

# N<sub>2</sub>O and N<sub>2</sub> formation dynamics during and after the regeneration of Lean NO<sub>x</sub> Trap

Petr Kočí<sup>1\*</sup>, David Mráček<sup>1</sup>, Miloš Marek<sup>1</sup>,  
Jae-Soon Choi<sup>2</sup>, Josh A. Pihl<sup>2</sup>, Todd J. Toops<sup>2</sup>, William P. Partridge<sup>2</sup>  
<sup>1</sup>Institute of Chemical Technology, Prague, CZ 16628, Czech Republic  
<sup>2</sup>Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA  
\*corresponding author: petr.koci@vscht.cz

## Introduction

The NO<sub>x</sub> storage and reduction catalyst (Lean NO<sub>x</sub> Trap, LNT) is used for abatement of NO<sub>x</sub> emissions from diesel and gasoline lean burn engines. While the NH<sub>3</sub> dynamics during LNT regeneration are relatively well understood, much less attention has been paid to the dynamics of N<sub>2</sub> and N<sub>2</sub>O. Ammonia appears at the reactor outlet in a single peak with certain delay that is determined by the breakthrough time of the reducing front [1]. On the other hand, both N<sub>2</sub> and N<sub>2</sub>O exhibit double-peak dynamics with a primary peak immediately after the start of regeneration and a secondary peak after the switch back to lean conditions [2]. In this contribution, we summarize our recent investigation of N<sub>2</sub>O and N<sub>2</sub> chemistry based on spatiotemporal resolution of reactions during lean/rich cycling experiments with a commercial LNT catalyst.

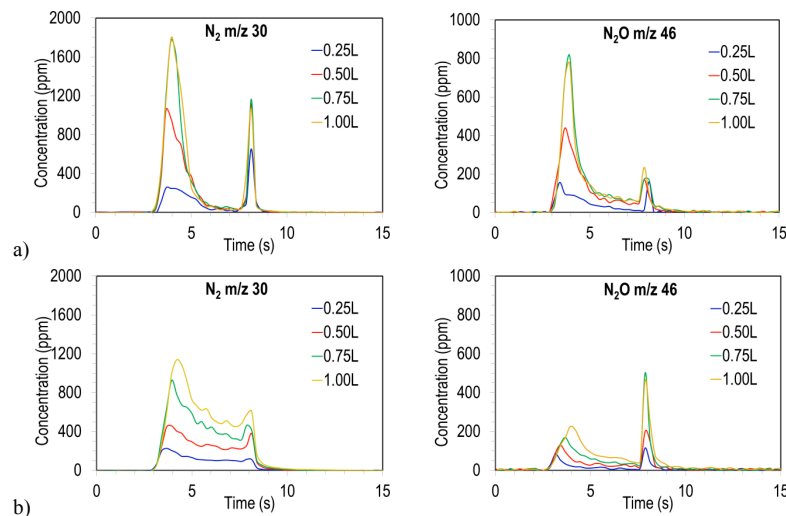
## Materials and Methods

The commercial catalyst used in this work contained platinum group metals (Pt, Pd, and Rh) as well as Ba, CeZr, MgAl and Al oxides. The catalyst was examined in a laboratory bench flow reactor, utilizing synthetic exhaust gas mixtures and rapid switching 4-way valve to alternate between the lean and rich gas mixtures. The length of the rich phase, reductant (CO, H<sub>2</sub> or C<sub>3</sub>H<sub>6</sub>) and regeneration temperature were varied, and the evolution of products at the reactor outlet was analyzed using a fast FTIR. Furthermore, spatiotemporal profiles inside the catalyst were obtained with an in-house developed spatially resolved capillary inlet mass spectrometer (SpaciMS), where gas was sampled continuously from different axial locations inside a catalyst channel using a small capillary probe (185-μm outer diameter, 50-μm inner diameter, ca. 10 μL/min sampling rate) and fed into a mass spectrometer for speciation. In order to analyze N<sub>2</sub>-product evolution during LNT regeneration with CO, isotopic <sup>15</sup>NO and Ar carrier gas were used in selected experiments; specifically <sup>15</sup>N<sub>2</sub> and <sup>15</sup>N<sub>2</sub>O were monitored at 30 and 46 m/z, respectively. The dynamics of key species on the catalyst surface were further studied by means of *in situ* DRIFTS.

## Results and Discussion

The experimental results suggest that the temporal profiles of N<sub>2</sub> and N<sub>2</sub>O generally follow similar two-peak dynamics; however, the N<sub>2</sub>O/N<sub>2</sub> selectivity changes with temperature and reductant (Figure 1). N<sub>2</sub>O formation is favored at lower temperatures and with a less active reductant (activity: H<sub>2</sub> > CO > C<sub>3</sub>H<sub>6</sub>). The primary N<sub>2</sub>O peak results from initial reaction of any reductant (H<sub>2</sub>, CO, C<sub>3</sub>H<sub>6</sub>, or NH<sub>3</sub>) with the stored NO<sub>x</sub> over poorly reduced PGM sites at the head of the reducing front [1, 2]. Secondary N<sub>2</sub>O peaks, on the other hand, result from reaction of residual stored NO<sub>x</sub> with adsorbed reductants. Secondary N<sub>2</sub>O peaks are

therefore greater after an incomplete LNT regeneration, and diminish with increasing temperature, regeneration length, or with the use of more active reductant [2]. This presentation will discuss the underlying reaction mechanisms, as well as LNT regeneration strategies for minimizing N<sub>2</sub>O formation.



**Figure 1.** Details of N<sub>2</sub> and N<sub>2</sub>O profiles at different locations along the catalyst sample (0.00L corresponds to the inlet, 1.00L to the outlet) measured during the LNT lean(60s)/rich(5s) cycling using SpaciMS with isotopic <sup>15</sup>NO. The 5s long rich phase (LNT regeneration) takes place from *t*=3s to *t*=8s. a) Regeneration by CO at 250°C, b) regeneration by C<sub>3</sub>H<sub>6</sub> at 250°C.

## Significance

N<sub>2</sub>O is a significant greenhouse gas, and even low emissions levels can be significant over typical drive cycles. The presented results significantly extend the understanding of highly dynamic processes taking place during regeneration of LNT catalysts, and modeling of the same. The selectivity of NO<sub>x</sub> reduction in automotive exhaust-gas catalysts is a highly relevant topic, particularly with respect to minimizing N<sub>2</sub>O emissions.

## References

1. Kočí P., Bártová Š., Mráček D., Marek M., Choi J.-S., Kim M.-Y., Pihl J.A., Partridge W.P. *Topics in Catalysis* **2013**, *56*, 118-124.
2. Bártová Š., Kočí P., Mráček D., Marek M., Pihl J.A., Choi J.-S., Toops T.J., Partridge W.P. *Catalysis Today* **2014**, in press, DOI:10.1016/j.cattod.2013.11.050