

Lean NO_x Trap Regeneration Selectivity Towards N₂O

Similarities and Differences Between H₂, CO and C₃H₆ Reductants



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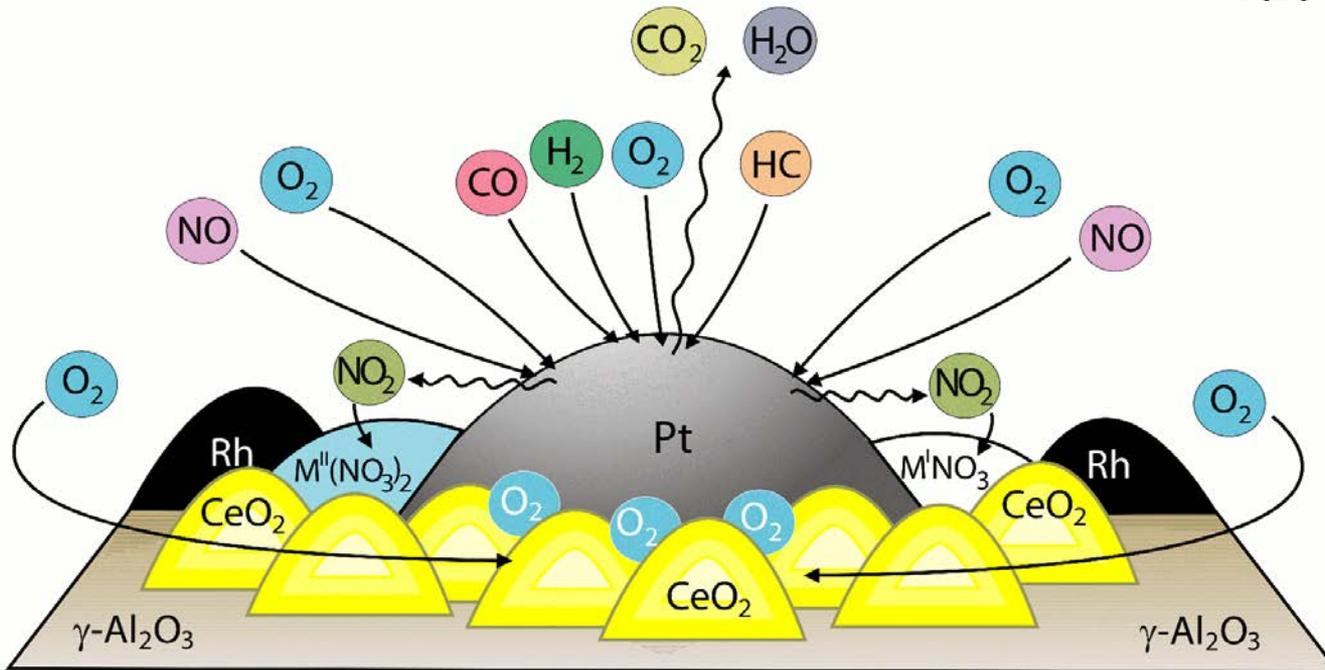
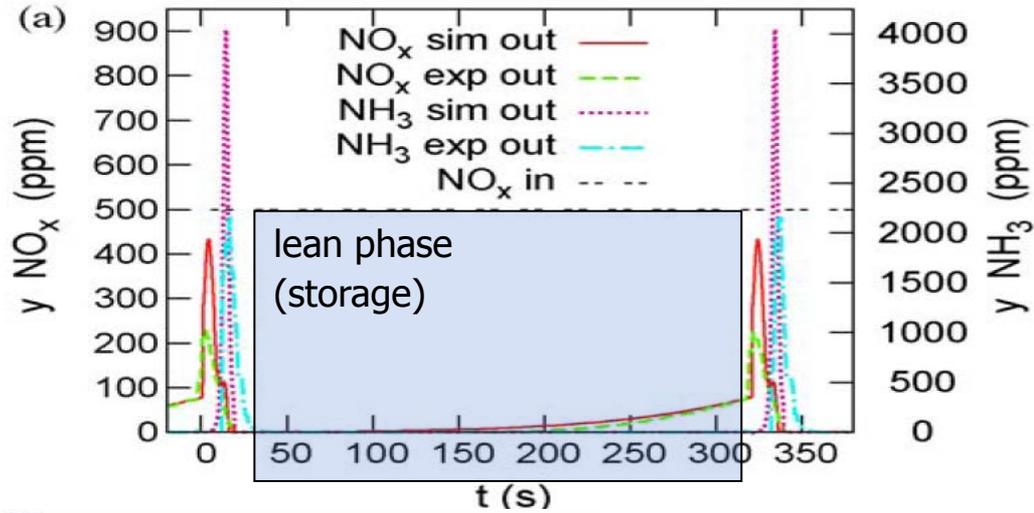
Jae-Soon Choi, Josh Pihl, C. Stuart Daw, William Partridge
Oak Ridge National Laboratory

N₂O emissions in automotive exhaust gas aftertreatment

- **Undesired by-product** of catalytic NO_x reduction in exhaust gas aftertreatment systems, particularly of lean-burn engines.
 - **DOC** – non-selective HC-SCR at lower-intermediate T
 - **NH₃-SCR** – too high NO₂/NO_x ratio, NH₄NO₃ decomposition, NH₃ oxidation
 - **NH₃ slip** catalyst (=ASC) – non-selective NH₃ oxidation
 - **LNT** (=NSRC) 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, therefore overall GHG contribution of N₂O in automotive exhaust gas can vary from 0.1 % up to several %.
- **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 have **been unregulated**, but EU and US limits are expected in near future.

NO_x storage catalyst – lean fuel mixture, oxidising conditions

- CO & HC oxidation
- NO oxidation to NO₂
- NO_x storage
- Oxygen storage

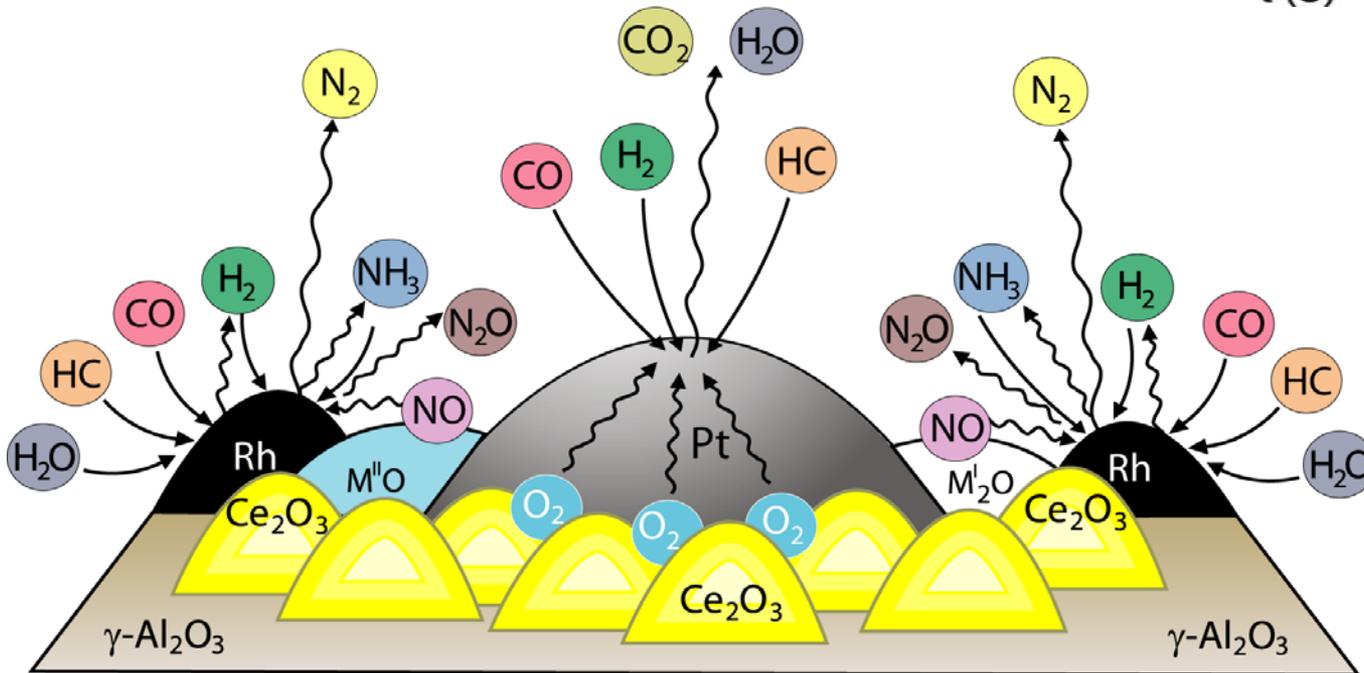
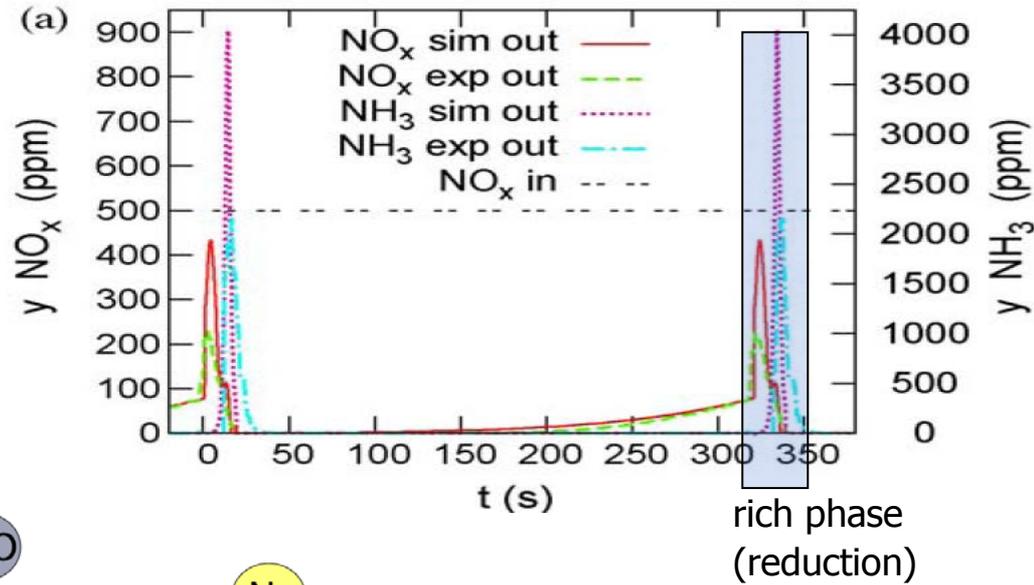


