Rapid Propylene Pulsing for Enhanced Low Temperature NO_x Conversion on Combined LNT-SCR Catalysts

Yang Zheng^a, Mengmeng Li^a, Di Wang^b, Michael P. Harold^{a,*}, Dan Luss^{a,*}

^a Department of Chemical & Biomolecular Engineering
University of Houston
Houston, TX 77204

^b Cummins Inc.
Columbus, IN 47201

*Corresponding author: Tel. 1-713-743-4322; Fax. 1-713-743 432
mharold@uh.edu (M.P. Harold), dluss@uh.edu (D. Luss)

Abstract

Lean reduction of NO_x (NO + NO₂) was conducted over combined LNT-SCR dual-layer and zoned monolithic catalysts using rapid propylene periodic pulsing into a lean feed. We investigated the effects of cycling frequency, reaction exotherm, hydrocarbon (HC) intermediates, top-layer material, LNT ceria content and catalyst configuration on the performance of dual-layer catalysts under fast propylene pulsing. High frequency propylene injection expands the operating temperature window of a conventional NO_x storage and reduction (NSR) system in both low and high-temperature regions. The combination of rapid propylene pulsing and the dual-layer catalyst architecture achieves a low-temperature NO_x conversion of up to 80% at a feed temperature of ca. 200 °C and relevant space velocities (~ 70k h⁻¹). The working mechanisms of rapid propylene pulsing on both LNT and LNT-SCR catalysts are discussed. Fast cycling facilitates the generation of partially oxidized hydrocarbon intermediates over the LNT that can then either directly react with NO_x or act as oxygen scavenger to maintain Pt in a reduced state for direct NO decomposition. The SCR top-layer traps partially oxygenated species that desorb from the LNT layer, enabling further production of N₂ through a LNT-assisted HC-SCR pathway. Optimization of ceria content, top-layer material and catalyst configuration like SCR and PGM zoning can improve system performance at lower cost.

Keywords: NO_x; Propylene; Selective Catalytic Reduction; Platinum; Low temperature NO_x reduction; HC-SCR

1. Introduction

The mandate for higher fuel-efficiency vehicles that meet emerging greenhouse gas (GHG) emission limits arouses an increased interest in lean burn engines with higher fuel-combustion efficiency (~20% gain in fuel economy compared to the stoichiometric combustion) [1]. Advanced powertrain strategies such as hybrid electric, turbo charging and start/stop techniques boost the fuel efficiency but produces a lower enthalpy exhaust; e.g., typical turbochargers can lower the exhaust gas temperature by more than 100 °C [2]. The lower temperature poses a great challenge to the catalytic abatement of NO_x (NO + NO₂) under both excess oxygen (lean feed) and low exhaust temperature. The reduction of NO_x in excess oxygen must compete with oxygen reduction by available reductants which increases fuel consumption. Lower exhaust temperature leads to slower conversion rates and correspondingly lower conversion efficiencies. Meeting stricter tailpipe emission standards like Tier 3, LEV III and Euro 6 will necessitate new deNO_x technologies that achieve higher lean NO_x conversions, particularly in the low temperature range (~150 to 250 °C) [2, 3].

Commercial lean NO_x abatement technologies include selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) and NO_x storage reduction (NSR). SCR is a more mature and implemented technology that efficiently reduces NO_x to N₂ over vanadium-based or transition metal exchanged zeolite catalysts with NH₃ generated upstream from urea thermal hydrolysis. A minimum urea dosing temperature of ~200 °C limits the

low-temperature functionality of SCR. In contrast, NSR technology, also referred to as lean NO_x trap (LNT) technology, involves cyclic operation comprising a sequential lean phase (typically 30-90 s) and much shorter rich phase (3-10 s). LNT catalyst contains noble metals (e.g., Pt, Rh) and NO_x storage materials (e.g., K₂O, BaO) supported on high surface area γ -Al₂O₃ [4, 5, 6]. Ceria (CeO₂) is often added to the LNT catalyst as a promotor. The underlying process involves the combination of Pt-catalyzed NO oxidation to NO₂ which is trapped on the storage material in the form of nitrates/nitrites during the lean phase. This is followed by reductive conversion of the stored NO_x species to a mixture of N₂, NH₃, and N₂O during the shorter rich phase [5]. Intermittent in-cylinder rich combustion or injection of fuel into the exhaust produce an exhaust containing a stoichiometric surplus of CO, H₂ and hydrocarbons (HC) [5, 6]. The operation temperature window for LNT catalysts is relatively narrow (250-400 °C) [7]. The low-temperature LNT performance is limited by an incomplete regeneration, as well as by low rates of NO oxidation. High-temperature performance suffers from decreased NO_x storage capacity as nitrates/nitrites become thermally unstable.

Improvements are required in either SCR or NSR system to provide high NO_x removal efficiency over a broad range of operating conditions encountered in practice. An intriguing yet sparsely applied concept combines the NSR and SCR technologies, based on the premise that the LNT catalyst generates NH₃ for use by the SCR catalyst positioned in sequence (dual brick design) or in parallel (dual layer design) [8-11].

