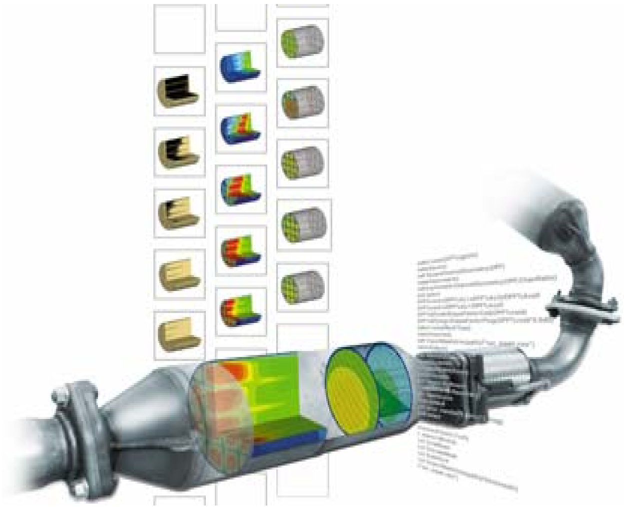
Exothermia
modeling efficiency

Modeling of multi-layer catalysts and application in deNOx systems



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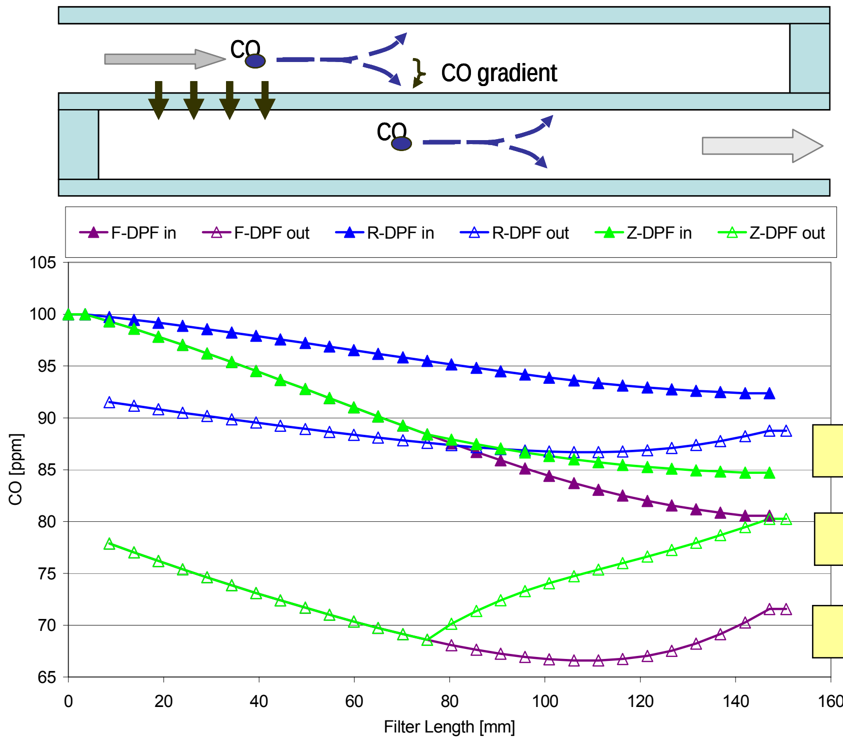
Scope and targets

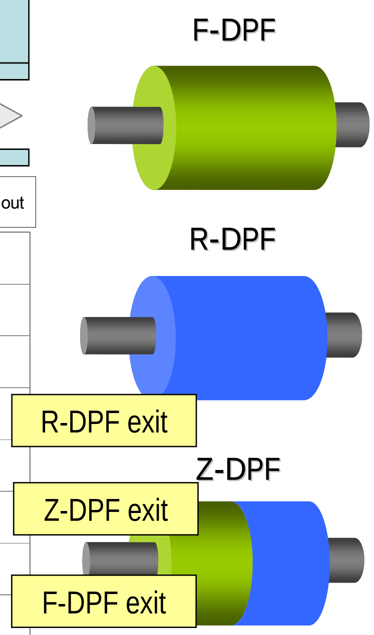
- Combined LNT-SCR w/o urea injection has been already introduced, to meet “moderate” NO_x reduction efficiencies
  - In-series systems
  - Dual-layer systems
- Published models are capable of dealing with in-series systems
- This work introduces a modeling approach for dual-layer systems
- Main targets:
  - illustrate modeling potential in benchmarking various $deNO_x$ concepts
  - preliminary investigation of washcoat properties effects
  - Indicate areas of further research

Contents

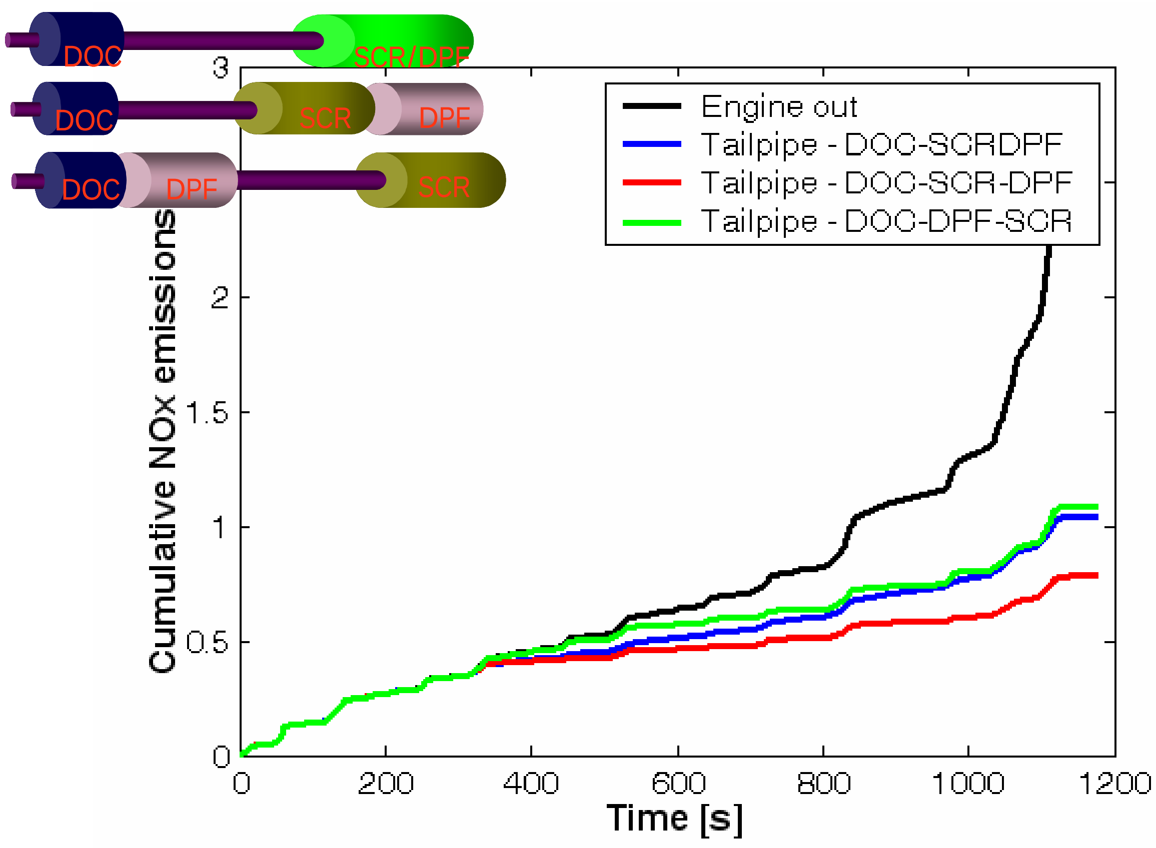
- Washcoat modeling
- LNT model calibration
- SCR model calibration
- “Numerical benchmarking”
  - LNT only
  - LNT + SCR in series
  - 2-layer LNT/SCR
- Model sensitivity on washcoat diffusivity
- Conclusions

- *"Modeling of Wall-flow Particulate Filters with Catalyst Zoning"*
  - Transport-reaction coupling in catalyzed filters
  - Application in zoned DPF systems

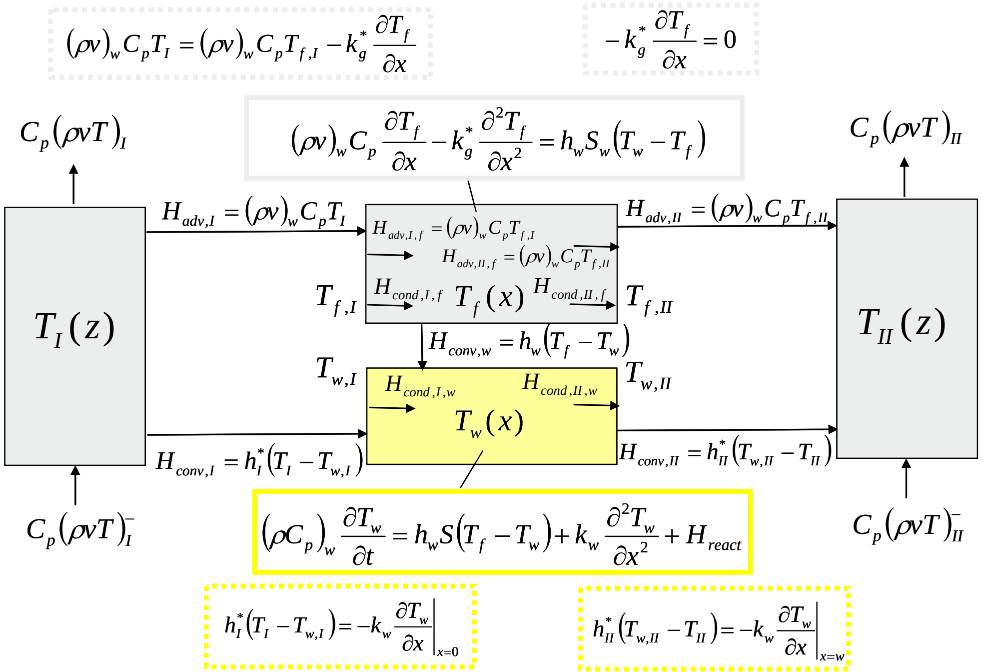


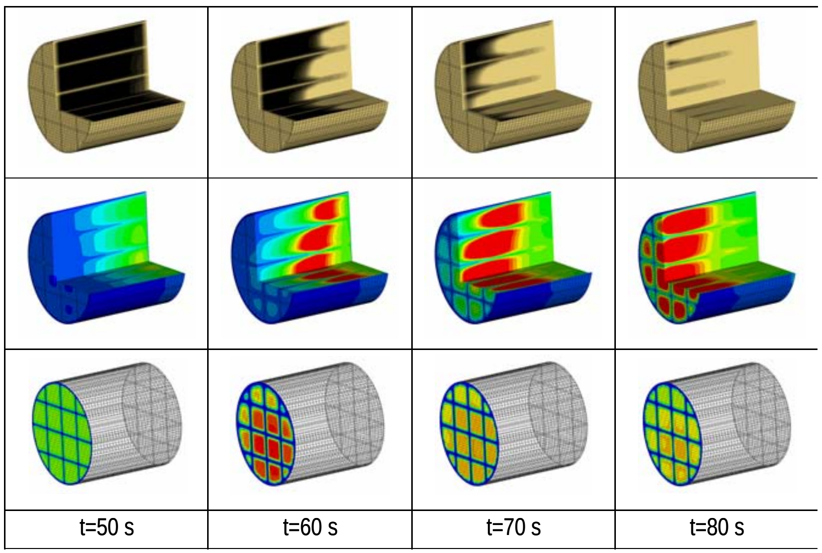


- *"4-way Catalyst Modeling in Wall-Flow and Deep-bed Substrates"*
  - Modeling of 4-way systems, incl. deNO$_x$ coated DPFs (DPNR, *SCRF*)

