Resolving N₂O formation dynamics during lean/rich cycling of a commercial LNT

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Significant N₂O 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 N₂O peaks
 - At regeneration inception: primary peak
 - At rich-to-lean transition: secondary peak
- Mechanisms not well understood



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This study aimed to clarify N₂O **UCT Prague-ORNL** formation mechanisms collaboration (2010-2015)

Experiments Develop N₂O models & mitigation strategies Commercial catalysts BMW Lean GDI LNT Rich Ê 1600 Lean udd)²1200 HN 800 NH₃ 2 🛞 $S_{NO} + S_{N2O} + S_{N2} + S_{NH3} = 1.0$ in entire range Bench reactor experiments co 8 sec V20, 400 reduction 0.8 NH₃ N₂O NO Fast lean/rich cycling Local reduction of PGM sites at Ê 1600 lean lean liahth 3 0.6 the rich regeneration front id 1200 Selectivity of NO_X Transient response method 2 🖇 Ϋ́ N₂O 800 N₂ NH: 8 small sec. N20, 0.4 400 Specialized measurements N₂O (ju 1600 dig 1200 lean 3 High speed FTIR 0.2 2 8 800 8 **SpaciMS** no sec 20 400 N₂O 0 (Covered by 0.2 0.4 0.6 0.8 Covered by ¹⁵NO 50 55 60 65 70 75 80 85 90 95 100 reductive species PGM sites redox state oxidative species t (s) - N₂O - NH₃ - CO DRIFTS **Simulation & Analysis** 1400 1400 (mdd) O^ZN ¹²⁰⁰ ¹⁰⁰⁰ ⁰⁰⁰ ⁴⁰⁰ Conversion (%) 08 08 08 08 NO_x conv N₂C 1200 80 1000 **(udd**) ⁰⁶ Yield (%) NO 800 ٣ 600 SpaciMS 400 NH 20 200 200 0 Cat-In Cat-Out 100 200 300 400 500 600 40 45 50 55 60 65 70 L (mm) Temperature (°C) Time (s) OAK RIDGE UNIVERSITY OF



Results

N₂O formation in rich phase (regeneration)







NO_x reduction over incompletely reduced PGM sites leads to N_2O

Spatial profile along catalyst reduction front moves CO H₂

N₂O

4

z (cm)



• N₂O formed locally at the reduction front

7

 \rightarrow outlet

greater chance to have this surface composition

- Reductants first reach oxidized zone (early regen)

5

6

N₂O yields highest near "light-off" temperature for each reductant type

8

-H₂, NH₃ (intermediate), CO, HCs



NH₃

1

 $0 \quad 1$

2

3

Implementation of variable selectivity in global kinetic model

- Local selectivity of the stored NO_x reduction to NO, N₂O, N₂ or NH₃ linked with coverage of oxidative or reductive species on locally available PGM sites
- Approximate selectivity functions are used in the global kinetics LNT model





Implementation of variable selectivity in global kinetic model (cont.)

Full range of possible N-products considered

$$\begin{array}{l} Ba(NO_{3})_{2} + S_{N0}^{*3} H_{2} + S_{N20}^{*4} H_{2} + S_{N2}^{*5} H_{2} + S_{NH3}^{*8} H_{2} \rightarrow \\ \rightarrow BaO + S_{N0}^{*2} NO + S_{N20}^{*1} N_{2}O + S_{N2}^{*1} N_{2} + S_{NH3}^{*2} NH_{3} + \dots H_{2}O \\ Ba(NO_{3})_{2} + S_{N0}^{*3} CO + S_{N20}^{*4} CO + S_{N2}^{*5} CO + S_{NH3}^{*8} (8 CO + 3 H_{2}O) \rightarrow \\ \rightarrow BaO + S_{N0}^{*2} NO + S_{N20}^{*1} N_{2}O + S_{N2}^{*1} N_{2} + S_{NH3}^{*2} NH_{3} + \dots CO_{2} \\ Ba(NO_{3})_{2} + S_{N0}^{*3} / 9 C_{3}H_{6} + S_{N20}^{*4} / 9 C_{3}H_{6} + S_{N2}^{*5} / 9 C_{3}H_{6} \rightarrow \\ \rightarrow BaO + S_{N0}^{*2} NO + S_{N20}^{*1} N_{2}O + S_{N2}^{*1} N_{2} + \dots CO_{2} + \dots H_{2}O \\ Ba(NO_{3})_{2} + S_{N0}^{*6} / 5 NH_{3} + S_{N20}^{*2} NH_{3} + S_{N2}^{*1} 0 / 3 NH_{3} \rightarrow \end{array}$$

 $\rightarrow BaO^{3/2} + S_{NO}^{*16/5} NO^{-1} + S_{N20}^{*2} N_2O^{-1} + S_{N2}^{*8/3} N_2^{-1} + \dots CO_2^{-1} + \dots H_2O^{-1}$



Results

N₂O formation at rich-tolean transition





NO_x reduction can be significant at rich-tolean transitions







Secondary N₂O more significant with less complete regeneration (cont.)