Thus, the LNT + SCR system exploits the NH_3 generation capability of the LNT catalyst and the NH_3 sorption and NO_x reduction capability of the SCR catalyst. The combined system offers the potential of enhancing NO_x conversion, reducing NH_3 slip, and lowering the required precious group metal (PGM) load. The LNT + passive SCR system was commercially applied on several vehicle models such as the Mercedes E320 Blutec. [12]. In most previous LNT+SCR studies the overall NO_x conversion was primarily accomplished in the LNT. Efforts have been made to improve LNT regeneration in order to achieve high NH_3 yield at minimum fuel penalty ($< 2\%$). Wittka et al. [8] proposed a novel configuration for the LNT + passive SCR system featuring the use of an out-line fuel reformer and an exhaust bypass around the LNT. In addition to the classic NH_3 -pathway for the combined system, Ford researchers found that non- NH_3 reductants like HC derivatives produced from the reaction of HC and stored NO_x during LNT regeneration, could enable additional NO_x conversion by the SCR [9, 13].

Toyota researchers reported in recent years an interesting technology called “Di-Air” (standing for diesel NO_x aftertreatment by adsorbed intermediate reductants) that achieves much higher NO_x conversion over a LNT catalyst at elevated temperatures [14, 15, 16]. The unique operational feature of Di-Air is the high frequency injection of HC into a lean exhaust stream with cycle times shorter than $\sim 5\text{s}$ flowing continuously over a LNT catalyst. The enhanced NO_x conversion performance was attributed to adsorbed, N-containing HC intermediates, which are generated during

the high-frequency HC pulsing, through reaction between adsorbed NO_x and partially oxidized hydrocarbons. These short-lived intermediates are readily converted through reaction with surface and/or gas phase NO_x species to N₂ during the lean part of the cycle. Compared to NSR, the Di-Air operation shifts the N₂ formation from one that occurs primarily during the rich phase to one that primarily occurs during the lean phase. The system was demonstrated to significantly improve the deNO_x performance under high-temperature and high-SV operations conditions for which conventional NSR (cycle time 0.5-2 min) performs unsatisfactorily. In a recent study our group found that fast cycling of propylene enhanced the deNO_x activity of LNT catalysts even at low temperatures, albeit to a smaller extent than at high temperatures [17].

A definitive mechanism has yet to be established for the Di-Air process although progress is being made. Toyota researchers advanced a mechanism that is similar to the aforementioned “non-NH₃” pathway encountered with the LNT-SCR system. Both involve the formation of HC intermediates (C_xH_yO_z, C_xH_yO_zN_t) through reaction of adsorbed NO_x and oxygenated hydrocarbon species that accumulate on the LNT catalyst during the rich purge. Zheng et al. [18] showed that these surface HC intermediates play an important role in the low-temperature NO_x conversion enhancement in the combined LNT-SCR system. Our recent preliminary study showed that a Di-Air process with high-frequency HC pulsing can benefit a combined LNT+ passive SCR system, especially at low temperatures [19].

The aim of this follow-up study is to gain insight into the working mechanism of rapid propylene pulsing on integrated LNT-SCR catalysts, with the objective to expand the operating temperature window of a conventional NSR system. We first demonstrate the enhanced NO_x conversion by the use of high injection frequency and/or SCR top-layer. We then investigate the impacts of relevant factors, including cycle timing (NSR and Di-Air operation), exothermic heat effects, SCR catalyst types (Cu-zeolites and Ag/Al₂O₃), and loadings of ceria and PGM, on the catalyst system performance in terms of catalytic activity, product distribution and catalyst durability. An overall mechanism for fast HC pulsing in both the standalone LNT and combined catalyst system is proposed. We also show how the deNO_x performance may be enhanced by configuring the catalyst architecture through, layering and zoning.

2. Experimental

2.1 Catalysts

The monolithic LNT catalysts provided by BASF (Iselin, NJ) have a cell density of 400 cpsi (cells per square inch) and washcoat loading of 4.6 g/in³ monolith, corresponding to a peripheral-averaged thickness of ~80 μm. The catalyst contains Pt/Rh/BaO/CeO₂/Al₂O₃ with an overall PGM (precious group metal) loading of 90 g/ft³ monolith, 15 wt.% (washcoat basis) BaO and 34 wt.% CeO₂ on a γ-alumina support. In some experiments, a LNT with the same specifics except for no CeO₂ addition was used which was also provided by 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 with chabazite (CHA) framework and Ag (2 wt.%)/Al₂O₃ catalyst powders were prepared via solid-state ion exchange [20] and incipient wetness impregnation methods [21], respectively. The as-prepared catalyst powder was washcoated onto the LNT monoliths by a dip-coating technique described elsewhere [22]. A uniform washcoat layer of 0.8-0.9 g/in³ was deposited on top of the LNT layer creating dual-layer catalysts (LNT-SCR, LNT-Ag/Al₂O₃). All catalysts were aged at 700 °C for 33 hours in air, equivalent to 160,000-km aging, prior to bench reactor experiments [14].

2.2 Reactor System

A schematic of the bench-scale reactor system was provided in a previous paper [19]. 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 line contained inert species (CO₂, H₂O, Ar), another the lean feed components (NO, O₂, Ar), and a third the rich feed components (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 ThermocraftTM tube furnace. Local 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 another was positioned at the midpoint of the monolith (radial and axial) to measure the temperature at the center of the catalyst (T_c). Note that T_c is a dependent variable, which varied markedly during the aerobic regenerations. 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.