NO_x storage catalyst – rich fuel mixture, reducing conditions

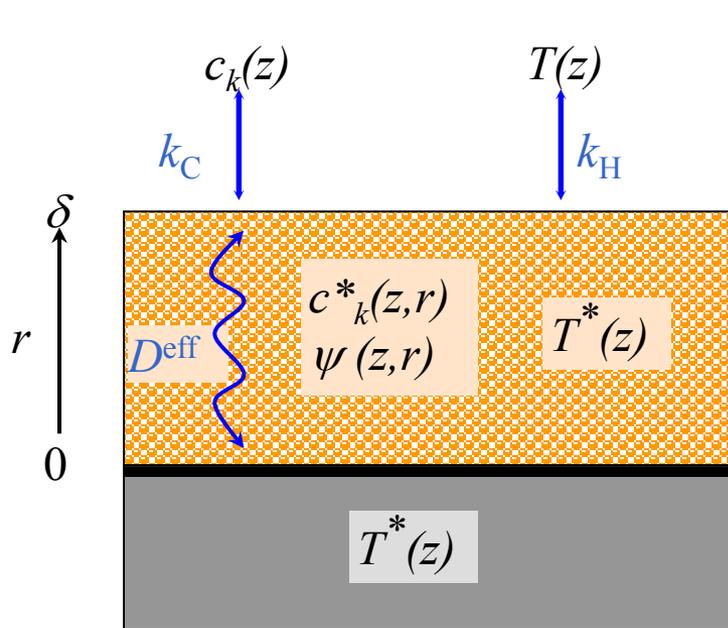
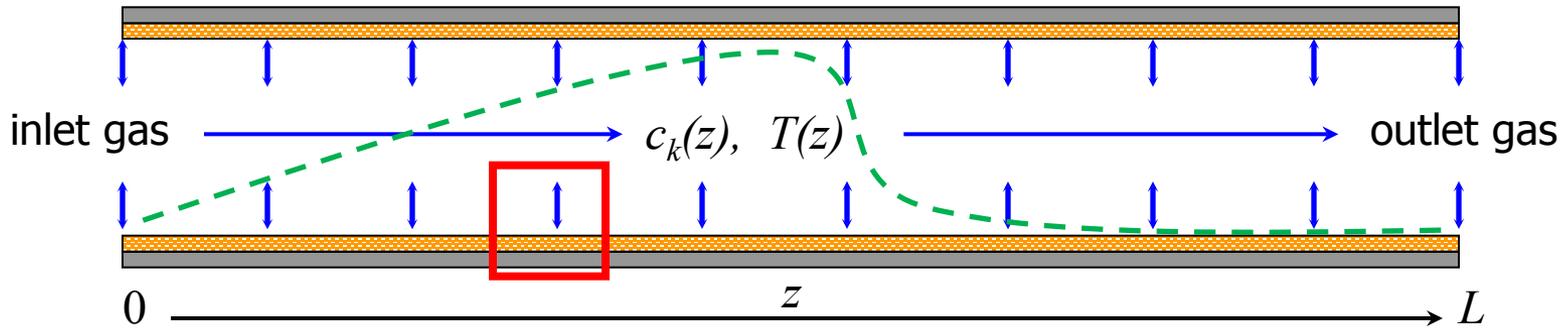
- NO_x desorption
- NO_x reduction
- Water gas shift & steam reforming
- NH₃ formation
- NH₃ oxidation
- Oxygen release

Range of NO_x reduction products:

N₂, NH₃, N₂O + desorbed NO_x



Coupling of reaction and transport – monolith channel model



flowing gas

- convection
- mass & heat transfer

porous washcoat

- diffusion (lumped with kinetics)
- adsorption, catalytic reactions
- heat accumulation & conduction

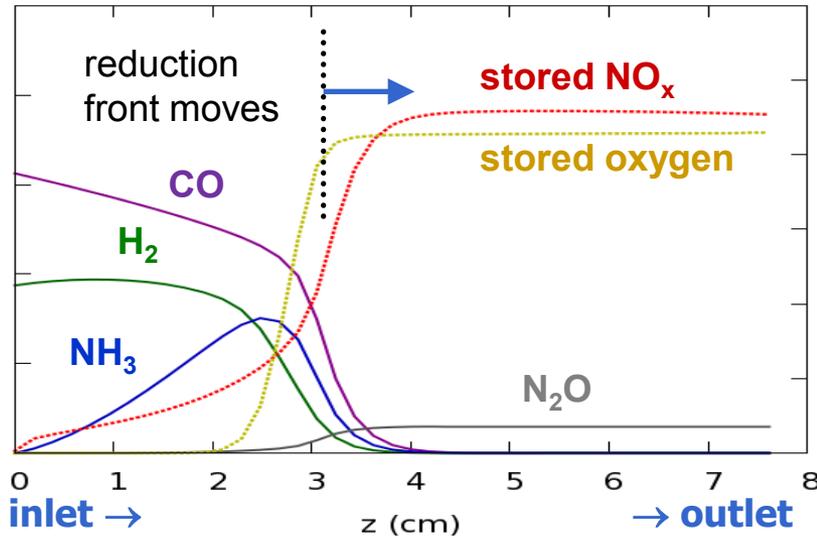
wall

- heat accumulation & conduction
- no reactions

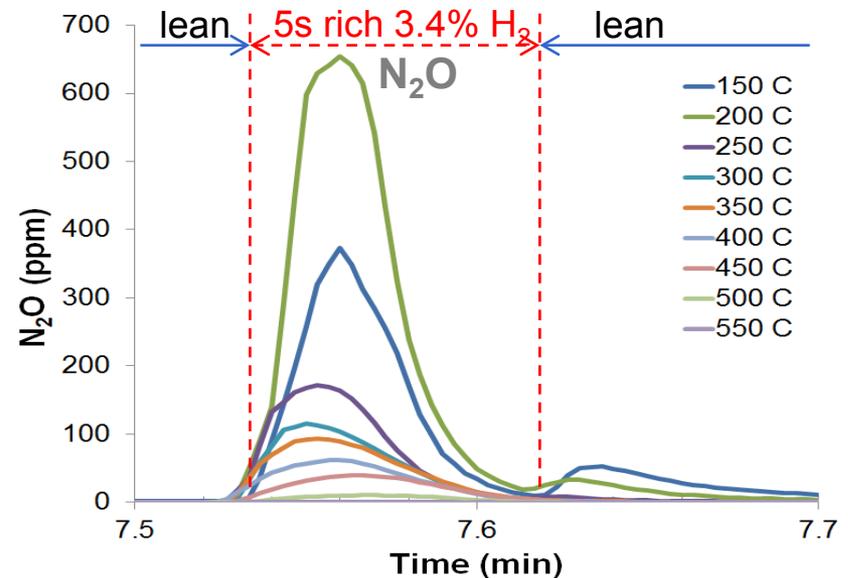
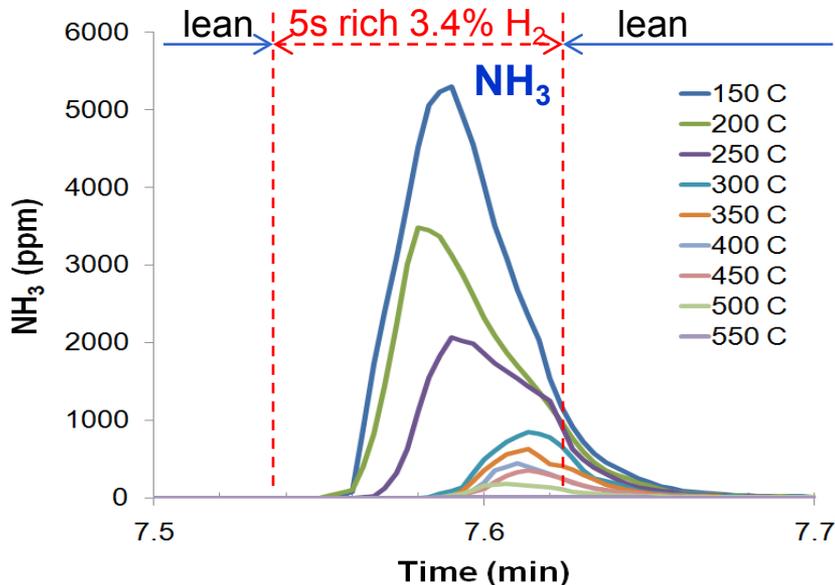
⇒ Standard heterogeneous 1D model