- Contribution of secondary peaks increases with decreasing regeneration length
 - More residual NO_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 N₂O most significant around light-off temperatures (as for primary N₂O)

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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_2O formation
- Accumulation of isocyanate (-NCO) species
- Other potential surface reductants: NH₃, HCs

After switch back to lean:

- O₂ + –NCO highly selective to N₂
 → not a source of the secondary N₂O peak
- Interactions of –NCO & PGM-CO with the NO_x released from the storage sites → secondary N₂O





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_x and adsorbed reductants/intermediates
 - Reductant ads/des steps added to the model

$$\begin{array}{c} \mathsf{H}_2 \texttt{+}^* \leftrightarrow \mathsf{H}_2^* \\ \mathsf{CO} \texttt{+}^* \leftrightarrow \mathsf{CO}^* \\ \mathsf{C}_3 \mathsf{H}_6 \texttt{+}^* \leftrightarrow \mathsf{C}_3 \mathsf{H}_6^* \\ \mathsf{NH}_3 \texttt{+}^* \leftrightarrow \mathsf{NH}_3^* \end{array}$$

 $\Theta^{\text{void}} = \mathbf{1} - (\Theta_{\text{H2}^*} + \Theta_{\text{CO}^*} + \Theta_{\text{C3H6}^*} + \Theta_{\text{NH3}^*})$

PGM oxidation rate

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Gained mechanistic insights led to an enhanced LNT model

Model prediction of N₂O dynamics

BMW LNT (250 °C, 30000 hr⁻¹) All: 300 ppm NO, 5% H₂O, inert balance Lean (60 s): 10% O₂ Rich (5 s): 0.378% C₃H₆ **BMW LNT (250 °C, 30000 hr⁻¹)** All: 300 ppm NO, 5% H₂O, inert balance Lean (60 s): 10% O₂ Rich (5 s): 3.4% CO





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 NO_x release rate + PGM reduction rate
- Secondary N₂O peak at rich-to-lean transition
 - Caused by reaction btwn. residual NO_x and reductive species on the surface
 - Selectivity determined by amount of residual stored NO_x 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





N₂O trend consistent w/ PGM redox state



- N₂O maximized near light-off temperature for a given reductant
 - H₂ < CO < C₃H₆ (consistent with reduction efficiency)
- One exception: H₂ produces high N₂O above light-off T (<150 °C)
 - Likely due to large NH₃-intermediate formation (major product)
 - NH₃ 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 H₂ at T=150°C

Note: complete NO_x conversion (no breakthrough) in both cases

- Without CO₂, higher NH₃, but negligible secondary N₂O
- CO₂ involved in surface intermediate formation?

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Lean-phase reduction of residual surface NO_x leads to secondary N_2O



by delaying regeneration (see NO_x breakthrough profiles)



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Possible surface reductants for secondary N₂O formation during regeneration with H₂ (150-200 °C): NH₃, C



- Switch from NH_3 (rich) to inert $\rightarrow 2^{nd} N_2O$
 - Destabilization of $\rm NH_3$ strongly held by PGM and reaction with $\rm NO_x$



- -NCO not observed
- PGM-CO formed readily
- Inhibition of reactions over PGM
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Possible surface reductants responsible for secondary N₂O formation during regeneration with CO (200-250 °C): CO

Regeneration with CO at T=250°C



- Stable PGM-CO formed in rich & gradually disappeared in lean
- -NCO formed but not very stable
- NH₃ is effective at this temperature (not strongly bound to PGM)

 \rightarrow CO adsorbed on PGM sites likely reductant



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Possible surface reductants responsible for secondary N_2O formation during regeneration with C_3H_6 (250-300 °C): C_xH_y

Regeneration with C₃H₆ at T=300°C



- No significant -NCO or PGM-CO on the surface (DRIFTS results not shown)
- Sharp CO₂ peak observed at rich/lean transition indicates presence of surface C species (results not shown)
- H₂, CO, NH₃ all effective at 300°C (not strongly bound to PGM)

 \rightarrow PGM-H_xC_y likely reductant

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