N₂O Formation During the Regeneration of Lean NO_x Traps





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N₂O Emissions Background

- N_2O in low concentrations pose **no health risk.** The global average atmospheric concentration is ~ 0.3 ppm.
- N₂O is a strong **greenhouse gas** (global warming potential 310 x higher than CO₂) with a long atmospheric life (~120 years). However, the mean N₂O tailpipe concentrations in automotive exhaust are typically 10^3 - 10^5 lower than those of CO₂.
- Natural sources (wide variety of biological sources in soil and water) account for over 60% of the total N₂O emissions. The main human-related source of N₂O is agricultural soil management (fertilizers), adipic and nitric acid production, and stationary and mobile combustion of fossil fuel.
- Exhaust catalysts can form N₂O by incomplete NO_x reduction or non-selective NH₃ oxidation.
- Mobile N₂O emissions are **not regulated** (yet), but there is a general effort to minimize tailpipe N₂O when designing exhaust aftertreatment systems.





NO_x Storage Catalyst Schematic: <u>lean</u> fuel mixture, <u>oxidizing</u> conditions







NO_x Storage Catalyst Schematic: <u>rich</u> fuel mixture, <u>reducing</u> conditions







Model Background & Approach

- 1D spatially distributed, dynamic, non-isothermal, physically and chemically based model.
- **Global reaction kinetics** including inhibition effects.
 - Only the key species on the surface considered explicitly (stored O_2 and stored NO_x).
- Kinetic parameters evaluated from **lab experiments with synthetic gases**.
 - Individual reactions or smaller reaction sub-systems are studied first, then the full system.
- The global reaction kinetic model published by Kočí et al., *Catalysis Today* (2009).
 - Fully formulated NO_x storage and reduction (NSRC, LNT) catalyst
 - Includes NH₃ as an active reduction intermediate
 - Validated by real driving cycle data.
 - $-N_2O$ was not considered.
- In this work we extend the existing model to include the reactions describing N₂O formation during LNT regeneration.





Model of Catalyst Monolith Channel







Existing LNT Model Reactions – Part 1

Kočí et al., Catalysis Today (2009)

CO, H₂ and hydrocarbons oxidation

 $CO + \frac{1}{2}O_2 \rightarrow CO_2$ $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $C_3H_6 + \frac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O$

$$R_{1} = k_{1} \Psi_{cap,Pt} y_{CO} y_{O_{2}} \frac{1}{G_{1}}$$

$$R_{2} = k_{2} \Psi_{cap,Pt} y_{H_{2}} y_{O_{2}} \frac{1}{G_{1}}$$

$$R_{3} = k_{3} \Psi_{cap,Pt} y_{C_{3}H_{6}} y_{O_{2}} \frac{1}{G_{1}}$$

Water gas shift and steam reforming

 $CO+H_2O \rightarrow CO_2+H_2$ $C_3H_6+3H_2O \rightarrow 3CO+6H_2$

Steady NO reduction

 $NO+CO \rightarrow CO_{2} + \frac{1}{2}N_{2}$ $NO + \frac{5}{2}H_{2} \rightarrow H_{2}O + NH_{3}$ $9NO+C_{3}H_{6} \rightarrow 3CO_{2} + 3H_{2}O + \frac{9}{2}N_{2}$ $\frac{NO/NO_{2} \text{ transformation}}{NO + \frac{1}{2}O_{2} \rightarrow NO_{2}}$ $NO_{2} + CO \longrightarrow NO + CO_{2}$ $9NO_{2} + C_{3}H_{6} \longrightarrow 9NO + 3CO_{2} + 3H_{2}O$



$$R_{4} = k_{4} \Psi_{\text{cap,Pt}} (y_{\text{CO}} y_{\text{H}_{2}\text{O}} - \frac{y_{\text{CO}_{2}} y_{\text{H}_{2}}}{K_{\text{cap}}^{\text{eq}}})$$

$$R_{5} = k_{5} \Psi_{\text{cap,Pt}} (y_{\text{C}_{3}\text{H}_{6}} y_{\text{H}_{2}\text{O}} - \frac{y_{\text{CO}_{2}}^{y} y_{\text{H}_{2}}^{6}}{K_{y,5}^{\text{eq}} y_{\text{H}_{2}\text{O}}^{2}})$$

