Kinetics of $N_2O$ and $N_2$ Peaks During and After the Regeneration of Lean NO$_x$ Trap

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Introduction

- Understanding mechanism of dynamic processes during **LNT regeneration**.
- **Selectivity** of formed products (N₂, N₂O, NH₃) in dependence on actual conditions:
  - temperature (150-550 °C),
  - gas mixture composition (reducing agents: H₂, CO, C₃H₆),
  - regeneration length.

- Set of **experiments** performed in bench flow reactor:
  - fast FTIR analyzer (5 Hz),
  - SpaciMS system (spatiotemporal profiles),
  - DRIFTS (surface species evaluation).

- Formulation of possible **reaction pathways** under specific conditions.

- **Particular attention given to N₂O formation.**
**N₂O emissions in automotive exhaust gas aftertreatment**

- **Undesired by-product** of catalytic NOₓ reduction in exhaust gas aftertreatment systems, particularly from lean-burn engines.

- Can be produced during **LNT regeneration**.

- In low concentrations pose **no health risk**.
- Global average in atmosphere ~ 0.3 ppm.
- Strong **greenhouse gas** (global warming potential ~300 x higher than CO₂).
- Mean N₂O tailpipe concentrations are typically 10³-10⁵ lower than those of CO₂.

- **Natural sources** (biological processes in soil and water) ~ 60% of total N₂O emissions. The main human-related source of N₂O is **agricultural soil management** (fertilizers), **adipic and nitric acid production**, and **combustion of fossil fuels**.

- **Mobile N₂O emissions not regulated (yet), limits expected in near future.**
Reduction of the stored NO\textsubscript{x}

- A large part of the stored NO\textsubscript{x} is reduced in the rich zone producing NH\textsubscript{3}.
- The formed NH\textsubscript{3} is transported downstream where it reacts with stored NO\textsubscript{x} and oxygen → delay of the NH\textsubscript{3} peak.
- N\textsubscript{2}O formed locally at the reduction front (reductants first reaching oxidized zone).
- N\textsubscript{2}O is emitted before reductants breakthrough → primary N\textsubscript{2}O peak.
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- N\textsubscript{2}O is emitted before reductants breakthrough → primary N\textsubscript{2}O peak.
- Secondary N\textsubscript{2}O peak may appear at the switch back to lean conditions (reactions of adsorbed intermediates).
**Reduction of the stored NO\textsubscript{x}**

- Main contribution to the **secondary N\textsubscript{2}O peak** at the **end of NO\textsubscript{x} storage zone** (0.25-0.50L).
- Most **NO\textsubscript{x} stored** in the **front zone** (0.00-0.25L).

- Surface NO\textsubscript{x} gradient along the channel at the **end of the 60 s lean phase**:

![Diagram of NO\textsubscript{x} storage zone and gradient along the channel](image)
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Surface NO\textsubscript{x} high, **long** exposure time
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- Surface NO\textsubscript{x} gradient along the channel at the end of the 60 s lean phase:

Surface NO\textsubscript{x} high, long exposure time

Surface NO\textsubscript{x} low, short exposure time
**Reduction of the stored NO\textsubscript{x}**

- Main contribution to the *secondary N\textsubscript{2}O peak* at the *end of NO\textsubscript{x} storage zone* (0.25-0.50L).
- Most NO\textsubscript{x} *stored* in the *front zone* (0.00-0.25L).
- Surface NO\textsubscript{x} gradient along the channel at the *beginning of the rich phase*:

Surface NO\textsubscript{x} high, **long** exposure time

Surface NO\textsubscript{x} low, **short** exposure time
**Reduction of the stored NO\textsubscript{x}**

- Main contribution to the **secondary N\textsubscript{2}O peak** at the **end of NO\textsubscript{x} storage zone** (0.25-0.50\(L\)).
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- Surface NO\textsubscript{x} gradient along the channel at the **beginning of the rich phase**:

- Surface NO\textsubscript{x} high, **long** exposure time

- Surface NO\textsubscript{x} low, **short** exposure time

\(L\) = Length of the catalyst channel

**Regeneration front**

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**Primary N\textsubscript{2}O peak**

**NO\textsubscript{x} storage zone**

**N\textsubscript{2}O**

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**Kinetics of N\textsubscript{2}O and N\textsubscript{2} Peaks During and After the Regeneration of LNT**
Reduction of the stored NO\textsubscript{x}

- Main contribution to the secondary N\textsubscript{2}O peak at the end of NO\textsubscript{x} storage zone (0.25-0.50\textdegree).
- Most NO\textsubscript{x} stored in the front zone (0.00-0.25\textdegree).
- Surface NO\textsubscript{x} gradient along the channel at the end of the rich phase:

![Diagram showing the reduction of stored NO\textsubscript{x} and the formation of N\textsubscript{2}O peaks during the regeneration of LNT catalyst.]
Reduction of the stored NO\textsubscript{x}

- Main contribution to the \textit{secondary N}_2\textsubscript{O} peak at the \textit{end of NO}_x storage zone (0.25-0.50\textit{L}).
- Most NO\textsubscript{x} \textit{stored} in the \textit{front zone} (0.00-0.25\textit{L}).

