

Optimization of LNT-SCR Dual-Layer Catalysts for Diesel NO_x Emission Control

Yang Zheng, Dan Luss, and Michael P. Harold
University of Houston

ABSTRACT

Monolithic catalysts consisting of a layer of SCR catalyst deposited on top of a LNT catalyst were optimized to provide high NO_x conversion at both low and high temperatures with minimal precious group metal (PGM) loading for effective diesel NO_x emission control. In this study we demonstrate the application of LNT & SCR zoning in dual-layer catalyst to improve NO_x reduction efficiency and show the potential to reduce the expensive PGM loading by up to 40% from that of LNT only catalyst without degrading its deNO_x performance under simulated diesel exhaust conditions. We investigated the NO_x reduction pathway in the SCR layer of the dual-layer catalyst using simulated rich exhaust of C₃H₆/CO/H₂ as reductants. The non-NH₃ reduction pathway by N-containing organic intermediates via the synergy of LNT and SCR catalysts can play a major role in the incremental NO_x conversion over SCR layer at low temperatures (≤ 225 °C). The roles of NH₃ and C₃H₆ as reductants for NO_x conversion over the SCR catalyst increase with temperature (> 225 °C). The impact of SCR and LNT zoning as well as SCR layer thickness, were studied. Zoning of either or both the SCR and LNT in the dual-layer catalysts improved the low-temperature NO_x conversion, and minimized the high-temperature (300-400 °C) conversion loss caused by the SCR layer diffusion resistance and undesired NH₃ oxidation. The performance decline due to the Cu-zeolite layer diffusion resistance was confirmed by replacing it with an inert Na-zeolite layer with a high Si/Al ratio.

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INTRODUCTION

Upcoming emission regulations like LEV III set stricter limitations on NO_x, PM and HC emissions from lean burn gasoline and diesel engines. The increasing demands on high performance, small-size and cost-effective aftertreatment systems to meet the regulations have motivated the integration of multiple catalytic technologies such as selective catalytic reduction (SCR), lean NO_x traps (LNT) and HC adsorber catalysts [1]. One typical example is combined LNT+SCR systems wherein the SCR catalyst stores and utilizes the reductants, generally NH₃, produced over the LNT during rich purges for additional NO_x reduction. This combination enables enhanced NO_x removal performance while lowering the cost by the reduction of the volume of the expensive PGM-containing LNT and the elimination of the need for urea injection to the SCR catalyst.

Several LNT+SCR configurations have been proposed, including zoned or layered configurations [2, 3, 4, 5, 6, 7]. Daimler commercialized the first LNT+SCR dual-zone deNO_x system on the Mercedes-Benz E-Class in 2007 [8]. Xu et al. [4] from Ford demonstrated the ability of the LNT+SCR dual-zone approach to achieve the Tier 2 Bin 2 standard with up to 30% saving in PGM loading compared to the LNT alone. They also

proved the existence of a non-NH₃ reduction pathway over the SCR for incremental NO_x reduction [9]. Morita et al. [10] from Honda presented the first report of a LNT+SCR dual-layer system that meets the Tier 2 Bin 5 standard. Recently, Honda researchers Matsuo et al. [6] further improved the dual-layer system by introducing a zirconia-based intermediate layer that minimized the negative interaction between LNT and SCR layers of opposite acid-base properties. The improved system showed high NO_x reduction performance even for low exhaust gas temperature.

Multi-layered architectures enable the potential downsizing of the aftertreatment system from that of a sequential configuration. This is desirable for application in cars with limited space. Moreover, the intimate contact between LNT and SCR layers is expected to enhance the utilization efficiency of reductants like NH₃. In the dual-zone configuration, a considerable amount of NH₃ released from the front LNT section may be oxidized by stored NO_x and oxygen in the LNT downstream before it can reach the SCR brick, limiting the NH₃ supply to the SCR reaction [2]. Inherent drawbacks are also associated with the dual-layer architecture. The foremost issue is the inevitable diffusion resistance of the SCR upper layer, which inhibits the transport of NO_x to the downstream for storage during the lean feed and of reductants for

regeneration during the rich feed. Koltsakis [11] reported that at either high temperature or high space velocity, the dual-layer deNO_x efficiency was severely reduced by the additional resistance of the SCR layer and was lower than either a LNT alone or a dual-bed system. Another deficiency is the undesired oxidation of stored NH_3 to NO_x by the adjacent LNT layer at high temperatures [12]. In addition, there is a concern on inter-layer mixing of elements in LNT and SCR coatings, which might become significant after high-temperature aging. Such detrimental effects may counterbalance or even outweigh the benefit of adding the SCR layer.

