accounted for in the data processing through tracer measurements.

Table 1. Lean-rich feed concentrations. GHSV = ca. 74,000 h⁻¹ and $S_N = 8.04$ and $S_{N,p} = 0.62$.

Gas	Lean	Rich
NO	300 ppm	300 ppm
C ₃ H ₆	—	1.8%
O ₂	10%	5%
CO ₂	5%	5%
H ₂ O	3.5%	3.5%

Lean-rich cycling experiments were conducted over either the LNT only, LNT-SCR dual-layer, or LNT-SCR dual-brick catalysts. Table 1 describes the feed compositions. Two different cycle timing, 30s lean/5s rich and 6s lean/1s rich, were mainly used corresponding to conventional and high-frequency NSR operations, respectively. The Di-Air operation periodically oscillates the air:fuel ratio (A/F) in the lean regime. We used high O₂ concentration of 10% in the lean feed and 5% in the rich feed. Previous studies found that a rich duty cycle (rich phase duration divided by total cycle time) of 14.3% achieved a high NOx conversion [21]. Hence, this value was used in all cycling experiments. Prior to testing, each catalyst was pretreated by exposing it at 400 °C for 15 min to lean/rich 30/5s and 6/1s cycling conditions, respectively. For catalyst activation, a periodic lean/rich pretreatment was superior to oxidative pretreatment in terms of faster light-off. The stoichiometric number is the molar ratio of the oxidizing to reducing components

$$S_N = \frac{2[O_2] + [NO]}{9[C_3H_6]}$$

A S_N value greater than unity represents a lean mixture, whereas a value less than unity a rich mixture. $S_{N,p}$ and S_N denote the stoichiometric number of the feed stream during the rich pulse and the cycle-averaged value, respectively. Based on the feed composition in Table 1, the corresponding $S_{N,p}$ and S_N used in this study was fixed as 0.62 and 8.04, respectively. The cycle-averaged conversions of NOx (NO + NO₂) and propylene were respectively determined by the fraction of NOx and propylene feed that were consumed (formula provided in [9]), during the final ten cycles after the system reached a stable periodic state.

Results and Discussion

Enhanced NOx Conversion by Combining Rapid Pulsing with SCR Layer Addition

Fig. 2a compares the cycle-averaged NOx conversions over the LNT catalyst as a function of the feed temperature for two different cycle times at the same rich cycle duty (14.3%). The rapid propylene pulsing into the lean stream clearly enhances NOx conversion over the entire temperature range, especially at low temperatures below 250 °C. Rapid injection also significantly enhances the high-T NOx conversion at feed temperatures above 400 °C (data not shown). This is consistent with the high temperature trend reported by Toyota researchers [1]. Fig. 2b shows that deposition of an SCR top-layer increases the low-T NOx conversion and that it exceeds that of the LNT with a fixed long cycle time. Due to negligible NH₃ generation at low temperatures (< 250 °C) as shown later in Fig. 5, the low-T enhancement by the SCR layer is mainly attributed to the non-NH₃ reductants, oxygenated propene derivatives. These are produced in the underlying LNT layer during the rich purge and are then stored and reacted in the upper SCR layer [12]. Hence, the low-T NOx conversion can be increased by use of either high-frequency HC pulsing or deposition of an SCR top layer on the LNT.