Resolving $\text{N}_2\text{O}$ formation dynamics during lean/rich cycling of a commercial LNT

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LNTs remove NO\textsubscript{x} via cyclic lean/rich operation

Storage (lean)
30-120 s

Regeneration (rich)
1-10 s

complex spatiotemporal development of regeneration reactions
Significant $\text{N}_2\text{O}$ can form during LNT regeneration

- Cycle-averaged yield can reach ~20% (lab reactor study, 60/5-s cycling, no reductant in lean)
- Sensitive to temperature and reductant type
- Two $\text{N}_2\text{O}$ peaks
  - At regeneration inception: primary peak
  - At rich-to-lean transition: secondary peak
- Mechanisms not well understood

![Temporal profiles of $\text{N}_2\text{O}$ formation](image)

- Cycle-averaged data

- NITROUS OXIDE

  strong greenhouse gas (need to minimize)
This study aimed to clarify N₂O formation mechanisms

Develop N₂O models & mitigation strategies

Experiments
- Commercial catalysts
  BMW Lean GDI LNT
- Bench reactor experiments
  Fast lean/rich cycling
  Transient response method
- Specialized measurements
  High speed FTIR
  SpaciMS
  \(^{15}\)NO
  DRIFTS

Simulation & Analysis

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Results

$\text{N}_2\text{O}$ formation in rich phase (regeneration)
NO\textsubscript{x} reduction over incompletely reduced PGM sites leads to N\textsubscript{2}O

Spatial profile along catalyst

- N\textsubscript{2}O formed locally at the reduction front
  - Reductants first reach oxidized zone (early regen)

- N\textsubscript{2}O yields highest near “light-off” temperature for each reductant type
  - H\textsubscript{2}, NH\textsubscript{3} (intermediate), CO, HCs

NO reduction over partially reduced PGM

*: PGM sites

2NO

N\textsubscript{2}O

greater chance to have this surface composition
Implementation of variable selectivity in global kinetic model

- **Local selectivity** of the stored NO\textsubscript{x} reduction to NO, N\textsubscript{2}O, N\textsubscript{2} or NH\textsubscript{3} linked with coverage of oxidative or reductive species on locally available PGM sites
- Approximate **selectivity functions** are used in the global kinetics LNT model

**Simplified PGM state reactions**

- \( \text{Pt} + \frac{1}{2} \text{O}_2 \rightarrow \text{Pt-O} \)
- \( \text{Pt-O} + \text{CO} \rightarrow \text{Pt} + \text{CO}_2 \)
- \( \text{Pt-O} + \text{H}_2 \rightarrow \text{Pt} + \text{H}_2\text{O} \)
- \( \text{Pt-O} + \frac{1}{9} \text{C}_3\text{H}_6 \rightarrow \text{Pt} + \frac{1}{3} \text{H}_2\text{O} + \frac{1}{3} \text{CO}_2 \)
- \( \text{Pt-O} + \frac{2}{5} \text{NH}_3 \rightarrow \frac{2}{5} \text{NO} + \frac{3}{5} \text{H}_2\text{O} \)

(Pt-O represents a lumped characteristic of the PGM state, not the real oxygen coverage)
Implementation of variable selectivity in global kinetic model (cont.)

- Full range of possible N-products considered

\[
\begin{align*}
\text{Ba(NO}_3\text{)}_2 + S\text{NO}^*3 \text{ H}_2 + S\text{N}_2\text{O}^*4 \text{ H}_2 + S\text{N}_2^*5 \text{ H}_2 + S\text{NH}_3^*8 \text{ H}_2 & \rightarrow \\
\rightarrow \text{BaO} + S\text{NO}^*2 \text{ NO} + S\text{N}_2\text{O}^*1 \text{ N}_2\text{O} + S\text{N}_2^*1 \text{ N}_2 + S\text{NH}_3^*2 \text{ NH}_3 + ... \text{ H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{Ba(NO}_3\text{)}_2 + S\text{NO}^*3 \text{ CO} + S\text{N}_2\text{O}^*4 \text{ CO} + S\text{N}_2^*5 \text{ CO} + S\text{NH}_3^*(8 \text{ CO} + 3 \text{ H}_2\text{O}) & \rightarrow \\
\rightarrow \text{BaO} + S\text{NO}^*2 \text{ NO} + S\text{N}_2\text{O}^*1 \text{ N}_2\text{O} + S\text{N}_2^*1 \text{ N}_2 + S\text{NH}_3^*2 \text{ NH}_3 + ... \text{ CO}_2
\end{align*}
\]