⇒ Transient solution of all components necessary (no steady state)

Rich reduction of the stored NO_x – moving regeneration front



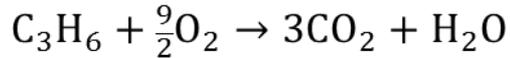
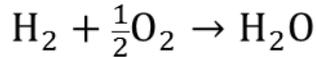
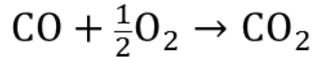
- A large part of the stored NO_x is reduced in the **rich zone up to NH₃**.
- The formed NH₃ is transported downstream where it reacts with the stored NO_x → **delay of the NH₃ peak**.
- N₂O is emitted before the reductants breakthrough → **primary N₂O peak**.
- **Secondary N₂O peak** may appear at the switch back to lean conditions due to oxidation of adsorbed intermediates.



Global model reactions – oxidation/reduction over NM sites

Reductant oxidation

(Kočí et al., 2009)

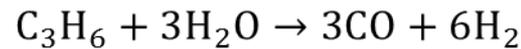
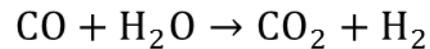


$$R_1 = k_1 \Psi_{\text{cap,Pt}} Y_{\text{CO}} Y_{\text{O}_2} \frac{1}{G_1}$$

$$R_2 = k_2 \Psi_{\text{cap,Pt}} Y_{\text{H}_2} Y_{\text{O}_2} \frac{1}{G_1}$$

$$R_3 = k_3 \Psi_{\text{cap,Pt}} Y_{\text{C}_3\text{H}_6} Y_{\text{O}_2} \frac{1}{G_1}$$

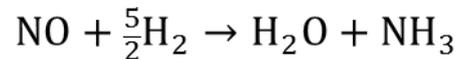
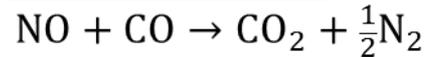
Water gas shift and steam reforming



$$R_4 = k_4 \Psi_{\text{cap,Pt}} \left(Y_{\text{CO}} Y_{\text{H}_2\text{O}} - \frac{Y_{\text{CO}_2} Y_{\text{H}_2}}{K_{y,4}^{\text{eq}}} \right)$$

$$R_5 = k_5 \Psi_{\text{cap,Pt}} \left(Y_{\text{C}_3\text{H}_6} Y_{\text{H}_2\text{O}} - \frac{Y_{\text{CO}}^3 Y_{\text{H}_2}^6}{K_{y,5}^{\text{eq}} Y_{\text{H}_2\text{O}}^2} \right)$$

NO reduction

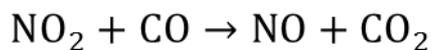
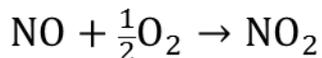


$$R_6 = k_6 \Psi_{\text{cap,Pt}} Y_{\text{CO}} Y_{\text{NO}}^{0.5} \frac{1}{G_2} \frac{1}{G_1}$$

$$R_7 = k_7 \Psi_{\text{cap,Pt}} Y_{\text{H}_2} Y_{\text{NO}}^{0.5} \frac{1}{G_2} \frac{1}{G_1}$$

$$R_8 = k_8 \Psi_{\text{cap,Pt}} Y_{\text{C}_3\text{H}_6} Y_{\text{NO}}^{0.5} \frac{1}{G_2} \frac{1}{G_1}$$

NO/NO₂ transformation



$$R_9 = k_9 \Psi_{\text{cap,Pt}} \left(Y_{\text{NO}} Y_{\text{O}_2}^{0.5} - \frac{Y_{\text{NO}_2}}{K_{y,9}^{\text{eq}}} \right) \frac{1}{G_1}$$

$$R_{10} = k_{10} \Psi_{\text{cap,Pt}} Y_{\text{NO}_2} Y_{\text{CO}} \frac{1}{G_{\text{NO}_2, \text{red}}}$$

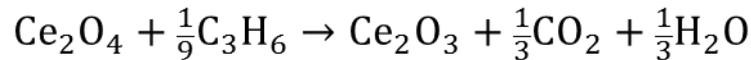
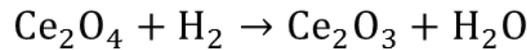
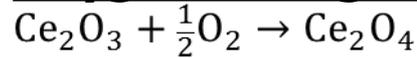
$$R_{11} = k_{11} \Psi_{\text{cap,Pt}} Y_{\text{NO}_2} Y_{\text{C}_3\text{H}_6} \frac{1}{G_{\text{NO}_2, \text{red}}}$$

$$G_1 = (1 + K_{a,1} Y_{\text{CO}} + K_{a,2} Y_{\text{C}_3\text{H}_6})^2 \cdot (K_{a,3} Y_{\text{CO}}^2 Y_{\text{C}_3\text{H}_6}^2) \cdot (1 + K_{a,4} Y_{\text{NO}_x}^{0.7}) T^s$$

$$G_2 = 1 + K_{a,5} Y_{\text{O}_2}$$

Global model reactions – storage and release

Oxygen storage & reduction



(Kočí et al., 2009, Chatterjee et al., 2010)

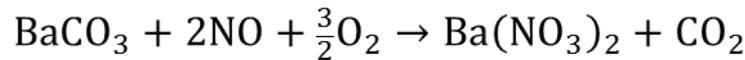
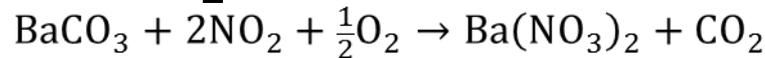
$$R_{12} = k_{12} \Psi_{\text{cap,CeO}_2} y_{\text{O}_2} (\psi_{\text{O}_2}^{\text{eq}} - \psi_{\text{O}_2})$$

$$R_{13} = k_{13} \Psi_{\text{cap,CeO}_2} y_{\text{CO}} \psi_{\text{O}_2}$$

$$R_{14} = k_{14} \Psi_{\text{cap,CeO}_2} y_{\text{H}_2} \psi_{\text{O}_2}$$

$$R_{15} = k_{15} \Psi_{\text{cap,CeO}_2} y_{\text{C}_3\text{H}_6} \psi_{\text{O}_2}$$

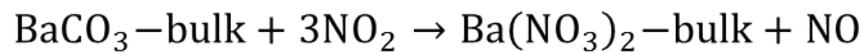
Fast NO_x storage (Ba sites in proximity of Pt)



$$R_{16} = k_{16} \Psi_{\text{cap,Ba}_A} y_{\text{NO}_2} (\psi_{\text{NO}_{x,A}}^{\text{eq}} - \psi_{\text{NO}_{x,A}})^2$$

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

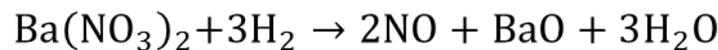
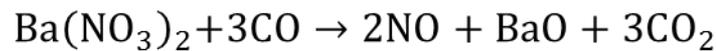
Slow NO_x storage (bulk Ba sites)



$$R_{29} = k_{29} \Psi_{\text{cap,Ba}_B} y_{\text{NO}_2} (\psi_{\text{NO}_{x,B}}^{\text{eq}} - \psi_{\text{NO}_{x,B}})^2$$

$$R_{30} = k_{30} \Psi_{\text{cap,Ba}_B} y_{\text{NO}_2} (\psi_{\text{NO}_{x,B}} - \psi_{\text{NO}_{x,A}})$$