A solenoid actuated four-way valve (Valco Inc., Micro-electric two position valve) generated the high-frequency propylene pulses via fast switching between lean and rich feeds. The lean and rich 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 the inert gas in the main line was kept at 800 cm³/min, lower than the 2200 cm³/min for 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 also helps avoid flow maldistribution. This was important as Toyota researchers recently pointed out that high radial uniformity of HC concentration was essential for Di-Air performance [23]. In order to minimize upstream axial mixing of lean and rich streams, the switching valve was placed close to the monolith catalyst (~ 0.6 m upstream), but sufficiently far to enable sufficient preheating of the feed stream. We

found that too long a distance between the switching valve injection point and the catalyst resulted in an unacceptable level of axial mixing due to dispersion in the tubing. The axial mixing decreased NO_x conversion during high frequency operation. (We did not investigate in detail this design variable in the current study so the 0.6 m distance may not be the optimal value.). The injection valve, thermocouples and MFCs were all controlled and monitored using LABVIEWTM software. Time delays between the feed point, reactor and the analytical equipment were accounted for in the data processing through tracer measurements.

Lean-rich cycling experiments were conducted over either the LNT only, LNT-SCR dual-layer, LNT-Ag/Al₂O₃ dual-layer or LNT-SCR dual-brick catalysts. Table 1 describes the cycling conditions. Three different cycle timing protocols, 60s lean/10s rich, 30s lean/5s rich, and 6s lean/1s rich, were used. The 60/10 and 30/5 timing are representative of conventional NSR operation while the 6/1 is representative of high-frequency NSR (simulated Di-Air). Due to the system limitation (switching delay time, mixing design to get rectangular plug flow HC pulses) higher injection frequency could not be realized. In the Di-Air process studies of Toyota the air:fuel ratio (A/F) was varied periodically through reductant injection into a flowing lean gas. To mimic this approach, we used a high O₂ concentration of 10%, typical of real diesel exhaust, 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% achieved a high NO_x conversion [24]. Hence, this value was used in all cycling experiments. The

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

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 S_N value less than unity represents 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. At each temperature the final ten periodic cycles were averaged after the system reached a periodic state to determine the cycle-averaged NOx and C₃H₆ conversions, product selectivities and T_c according to standard expressions preciously reported [17].

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. Different pretreatment methods caused different low-temperature cycle-averaged NOx conversions with the above periodic lean/rich pretreatment superior to that following an oxidative pretreatment (i.e. 5% O₂ for 30 min).

3. Results and discussion

3.1 Effects of combining rapid propylene pulsing with SCR layer addition

Fig. 1a compares the cycle-averaged NOx conversion over the standalone LNT catalyst as a function of the feed temperature for cycle times spanning 60/10s to 6/1s for a fixed rich duty cycle (14.3%). The dual-layer LNT-SCR catalyst at the fastest cycling (6/1s) is shown for comparison. For each of the cases the NOx conversion exhibits a rather broad maximum over a range of feed temperatures. The extent of the

fall-off at low temperature is a sensitive function of the cycle timing and SCR top-layer.

For the longest cycle time the LNT has a NO_x conversion exceeding 80% between 250 and 350 °C. For feed temperatures below 225 °C the conversion is 10-20% while at 400 °C the conversion is ~70%. As the cycle time is shortened to 30/5s and 6/1s, both the low and high-temperature NO_x conversions increase with the larger increase occurring at low feed temperatures (≤ 250 °C). Finally, adding a Cu-SCR top-layer combined with fast propylene pulsing further increases the low-temperature NO_x conversion. The combination of fast cycling and SCR top-layer decreases the light-off temperature by ca. 50 °C below that of the standalone LNT with 60/10s cycle timing. For example, for a feed temperature at 225 °C, a 80% NO_x conversion was achieved for the dual-layer with rapid injection, compared to 51% and 24% conversion for the standalone LNT with the fast (6/1s) and slower (30/5s) cycling, respectively. We expand on the noted low temperature enhancement by the faster cycling and addition of the SCR layer below. At high feed temperature (400 °C) faster cycling enhances the NO_x conversion for the standalone LNT, consistent with previous studies [14, 17]. However, addition of the SCR top-layer decreases the NO_x conversion. This decrease is primarily attributed to increased mass transfer resistance which limits C₃H₆ supply to the underlying LNT layer.

The exothermic oxidation of propylene occurs during the propylene injection, and therefore non-isothermal behavior is expected. Kabin et al. [25] reported significant temperature excursion of up to 150 °C during conventional NSR using propylene as a reductant in cases when the rich feed contained up to 5% O₂. Epling et al. [26] reported an evolving and non-uniform axial temperature profile along the LNT monolith owing to the rich purge. This affected the dynamic NO_x storage capacity during a cycle period. Fig. 1b shows the same cycle-averaged NO_x conversion plotted as a function of the corresponding cycle-averaged T_c (at the monolith center). A comparison of Fig. 1a and 1b reveal an expansion in the temperature range due to the substantial temperature rise after ignition (T_f > 225 °C). Although T_c spans a broader temperature window than T_f, the same qualitative trends in the data are apparent. One notable difference is the more significant difference in the high temperature NO_x conversions for the different cycle times. These trends are in line with results reported by Bisaiji et al. [14]. It is noted that the actual temperature of the catalyst (washcoat) at the monolith midpoint is likely higher than the local gas phase temperature because of gas-to-solid heat transfer limitations.