\[
\begin{align*}
\text{Ba(NO}_3\text{)}_2 + S\text{NO}^*3/9 \text{ C}_3\text{H}_6 + S\text{N}_2\text{O}^*4/9 \text{ C}_3\text{H}_6 + S\text{N}_2^*5/9 \text{ C}_3\text{H}_6 & \rightarrow \\
\rightarrow \text{BaO} + S\text{NO}^*2 \text{ NO} + S\text{N}_2\text{O}^*1 \text{ N}_2\text{O} + S\text{N}_2^*1 \text{ N}_2 + ... \text{ CO}_2 + ... \text{ H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{Ba(NO}_3\text{)}_2 + S\text{NO}^*6/5 \text{ NH}_3 + S\text{N}_2\text{O}^*2 \text{ NH}_3 + S\text{N}_2^*10/3 \text{ NH}_3 & \rightarrow \\
\rightarrow \text{BaO} + S\text{NO}^*16/5 \text{ NO} + S\text{N}_2\text{O}^*2 \text{ N}_2\text{O} + S\text{N}_2^*8/3 \text{ N}_2 + ... \text{ CO}_2 + ... \text{ H}_2\text{O}
\end{align*}
\]

- High N\textsubscript{2} selectivity of OSC reduction with NH\textsubscript{3}

\[
\text{Ce}_2\text{O}_4 + 2/3 \text{ NH}_3 \rightarrow \text{Ce}_2\text{O}_3 + 1/3 \text{ N}_2 + \text{H}_2\text{O}
\]

Results

$\text{N}_2\text{O}$ formation at rich-to-lean transition

“secondary peak”
**NO\textsubscript{x} reduction can be significant at rich-to-lean transitions**

- **Regeneration by CO at 300°C**
  - High conversion (~100 %)
  - No breakthrough of NO\textsubscript{x} in lean

\[ L=0 \text{ (inlet)} \quad \quad \text{ (outlet) } L=1 \]

\[ \text{NO}_x \text{ storage zone} \quad \quad \text{O}_2 \text{ storage only} \]

![Graphs showing NO\textsubscript{x} and O\textsubscript{2} storage](image-url)
NO$_x$ reduction can be significant at rich-to-lean transitions

- **Regeneration by CO at 300°C**
  - High conversion (~100%)
  - No breakthrough of NO$_x$ in lean

L=0 (inlet) (outlet) L=1

- NO$_x$ storage zone
- O$_2$ storage only
Secondary $\text{N}_2\text{O}$ more significant with less complete regeneration

- Regeneration by $\text{C}_3\text{H}_6$ at 250 °C
  - Slow regen, low conversion
  - $\text{NO}_x$ breakthrough in lean phase
  - Residual stored NOx at end of regen.

$L=0$ (inlet), $(outlet) \ L=1$

$\text{NO}_x$ storage zone

Graphs showing:

- $\text{N}_2$ and $\text{N}_2\text{O}$ emissions over time at different L values (0.25L, 0.50L, 0.75L, 1.00L).
- The emissions are labeled as primary ($\text{N}_2$) and secondary ($\text{N}_2\text{O}$) for both lean and rich phases.

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Secondary N\textsubscript{2}O more significant with less complete regeneration (cont.)

- Contribution of secondary peaks increases with decreasing regeneration length
  - More residual NO\textsubscript{x} remaining on the surface
- Secondary peaks observed up to 400 °C for short regeneration
  - May be relevant to high-temperature activity during rapid cycling (Di-Air)
- Secondary N\textsubscript{2}O most significant around light-off temperatures (as for primary N\textsubscript{2}O)
A variety of reductive species available on the surface at the end of regeneration

- Proposed general mechanism for secondary peaks formation: residual stored NO$_x$ + adsorbed reductants & intermediates
- High PGM-CO coverage – “simple” adsorbed reductant can contribute to secondary N$_2$ and N$_2$O formation
- Accumulation of isocyanate (-NCO) species
- Other potential surface reductants: NH$_3$, HCs

After switch back to lean:
- O$_2$ + –NCO highly selective to N$_2$ → not a source of the secondary N$_2$O peak
- Interactions of –NCO & PGM-CO with the NO$_x$ released from the storage sites → secondary N$_2$O
Extension of global kinetic model to capture peaks at rich-to-lean transitions

Selectivity at rich to lean transition is determined by:

- Amount of residual stored NO\textsubscript{x} and adsorbed reductants/intermediates
  - Reductant ads/des steps added to the model
    \[ \text{H}_2 + * \leftrightarrow \text{H}_2^* \]
    \[ \text{CO} + * \leftrightarrow \text{CO}^* \]
    \[ \text{C}_3\text{H}_6 + * \leftrightarrow \text{C}_3\text{H}_6^* \]
    \[ \text{NH}_3 + * \leftrightarrow \text{NH}_3^* \]
  
  \[ \Theta_{\text{void}} = 1 - (\Theta_{\text{H}_2^*} + \Theta_{\text{CO}^*} + \Theta_{\text{C}_3\text{H}_6^*} + \Theta_{\text{NH}_3^*}) \]