Desorption of stored NO_x

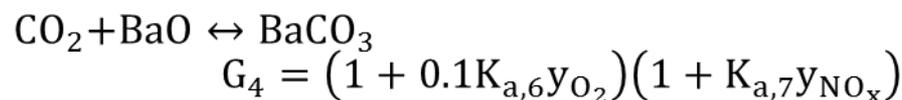


$$R_{22} = k_{22} \Psi_{\text{cap,Ba}_A} y_{\text{CO}} \psi_{\text{NO}_{x,A}}^2 \frac{1}{G_4}$$

$$R_{23} = k_{23} \Psi_{\text{cap,Ba}_A} y_{\text{H}_2} \psi_{\text{NO}_{x,A}}^2 \frac{1}{G_4}$$

$$R_{24} = k_{24} \Psi_{\text{cap,Ba}_A} y_{\text{C}_3\text{H}_6} \psi_{\text{NO}_{x,A}}^2 \frac{1}{G_4}$$

CO₂ adsorption on NO_x storage sites

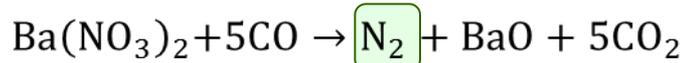


$$R_{31} = \sum_{j=18}^{25} R_j$$

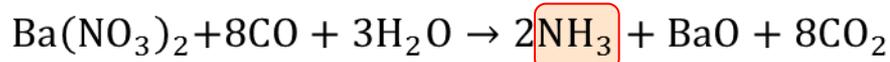
Global model reactions – reduction of nitrates

“Classical” approach with NH₃ intermediate and N₂ product

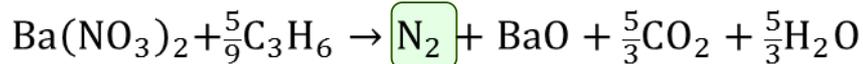
Direct reduction of stored NO_x (Ba sites in proximity of Pt) (Kočí et al., 2009)



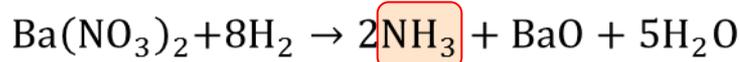
$$R_{18} = k_{18} \Psi_{\text{cap,Ba}_A} y_{\text{CO}} \psi_{\text{NO}_{x,A}}^2 \frac{1}{G_3}$$



$$R_{19} = k_{19} \Psi_{\text{cap,Ba}_A} y_{\text{CO}} \psi_{\text{NO}_{x,A}}^2 \frac{1}{G_3} \frac{1}{G_5}$$

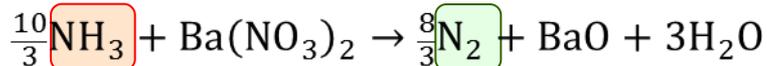


$$R_{21} = k_{21} \Psi_{\text{cap,Ba}_A} y_{\text{C}_3\text{H}_6} \psi_{\text{NO}_{x,A}}^2 \frac{1}{G_3}$$

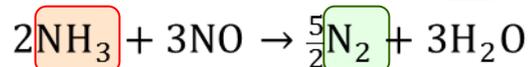


$$R_{20} = k_{20} \Psi_{\text{cap,Ba}_A} y_{\text{H}_2} \psi_{\text{NO}_{x,A}}^2 \frac{1}{G_3} \frac{1}{G_5}$$

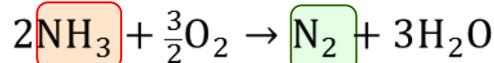
NH₃ oxidation reactions – only N₂ formation considered



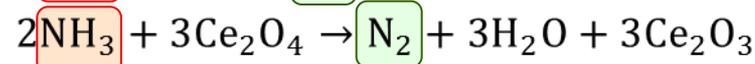
$$R_{25} = k_{25} \Psi_{\text{cap,Ba}_A} y_{\text{NH}_3} \psi_{\text{NO}_{x,A}}^2$$



$$R_{26} = k_{26} \Psi_{\text{cap,Pt}} y_{\text{NH}_3} y_{\text{NO}}^{0.5}$$



$$R_{27} = k_{27} \Psi_{\text{cap,Pt}} y_{\text{NH}_3} y_{\text{O}_2}$$



$$R_{28} = k_{28} \Psi_{\text{cap,CeO}_2} y_{\text{NH}_3} \psi_{\text{CeO}_2}$$

$$G_3 = 1 + K_{a,6} y_{\text{O}_2} \quad G_5 = 1 + K_{a,8} y_{\text{CO}}$$

The conventional global kinetic model does not consider N₂O.

Motivation: Extend the existing model in order to enable N₂O prediction, using minimum number of new reactions and components.

Primary N₂O peak during the rich phase

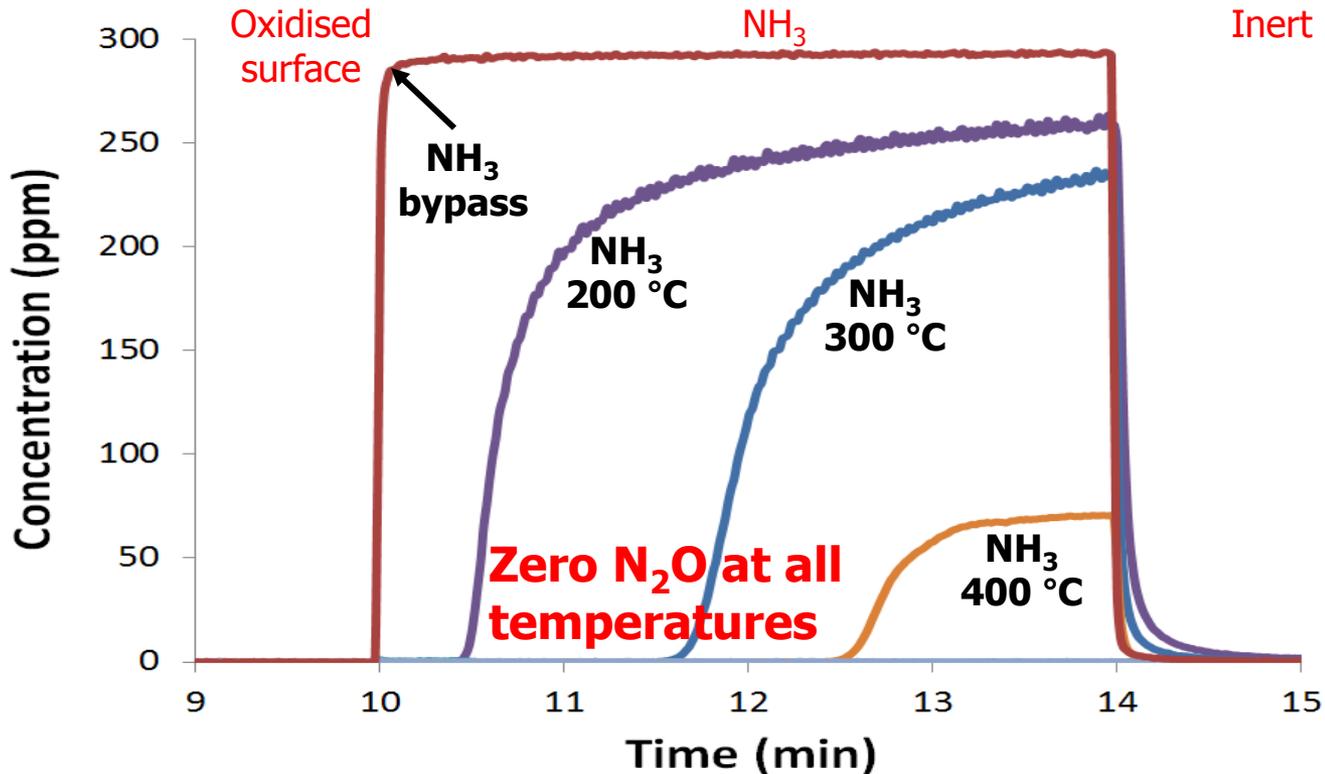
Identification of the mechanism...

Several candidate reactions:

- Non-selective NH₃ re-oxidation – poor selectivity of PGM catalysts in NH₃ oxidation is known. There are two main species for NH₃ to react with:
 - Stored oxygen
 - Stored NO_x
- Formation of N₂O during reduction of stored NO_x by primary reductants (H₂, CO and HC)
 - Most of the stored NO_x are reduced under locally rich conditions (leading mainly to NH₃), but at the head of the reducing front the reductants initially reach oxidized sites surrounded by stored NO_x – local formation of N₂O possible.

Source of primary N₂O peak during the rich phase Reaction of NH₃ + stored oxygen ?