Locations relative to \textit{L} = catalyst length:
- \textbf{0.00L}  
- \textbf{0.50L}  
- \textbf{1.00L}  
- \textbf{0.25L}  
- \textbf{0.75L}

- The \textit{reducing front} reaches downstream zones with a progressive \textit{delay}.
- Therefore, the actual \textit{regeneration times} for the downstream zones are \textit{shorter} than near the inlet.
- A higher local concentration of \textit{residual adsorbed NO}_x after the \textit{incomplete reduction} results in a higher \textit{secondary N}_2\textsubscript{O} peak.
**N₂ formation trends**

- N₂O and N₂ exhibit similar behavior during the LNT regeneration → **N₂ is formed in two peaks**.
- Difficult to measure N₂ experimentally → Ar carrier gas, isotopically labelled ¹⁵NO feed → SpaciMS.
- Proceeding investigation...

- 60 s lean / 5 s rich phase, regeneration by CO, 250 °C
Regeneration length effect

300 s lean (near full saturation), varied rich phase length

- Short rich phase → less efficient reduction → secondary N\(_2\)O peak
- Long rich phase → more complete reduction → no secondary N\(_2\)O peak
**Inhibition effect of CO₂**

60 s lean / 5 s rich phase, regeneration by H₂, 150 °C

- Without CO₂ → no secondary N₂O, more efficient regeneration (more NH₃, less N₂O)
- With CO₂ → secondary N₂O peak, **CO₂ inhibition** effect (reverse WGS, the formed CO blocks PGM sites)
**Inhibition effect of CO₂**

DRIFTS surface scan, regeneration by H₂, 150 °C

- **Pt-CO formation**, no further reactions (too low temperature), no gaseous CO detected
- Inhibition by CO₂ → **surface carbonyls blocking PGM sites**
  (transient reverse water gas shift reaction)

Upon switch to the rich phase

Upon switch to the lean phase
Effect of NO\textsubscript{x} feed after the regeneration

300 s lean / 5 s rich, regeneration by CO, 300 °C

- Almost the same **secondary N\textsubscript{2}O peak** was produced in the **absence of NO\textsubscript{x}** in the lean feed after the LNT regeneration.

![Graphs showing kinetics of N\textsubscript{2}O and N\textsubscript{2} peaks during and after regeneration.](image)
**Effect of O₂ feed after the regeneration**

300 s lean / 120 s purge / 60 s rich / 120 s purge, slow regeneration by NH₃, 200 °C

- Purging (by N₂) to avoid additional N₂O formation (rich and lean gas phase mixing)
- **Secondary N₂O peak** was produced even in the **absence of O₂** in the lean feed
- At 150-200 °C NOₓ stored mainly as nitrites → NH₄NO₃ probably not the source for N₂O formation
- NH₄NO₂ unstable and decomposes to nitrogen → no N₂O

General scheme suggested:

- **Residual stored NOₓ** react with the **adsorbed reductant**.
- After the end of the rich phase, surface concentration of the reductant decreases and residual NOₓ become **locally excessive** → N₂O formation.
- After complete consumption of the reductant, the NOₓ release continues (in absence of O₂).
**Surface intermediates during regeneration by CO**

- **Isocyanate species detected by DRIFTS** even in the presence of water
- \( \text{O}_2 + \text{–NCO} \) highly selective to nitrogen \( \rightarrow \) not a source of the secondary \( \text{N}_2\text{O} \) peak
- Interactions of \( \text{–NCO} \) and PGM-CO with the \( \text{NO}_x \) released from the storage sites \( \rightarrow \) secondary \( \text{N}_2\text{O} \) formation
- In line with the proposed general mechanism (adsorbed reductant + residual stored \( \text{NO}_x \))

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60 s lean / 60 s purge / 300 s rich / 60 s purge

DRIFTS surface scan

Regeneration by CO, 250 °C
Conclusions

• \( \text{N}_2\text{O} \) can be formed on PGM sites with any type of reductant, whenever the PGM sites are poorly reduced or the released NO\(_x\) are in local excess over the reductant. This may occur during switching from lean to rich (primary \( \text{N}_2\text{O} \) peak) as well as during switching back from rich to lean (secondary \( \text{N}_2\text{O} \) peak).

• **Primary \( \text{N}_2\text{O} \) peak:**
  - Selectivity of NO\(_x\) reduction depends on local state of PGM sites,
  - Overall selectivity depends on the ratio of individual rates, specific for each reductant (PGM reduction rate, NO\(_x\) release rate, stored oxygen reaction rate).

• **Secondary \( \text{N}_2\text{O} \) peak sources:**
  - adsorbed intermediates (PGM-CO, isocyanates, adsorbed NH\(_3\)),
  - residual NO\(_x\) released from the storage sites,
  - mutual ratio between these two groups = major contributor to secondary \( \text{N}_2\text{O} \).

• Secondary \( \text{N}_2\text{O} \) peak diminishes with more complete regeneration.

• **\( \text{N}_2 \) peaks dynamics** similar to \( \text{N}_2\text{O} \):
  - \( \text{N}_2/\text{N}_2\text{O} \) peaks ratio currently investigated at various conditions.
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