The main goal of the present study is to determine whether and which zoned dual layer LNT-SCR catalyst can improve the overall NO_x reduction performance at both low and high temperatures. We study the NO_x reduction pathway in the SCR layer of the dual-layer catalyst by simulated rich exhaust gas of a $\text{C}_3\text{H}_6/\text{CO}/\text{H}_2$ mixture. The non- NH_3 reductant species, likely nitrogen-containing organic compounds formed by the reaction of propene with adsorbed NO_x in the LNT layer, contributes to the incremental NO_x conversion over SCR layer at low temperatures ($< 250^\circ\text{C}$). The performance loss caused by the top-layer diffusion resistance is determined by replacing it with an inert Na-zeolite layer. Finally, zoning of both the SCR and LNT in the dual-layer catalysts has the potential to reduce the expensive PGM loading by up to 40% from that of LNT-only catalyst under laboratory conditions.

EXPERIMENTAL

Catalysts

Monolithic LNT ($\text{Pt}/\text{Rh}/\text{BaO}/\text{CeO}_2/\text{Al}_2\text{O}_3$) and SCR (Cu-SSZ-13) bricks were supplied by BASF Catalysts (Iselin, NJ). The LNT sample had a cell density of 400 cpsi and a washcoat loading of 4.6 g/in^3 , corresponding to $60\text{--}80 \mu\text{m}$ in thickness. It contained a PGM loading of 90 g/ft^3 , 14 wt% BaO and 34 wt% CeO_2 in washcoat. The Cu-SSZ-13 catalyst, referred to as CuC, has an 8-membered ring, small-pore chabazite (CHA) crystal structure. Its cell density was 400 cpsi and the washcoat loading was about 2.4 g/in^3 . Cylindrical cores ($D=2.54 \text{ cm}$, $L=7.6 \text{ cm}$) were drilled out of a monolithic brick. Then small monolithic pieces were prepared with a specific shape ($D=0.8 \text{ cm}$, $L=2.0 \text{ cm}$, 28 channels).

LNT-SCR dual-layer monolithic catalysts, provided by BASF Catalysts (Iselin, NJ), comprised a Cu-SSZ-13 layer deposited on top of the LNT catalyst. We refer to these dual-layer catalysts as $\text{CuC}(\text{Y})/\text{L}(\text{X})$, in which the “Y” is the top-layer washcoat loading of the CuC while the “X” indicates the bottom-layer loading of the LNT denoted by “L”. The compositions of the LNT and SCR in the dual-layer catalysts are the same as above. A series of CuC-L dual-layer catalysts with varying LNT ($1.15, 2.3, 3.45, 4.6 \text{ g/in}^3$) and SCR ($0.8, 1.6 \text{ g/in}^3$) loadings were prepared for our study. Catalyst notation and configurations used in our experiments are reported in [Table 1](#).

In order to investigate the washcoat diffusion resistance by the top layer, an inert Na-ZSM-5 (NaZ) with a high Si/Al ratio was deposited on top the LNT monolith to form a dual-layer catalyst, $\text{NaZ}(\text{Y})/\text{L}(\text{X})$. The in-house synthesized Na-ZSM-5 catalyst powder with Si/Al ratio of up to 280 was prepared via a wet-ion exchange method described elsewhere [13]. Then the as-prepared Na-ZSM-5 powder was washcoated onto the bare cordierite or LNT monoliths for testing. The high Si/Al ratio was used to minimize the adsorptive or catalytic properties of the zeolite catalyst.