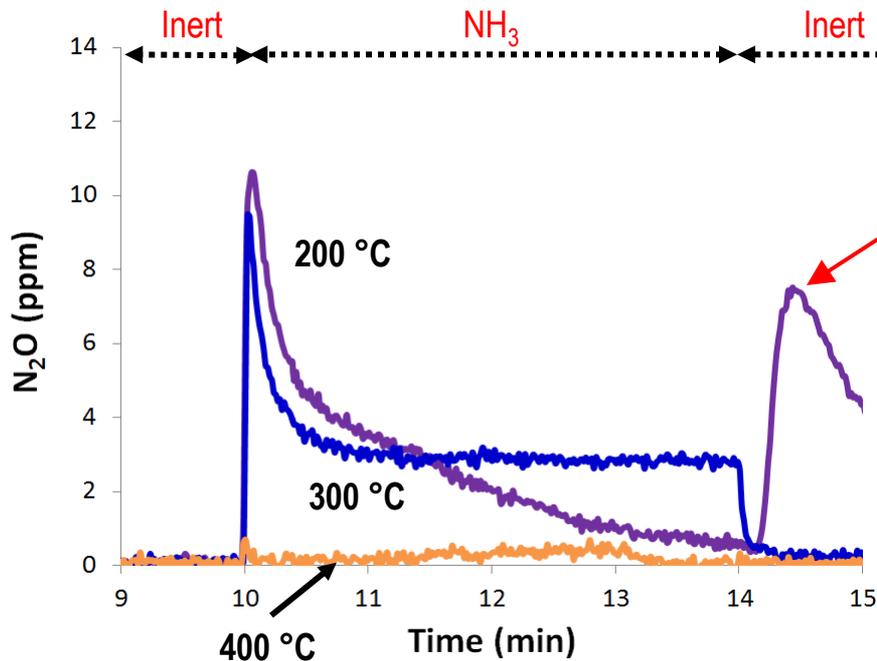
- Pre-oxidised surface (followed by inert purge), then NH₃ introduced.
- The reaction with stored oxygen is very rapid ⇒ plug-like behaviour
- Contrary to steady-state NH₃ oxidation, no N₂O is detected. NH₃ decomposition at high T.
⇒ This reaction does not contribute to N₂O formation.



Source of primary N₂O peak during the rich phase

Reaction of NH₃ + stored NO_x ?

- Nitrated surface (NO_x + O₂ storage), then inert purge, then NH₃ introduced
 - N₂O is formed all the time before NH₃ breakthrough.
- ⇒ This reaction definitely contribute to N₂O formation.

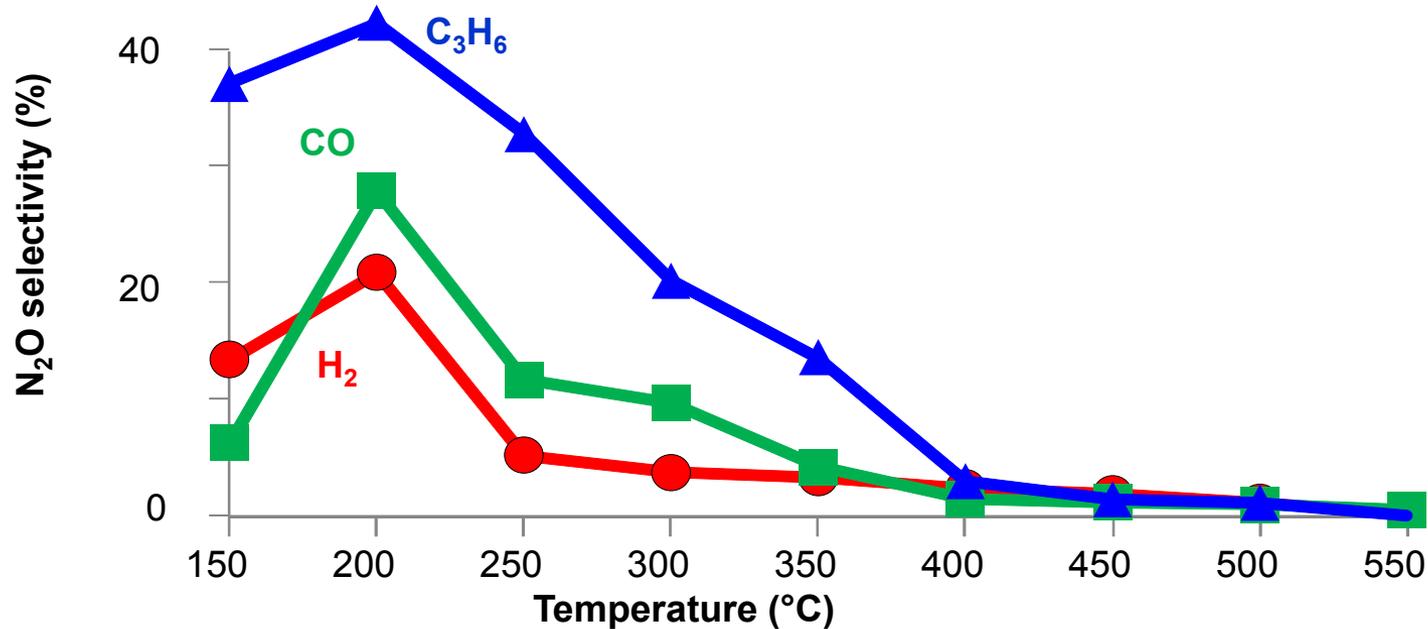


At 200°C self-inhibition of the reaction is observed as well as secondary N₂O peak after switching to inert atmosphere – probably NH₄NO₃ formation and decomposition

Choi et al., Catalysis Today (2012)

However, is this a unique reaction, and is the NH₃ intermediate necessary for N₂O formation during LNT regeneration?

N₂O selectivity in short cycles (60s lean + 5s rich)



- N₂O by-product formed at lower T with all reductants, particularly C₃H₆ >> CO > H₂. The unique NH₃ intermediate route cannot explain the trend – C₃H₆ at lower temperatures gives practically no NH₃ but significant N₂O.

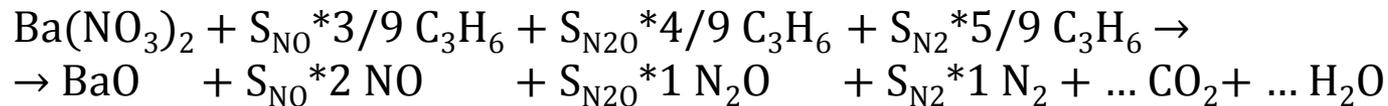
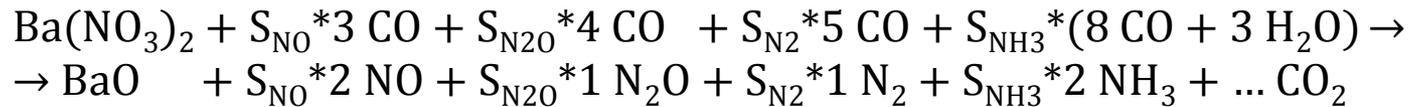
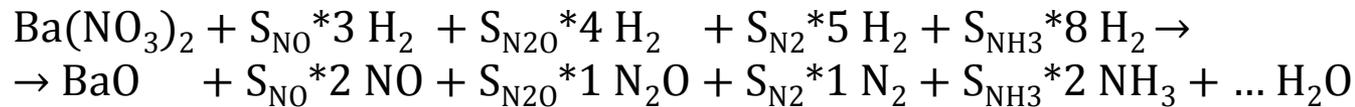
⇒ N₂O can be formed by the interaction of stored NO_x with any reductant. The ammonia intermediate is not necessary.

Generalized approach to reduction of stored NO_x

Full range of N-products considered

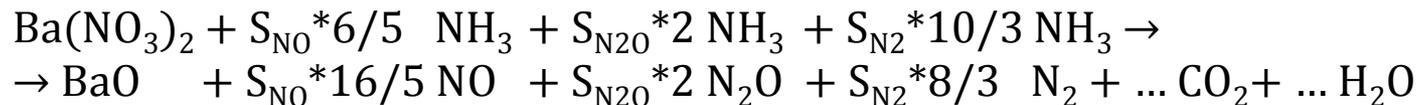
Reduction of stored NO_x (Ba sites in proximity of Pt)

Sum of selectivities ($S_{NO} + S_{N_2O} + S_{N_2} + S_{NH_3}$) = 1.0



Reduction of stored NO_x by NH₃ (Ba sites in proximity of Pt)