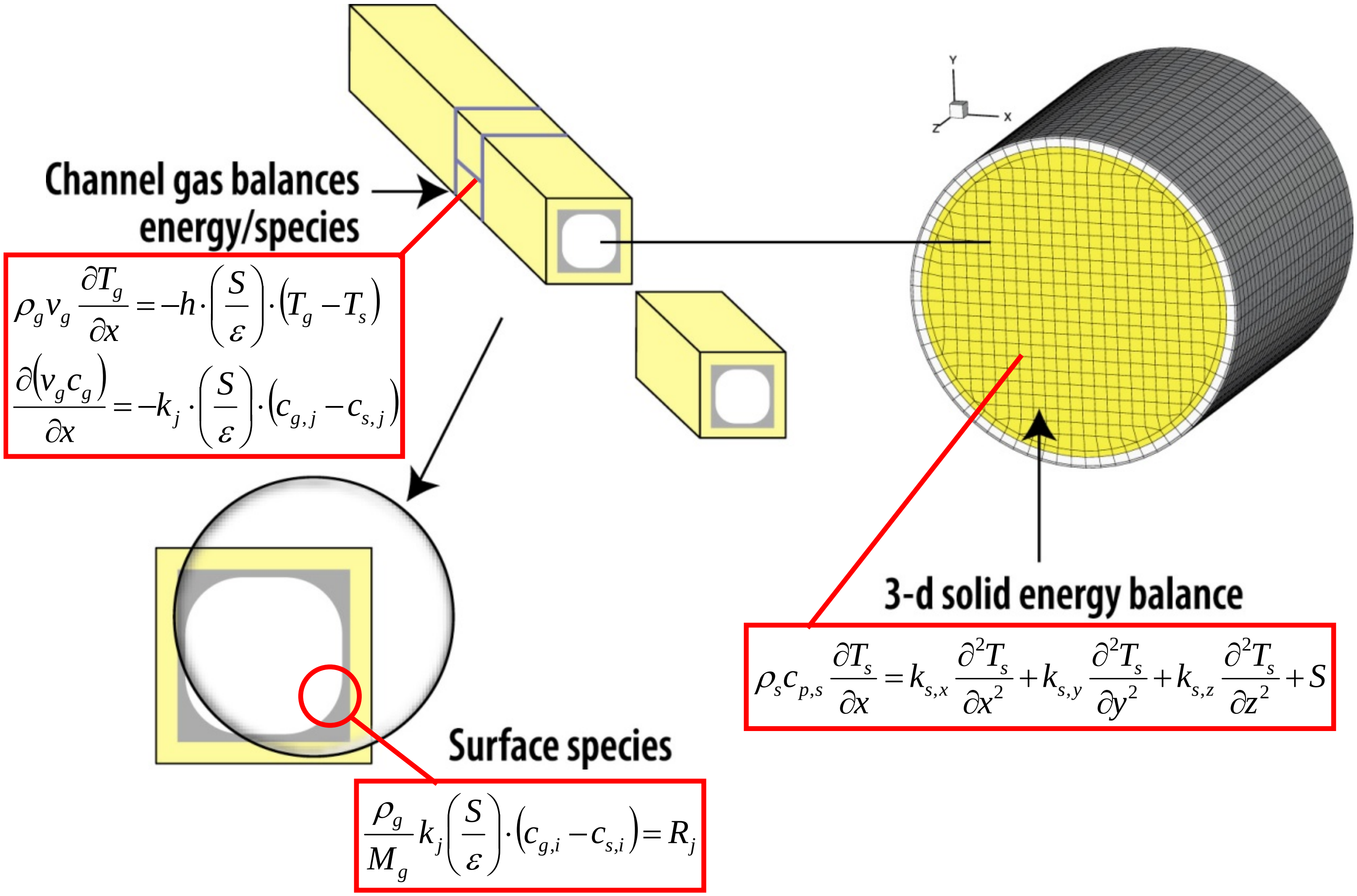


- *"From zero to four-dimensional after-treatment models: needs and challenges"*
  - Discussion of species/energy balance derivations for 0-d to 4-d models
  - How many dimensions we need for each modeling application





Basic equations of flow-through catalyst modeling



Intra-layer washcoat model equations

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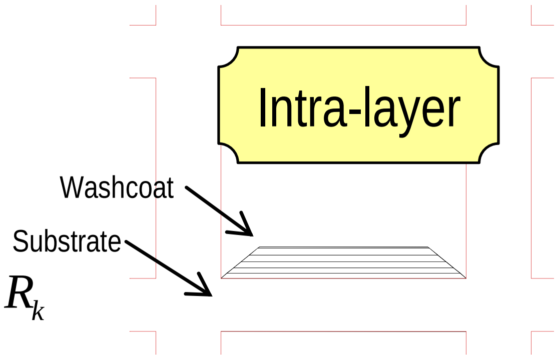

Washcoat:

$$-D_j \frac{\partial}{\partial x}\left(f_x \frac{\partial y_j}{\partial x} \right) = \frac{f_x}{c_m} \sum_k c_{j,k} R_k$$

Channel gas species balance:

$$\frac{\partial}{\partial z}\left(v_1 y_{1,j}\right) = \frac{1}{df_{-w}} k_{1,j}\left(y_{1s,j} - y_{1,j}\right), \qquad k_{i,j} = \frac{Sh \cdot D_{mol,j}}{d_i}$$

Boundary conditions:

$$-D_j f_{-w} \left.\frac{\partial y_j}{\partial x}\right|_{1s} = -df_{-w}{}^2 \frac{\partial}{\partial z}\left(v_1 y_{1,j}\right), \qquad \left.\frac{\partial y_j}{\partial x}\right|_{2s} = 0$$

Applications

- “Thick” washcoats
- Extruded catalysts
- Multi-layer catalysts

Washcoat diffusivity

“mixed” (parallel pore) model

$$\frac{1}{D_{w,j}} = \frac{\tau}{\varepsilon_p}\left(\frac{1}{D_{mol,j}} + \frac{1}{D_{knud,j}} \right)$$

$$D_{knud,j} = \frac{d_p}{3}\sqrt{\frac{8\Re T}{\pi M_j}}$$

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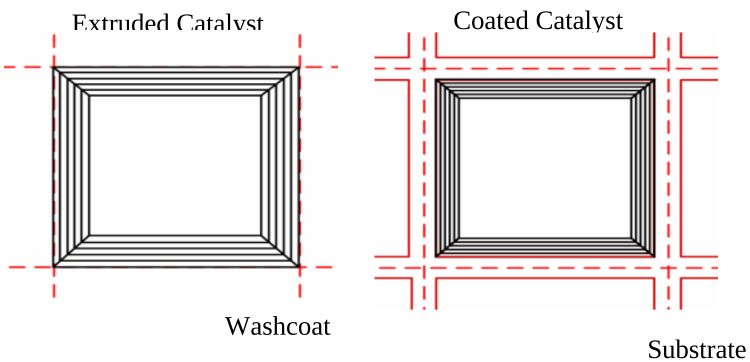
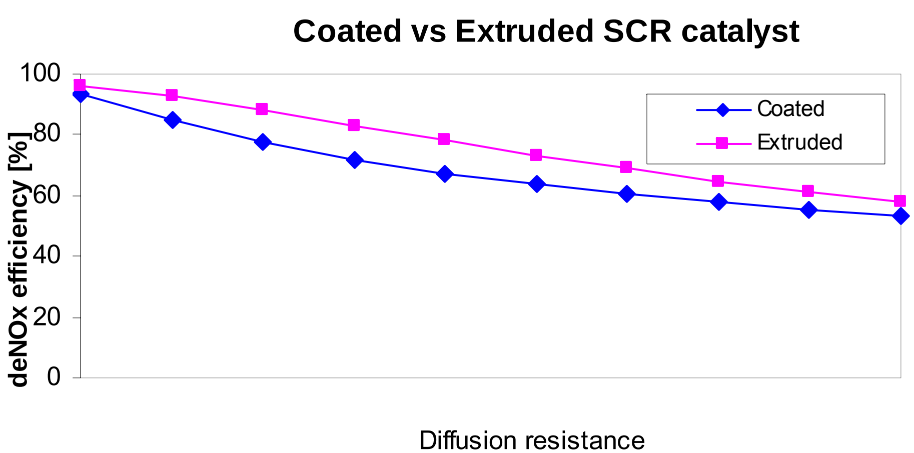
Significance of 4th dimension in flow-through catalyst modeling

- Comparison between coated and extruded SCR catalysts





- Exhaust gas scenario
  - ~350 kg/h mass flow rate
  - 400° gas temperature
  - NO2/NOx= 0.1
  - NH3:NOx = 1:1
- Catalysts
  - 3.2lt volume
  - 300 cpsi
  - Same frontal area (~88%)

Intra-layer modeling
Application in dual layer concepts

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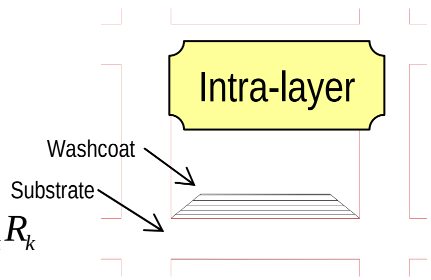
Intralayer modeling equations