- PGM oxidation rate
Gained mechanistic insights led to an enhanced LNT model

Model prediction of $N_2O$ dynamics

**BMW LNT (250 °C, 30000 hr$^{-1}$)**
All: 300 ppm NO, 5% $H_2O$, inert balance
Lean (60 s): 10% $O_2$
Rich (5 s): 0.378% $C_3H_6$

**BMW LNT (250 °C, 30000 hr$^{-1}$)**
All: 300 ppm NO, 5% $H_2O$, inert balance
Lean (60 s): 10% $O_2$
Rich (5 s): 3.4% CO
Lambda control impact on secondary peak selectivity

BMW LNT (225 °C, 30000 hr⁻¹)
All: 300 ppm NO, 5% H₂O, inert balance
Lean (60 s): 10% O₂
Rich (5 s): 3.4% CO
Slightly lean (6 or 25 s): 0.5% CO, 0.28% O₂

...and N₂O control strategies
Summary

• LNT regeneration dynamics & mechanisms controlling N-product selectivity clarified by reactor study and modeling

• Primary N₂O peak in rich phase
  — Caused by reaction btwn. N* + NO* formed over partially reduced PGM
  — High at early regen. times, at low temperature, with less effective reductants
  — Selectivity determined by NOₓ release rate + PGM reduction rate

• Secondary N₂O peak at rich-to-lean transition
  — Caused by reaction btwn. residual NOₓ and reductive species on the surface
  — Selectivity determined by amount of residual stored NOₓ and adsorbed reductants/intermediates + PGM oxidation rate

• Insights led to enhanced kinetic model & N₂O mitigation strategies
  — Avoid regeneration at low temperatures
  — Minimize hydrocarbon content at low-intermediate temperatures (via engine control, reforming catalyst utilization upstream)
  — Lambda control after rich regeneration
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Additional Slides
N$_2$O trend consistent w/ PGM redox state

- N$_2$O maximized near light-off temperature for a given reductant
  - $H_2 < CO < C_3H_6$ (consistent with reduction efficiency)
- One exception: $H_2$ produces high N$_2$O above light-off T (<150 °C)
  - Likely due to large NH$_3$-intermediate formation (major product)
  - NH$_3$ is not effective at low temperatures
Oxidation of “stored” NH$_3$ not likely a major contributor to 2$^{nd}$ N$_2$O peak

- Gas-phase NO in lean not critical (results not shown)

Regeneration with H$_2$ at T=150°C

Note: complete NO$_x$ conversion (no breakthrough) in both cases

- Without CO$_2$, higher NH$_3$, but negligible secondary N$_2$O
- CO$_2$ involved in surface intermediate formation?
Lean-phase reduction of residual surface NO\textsubscript{x} leads to secondary N\textsubscript{2}O

Regeneration with H\textsubscript{2} at T=150°C

- CO\textsubscript{2} not critical in secondary N\textsubscript{2}O formation, but seems to “promote” by delaying regeneration (see NO\textsubscript{x} breakthrough profiles)
Possible surface reductants for secondary \( \text{N}_2\text{O} \) formation during regeneration with \( \text{H}_2 \) (150-200 °C): \( \text{NH}_3, \text{ C} \)

- Switch from \( \text{NH}_3 \) (rich) to inert \( \rightarrow \) 2\(^{nd} \) \( \text{N}_2\text{O} \)
  - Destabilization of \( \text{NH}_3 \) strongly held by PGM and reaction with \( \text{NO}_x \)

Regeneration with \( \text{NH}_3 \) at \( T=200^\circ\text{C} \) with \( \text{CO}_2 \)

Regeneration with \( \text{H}_2 \) (DRIFTS) at \( T=200^\circ\text{C} \) with \( \text{CO}_2 \)

- \( \text{-NCO} \) not observed
- PGM-CO formed readily
- Inhibition of reactions over PGM
**Possible surface reductants responsible for secondary N\textsubscript{2}O formation during regeneration with CO (200-250 °C): CO**

- **Regeneration with CO at T=250°C**

  ![Graph showing regeneration with CO at T=250°C](image)

- Stable PGM-CO formed in rich & gradually disappeared in lean
- -NCO formed but not very stable
- NH\textsubscript{3} is effective at this temperature (not strongly bound to PGM)

  → CO adsorbed on PGM sites likely reductant
Possible surface reductants responsible for secondary \( \text{N}_2\text{O} \) formation during regeneration with \( \text{C}_3\text{H}_6 \) (250-300 °C): \( \text{C}_x\text{H}_y \)

**Regeneration with \( \text{C}_3\text{H}_6 \) at \( T=300^\circ\text{C} \)**

- No significant -NCO or PGM-CO on the surface (DRIFTS results not shown)
- Sharp CO\(_2\) peak observed at rich/lean transition indicates presence of surface C species (results not shown)
- \( \text{H}_2 \), CO, \( \text{NH}_3 \) all effective at 300°C (not strongly bound to PGM)

\[ \rightarrow \text{PGM-} \text{H}_x\text{C}_y \text{ likely reductant} \]