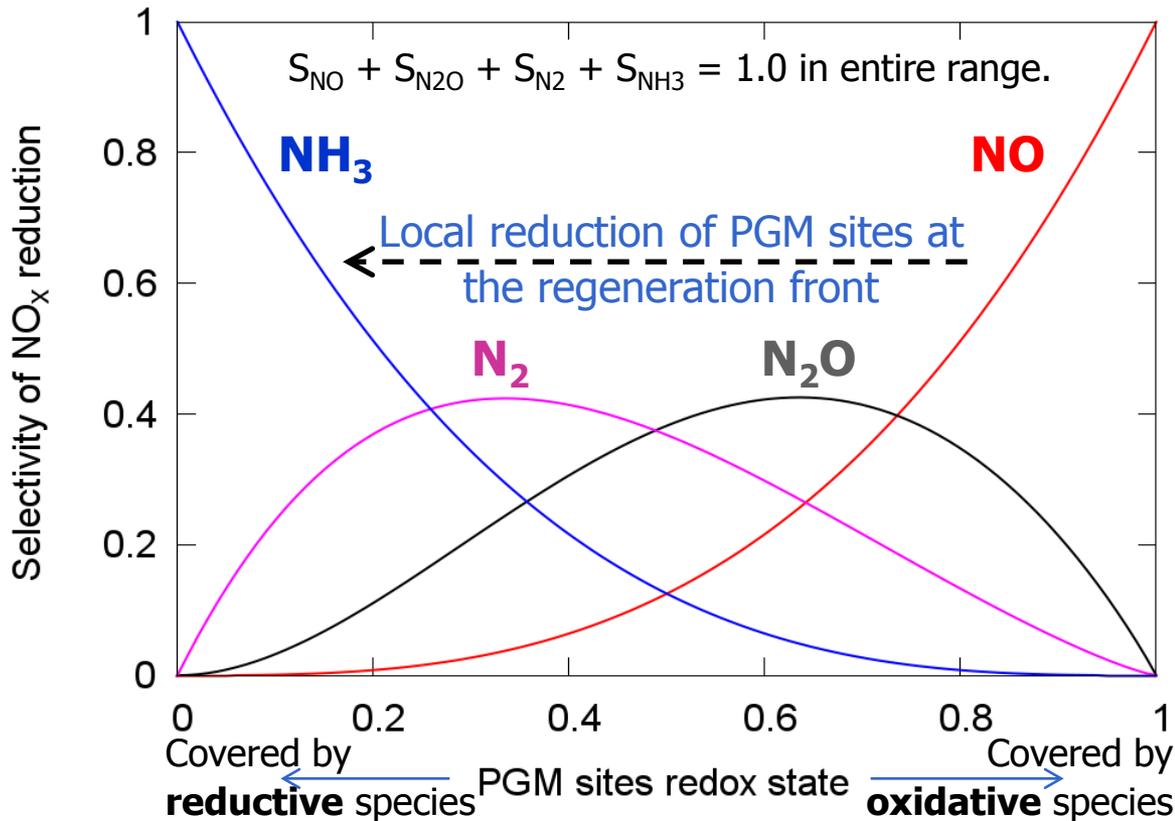
Sum of selectivities ($S_{NO} + S_{N_2O} + S_{N_2}$) = 1.0



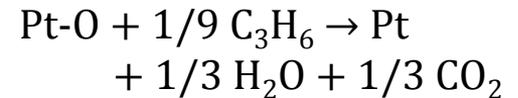
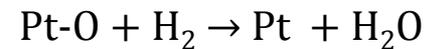
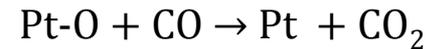
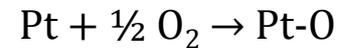
Is there an approximate measure in global kinetic model that can give prediction of actual local NO_x reduction selectivity?

Implementation of variable selectivity to global kinetic model – Selectivity as a function of local Pt (PGM) sites state

- Local selectivities of the stored NO_x reduction to NO, N₂O, N₂ or NH₃ are linked with coverage of oxidative or reductive species on locally available PGM sites. Smooth polynomial functions are used and this approximate map is employed in global kinetics LNT model.



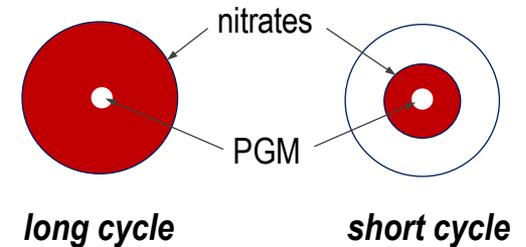
Simplified PGM state reactions



The rates determining selectivity of NO_x reduction in LNT

- Three types of sites need to be reduced during the LNT regeneration:
 - Precious group metal (PGM) sites
 - NO_x storage sites
 - Oxygen storage sites

- Ratio between the respective reduction rates determines local selectivity:
 - If PGM reduction is slow and inefficient => higher N₂O formation
 - lower T
 - inefficient reductant of PGM (C₃H₆)
 - If PGM reduction is fast and efficient => N₂, NH₃
 - higher T
 - efficient reductant (H₂)
 - Slower release of stored NO_x for reduction => NH₃
 - longer lean phase
 - NO_x adsorption on the storage sites farther from PGM redox sites

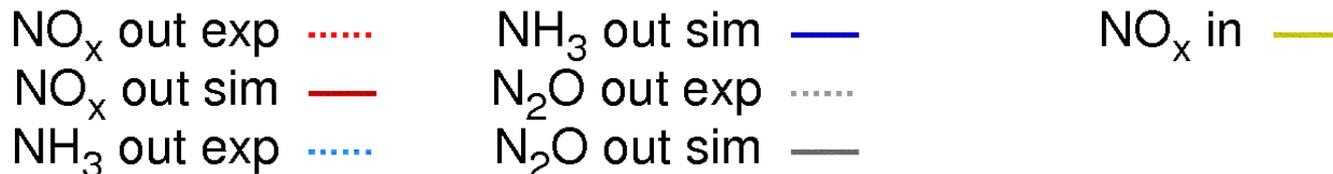
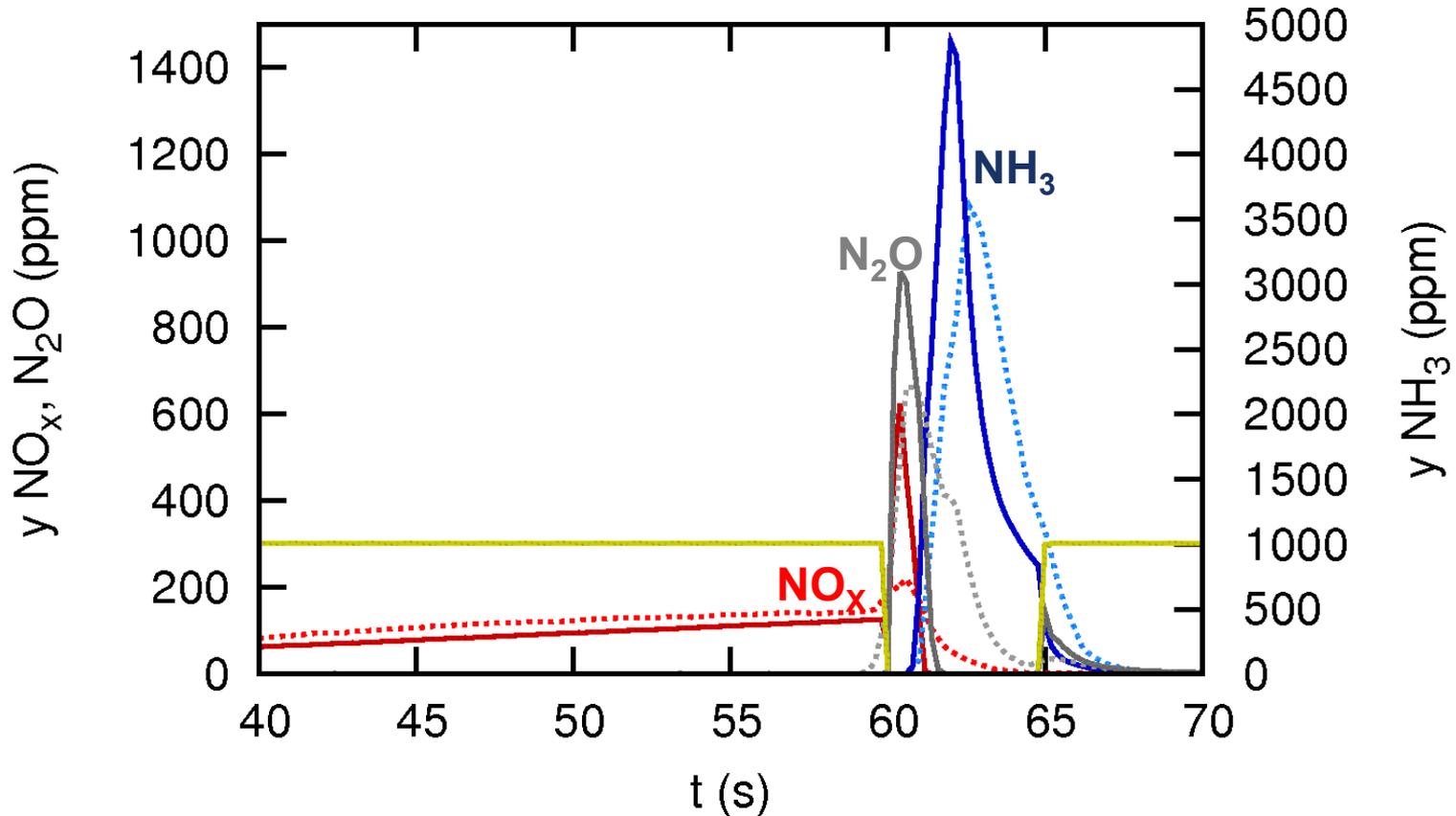