$$R_{6} = k_{6} \Psi_{cap,Pt} y_{CO} y_{NO}^{0.5} \frac{1}{G_{2}} \frac{1}{G_{1}}$$

$$R_{7} = k_{7} \Psi_{cap,Pt} y_{H_{2}} y_{NO}^{0.5} \frac{1}{G_{2}} \frac{1}{G_{1}}$$

$$R_{8} = k_{8} \Psi_{cap,Pt} y_{C_{3}H_{6}} y_{NO}^{0.5} \frac{1}{G_{2}} \frac{1}{G_{1}}$$

$$R_{9} = k_{9} \Psi_{\text{cap,Pt}} (y_{\text{NO}} y_{\text{O}_{2}}^{0.5} - \frac{y_{\text{NO}_{2}}}{K_{v,0}^{\text{eq}}}) \frac{1}{G_{1}}$$

$$R_{10} = k_{10} \Psi_{\text{cap,Pt}} y_{\text{NO}_{2}} y_{\text{CO}} \frac{1}{G_{\text{NO}_{2\text{red}}}}$$

$$R_{11} = k_{11} \Psi_{\text{cap,Pt}} y_{\text{NO}_{2}} y_{\text{C}_{3}} H_{6} \frac{1}{G_{\text{NO}_{2\text{red}}}}$$



Existing LNT Model Reactions – Part 2 Kočí et al., Catalysis Today (2009)

Oxygen storage & reduction

 $Ce_{2}O_{3} + \frac{1}{2}O_{2} \rightarrow Ce_{2}O_{4}$ $Ce_{2}O_{4} + CO \rightarrow Ce_{2}O_{3} + CO_{2}$ $Ce_{2}O_{4} + H_{2} \rightarrow Ce_{2}O_{3} + H_{2}O$ $Ce_{2}O_{4} + \frac{1}{9}C_{3}H_{6} \rightarrow Ce_{2}O_{3} + \frac{1}{3}CO_{2} + \frac{1}{3}H_{2}O$

$$R_{12} = k_{12} \Psi_{cap,CeO_2} y_{O_2} (\psi_{O_2}^{eq} - \psi_{O_2})$$

$$R_{13} = k_{13} \Psi_{cap,CeO_2} y_{CO} \psi_{O_2}$$

$$R_{14} = k_{14} \Psi_{cap,CeO_2} y_{H_2} \psi_{O_2}$$

$$R_{15} = k_{15} \Psi_{cap,CeO_2} y_{C_3H_6} \psi_{O_2}$$

Fast NO_x storage (Ba sites in proximity of Pt)

 $BaCO_{3} + 2NO_{2} + \frac{1}{2}O_{2} \rightarrow Ba(NO_{3})_{2} + CO_{2}$ $BaCO_{3} + 2NO + \frac{3}{2}O_{2} \rightarrow Ba(NO_{3})_{2} + CO_{2}$

Slow NO_x storage (bulk Ba sites)

 $3NO_2 + BaCO_3 - bulk \rightarrow Ba(NO_3)_2 - bulk + NO Ba(NO_3)_2 - bulk \rightarrow Ba(NO_3)_2$

$$R_{16} = k_{16} \Psi_{\text{cap},\text{Ba}_{\text{A}}} y_{\text{NO}_{2}} (\psi_{\text{NO}_{x,\text{A}}}^{\text{eq}} - \psi_{\text{NO}_{x,\text{A}}})^{2}$$

$$R_{17} = k_{17} \Psi_{\text{cap},\text{Ba}_{\text{A}}} y_{\text{NO}} (\psi_{\text{NO}_{x,\text{A}}}^{\text{eq}} - \psi_{\text{NO}_{x,\text{A}}})^{2}$$

$$R_{29} = k_{29} \Psi_{cap, Ba_B} y_{NO_2} (\Psi_{NO_{x,B}}^{eq} - \Psi_{NO_{x,B}})^2$$

$$R_{30} = k_{30} \Psi_{cap, Ba_B} (\Psi_{NO_{x,B}} - \Psi_{NO_{x,A}})$$

Desorption of the stored NO_x in reducing atmosphere

$$Ba(NO_3)_2 + 3CO \rightarrow 2NO + BaO + 3CO_2$$

$$Ba(NO_3)_2 + 3H_2 \rightarrow 2NO + BaO + 3H_2O$$

$$Ba(NO_3)_2 + \frac{1}{3}C_3H_6 \rightarrow 2NO + BaO + CO_2 + H_2O$$

$$R_{22} = k_{22} \Psi_{cap,Ba_A} \mathcal{Y}_{CO} \Psi_{NO_{x,A}}^2 \frac{1}{G_4}$$