3.1.1 Effect of rapid propylene injection

Detailed information on the effect of cycle timing is gotten from the instantaneous concentration and temperature profiles. Fig. 2 shows the transient effluent NO_x (C₃H₆) concentration and catalyst temperature at the low feed temperature of 225 °C. The first and second columns of the figure are for the standalone LNT with 30/5s and 6/1s

cycle timing, respectively. The third column shows results for the LNT-SCR dual-layer catalyst which we discuss later.

The cycle-averaged NO_x conversions for the two LNT cases are ~24 and 51%, respectively, while the corresponding cycle-averaged C₃H₆ conversions are ~8 and 40%, respectively. Under the slower NSR cycling (30/5s), NO_x breakthrough gradually increases during the lean period, followed by a sharp NO_x spike upon switching to rich phase. This trend is typical of conventional NSR operation [5]. Generally, the inefficient low-temperature NO_x conversion is a result of low rates of NO oxidation, NO_x storage, and/or incomplete regeneration. Forzatti et al. [6] suggested that the slow diffusion of NO₂ from Pt to distant BaO storage sites accounts for the slower uptake of NO_x at the later stages of the lean phase. This is consistent with the studies of Bhatia et al. [27], Kumar et al. [28] and Shakya et al. [29] who showed through experiments and modeling that stored-NO_x diffusion during both storage and release processes may limit the overall NO_x conversion. In this context, proximal adsorption sites quickly saturate first then the storage slows down due to the longer diffusion distances on the surface or in the bulk of BaO/BaCO₃ particles. Thus, a prolonged lean phase leads to considerable NO_x slip as observed (Fig. 2a). Epling et al. [30] attributed the inefficient low-temperature rich purge using hydrocarbon reductants to both slow kinetics of propylene reaction with the stored NO_x and Pt site poisoning by hydrocarbon intermediates, limiting the regeneration extent.

Lower NO_x and C₃H₆ effluent concentrations are observed along with a higher and steadier catalyst temperature (see middle column of Fig. 2) upon increasing the cycling frequency (6/1s). Similar fast cycling trends were reported by Perng et al. [17]. Lietti et al. [31] suggested that at low temperatures NO may be stored in the form of nitrites and that this mechanism requires the cooperative interaction between Pt and nearby storage materials. This mechanism involves the following sequential steps:

This mechanism known as nitrite pathway does not require the formation of NO₂. Xu et al. [32] modeled NO uptake at high temperatures and showed that for a NO+O₂ feed NO_x storage proceeds through NO₂ formation and uptake on proximal storage as well. These studies suggest that under fast cycling, NO uptake would only be possible through a fast pathway so that only kinetically accessible storage sites would be utilized. That is, fast cycling mitigates the kinetic challenge of low-temperature NO_x uptake by confining NO_x storage to surface Ba sites in close proximity to Pt via a spillover process. The fraction of Ba that effectively participates in the storage process is smaller than during conventional NSR operation. This diminishes the importance of NO_x storage capacity that is gradually reduced with elevated temperature, thereby extending the operating window to high temperatures (> 400 °C) as shown in Fig. 1 and in the Toyota reports [14]. Perng et al. [17] showed that storage and reduction under fast cycling experiments is less sensitive to CO₂. They

argued that this is evidence for a NO_x reduction mechanism that does not rely on NO_x storage on BaCO₃ sites that are less effective in trapping NO_x than BaO or Ba(OH)₂.

Once the proximal storage sites are saturated, a short propylene pulse is injected to purge stored NO_x. Bisaiji et al. [14] proposed that the rapid HC pulsing plays a pivotal role in the Di-Air reaction pathway. HC efficiently reacts with adsorbed NO_x and O₂ over Pt to generate N-containing intermediates (denoted by C_xH_yO_zN_t) which can be stabilized by the nearby basic oxide (BaO) component and retained on the catalyst surface until the end of a sufficiently short rich phase. Such active intermediates are then either converted to N₂ directly or react with adsorbed and/or gaseous NO_x generating N₂ during the subsequent lean period. Bisaiji et al. [16] further conducted an *in operando* XAFS (X-ray Adsorption Fine Structure) study to monitor the valence state of Pt and determined that HC intermediates are capable of maintaining Pt in a metallic state through scavenging O adatoms even within several seconds (up to ~ 4s) into the subsequent lean phase. In other words, Pt is kept in a reduced state all the time under rapid HC pulsing. The presence of reduced Pt sites may imply a different pathway via the direct NO decomposition on metallic Pt sites as reported by Burch et al. [33], compared to Toyota's pathway involving organo-nitrate species as key intermediates. In either pathway, the initial formation of partially oxidized HC intermediate is critical. Bisaiji et al. [14] and Perng et al. [17] reported that a high injection frequency sustains the gas phase O₂ at a higher level and that this

promotes propylene oxidation, given the positive reaction order with respect to O_2 for propylene oxidation. It is noted that the high ceria content (34 wt.%) in the LNT catalyst used in the current study also acts as oxygen buffer to maintain surface oxygen concentration. The functionality of ceria for fast cycling is further discussed later. In summary, fast injection of propylene encounters relatively high-levels of both stored and gaseous O_2 . This enables improved utilization of the propylene reductant, evidenced by the much lower C_3H_6 breakthrough. In addition, better propylene oxidation results in higher catalyst temperature which, in turn, benefits efficient NO_x storage and regeneration, especially at low temperatures.