Still, the overall NH₃ yield remains limited by NH₃ consumption in oxidized zone (reactions with stored oxygen and NO_x)

Lean/rich cycles example – 200°C, H₂ reductant

60 s lean + 5 s rich, fast regeneration by 3.4 % H₂

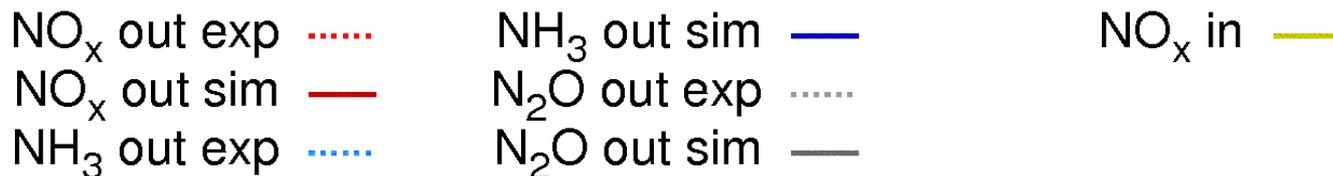
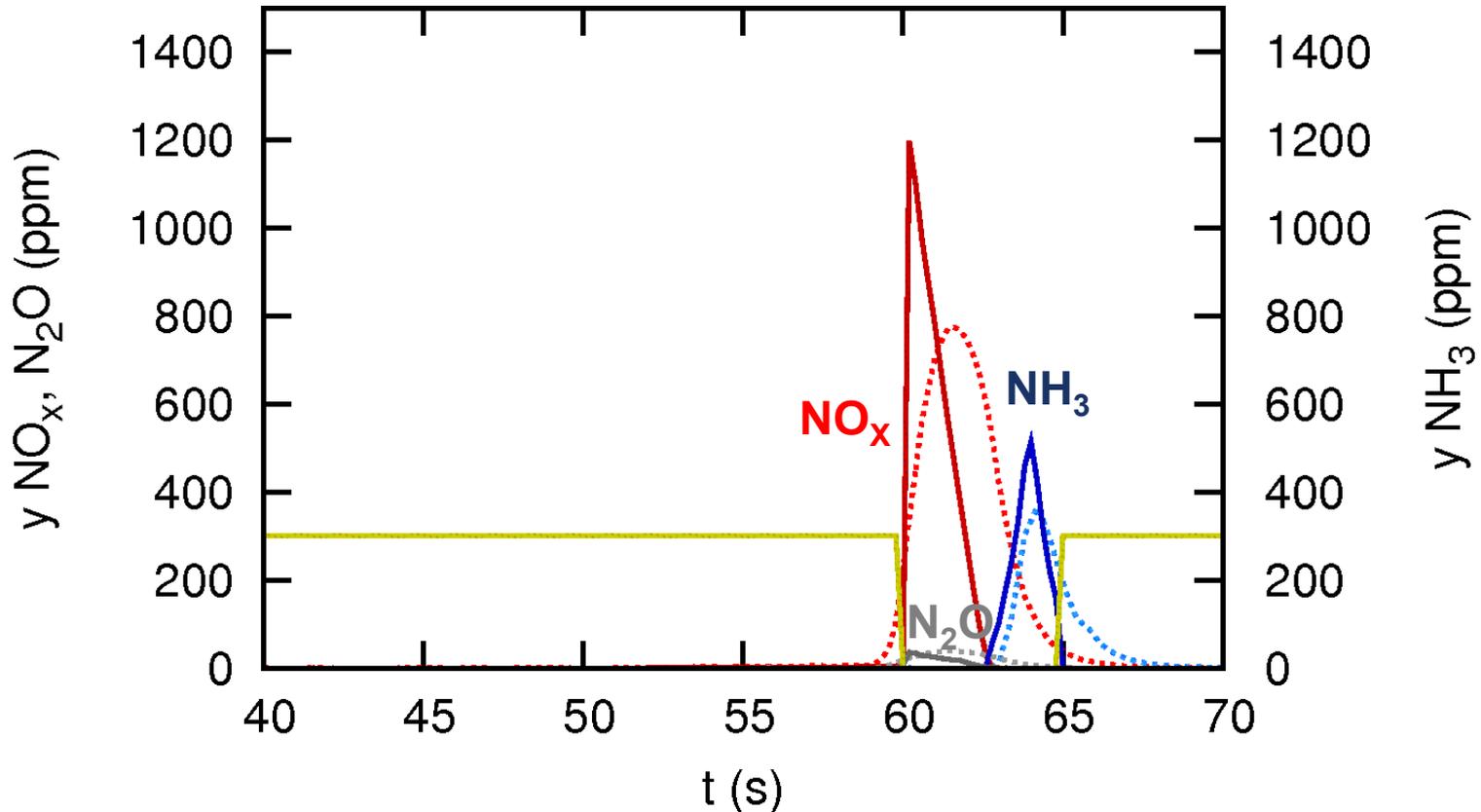
Slower NO_x release, slow PGM reduction ⇒ high N₂O, high NH₃.



Lean/rich cycles example – 400°C, H₂ reductant

60 s lean + 5 s rich, fast regeneration by 3.4 % H₂

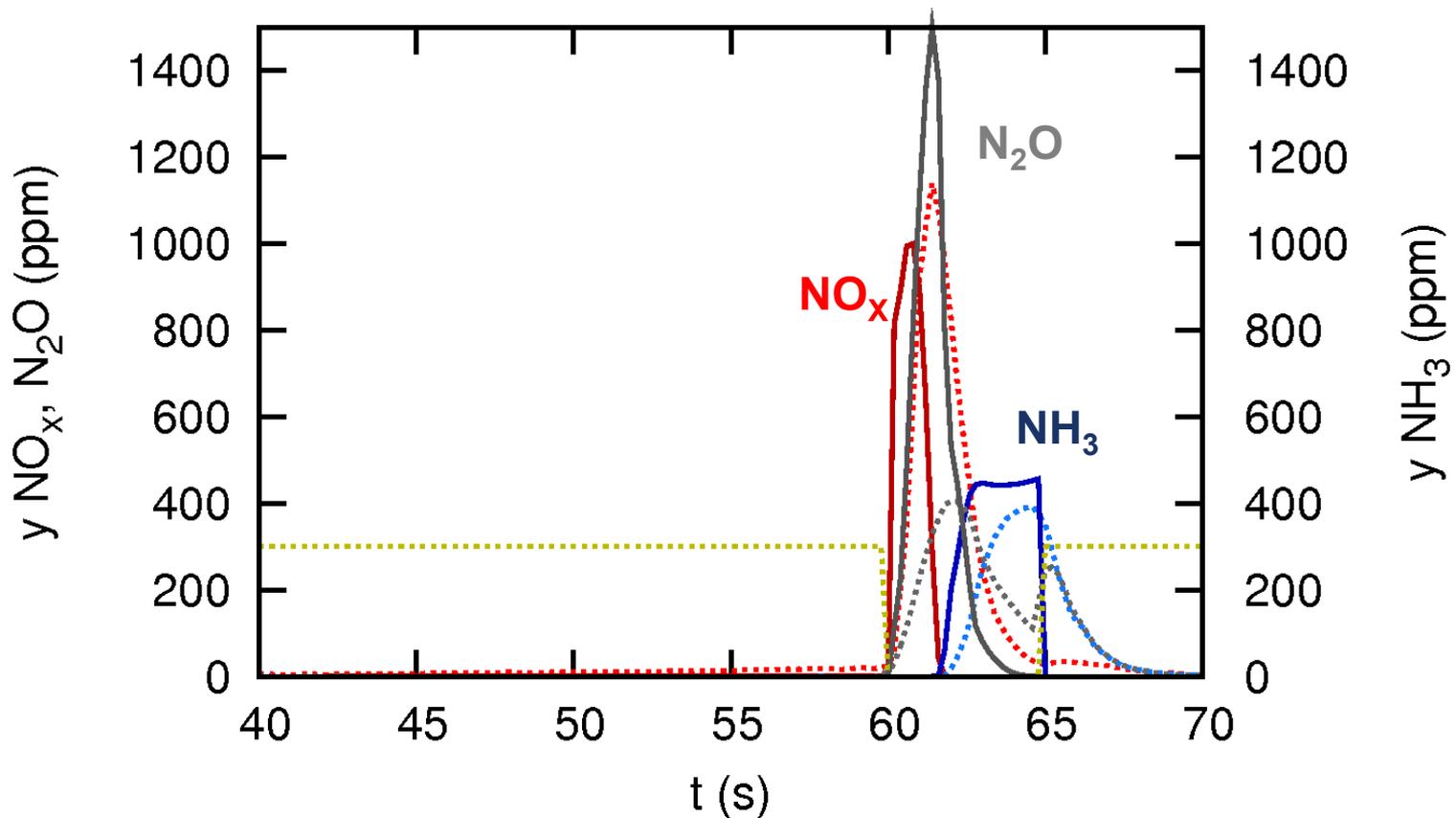
Facile NO_x release, efficient PGM reduction ⇒ low N₂O, some NH₃ (changed scale).