$$R_{23} = k_{23} \Psi_{cap,Ba_A} \mathcal{Y}_{H_2} \Psi_{NO_{x,A}}^2 \frac{1}{G_4}$$

$$R_{24} = k_{24} \Psi_{cap,Ba_A} \mathcal{Y}_{C_3H_6} \Psi_{NO_{x,A}}^2 \frac{1}{G_4}$$





Existing LNT Model Reactions – Part 3

Kočí et al., Catalysis Today (2009)

Direct reduction of the stored NO_x (Ba sites in proximity of Pt)

$$Ba(NO_{3})_{2} + \frac{5}{9}C_{3}H_{6} \rightarrow N_{2} + BaO + \frac{5}{3}CO_{2} + \frac{5}{3}H_{2}O$$

$$Ba(NO_{3})_{2} + 8H_{2} \rightarrow 2NH_{3} + BaO + 5H_{2}O$$

$$Ba(NO_{3})_{2} + 5CO \rightarrow 2N_{2} + BaO + 5CO_{2}$$

$$Ba(NO_{3})_{2} + 8CO + 3H_{2}O \rightarrow 2NH_{3} + BaO + 8CO_{2}$$

<u>NH₃ oxidation reactions – selective to N₂</u>

$$\frac{10}{3} \mathbf{NH_3} + Ba(NO_3)_2 \rightarrow \frac{8}{3} \mathbf{N_2} + BaO + 3H_2O$$

$$2\mathbf{NH_3} + 3NO \rightarrow \frac{5}{2} \mathbf{N_2} + 3H_2O$$

$$2\mathbf{NH_3} + \frac{3}{2}O_2 \rightarrow \mathbf{N_2} + 3H_2O$$

$$2\mathbf{NH_3} + 3Ce_2O_4 \rightarrow \mathbf{N_2} + 3H_2O + 3Ce_2O_3$$

$$R_{18} = k_{18} \Psi_{cap, Ba_A} y_{CO} \Psi_{NO_{x,A}}^2 \frac{1}{G_3}$$

$$R_{19} = k_{19} \Psi_{cap, Ba_A} y_{CO} \Psi_{NO_{x,A}}^2 \frac{1}{G_3} \frac{1}{G_5}$$

$$R_{20} = k_{20} \Psi_{cap, Ba_A} y_{H_2} \Psi_{NO_{x,A}}^2 \frac{1}{G_3} \frac{1}{G_5}$$

$$R_{21} = k_{21} \Psi_{cap, Ba_A} y_{C_3 H_6} \Psi_{NO_{x,A}}^2 \frac{1}{G_3}$$

$$R_{25} = k_{25} \Psi_{cap, Ba_A} y_{NH_3} \Psi_{NO_{x,A}}^2$$

$$R_{26} = k_{26} \Psi_{cap, Pt} y_{NH_3} y_{NO}^{0.5}$$

$$R_{27} = k_{27} \Psi_{cap, Pt} y_{NH_3} y_{O_2}$$

$$R_{28} = k_{28} \Psi_{cap, CeO_2} y_{NH_3} \Psi_{CeO_2}$$

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<u>CO₂ adsorption on the NO_x storage sites</u>

 $CO_2 + BaO \leftrightarrow BaCO_3$

$$R_{31} = \sum_{j=18}^{25} R_j$$

 $\begin{array}{ll} \hline \textbf{Inhibition terms:} & G_1 = (1 + K_{a,1}y_{\text{CO}} + K_{a,2}y_{\text{C}_3\text{H}_6})^2 \cdot (K_{a,3}y_{\text{CO}}^2y_{\text{C}_3\text{H}_6}^2) \cdot (1 + K_{a,4}y_{\text{NO}_x}^{0.7})T^{\text{s}} \\ & G_2 = 1 + K_{a,5}y_{\text{O}_2}; \quad G_3 = (1 + K_{a,6}y_{\text{O}_2}) \\ & G_4 = (1 + 0.1K_{a,6}y_{\text{O}_2})(1 + K_{a,7}y_{\text{NO}_x}); \quad G_5 = 1 + K_{a,8}y_{\text{CO}} \end{array}$



