Spatiotemporal Distribution of $\text{NO}_x$ Storage: a Factor Controlling $\text{NH}_3$ and $\text{N}_2\text{O}$ Selectivities over a Commercial LNT Catalyst

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Lean $\text{NO}_x$ traps remove $\text{NO}_x$ from lean-burn engine exhausts in cyclic lean/rich operation

$LNT = 3\text{-way catalyst} + \text{NO}_x$ storage material

$Pt, Pd, Rh, Al_2O_3, CeO_2 \quad Ba, K$

Lean environment (long interval)  NO$_x$ storage

Rich environment (short interval)  NO$_x$ release & reduction
Commercialized variants of LNTs

Lean gasoline (TWC + LNT)

Diesel (LNT + SCR)

Diesel (LNT)
LNT catalysts represent non-urea aftertreatment option for lean engines: no need for urea storage & delivery systems

Technical barriers

• **Fuel penalty**
  – Regeneration & desulfation

• **Cost**
  – High cost of platinum group metals

• **Durability**
  – Large built-in catalyst margin

• **Byproduct emissions**
  – NH$_3$: useful in LNT+SCR application
  – N$_2$O: greenhouse gas to be controlled

*Fundamental insights can enable more efficient and cost effective technology development*
Understanding spatiotemporal distribution of reactions can lead to new insights

- LNT is an inherently transient & integral reactor
  - Transient chemistry evolves along the catalyst length

- Traditional, zero-dimensional (i.e., non-integral) consideration of reactions is not sufficient to describe relevant processes
  - Intermediate reductant roles of NH₃
  - Sulfation impact on catalyst performance
Objective: understand how spatiotemporal distribution of NO$_x$ storage coupled with local chemistry affects NH$_3$ & N$_2$O selectivity

1. Major storage during lean phase
2. Readsorption during rich phase
3. Sulfation-induced storage displacement
Approach: controlled lab reactor study with spatiotemporally resolved analysis

• Commercial LNT:
  – Pt/PdRh, Ba-based, oxygen storage capacity (OSC: Ce/Zr)

• Two types of experiments (base gas: 5% H₂O, 5% CO₂, N₂ balance)
  1. Lean/rich cycling (with or without sulfation)
     – Lean (60 s): 300 ppm NO, 10% O₂
     – Rich (5 s): 3.4% H₂
  2. Transient response
     – Initial LNT surface: oxidized or nitrated
     – NH₃ pulse input

• Spatiotemporal resolution of reactions

Bench reactor

Inside catalyst

In catalyst effluents
Upstream-slipped NO$_x$ during regeneration can be re-adsorbed and reduced downstream

Lean/rich cycling at 400°C

Spatiotemporal profiles

- Fraction of LNT sufficient for complete NO$_x$ storage under optimal conditions
  - Complete lean-phase trapping of inflow NO$_x$ in 1$^{st}$ half (“active NSR zone”)
- Upstream-slipped rich-phase NO$_x$ can be re-adsorbed & further reduced in 2$^{nd}$ half
  - Almost complete cycle averaged NO$_x$ conversion
Sulfation axially displaces lean NO$_x$ storage increasing rich NO$_x$ slip

Lean/rich cycling at 400°C (after sulfation; 1.7 g/L)

Spatiotemporal profiles

- Plug-like axial displacement of lean NO$_x$ storage
  - Complete lean-phase trapping of inflow NO$_x$ still maintained

- Earlier & greater rich-phase NO$_x$ slip
  - Due to less downstream storage buffer
  - Significant rich-phase NO$_x$ slip leading to a reduced cycle-averaged conversion
Sulfation-induced axial redistribution explains decreasing NO$_x$ conversion pattern

Lean/rich cycling at 400°C

![Graph showing NO$_x$ storage, NO$_x$ slip, and NO$_x$ readsorption](image)

- **< ~1 g S**, conversion increasingly limited by rich NO$_x$ slip
  - Continuous decrease in readsorption
- **> 1 g S**, accelerated decrease due to insufficient storage capacity
**Sulfation-induced axial redistribution explains increasing NH$_3$ selectivity**

Lean/rich cycling at 400°C

- **Significant increase in NH$_3$ selectivity (9-fold increase)**
  - Shortening of OSC-only zone: less NH$_3$ reaction with OSC
- **Minor change in N$_2$O selectivity (initial increase followed by continuous decrease)**

Integrated outlet measurement

![Graph showing selectivity against sulfur loading](image-url)

- Plot with NH$_3$ and N$_2$O selectivity against sulfur loading (g/L)
- Key observations:
  - NH$_3$ selectivity increases significantly (9-fold)
  - Shortening of OSC-only zone
  - N$_2$O selectivity shows initial increase followed by continuous decrease

Diagram with reaction pathways:

- Lean (late) and Rich (early) cycling
- Sulfated NO$_x$ storage
- NO$_x$ slip, readsorption, NH$_3$ slip, NH$_3$ oxidation
- Regeneration front

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Direct intra-catalyst measurements confirm the link between NO$_x$ distribution & NH$_3$
NH₃ reduction of surface oxygen does not lead to N₂O formation

Transient response experiment: NH₃ pulse input
LNT pre-oxidized with O₂ followed by inert purge

- NH₃ reduction of stored oxygen (CeO₂): efficient (plug-like front)
- Not a major contributor to N₂O formation
- Consistent with insignificant change in N₂O selectivity with sulfation
  - Despite 9-fold increase in NH₃ slip (i.e., less NH₃ reduction of OSC)
**NH₃** reaction with stored \( \text{NO}_x \) leads to \( \text{N}_2\text{O} \)

Transi\( \text{ent} \) response experiment: \( \text{NH}_3 \) pulse input

LNT pre-nitrated with 300 ppm \( \text{NO}_x \) + 10% \( \text{O}_2 \) followed by inert purge

- \( \text{NH}_3 \) reduction of stored \( \text{NO}_x \): efficient
- Major contributor to \( \text{N}_2\text{O} \) formation
- Consistent with insignificant change in \( \text{N}_2\text{O} \) selectivity with sulfation
  - Plug-like axial displacement of the active NSR zone (i.e., just location changes)
**NH₃ reaction with stored NOₓ relevant to LNT N₂O selectivity**

- NH₃ reaches unregenerated zone earlier than H₂
- Due to lower regeneration efficiency of NH₃
- Co-presence of CO and HCs can further alter N₂O selectivity

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**Long cycle test – 2nd of 3 cycles, 200°C, 30,000 hr⁻¹ space velocity**

- NOx conversion (%)
- Temperature (°C)
Conclusions

• **Distribution of stored NO\textsubscript{x} evolves continuously over space and time**
  - Primary storage with inflow NO\textsubscript{x} (lean)
  - Downstream readsorption of upstream-slipped NO\textsubscript{x} (rich)
  - Sulfation-induced axial displacement of active NO\textsubscript{x} storage (lean, rich)

• **NH\textsubscript{3} byproduct plays intermediate reductant roles**
  - NH\textsubscript{3} reduces efficiently stored oxygen (OSC) without N\textsubscript{2}O formation
  - NH\textsubscript{3} reduces efficiently stored NO\textsubscript{x} with N\textsubscript{2}O formation

• **Coupling of NO\textsubscript{x} storage distribution with local chemistry is an important factor determining LNT performance trends**
  - Example: sulfation impact
    - Increased NO\textsubscript{x} slips (both lean and rich)
    - Increased NH\textsubscript{3} selectivity
    - Minor change in N\textsubscript{2}O selectivity

• **Insights can facilitate modeling and development efforts**
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