3.1.2 Effect of Cu-SAPO-34 top-layer

The deposition of a Cu-SCR layer and fast cycling leads to an even higher NO_x and C_3H_6 conversion. As shown in the right column of Fig. 2, the addition of a Cu-SAPO-34 top-layer to the LNT catalyst while maintaining the 6/1s cycling results in a noted drop in the NO_x and C_3H_6 effluent concentrations. The cycle-averaged NO_x conversion is $\sim 80\%$, an absolute increase of 29% from the standalone LNT under fast cycling. Moreover, the resulting T_c is higher by over $30^\circ C$. A previous study showed that due to the higher oxygen level and short rich duration, negligible NH_3 slips from the LNT upon fast cycling over the almost entire temperature range [19]. Thus, the classic NH_3 -pathway cannot account for the increased NO_x conversion on the dual-layer catalyst.

An alternative mechanism for the LNT + SCR system that does not require NH_3 was advanced by Ford researchers [9, 13]. Bisaiji et al. [14] reported the detection of several stable gas phase intermediates in LNT effluent during rapid HC pulsing, including amines (CH_3NH_2 , $\text{C}_2\text{H}_5\text{NH}_2$, NH_2OH), carboxylic acids (HCOOH , CH_3COOH) and aldehydes (CH_3CHO). In the current study, we observed both HCHO and HNCO in the effluent during fast cycling to the standalone LNT catalyst at a feed temperature of 225°C . Other propene oxidation derivatives in addition to HCHO and HNCO are likely to exist but only HCHO and HNCO were reported due to measurement limitations. It is expected that such intermediates released from the LNT may be trapped and utilized as reductants in the SCR top-layer via a HC-SCR pathway. These species have been previously reported as NO_x reductants via a HC-SCR pathway on zeolite catalysts [34-36]. For example, Peden et al. [37] reported that the partially oxidized propylene species are more active than propylene for NO_x reduction over Ba- or Na- exchanged zeolite catalysts. In fact, a feed containing aldehyde species like HCHO , CH_3CHO , etc., included in a lean NO_x stream resulted in 80% NO_x conversion over a BaY zeolite catalyst at 200°C [37]. This supports our conjecture that the added SCR layer can utilize released intermediates for additional NO_x reduction.

To gain further insight into the catalytic oxidation chemistry, DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) measurements were conducted to identify and monitor the evolution of surface organic intermediates over powder LNT

and SCR catalysts. Fig. 3a-b show the temporal changes of the in situ DRIFTS spectra when exposing a NO_x pre-adsorbed LNT to a feed of 0.1% C₃H₆ + 1% O₂ at 200 °C. After a 1h pre-conditioning, the catalyst was exposed to a feed containing 500 ppm NO + 5% O₂. Three intense peaks were observed at 1270, 1300 and 1575 cm⁻¹, which can be assigned to the bulk nitrates, surface nitrites and surface nitrates, respectively [38, 39]. Upon the introduction of propylene the spectra exhibited a temporal decrease in the intensity of the surface nitrates peaks at 1300 and 1575 cm⁻¹, and a near-simultaneous evolution of four new bands at 1650, 1680, 2190 and 2215 cm⁻¹. Compared to the nearly constant peak at 1270 cm⁻¹ corresponding to bulk nitrates, the dramatic decrease in the spectral intensity of the surface nitrates peak suggests that NO_x stored at surfaces sites close to the Pt are prone to conversion at low temperatures. This corroborates our previous argument that fast cycling favors the efficient utilization of fast (proximal) NO_x storages sites. The band at 1650 cm⁻¹ is most likely a C=O group of either surface acrylate (R-COO⁻) or aldehydes (R-CHO) like acrolein [40]. The bands at 1680, 2190 and 2215 cm⁻¹ are assigned to C=N stretching vibration of acetone oxime [35], isocyanate (R-NCO) over barium [41] or cyanide species (R-CN) over alumina [42], and surface isocyanate over alumina [41], respectively. Thus, these surface species measurements together with the gas phase species HNCO and HCHO, as well as the additional species reported by Toyota researchers suggest either a direct release or hydrolysis of activated surface intermediates over the LNT during the rapid HC pulsing into a lean NO_x stream.

Fig. 3c shows the temporal DRIFTS spectra when exposing a NO_x pre-adsorbed SCR catalyst to a feed of 0.1% C₃H₆ + 1% O₂ at 200 °C in a separate experiment. The SCR powder used here is Cu-SSZ-13 provided by BASF. Its performance is comparable to our in-house synthesized Cu-SAPO-34 [20]. After feeding propylene for 5 min, a band at 2278 cm⁻¹ corresponding to R-CN [43] appears. Prolonged propylene exposure for 30 min results in a decrease in this peak intensity, accompanied with a gradual evolution of two new peaks at 2218 and 2254 cm⁻¹ that can be assigned to R-NCO on Cu⁺ and zeolite, respectively [44]. About 1 h after propylene admission, the peak for R-CN disappears and peaks for R-NCO stabilize at higher intensities. Isocyanates are well recognized as active intermediates that can rapidly hydrolyze to produce NH₃ or amine to further reduce NO_x [36]. The spectra clearly indicate a slow evolution of surface organic intermediates from R-CN (2278 cm⁻¹) towards R-NCO (2218 and 2254 cm⁻¹). Compared to nearly immediate evolution of R-NCO species on the LNT, the time taken to form R-NCO on the SCR is much longer. This suggests the formation of NCO may be the RDS for the HC-SCR pathway on the Cu-CHA catalysts, especially at low temperature. Thus, we speculate that the activated HC intermediates provided by the LNT facilitate the formation of R-NCO on the Cu-CHA catalyst, thereby promoting the LNT-assisted HC-SCR reaction. This hypothesis is consistent with the non-NH₃ pathway proposed by Ford researchers [9, 13].