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Model Additions to Include N₂O Formation





Assumptions for N₂O Formation During LNT Regeneration

- During the LNT regeneration:
 - a reduction front moves from the inlet towards outlet,
 - dividing the monolith into two zones
 - the front zone is already **reduced**,
 - the back zone is still **oxidized**.
- NH₃ is formed in the reduced zone:
 - then transported by convection into the downstream oxidized zone,
 - where NH_3 reacts with the Stored NO_x and oxygen.
- These NH₃ reactions are not 100 % selective to N₂;
 - N₂O is formed from nonselective NH₃ oxidation.







New LNT Model Reactions – N₂O extensions

<u>Non-selective NH₃ oxidation -> N₂O</u>

$2NH_3 + Ba(NO_3)_2 \rightarrow 2N_2O + BaO + 3H_2O$
$2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O$
$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$
$(\overline{\mathrm{NH}_{3}} + \mathrm{Ce}_{2}\mathrm{O}_{4} \ \overline{give} \ negligible \ \mathrm{N}_{2}\mathrm{O})$
(cf. Choi et al.)

<u>Non-selective NH₃ oxidation → NO</u> $2NH_3 + \frac{5}{2}O_2 \rightarrow 2NO + 3H_2O$ Each NH₃ oxidation reaction (NH₃+O₂, NH₃+NO_x, NH₃+sO₂, and NH₃+sNO_x) is now split into two parallel reactions, leading to N₂ or N₂O, respectively. The ratio of these two reaction rates is defined by a **tabulated selectivity factor S_{N2O}(T)**. This limits the number of kinetic parameters and enables calibration of the NH₃ oxidation rates independent of their selectivity.

For NH₃ oxidation by O₂, selectivity towards NO_x $S_{NOx}(T)$ is considered in the same way as $S_{N2O}(T)$; i.e., three parallel reactions to N₂, N₂O or NO are taken into account.

N₂O reduction – not considered in the first approximation

(Justification: N_2O is formed in the oxidized zone and when transported towards the outlet by convection, there are almost no available reducing species. This holds in most cases when the reduction front is sharp.)

LNT Model Reactions – Other Extensions

NH₃ adsorption/desorption (plays role at lower temperatures)

 $NH_3 + s \rightarrow s \cdot NH_3$ s \cdot NH_3 \rightarrow NH_3 + s **CLEERS 2011** -12-



Steady-State NH₃ + O₂ Selectivity Factors

- Analysis gives $S_{N2}(T) \& S_{N2O}(T)$ for this reaction
- The selectivity is almost insensitive to O₂ concentration (tested NH₃:O₂ 1:1 and 1:500)
- The selectivity of **NH₃ + stored oxygen is different** highly selective to N₂ (cf. Choi et al).
 - I.e., does not contribute significantly to N₂O formation during LNT regeneration.



Steady-State NH₃ + NO_x Selectivity Factors

- The selectivity is very sensitive to the $NO_x:NH_3$ ratio.
- N₂O formation dramatically increases with excess NO_x.



Selectivity Factor of NH₃ + <u>Stored</u> NO_x

- The reaction of NH₃ with Stored NO_x is the main source of N₂O during LNT regeneration.
- Despite the fact that steady-state selectivity for NH₃ + NO_x is very sensitive to NO_x:NH₃ ratio, the selectivity during regeneration with NH₃ + <u>Stored NO_x</u> can be approximated as a function of temperature only.
- Just one "mean" S_{N20}(T) was successfully used for simulations of both **slow**and **fast-cycling** regeneration.
- The "mean" S_{N20}(T) curve for reaction of NH₃ with the Stored NO_x lies between two limit cases shown for the steady-state NH₃ + NO_x reaction using:
 - @ lower T: the steady-state selectivity at slight excess NH₃ or an NH₃:NO ratio stoichiometric for N₂
 - @ higher T: the steady-state selectivity at slight excess NO_x.





Assessment of Improved LNT Model

- 1. Long Cycle Comparison
- 2. Long Cycle Spatiotemporal Distributions
- 3. Short Cycling Comparison





Long Cycle Comparison

900s Lean & 600s Rich 625ppm CO + 375ppm H₂ 200, 300 & 400°C





Long Cycles (Slow Regeneration) – 200°C

900 s lean + 600 s rich, slow regeneration by 625 ppm CO with 375 ppm H_2 .