Lean/rich cycles example – 300°C, C₃H₆ reductant

60 s lean + 5 s rich, fast regeneration by **3780 ppm C₃H₆**

Facile NO_x release, slow PGM reduction ⇒ high NO & N₂O, low NH₃.



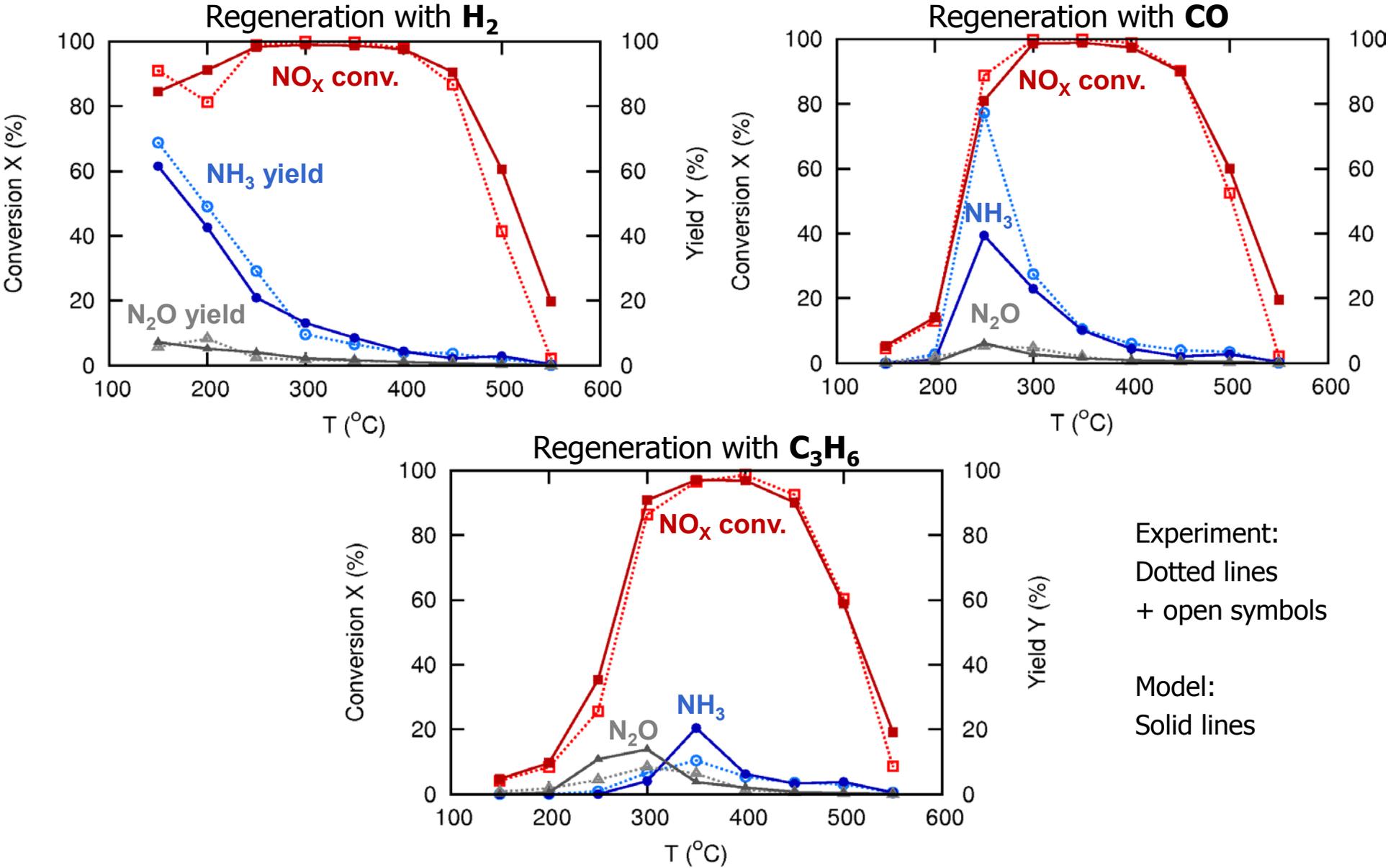
NO_x out exp
 NO_x out sim ———
 NH₃ out exp
 NH₃ out sim ———

NH₃ out sim ———
 N₂O out exp
 N₂O out sim ———

NO_x in
 NH₃ in
 N₂O in



Integral conversions and selectivities for individual reductants

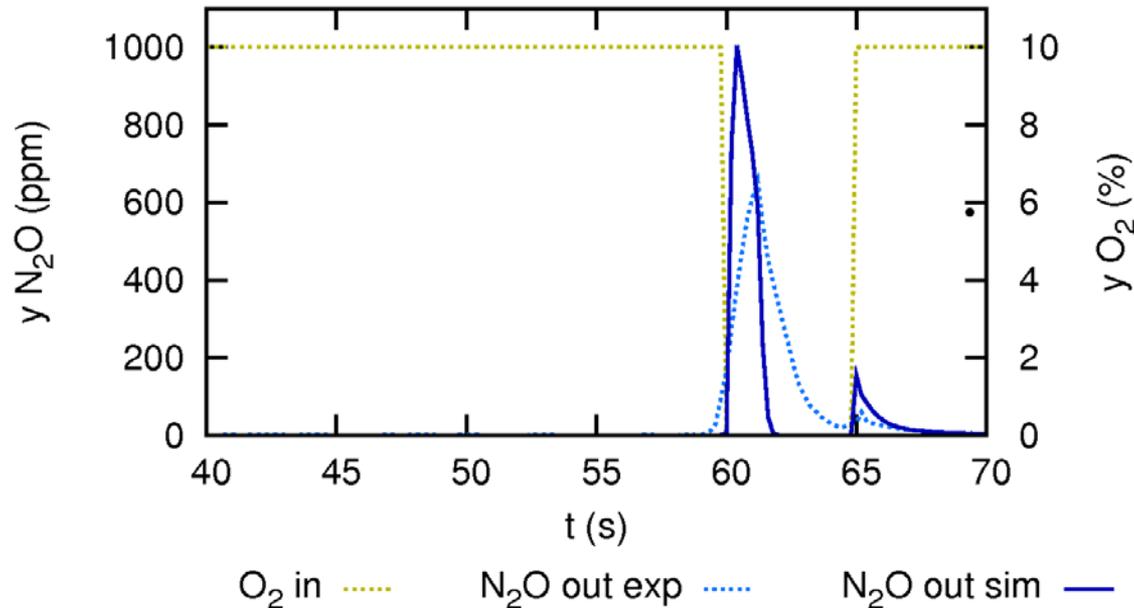


Secondary N₂O peak at transition back from rich to lean

Caused by oxidation of adsorbed reduction intermediates.

a) Ammonia-related species – mainly during regeneration with H₂ at low T (200°C)

- At least NH₃ adsorption, NH₃+O₂ and NH₃+NO→N₂O reactions need to be considered



b) Carbonaceous species – mainly during regeneration with HC at intermediate T (200-350°C)

- Isocyanates (R-CNO), but other candidates also exist
- Under investigation, not yet included in the current model

Conclusions

- At lower-intermediate temperatures, the **N₂O is emitted in two peaks**
- **NH₃ intermediate is not a unique route** for N₂O formation
- Global model for **primary N₂O peak**: Variable **selectivity** of the NO_x reduction depending on local **state of PGM sites**
 - At the head of reducing front, the PGM sites are not fully reduced yet → N₂O
 - Overall selectivity depends on the **ratio of individual rates**, specific for each reductant:
 - **PGM** reduction rate
 - **NO_x** release rate
 - **Stored oxygen** reaction rate
- Global model for **secondary N₂O peak**: Oxidation of adsorbed reduction intermediates
 - NH₃-related – relevant at low T: **adsorbed NH₃**, possibly NH₄NO₃
 - **Carbonaceous intermediates** – isocyanates, ...?
- **Main source** of N₂O at intermediate temperatures are **hydrocarbons**
 - Large N₂O peaks with C₃H₆ **up to 350°C**
 - Reforming to H₂ and CO can decrease N₂O yield (and increase NO_x conversion)

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