Washcoat:

$$-D_j \frac{\partial}{\partial x}\left(f_x \frac{\partial y_j}{\partial x} \right) = \frac{f_x}{c_m} \sum_k c_{j,k} R_k$$

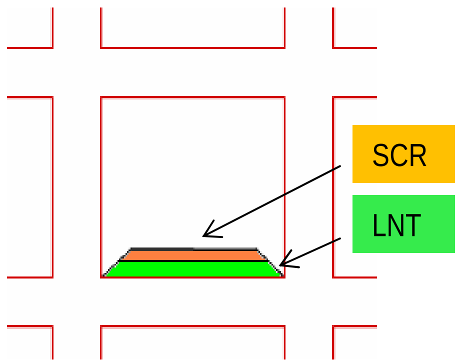
Channel gas species balance:

$$\frac{\partial}{\partial z}\left(v_1 y_{1,j}\right) = \frac{1}{df_{-w}} k_{1,j}\left(y_{1s,j} - y_{1,j}\right), \qquad k_{i,j} = \frac{Sh \cdot D_{mol,j}}{d_i}$$

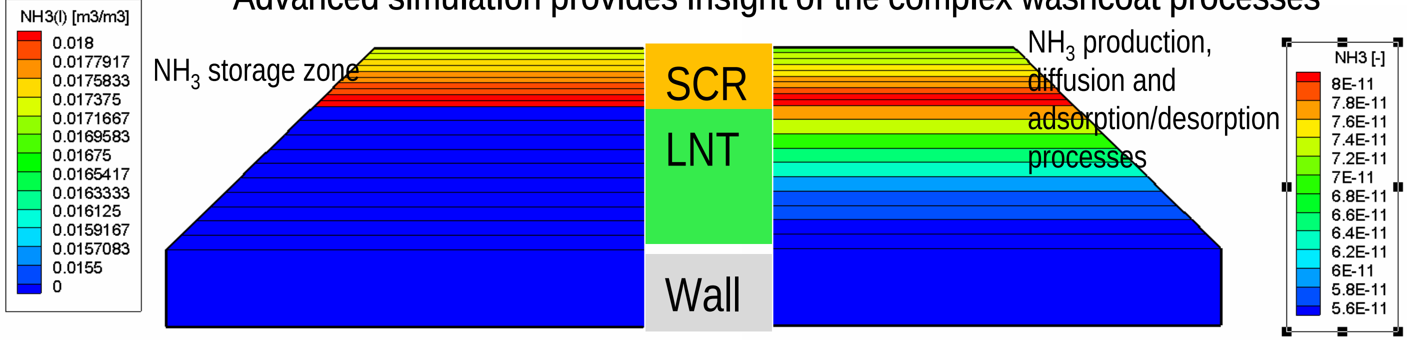
Boundary conditions:

$$-D_j f_{-w} \left.\frac{\partial y_j}{\partial x}\right|_{1s} = -df_{-w}^{\;2} \frac{\partial}{\partial z}\left(v_1 y_{1,j}\right), \qquad \left.\frac{\partial y_j}{\partial x}\right|_{2s} = 0$$

Double layer washcoat modeling



Advanced simulation provides insight of the complex washcoat processes



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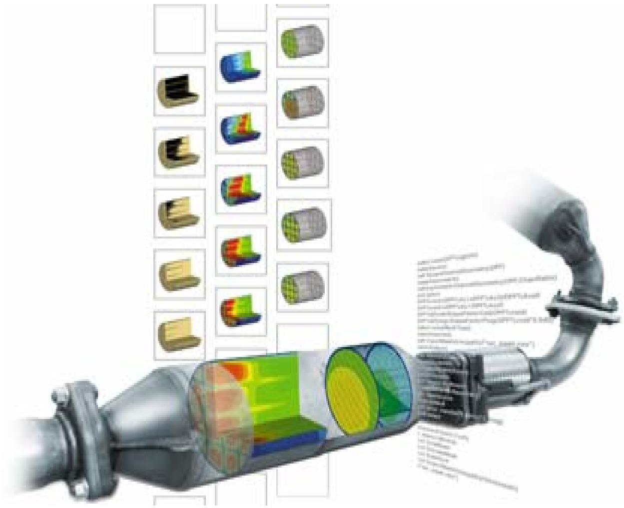
LNT catalyst

- Reaction scheme
- Calibration



LNT catalyst modeling

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Barium storage / desorption

$$BaO + 2NO_2 + \frac{1}{2}O_2 \rightarrow Ba(NO_3)_2$$
$$BaO + 2NO + \frac{1}{2}O_2 \rightarrow Ba(NO_2)_2$$

$$Ba(NO_2)_2 + O_2 \rightarrow Ba(NO_3)_2$$

$$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + \frac{1}{2}O_2$$
$$Ba(NO_2)_2 \rightarrow BaO + 2NO + \frac{1}{2}O_2$$

Oxidation reactions over Pt

$$NO + \frac{1}{2}O_2 \leftrightarrow NO_2$$
$$CO + \frac{1}{2}O_2 \leftrightarrow CO_2$$
$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$$

Ceria oxidation / reduction

$$Ce_2O_3 + \frac{1}{2}O_2 \rightarrow 2CeO_2$$
$$Ce_2O_3 + 2NO \rightarrow 2CeO_2 + N_2O$$

$$CO + 2CeO_2 \rightarrow Ce_2O_3 + CO_2$$
$$H_2 + 2CeO_2 \rightarrow Ce_2O_3 + H_2O$$

$$Ce_2O_3 + N_2O \rightarrow 2CeO_2 + N_2$$
$$NH_3 + 5Ce_2O_3 \rightarrow \frac{5}{2}CeO_2 + NO + \frac{3}{2}H_2O$$

Barium nitrate/nitrite decomposition

$$Ba(NO_3)_2 + 3CO \rightarrow BaO + 2NO + 3CO_2$$
$$Ba(NO_2)_2 + CO \rightarrow BaO + 2NO + CO_2$$

$$Ba(NO_3)_2 + 3H_2 \rightarrow BaO + 2NO + 3H_2O$$
$$Ba(NO_2)_2 + H_2 \rightarrow BaO + 2NO + H_2O$$

NO reduction mechanisms

$$CO + NO \rightarrow CO_2 + \frac{1}{2}N_2 \qquad H_2 + NO \rightarrow H_2O + \frac{1}{2}N_2$$
$$CO + 2NO \rightarrow CO_2 + N_2O \qquad 2.5H_2 + NO \rightarrow NH_3 + H_2O$$

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LNT catalyst calibration
Epling et al., 2007

Calibration of LNT kinetics based on published experimental data:

*W.S.Epling, A.Yezerets, N.W.Currier,“**The effects of regeneration conditions on NOx and NH_3 release from Nox storage/reduction catalysts”**, Appl.Catal.B: Environ. 74 (2007) 117*

Experimental data consist of NOx storage/reduction phases at different temperatures

- NO_x storage phase: 300 ppm NO ,10% O_2, 5% H_2O
- Regeneration phase: 625 ppm CO and 375ppm H_2

LNT catalyst calibration results

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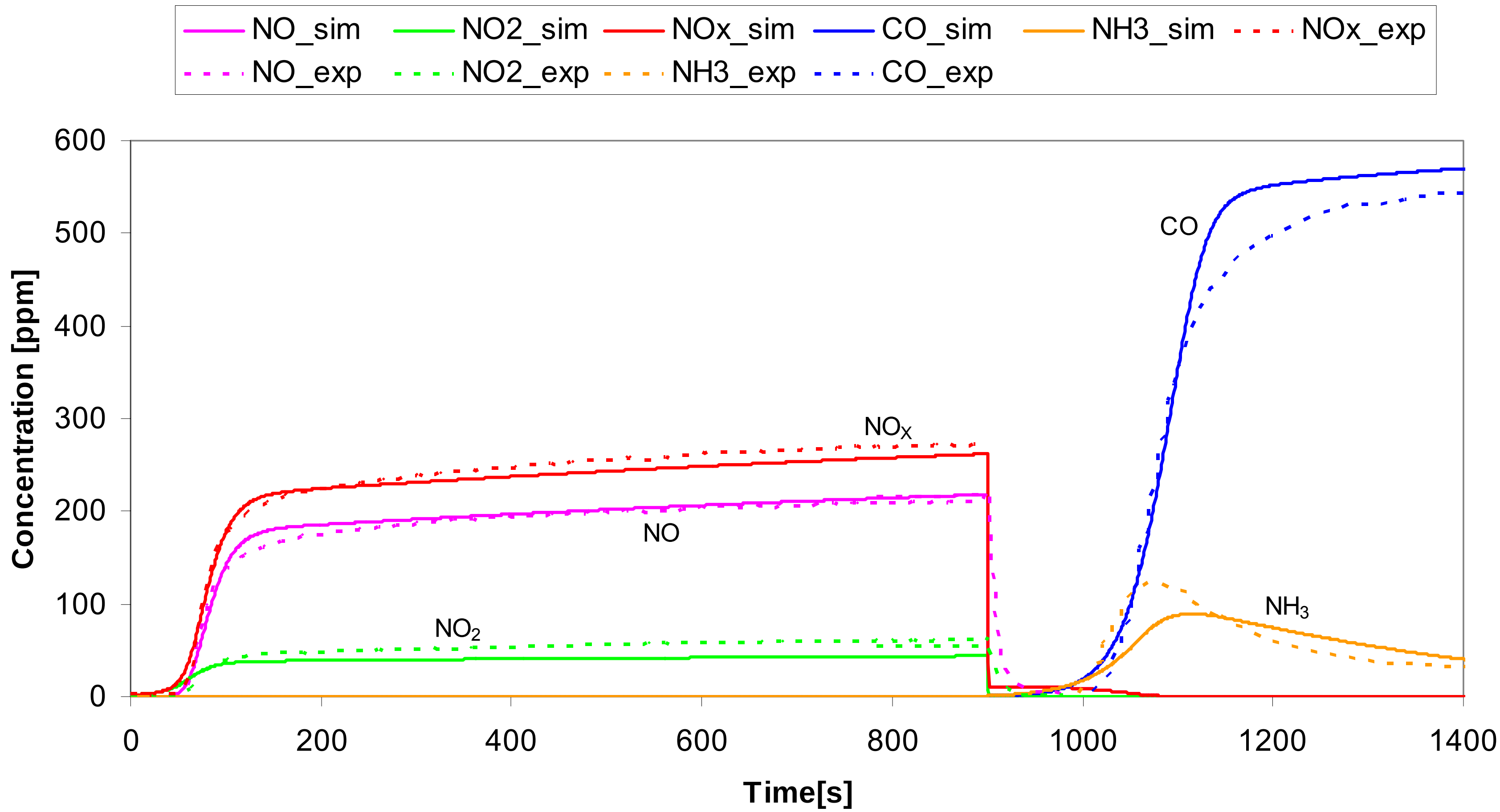
Loading - Regeneration @ 200°C