Reactor System

The bench-scale reactor set-up comprised a gas supply, a reactor, and analytical and data acquisition systems. Gas flow rates were controlled by mass flow controllers (MKS Inc.) before entering the inline static mixers. Water was fed by a syringe pump (ISCO Model 500D) and vaporized in a heated line. A LabTech interface controlled the switching valve and mass flow controllers for the feed streams. The monolith catalysts were wrapped with Fiberfrax® ceramic paper and inserted inside a quartz tube (40.6 cm long, 1.27 cm outer diameter) mounted in a tube furnace coupled to a temperature controller. The temperature inside the reactor was measured by two 0.5 mm type-K stainless steel sheathed thermocouples (Omega Engineering Inc.). One placed 0.5 cm in front of the monolith measured the feed temperature. The other located in the middle of the center monolith channel measured the monolith temperature. The gaseous effluent concentrations of NO , NO_2 , N_2O , NH_3 , CO , CO_2 and H_2O were measured by a FT-IR spectrometer (Thermo-Nicolet, Nexus 470). A quadrupole mass spectroscopy (QMS; Cirrus LM99, MKS Inc.) monitored the concentrations of H_2 and O_2 if needed. In the presence of CO , having the same m/e of 28 as N_2 , the cycle-averaged N_2 was determined by an overall nitrogen balance.

Lean-rich cycling experiments were conducted over either LNT-only or SCR-only or dual-layer catalysts. [Table 2](#) describes the 60s-lean and 5s-rich cycling conditions. A fixed operating condition makes it easy to focus on the impact of different catalyst design variables. The same lean phase conditions were used in all the experiments. Unless otherwise mentioned, the standard set of gas compositions with a lean gas feed and a rich gas feed #1 described in [Table 1](#) was used for the majority of the tests to simulate real diesel exhaust gas. A 3:1 ratio of $\text{CO}:\text{H}_2$ was used and propylene (C_3H_6) was chosen as the model HC reductant typical of light cracked hydrocarbons in a diesel exhaust. Prior to measurements, each catalyst was degreened by exposing it to 5% O_2 in Ar at 500°C for 30 min and then to lean/rich cycling conditions with rich feed #1 at 500°C for another 90 min.

The total flow rate was 1000 sccm. Unless specifically stated, the GHSV was $60,000 \text{ h}^{-1}$ (based on monolith volume, 2 cm long). In some cases, a series of shorter LNT pieces were used to construct spatial concentration profiles. The feed temperature was increased from 150 to 250°C in steps of 50°C , and then to 400°C in steps of 50°C . It took approximately

5~10 min to reach a periodic state. At each temperature the final ten cycles were averaged after a cyclic state was reached to determine the cycle-averaged NO_x conversion and NH₃ yield for a particular operating condition.

The fractional NO_x conversion was calculated by

$$X_{NOx} = 1 - \frac{\int_0^{\tau_r} [F_{NO}(t) + F_{NO_2}(t)] dt}{\int_0^{\tau_r} F_{NO}^i(t) dt}$$

The fractional NH₃ yield was calculated by

$$Y_{NH_3} = \frac{\int_0^{\tau_r} F_{NH_3}(t) dt}{\int_0^{\tau_r} F_{NO}^i(t) dt}$$

Here τ_l and τ_r are the duration of lean feed and the lean-rich cycle (s). $F_{NO}^i(t)$ is the NO feed rate and $F_{NO}(t)$, $F_{NO_2}(t)$, $F_{NH_3}(t)$, are the effluent molar flow rates of the various species (mole/s).

Several continuous flow experiments were conducted to evaluate the SCR catalyst properties. The standard SCR and HC-SCR reactions were used to assess the activity of the CuC and NaZ, both of which had a ~2.4 g/in³ loading. The feed contained 500 ppm reductant (NH₃ for standard SCR or C₃H₆ for HC-SCR), 500 ppm NO, and 5% O₂ in carrier gas of 2.5% H₂O, 2% CO₂, and Ar (balance). As for NH₃ and C₃H₆ storage experiments, each catalyst was pretreated by exposing it to a flow containing 5% O₂ in carrier gas at 500 °C for 1 h, followed by cooling to the desire temperature in the carrier gas. A carrier gas containing 500 ppm NH₃ or C₃H₆ was fed to the catalysts at 150 °C for 30 min until they were saturated. The adsorbate feed was then shut off and the catalysts were purged by a carrier gas for 30 min at 150 °C. The adsorption capacity of the catalyst was calculated from the difference between the uptake and the amount of released adsorbate during flushing.