3.2 Effect of ceria in LNT layer

Fig. 4 compares the NO_x conversion as a function of feed temperature under fast cycling obtained with two dual-layer catalysts, one with the same LNT formulation having ceria and the second without ceria. The effect of ceria is marked: in its absence the cycle-averaged NO_x conversion is significantly lower over the entire feed temperature range. A large number of previous studies have shown the important role of ceria in automotive emission control, including oxygen storage capacity, low-temperature NO_x storage and stabilization of Pt dispersion, etc [45-47]. As suggested earlier, ceria supplies oxygen to promote the oxidation of propylene to form surface intermediates that are critical for fast-cycling performance. Yi et al. [22] reported that ceria enhanced the resistance of LNT-SCR dual-layer catalysts to thermal aging by suppressing the migration of Pt and BaO from underlying LNT to the top SCR layer. Recently, Kapteijn et al. [48] argued that ceria might provide active sites for NO_x reduction under fast cycling conditions. Using Temporal Analysis of Products (TAP) they showed that propylene reduces the ceria surface layer from Ce⁴⁺ to Ce³⁺, thereby creating surface layer oxygen vacancies that are active for NO decomposition to N₂. It is speculated that HC surface species act to maintain the reduced state of surface ceria rather than directly reacting with surface NO_x species [48]. Further study is needed, especially operando monitoring of ceria valence state under realistic Di-Air condition and interaction of ceria with Pt and basic storage material. At any rate, ceria certainly plays a crucial role in the activity and durability of LNT and dual-layer catalysts under fast cycling operation.

3.3 Effect of top-layer material

Based on our hypothesis that the added SCR top-layer utilizes hydrocarbon intermediates generated and released from the underlying LNT layer via a HC-based SCR pathway, we compared the performance of three top-layer materials: Cu-SAPO-34, γ -Al₂O₃ and Ag/Al₂O₃. The Cu-exchanged aluminosilico phosphate SAPO-34 is of interest because it and the related Cu-exchanged SSZ-13 zeolite have very high NH₃-based SCR activity. Ag/Al₂O₃ is of interest because it is a known effective HC-SCR catalyst [21, 49]. The use of unimpregnated γ -Al₂O₃ is intended to check whether the NO_x conversion enhancement might be the result of storage and transport effects only. Fig. 5a compares the cycle-averaged NO_x conversions of dual-layer catalysts with the three top-layer materials. The data show that the Cu-SAPO-34 top-layer has the highest NO_x conversion at feed temperatures below 300 °C while the γ -Al₂O₃ top-layer has the highest NO_x conversion at high temperatures (≥ 350 °C) among all the samples.

We consider first the γ -Al₂O₃ results. The lower NO_x conversion obtained with the γ -Al₂O₃ top-layer for $T_f \leq 300$ °C compared to Cu-SAPO-34 top-layer is undoubtedly a result of the lower HC-SCR activity. The added γ -Al₂O₃ top-layer slightly enhances the low-temperature NO_x conversion of LNT. This follows from the study of Panov et al. [37] who reported that γ -Al₂O₃ is able to catalyze the reduction of NO_x by aldehydes, even though less effectively than metal-exchanged zeolite catalysts. This probably in part accounts for the minimal enhancement. In contrast, its higher

high-temperature NO_x conversion is attributed to its lower propylene oxidation activity. This enables more propylene to access to the underlying LNT layer.

The results obtained with the Ag/ γ -Al₂O₃ top-layer are somewhat surprising and would appear to contradict the explanations just provided for the selection of γ -Al₂O₃ top-layer. A dramatic performance decline was observed for the dual-layer LNT-Ag/Al₂O₃ catalyst spanning the entire temperature range. Ag/Al₂O₃ is generally regarded as an effective HC-SCR catalyst so one would expect NO_x reduction chemistry to occur in the top-layer. Rather, it appears that there is significant negative interaction between Ag/Al₂O₃ and LNT layers, apparently from the migration of Ag ions to the LNT base layer. To prove this conjecture, Fig. 5b shows the steady-state propylene oxidation light-off for the standalone LNT, LNT-Al₂O₃ and LNT-Ag/Al₂O₃ dual-layer catalysts. While the LNT and LNT-Al₂O₃ catalysts have similar light-off results, the presence of Ag in the top-layer significantly inhibits the propylene oxidation as evidenced by the increase in the light-off temperature by almost 100 °C. This suggests the poisoning effect of Ag on LNT catalyst, probably due to Ag migration to underlying LNT layer and block Pt sites, especially after high-temperature thermal aging. Further catalyst characterization is needed to verify the deactivation mechanism and will be reported elsewhere.