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LNT catalyst calibration results

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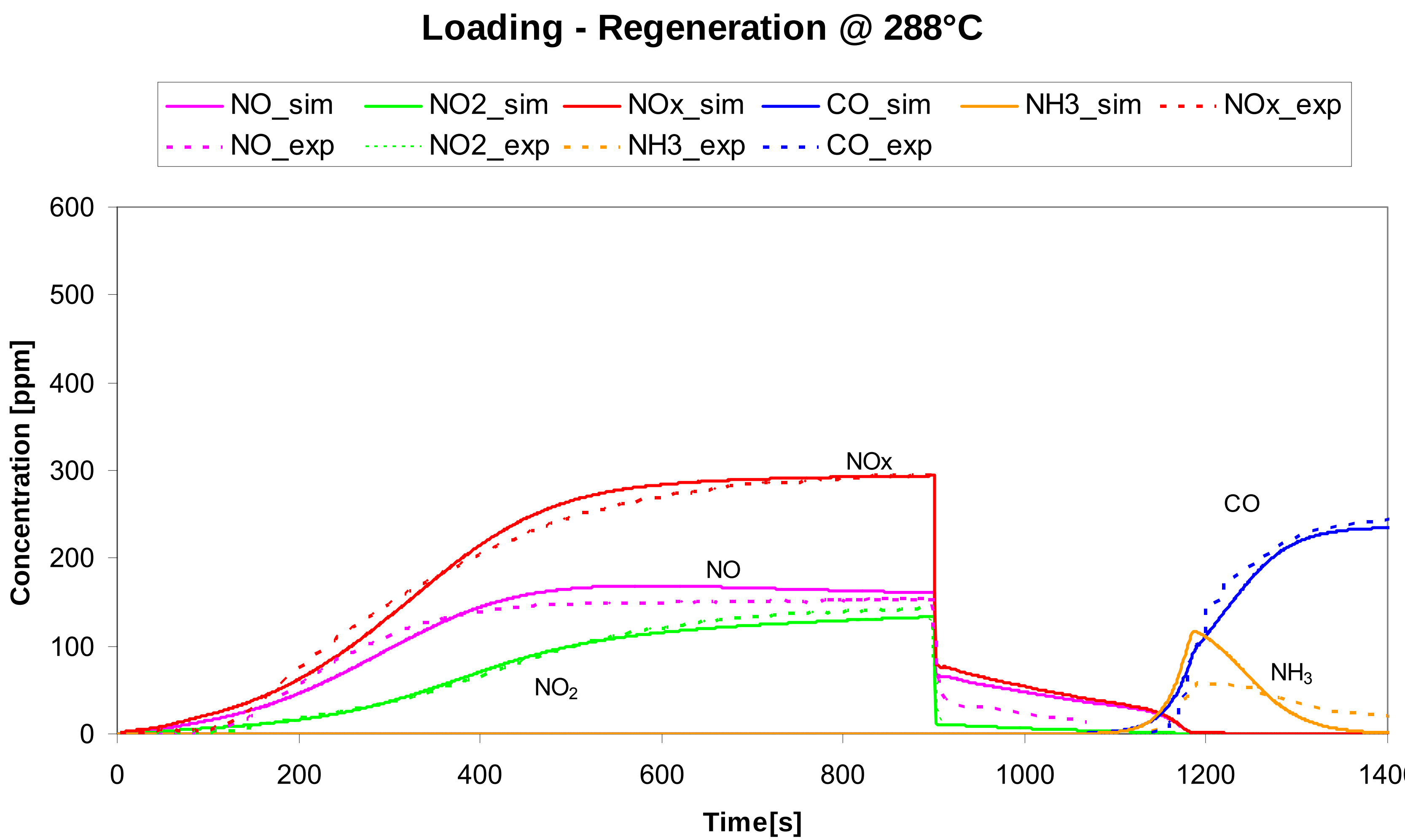

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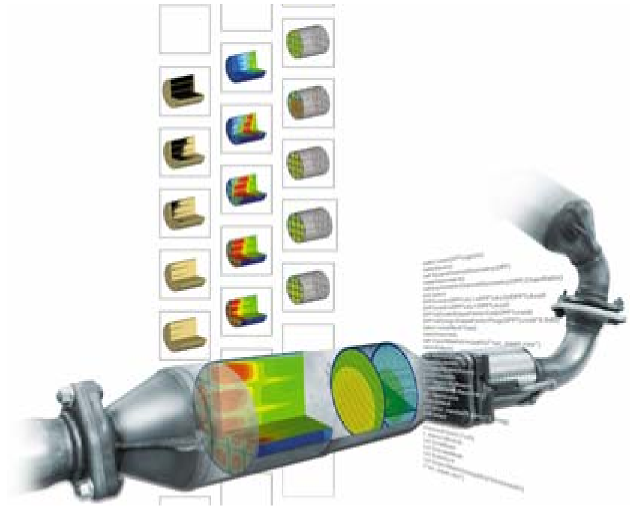
SCR catalysts

- Reactions scheme
- Calibration



SCR catalyst modeling

SCR reaction mechanism comprises of the three well-established reactions:

Standard SCR reaction	$NH_3 + NO + 1/4\ O_2 \rightarrow N_2 + 3/2\ H_2O$
Fast SCR reaction	$2\ NH_3 + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O$
NO2-SCR reaction	$NH_3 + 3/4\ NO_2 \rightarrow 7/8\ N_2 + 3/2\ H_2O$

Reaction rates are Ahrenius type expressions with inhibition terms, according to **Langmuir - Hinshelwood** heterogeneous catalytic reaction mechanism

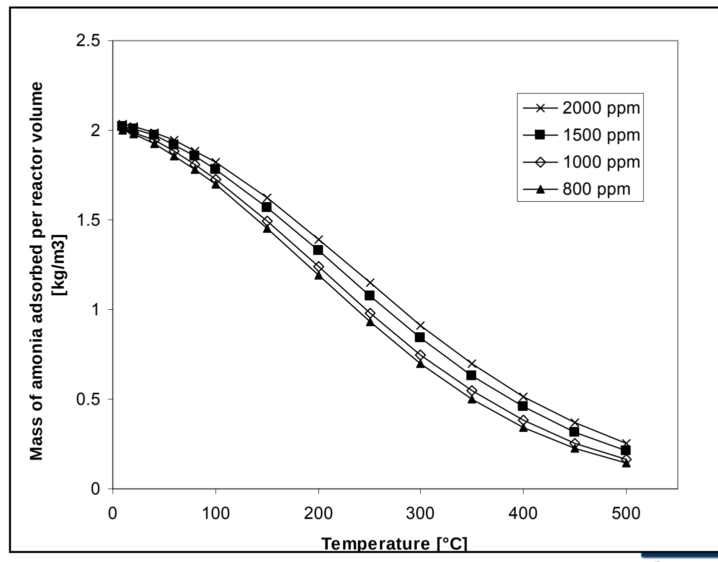
Adsorption/desorption phenomena are modeled using the **Dubinin-Radushkevich** adsorption isotherm and appropriate adsorption/desorption rates

$$\ln x = \ln(W_0\rho) - D\left[\ln\left(\frac{p_{NH_3}}{p_{sat,NH_3}}\right)\right]^2 \qquad D = A\left(RT/\beta\right)^2$$

$$\log p_{sat} = A - \frac{B}{C+T_s}$$

$$R_b = kW_0\phi_j\left(1-\phi_{eq,j}\right)$$

$$R_f = kW_0\,\phi_{eq,j}\,\phi_{free} \qquad \phi_j = \frac{x_j}{W_0\,\rho_j}$$



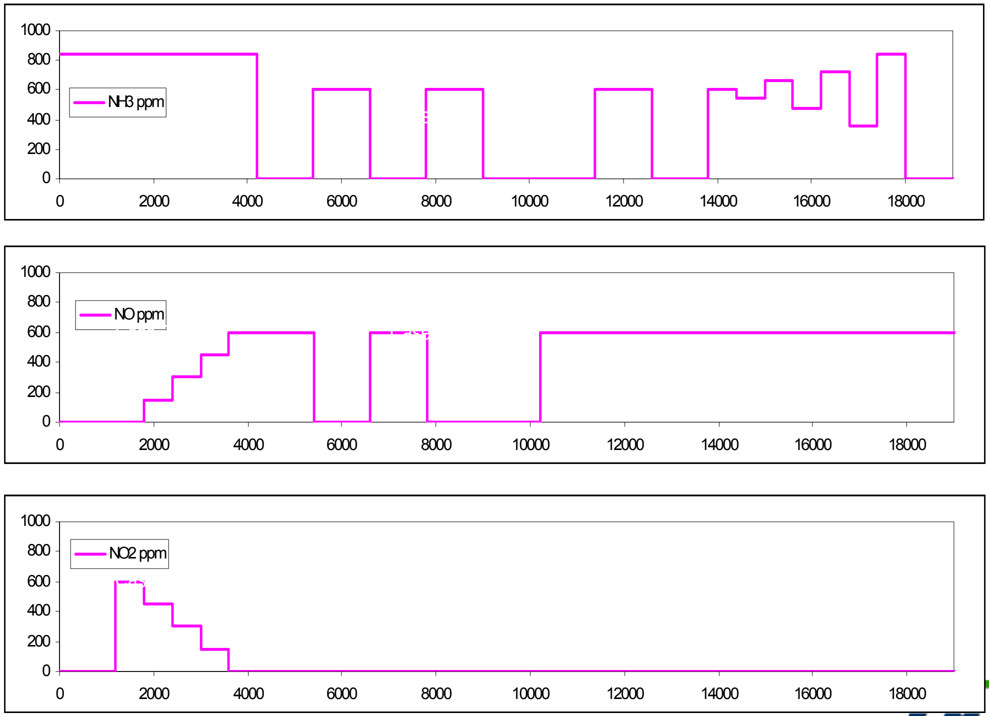
Zeolite SCR catalyst calibration

Calibration of Fe-zeolite SCR kinetics based on published experimental data:

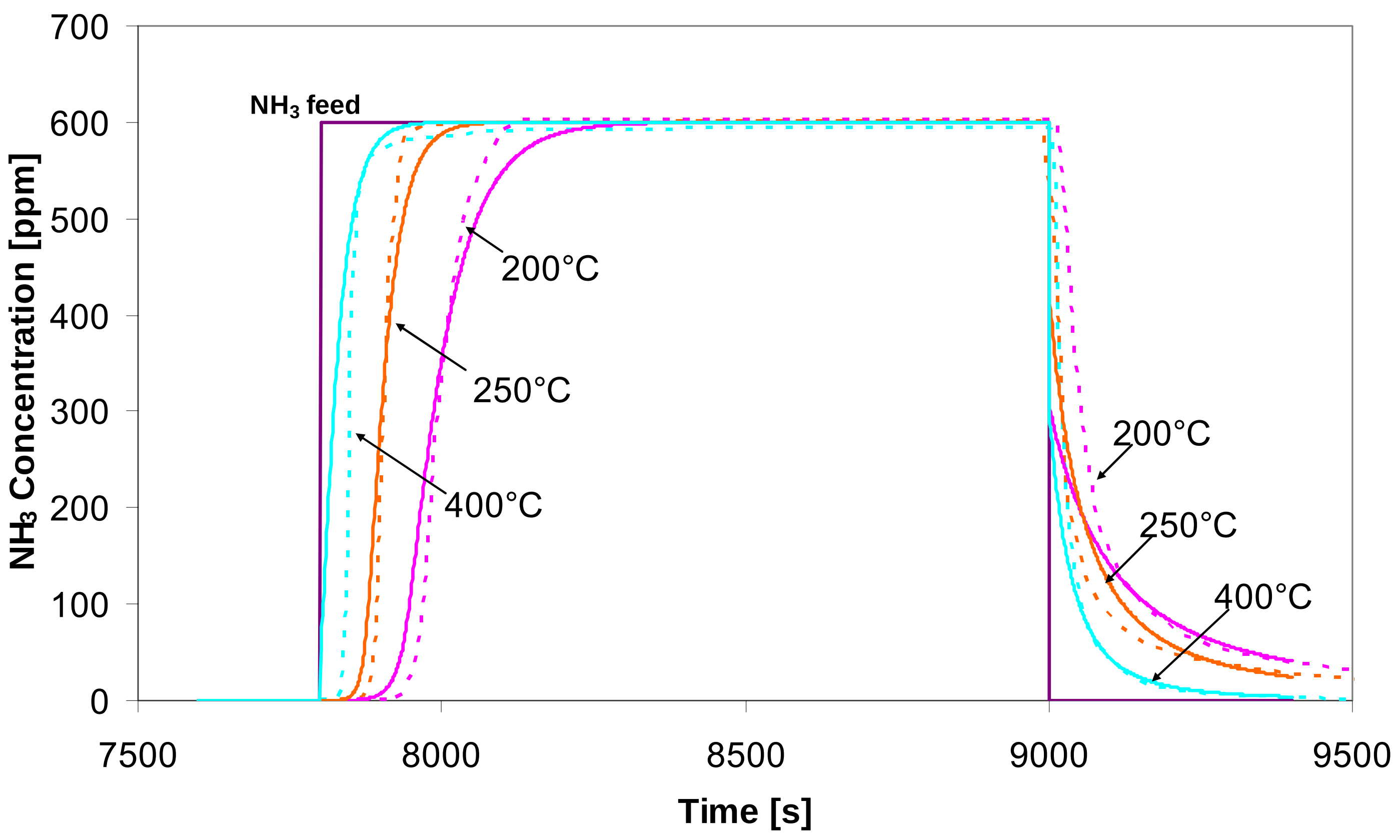
S. Malmberg, M. Votsmeier, J. Gieshoff, N. Söger, L. Mußmann, Umicore AG & Co. KG
A. Schuler, A. Drochner, TU Darmstadt
"Experimental Investigation and Simulation of NH_3-SCR Reaction on Fe-Exchanged Zeolites"
5th International CTI Forum, Nürtingen, 2007

Experimental data consist of:

- NH_3 adsorption-desorption experiments
- Variable NH_3/NO inlet concentrations
- Variable NH_3/NO/NO_2 inlet concentrations

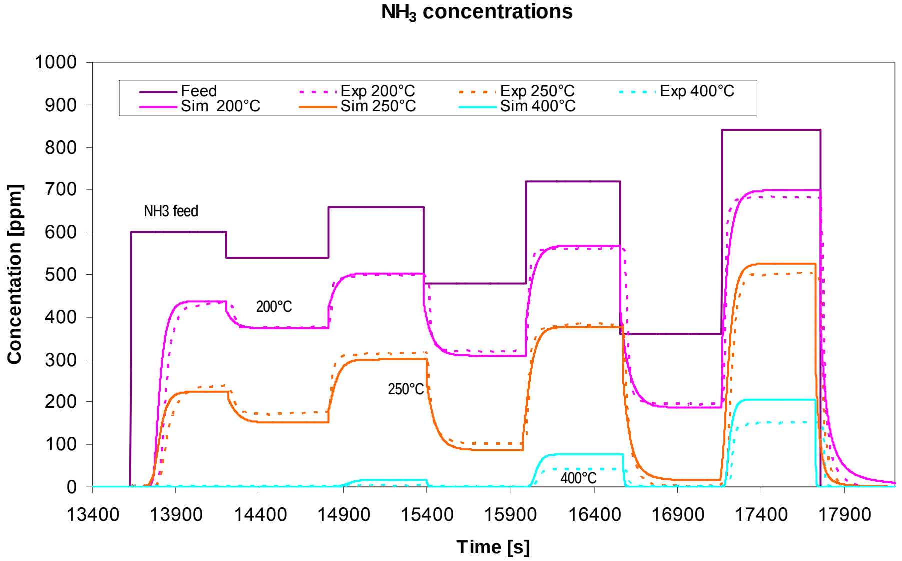


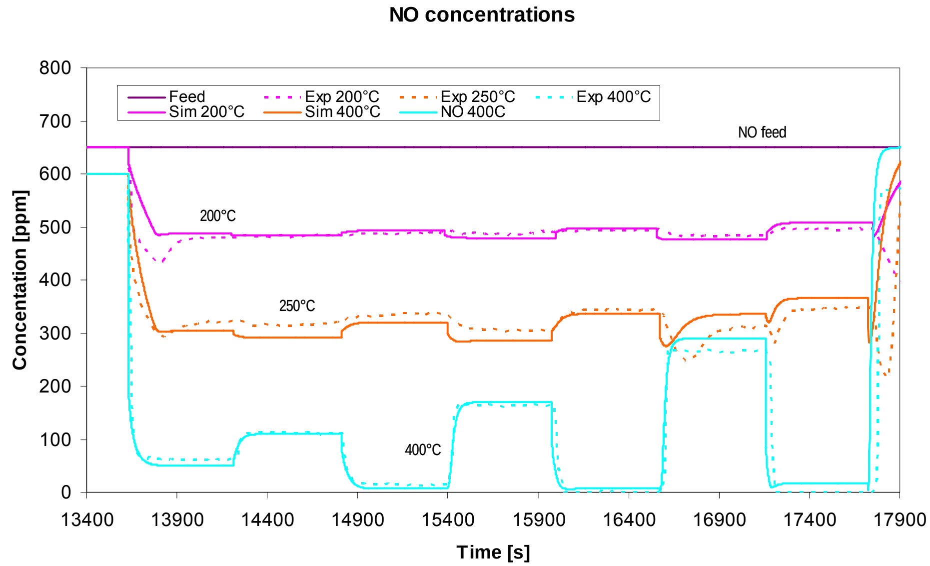
Adsorption/desorption model calibration



The model is able to predict the NH_3 storage-release dynamics without NO_x in the feed gas at various temperatures

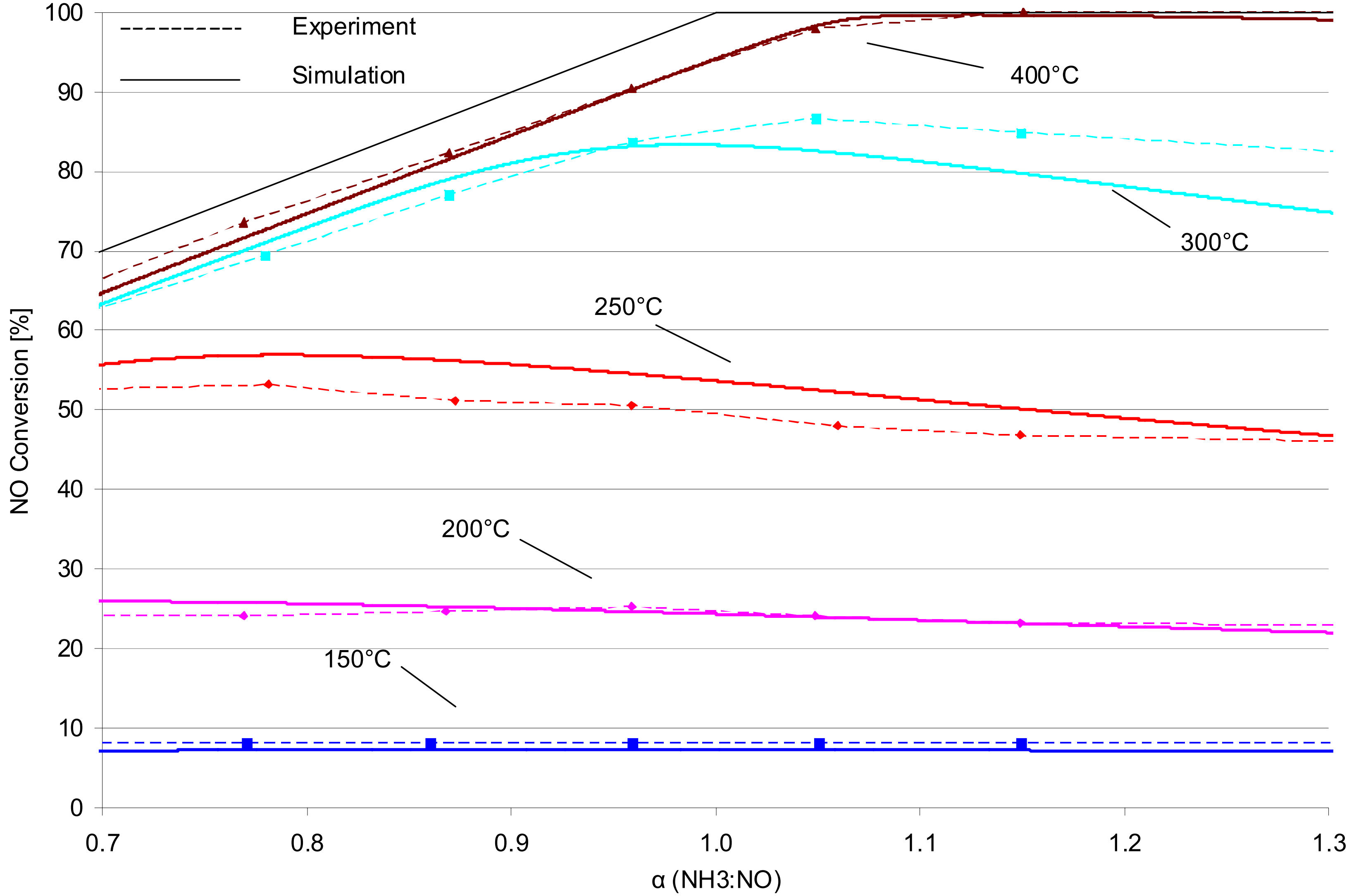
Calibration of "standard SCR" reaction
Variation of NH_3 /NO inlet concentrations





Variable NH_3/NO ratio allows for the calibration of the "Standard SCR" reaction. The self-inhibition effect of NH_3 is also calibrated by this experiment.