Table 1. Configuration and notation of zoned & layered catalysts.

Catalysts	Configurations	LNT, g/in ³	CuC*, g/in ³
L(X)		X	—
CuC*(Y)/L(X)		X	Y
L(X ₁)+CuC*(Y)/L(X ₂)		X ₁ /X ₂	Y

*CuC may be also NaZ in study.

*CuC, NaZ represent Cu-CHA, Na-ZSM-5, respectively.

RESULTS AND DISCUSSION

NO_x Reduction in the SCR Layer of the Dual-Layer Catalyst

Fig. 1 compares the cycle-averaged NO_x conversion under simulated diesel exhaust conditions (rich feed #1 in Table 2) for a high-loaded LNT catalyst, L(4.6), and one with a top SCR layer, CuC(0.8)/L(4.6). The added SCR layer improves the NO_x conversion in the low- and mid-temperature range (below 300 °C). Above 300 °C, the NO_x conversion from the dual-layer catalyst is slightly lower than that of the LNT-only catalyst. Hence, addition of a SCR top layer is beneficial for temperatures below 300 °C but somewhat detrimental above 300 °C. Fig. 2 shows the transient concentration profiles of NO_x (NO+NO₂), N₂O, NH₃, and C₃H₆ after cyclic behavior was achieved at 200 °C for the same LNT catalysts with and without a SCR top layer. The effluent lean-phase NO_x slip from the dual-layer catalyst is clearly lower than that from the LNT, while only a slight decrease is observed in the rich-phase NO_x puff. This suggests that the reductants stored in the SCR layer can react with NO_x in the lean phase to reduce its slip. Note that only a small amount of NH₃ is emitted from the LNT at 200 °C and slightly less C₃H₆ slip from the dual-layer catalyst is observed, apparently due to the HC adsorption by the SCR layer.

Table 2. Gas conditions for 60/5 cycling test.

Gas	Lean	Rich #1	Rich #2	Rich #3	Rich #4
NO	300 ppm	300 ppm	300 ppm	300 ppm	300 ppm
CO	—	2.4%	2.4%	—	—
H ₂	—	0.8%	0.8%	—	—
C ₃ H ₆	—	1000 ppm	—	1000 ppm	3550 ppm
O ₂	5%	1%	—	—	—
CO ₂	2%	2%	2%	2%	2%
H ₂ O	2.5%	2.5%	2.5%	2.5%	2.5%

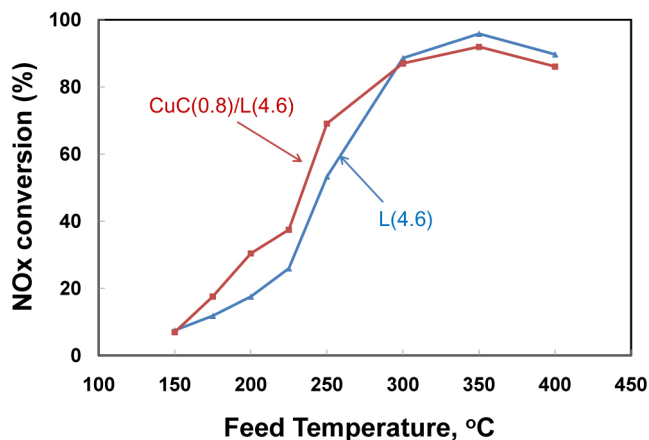


Figure 1. Comparison of cycle-averaged NO_x conversion for L(4.6) and CuC(0.8)/L(4.6) catalysts using 2.4% CO + 0.8% H₂ + 1000 ppm C₃H₆ as reductants (Rich #1).