3.4 N₂O yield and selectivity

One of the challenges with conventional NSR operation is the relatively high levels of N_2O generated at low to intermediate temperatures, especially compared to NH_3 -based SCR on metal-exchanged zeolites. N_2O is relatively stable in the atmosphere and is a potent greenhouse gas with a global warming potential ~300 times that of CO_2 . The recently enacted US EPA 2017-25 greenhouse gas regulations will require the reduction of N_2O from LD and HD vehicles [1]. Fig. 6 shows the N_2O selectivity and yield under both conventional and fast cycling on both single-layer LNT and dual-layer catalysts. For the standalone LNT, the use of fast cycling increases the N_2O selectivity and yield. These data are consistent with the earlier findings by Perng et al. [17]. Interestingly, the addition of the SCR top-layer lowers the N_2O selectivity under fast cycling. This is probably due to lower N_2O selectivity for NO_x reduction by SCR than LNT catalysts. This encouraging result provides additional incentive for the proposed fast cycling technology. However, the highest N_2O yield below 225°C of ca. 15% was observed for the dual-layer catalyst, due to the highest NO_x conversion in this temperature range. Efforts still need to be made to further reduce the N_2O formation.

3.5 Working mechanism of rapid propylene pulsing

To this point we have studied the effects of operating conditions (cycling frequency), catalyst design (top-layer material, LNT ceria content) and reaction phenomena (reaction exotherm, HC intermediates) to elucidate the performance of dual-layer catalysts under fast propylene pulsing. In contrast to conventional LNT+SCR system,

NH_3 is not a primary reductant of NO_x reduction in the SCR component. Here we describe a likely mechanism spanning the complete cycle.

A schematic of the proposed cyclic mechanism is shown in Fig. 7. The high-frequency pulse of propylene into the lean feed facilitates the generation of surface hydrocarbon intermediates on the LNT by the partial oxidation of propylene, both by surface NO_x and oxygen. These intermediates may desorb or accumulate. The oxidation process is enhanced by ceria, possibly through the spillover of oxygen to the precious metal crystallites. As discussed earlier, direct NO decomposition on reduced metal sites is another potential route for N_2 and N_2O formation. The complex set of surface catalyzed reactions generate organic oxygenates and nitrogenates which may react with NO , selectively producing N_2 and a lesser amount of byproduct N_2O . A key feature of this mechanism is the cycle timing. If the sustained supply of injected propylene, alternated with a lean feed, is accomplished at a sufficient frequency, then the desired HC-based SCR and/or NO decomposition may occur before the desorption of these intermediates, without the accumulation of surface nitrites and nitrates, and the production of deep reduction product NH_3 .

The role of the SCR top-layer is to trap partially oxygenated species that desorb from the LNT layer, enabling further production of N_2 through HC-SCR pathway. That a moderate level of additional NO_x reduction occurs even with a $\gamma\text{-Al}_2\text{O}_3$ top-layer suggests that the conversion of the intermediates is fast. Perhaps the elevated

temperature caused by the propylene oxidation enhances the reaction rates. The coupled chemical and thermal effects enhance the low-temperature NO_x conversion over that of the standalone LNT. Clearly, this proposed mechanism should be subjected to further validation with targeted experiments and modeling.

3.6 Effects of catalyst configuration and zoning

The intriguing behavior of the dual-layer catalysts under rapid periodic switching invites a study of the potential for alternative designs with improved performance. To illustrate, Fig. 8a compares the cycle-averaged NO_x conversion under fast cycling operation using the LNT, LNT-SCR dual-layer or LNT-SCR dual-brick catalyst. For a meaningful comparison, the SCR brick had the same composition as the SCR used in the dual-layer catalyst but had a higher washcoat loading (2.4 g/in³) than the dual-layer catalyst (0.9 g/in³).

The comparison study reveals that the best low-temperature deNO_x performance is achieved with a dual-layer catalyst, followed by the dual-brick, and then the standalone LNT. These data strongly suggest that the close proximity of the LNT and SCR is needed to fully exploit the HC-SCR NO_x reduction mechanism. On the other hand, the high-temperature deNO_x performance is negatively impacted by the addition of the SCR top-layer. This is likely attributed to the diffusion limitation contributed by the top-layer that limits the propylene supply to the underlying LNT layer, combined with unselective propylene oxidation in the SCR top-layer. This

behavior was encountered in earlier dual-layer LNT-SCR studies by Zheng et al. [18] and Shakya et al. [50] and was also encountered in dual-layer ammonia slip catalysts as reported by Shrestha et al. [51].

The conversion decline at high temperatures may be lessened by utilizing a combination of SCR layering and zoning. The idea is to move a fraction of the upstream SCR top-layer downstream, giving a hybrid architecture that strikes a better balance between low- and high-temperature NO_x removal (Fig. 8b). This follows a similar approach taken by Zheng et al. [10] for a conventional LNT-SCR. Because SCR zoning minimizes the detrimental impact of SCR-layer on the LNT at high temperatures while sustains the low-temperature enhancement. A detailed study of the SCR zoning effect can be found in [10].