Standard-SCR reaction
Summary of steady-state points



NO_2 effect: fast SCR, NO_2-SCR
Variable NH3 /NO/NO2 inlet concentrations

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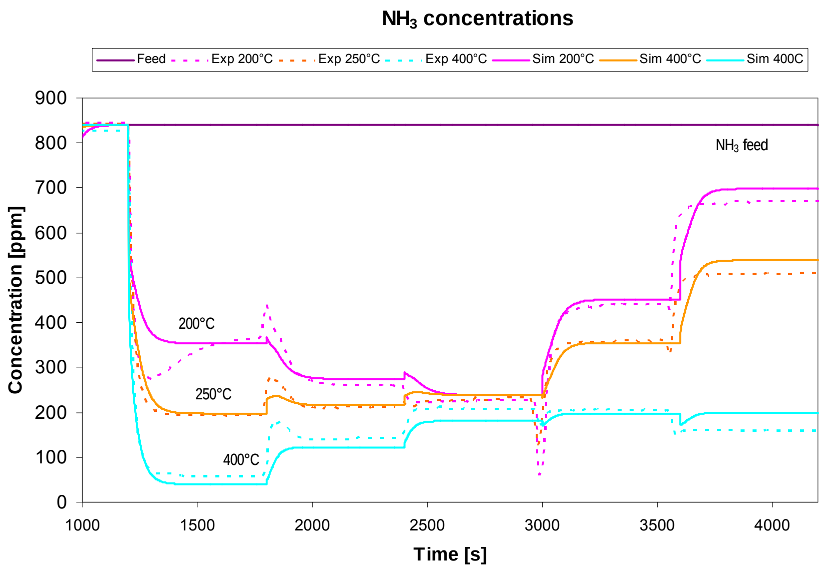

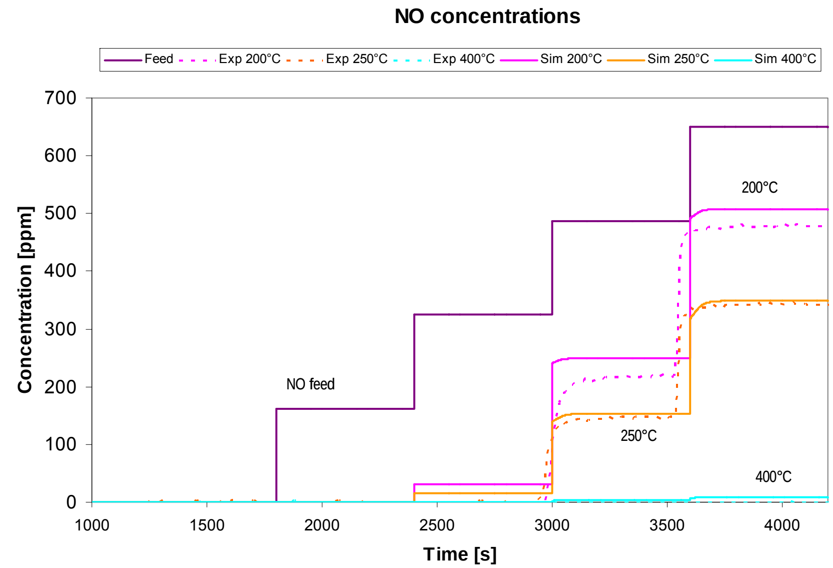

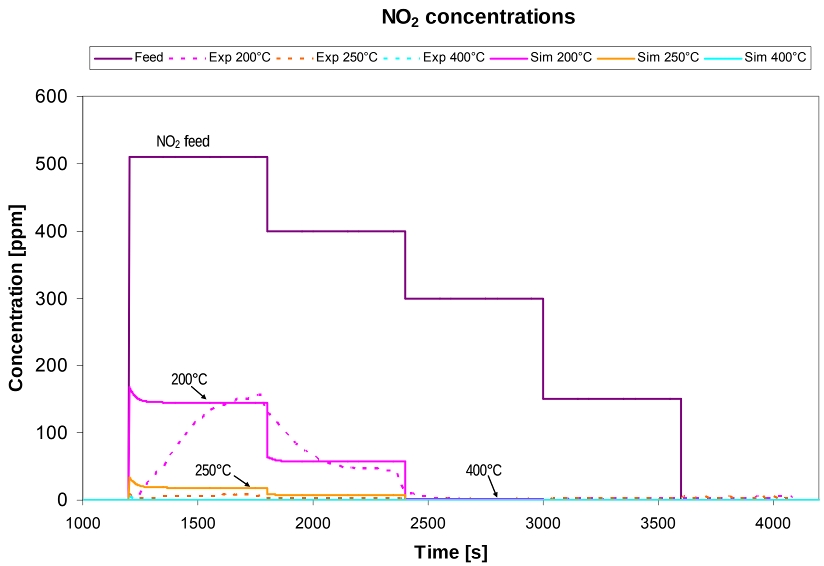

Variable NH_3/NO/NO_2 feed gas ratios enable the calibration of the “Fast and NO_2-SCR” reactions.

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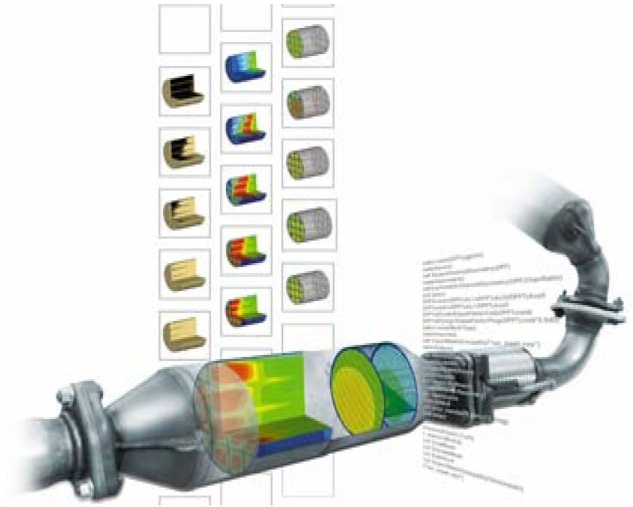
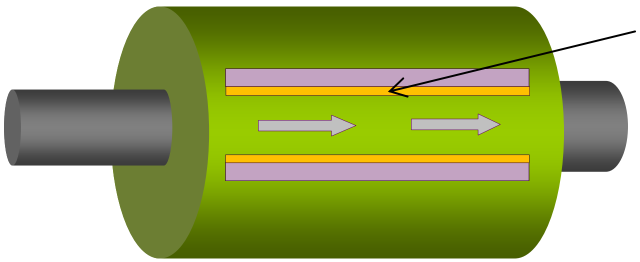
LNT-SCR systems numerical benchmarking

- Single LNT catalyst
- Double bed LNT-SCR catalysts
- Double layer LNT-SCR catalyst

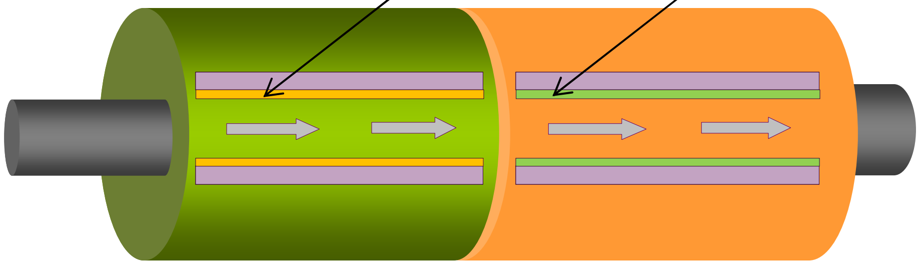


System definitions

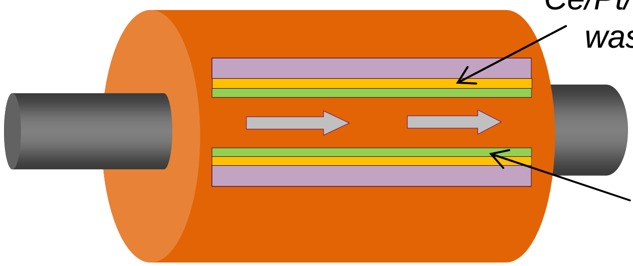
- Single LNT catalyst
  - V=2 l
  - Washcoat loading = 100 g/l



- Double bed LNT-SCR catalyst
  - V=2 l + 2 l
  - Washcoat loading =
    - 100 g/l LNT (1st bed)
    - 100 g/l SCR(2nd bed)



- Double layer LNT-SCR catalyst
  - V=2 l
    - 100 g/l LNT (1st layer)
    - 100 g/l SCR(2nd layer)



Inlet gas conditions used for the numerical benchmarking

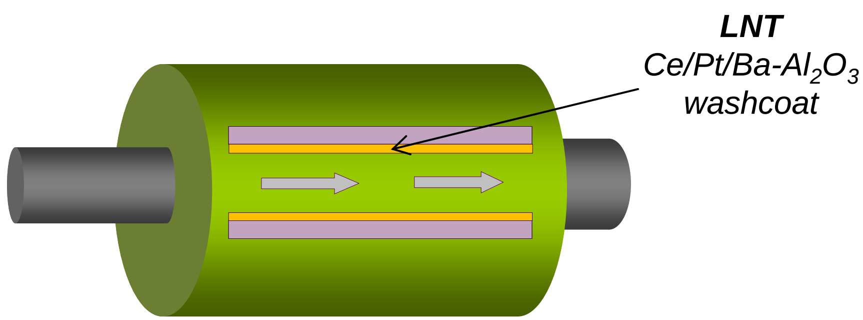
- Consecutive lean-rich cycles
  - T_{in}= 200°C, GHSV= 25000 1/h
  - T_{in}= 300°C, GHSV= 50000 1/h