Long Cycles (Slow Regeneration) – 300°C

900 s lean + 600 s rich, slow regeneration by 625 ppm CO with 375 ppm H_2 .







Long Cycles (Slow Regeneration) – 400°C

900 s lean + 600 s rich, slow regeneration by 625 ppm CO with 375 ppm H_2 .







Long Cycles – Trends

- The NH₃ peak *delay* increases with the effective NO_x storage capacity – maximum at 300°C
- The NH₃ peak magnitude decreases with increasing temperature, – As NH₃ reduction of surface oxygen becomes more facile.
- N₂O is always appears at reactor outlet before the NH₃ peak.
 Consistent with assumption that N₂O is formed by NH₃ oxidation.
- Selectivity towards N₂O decreases with increasing temperature.
- Dynamics of LNT outlet N₂O and NH₃ during the regeneration follow movement of the reducing front inside the monolith, as demonstrated in the next slides.





Long Cycle Spatiotemporal Distributions 900s Lean & 600s Rich 625ppm CO + 375ppm H₂ 300°C *10, 100, 200, 250 & 350s*





Moving reduction front.

Simulation results for a long cycle, slow regeneration at T=300°C.



Moving reduction front.

Simulation results for a long cycle, slow regeneration at T=300 °C.





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Moving reduction front.

Simulation results for a long cycle, slow regeneration at T=300°C.



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Moving reduction front.

Simulation results for a long cycle, slow regeneration at T=300°C.



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Moving reduction front.

Simulation results for a long cycle, slow regeneration at T=300°C.



Short Cycle Comparison

60s Lean & 5s Rich 3.4% H₂ 200, 300, 400 & 500°C





Short Cycles (Fast Regeneration) – 200°C

A stabilized cycle (60 s lean + 5 s rich), fast regeneration by $3.4 \% H_2$. Note the scale of y-axis for NH_3 and N_2O – large peaks.



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Short Cycles (Fast Regeneration) – 300°C

A stabilized cycle (60 s lean + 5 s rich), fast regeneration by 3.4 % H_2 . Note: Scale change for NH_3 and N_2O – decreasing magnitude, but still significant.



Short Cycles (Fast Regeneration) – 400°C

A stabilized cycle (60 s lean + 5 s rich), fast regeneration by 3.4 % H_2 . Note: Scale change for NH_3 and N_2O – decreasing magnitude.



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Short Cycles (Fast Regeneration) – 500°C

A stabilized cycle (60 s lean + 5 s rich), fast regeneration by 3.4 % H_2 . Note: Scale change for NH_3 and N_2O – small peaks; for NO_x – large desorption peak.



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Conclusions

- The existing global-kinetic LNT model has been extended
 - to include N_2O formation during the NH_3 oxidation.
 - Ammonia formed during LNT regeneration at the reductant front is transported downstream by convection to the rear part which is yet oxidized.
- The main N_2O source is non-selective reaction of NH_3 with Stored NO_x during regeneration
 - N_2O is emitted until the NH₃ peak appears at the outlet.
 - Contribution of the reaction with the Stored O_2 is negligible.
- N_2O yield during the regeneration is considerable at 200°C (~500 ppm peak during the fast regeneration) but decreases at higher temperatures.
- Although the steady-state selectivity of $NH_3 + NO_x$ is very sensitive to $NO_x:NH_3$ ratio,
 - selectivity during regeneration can be described as the function of temperature only.
 - the same parameters can be used for both slow- and fast-cycling simulations.
- A reasonable agreement between the model and experiments has been achieved with a **minimum number of new reactions and kinetic parameters**. The model is able to predict dynamics and magnitude of both N₂O and NH₃ by-products of NO_x reduction during LNT regeneration.





"Mean" Selectivity Function for NH₃ + NO_x

• The N₂O formation observed in NH₃+NO steady-state experiment with slight excess of NH₃, and the N₂O levels predicted by the model using the **"mean"** $S_{N20}(T)$.

• As discussed in the previous slide, the two curves are **identical at lower temperatures**.

• At higher temperatures, the "mean" $S_{N2O}(T)$ predicts higher N_2O formation (corresponding to a slight excess of NO).