Fast light-off of hydrocarbon oxidation to generate intermediates determines the low-temperature deNO_x performance. Many previous studies have demonstrated that PGM zoning enables a good compromise between fast light-off and minimal PMG load needed. To this end, we investigated the impact of potentially reducing the overall PGM loading by appropriately reconfiguring the catalyst architecture. Fig. 9a shows that increasing the PGM loading from 90 to 120 g/ft³ in the dual-layer catalysts decreases the light-off temperature to a feed temperature as low as ~ 175 °C. In practice, a low PGM loading is desired as it lowers the catalyst cost. Fig. 9b shows that the performance of zoned dual-layer catalyst with 25% lower PGM loading, LNT

(0.5 in. 4.6 g/in³) + LNT-SCR (0.5 in., 2.3 g/in³ for LNT and 0.9 g/in³ for SCR washcoat), is comparable to that of LNT alone with higher PGM load. Given the high axial temperature gradient existed along the LNT monolith, a high upstream PGM loading enables fast light-off and a low downstream loading decreases the PGM load while providing good warm-up performance.

4. Conclusions

High frequency propylene pulsing of LNT or dual-layer LNT-SCR catalysts under lean conditions can enhance low-temperature deNO_x efficiency and expand the operating temperature windows of a conventional NSR system. The main findings of this study are:

- High-frequency propylene pulsing expands the operating temperature window of a conventional NSR system in both the low and high-temperature regions.
- The combination of rapid propylene pulsing and the dual-layer catalyst increased low-temperature NO_x and C₃H₆ conversions. This may be useful for advanced fuel-efficient engines with low exhaust temperatures.
- HC intermediates generated over the LNT can either directly react with NO_x or act as oxygen scavenger to maintain Pt at reduced states for direct NO decomposition.
- Under fast cycling partially oxidized HC intermediates should be the primary NO_x reductants for SCR, in contrast to classic NH₃-pathway. The evolution of isocyanates is considered as the RDS of HC-SCR over Cu-zeolite catalysts.

The activated HC intermediates provided by the underlying LNT may facilitate isocyanates formation, thus promoting LNT-assisted HC-SCR pathway.

- A top-layer of Cu-SAPO-34 is beneficial while Ag/Al₂O₃ is detrimental.
- Ceria plays a crucial role in the activity, durability and likely reaction pathway of LNT and dual-layer catalysts under fast cycling operation.
- Optimization of catalyst configuration (i.e., zoning of SCR and PGM) can improve system performance and decrease the catalyst price.

Studies of the impact of different HC species and higher injection frequency on the performance of both LNT alone and combined LNT-SCR catalysts are currently being conducted. Preliminary results shows the type of HC species is critical for low-temperature enhancement. Light olefins, which have a relatively low light-off oxidation temperature and stronger affinity to Pt, are preferred. Propane that weakly adsorbs on Pt and has a higher light-off temperature, limit the performance enhancement by fast cycling and SCR-layer addition. HC mixture of short- and long-chain alkane and alkene may benefit from fast cycling operation. The results of this effort will be reported in a future study.

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Fig. 1. Cycle-averaged NO_x as a function of (a) feed temperature and (b) catalyst temperature (temperature at the center of monolith) for LNT alone and dual-layer catalysts with different cycle times.

Fig. 2. Effluent NO_x/C₃H₆ concentration and catalyst temperature for a set of cycling experiments at 225 °C feed temperature over LNT and dual-layer catalysts.

Fig. 3. Temporal DRIFTS spectra over (a-b) LNT and (c) SCR catalyst taken at 200 °C after a 1h pre-conditioning by 500 ppm NO + 5% O₂ and purge with He (a), subsequently exposed to a flow of 0.1% C₃H₆ + 1% O₂.

Fig. 4. Cycle-averaged NO_x as a function of feed temperature for dual-layer catalysts with and without ceria under fast cycling.

Fig. 5. (a) Cycle-averaged NO_x conversions as a function of feed temperature under fast cycling for LNT alone and dual-layer catalysts with either Cu-SAPO-34 or γ -Al₂O₃ or Ag/Al₂O₃. (b) Propene oxidation over LNT, LNT-Al₂O₃ and LNT-Ag/Al₂O₃ catalysts (1111ppm C₃H₆, 1% O₂, 3.5% H₂O, 5% CO₂).

Fig. 6. N₂O selectivity (a) and yield (b) as a function of feed temperature for LNT alone and dual-layer catalysts with different cycle times.

Fig. 7. Working mechanism for fast propylene pulsing over dual-layer catalyst.

Fig. 8. Cycle-averaged NO_x as a function of feed temperature for LNT, dual-layer plus either (a) dual-brick or (b) zoned dual-layer catalysts under fast cycling.

Fig. 9. Cycle-averaged NO_x as a function of feed temperature by LNT (4.6 g/in³ washcoat with PGM 90 g/ft³), LNT-SCR dual-layer (PGM 90 g/ft³, SCR 0.9 g/in³)

plus either (a) dual-layer with higher PGM load (120 g/ft^3) or (b) zoned dual-layer comprised of 0.5'' LNT (4.6 g/in^3 washcoat with PGM 90 g/ft^3) and 0.5'' dual-layer LNT(2.3 g/in^3)/SCR(1.6 g/in^3) with lower PGM load (45 g/ft^3).

Table 1

Gas condition for baseline cycling test		
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%

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9