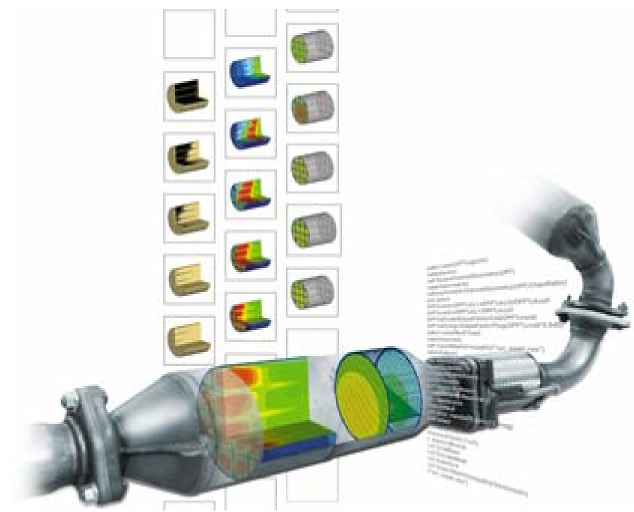
- Lean rich cycle durations: 60/8 s (indicative, not optimized)

- Inlet gas composition:
  - Lean mode:
  - 200 ppm NO, 50 ppm NO_2, 6% O_2, 5% H_2O
  - Rich mode: 3% CO and 1% H_2 in N_2

- *Oxygen storage capacity of the LNT deliberately reduced to allow for more NH_3 production in rich mode*

Single bed LNT catalyst





Single bed LNT catalyst
Results @ 200°C

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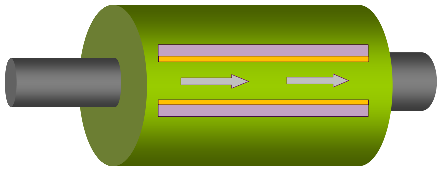
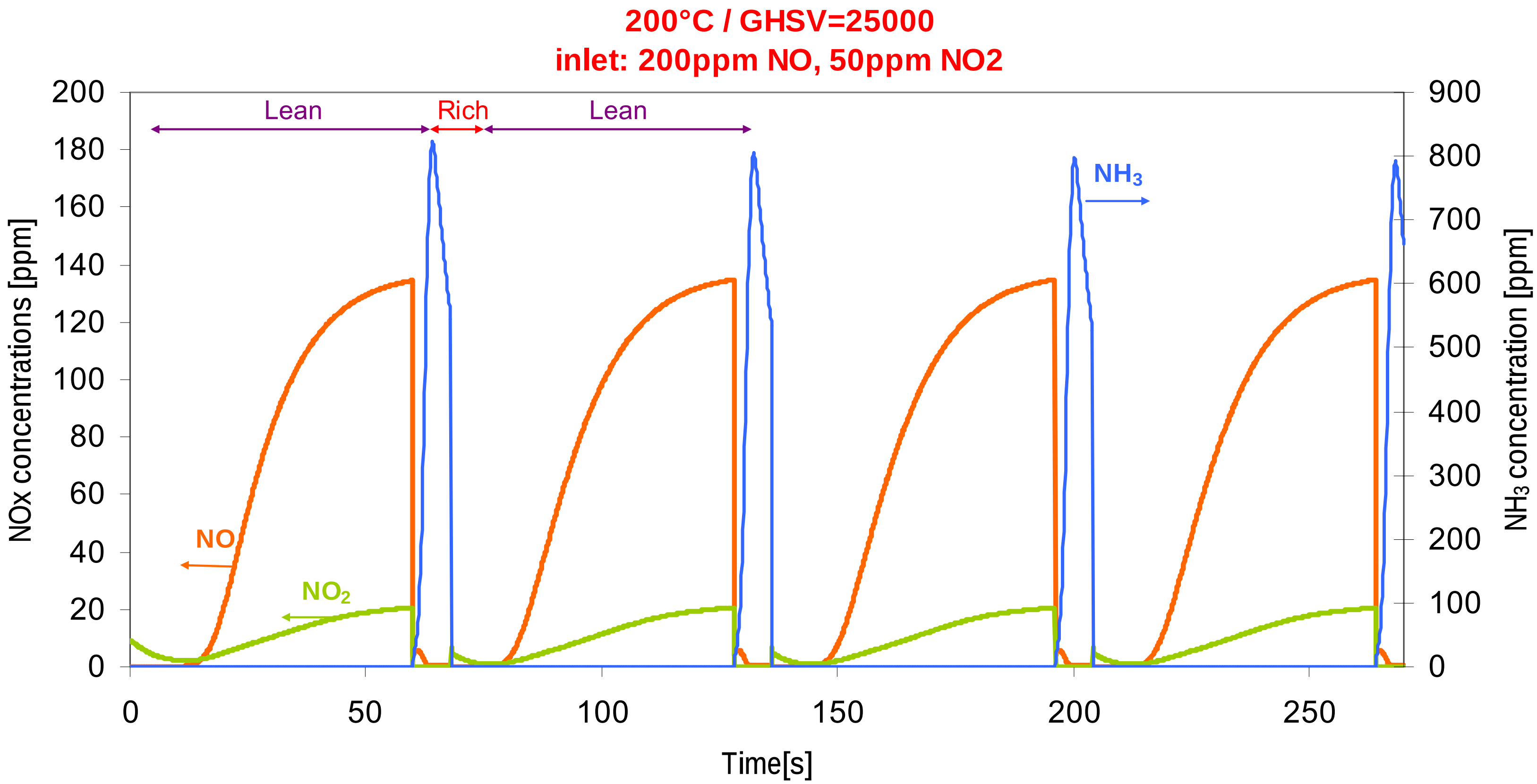
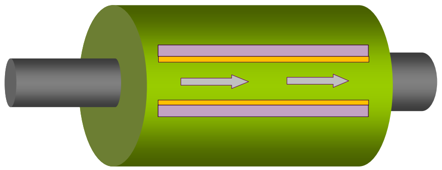
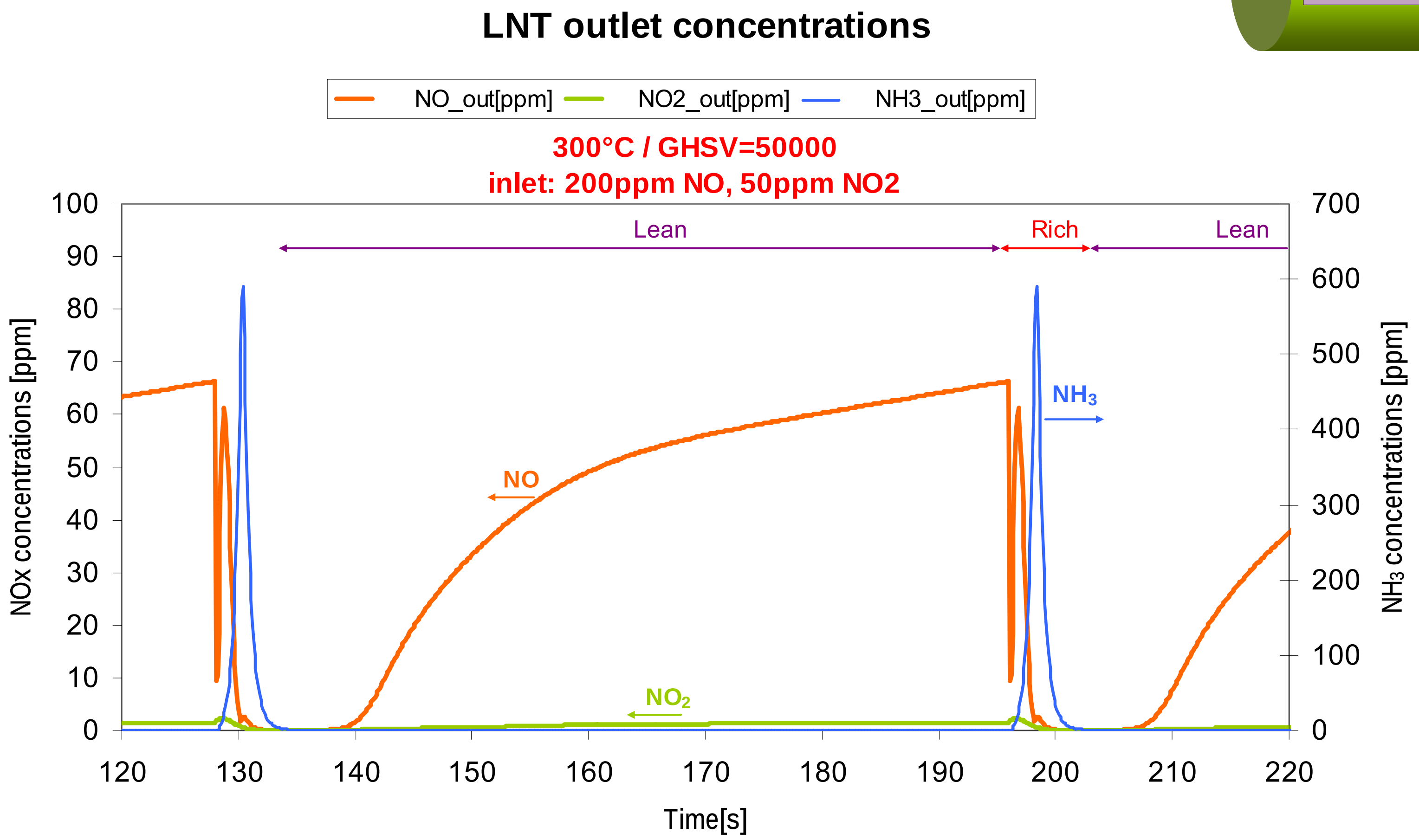




Significant amounts of NH_3 production predicted during rich mode

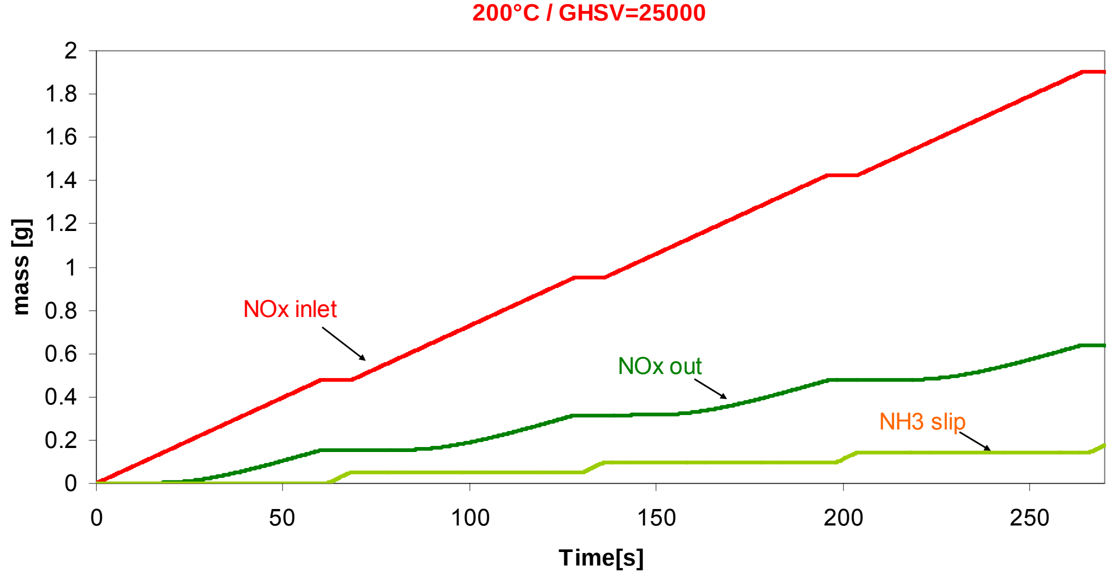
Single bed LNT catalyst
Results @ 300°C

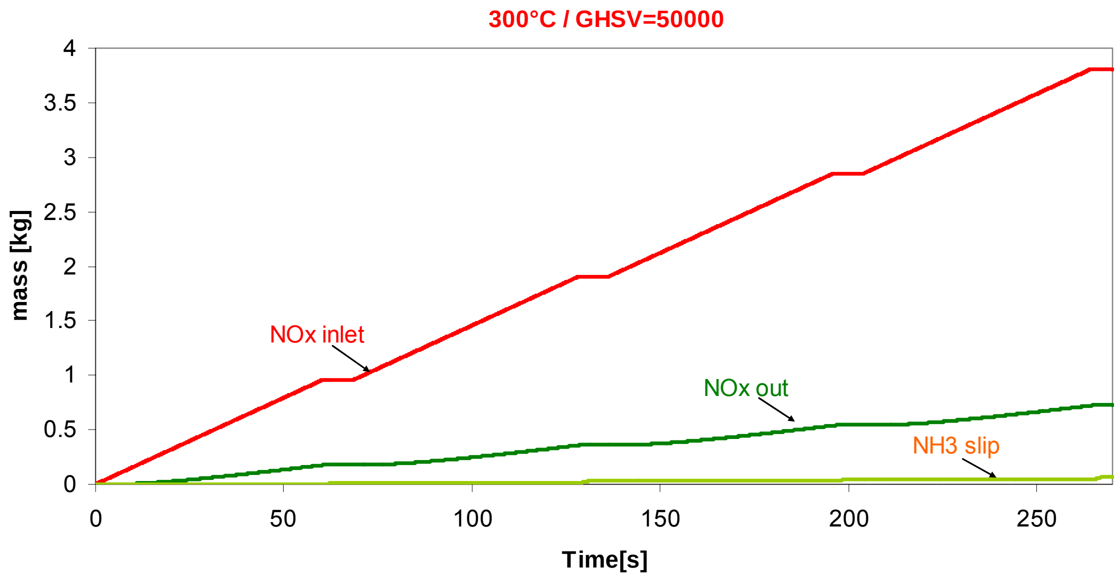


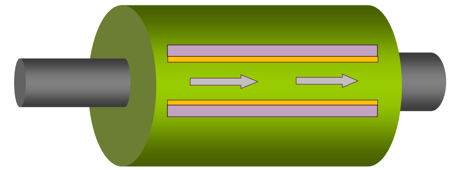


NH_3 slip following the NO spike during rich mode

Single bed LNT catalyst
Comparative cumulative emissions

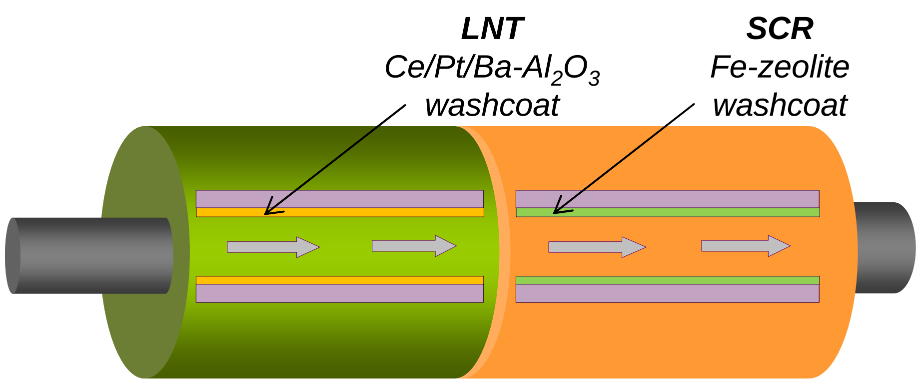


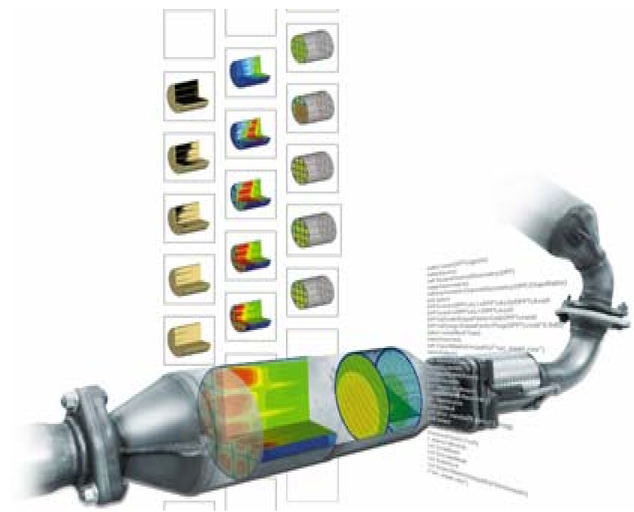




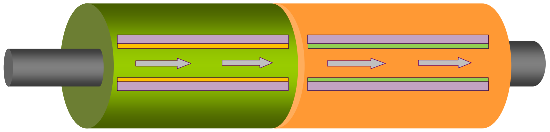
The cumulative NH_3 slip is comparatively higher at 200°C

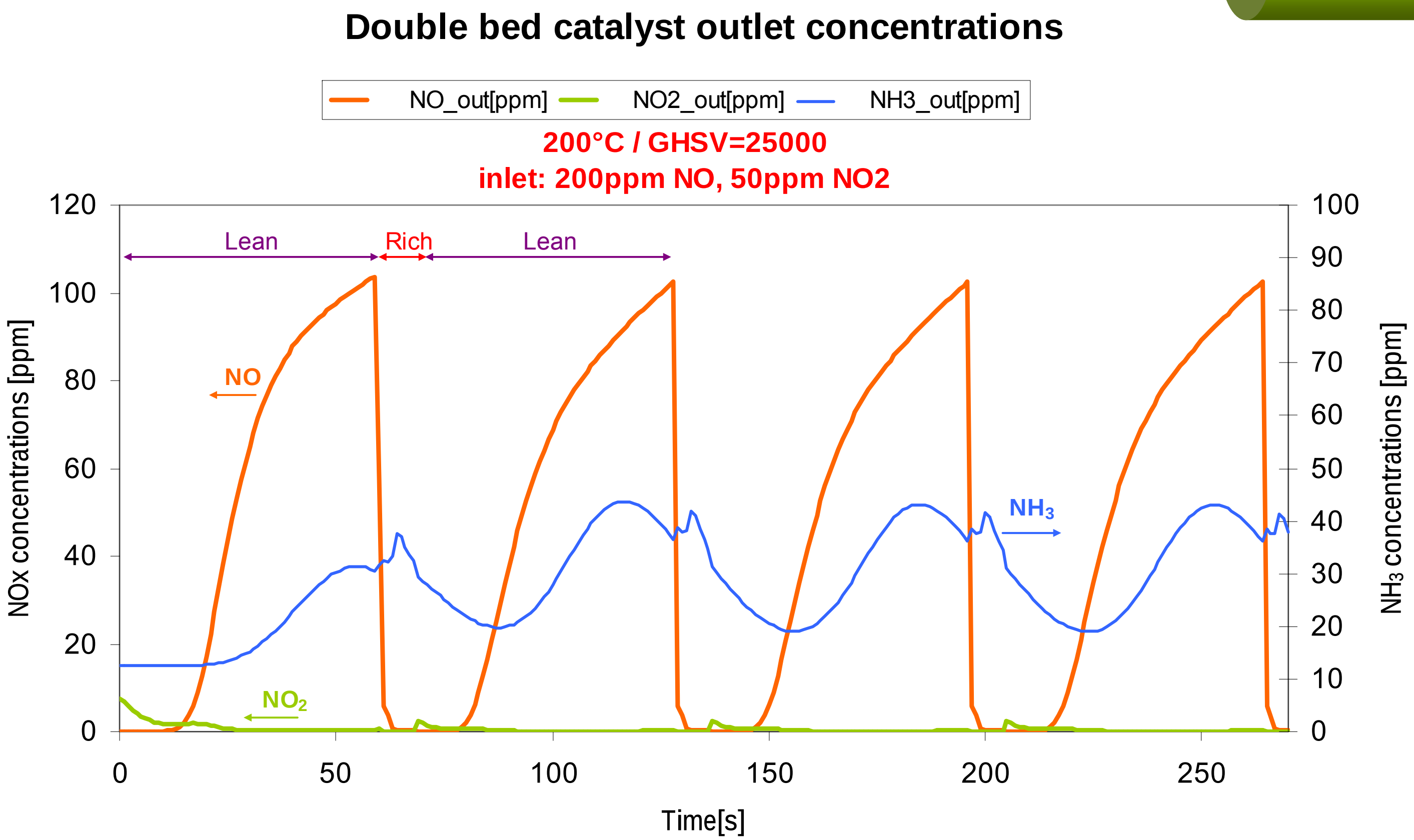
Double bed LNT-SCR catalyst





Double bed LNT-SCR catalyst
Results @ 200°C





Practically, all NO_2 disappears downstream the SCR
NH_3 slip during rich mode is strongly attenuated due to storage on the SCR
Some NH_3 desorbs during lean-mode

Double bed LNT-SCR catalyst
Results @ 300°C

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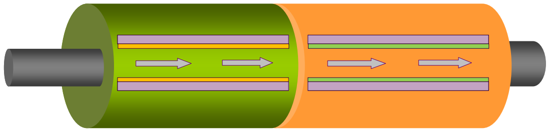

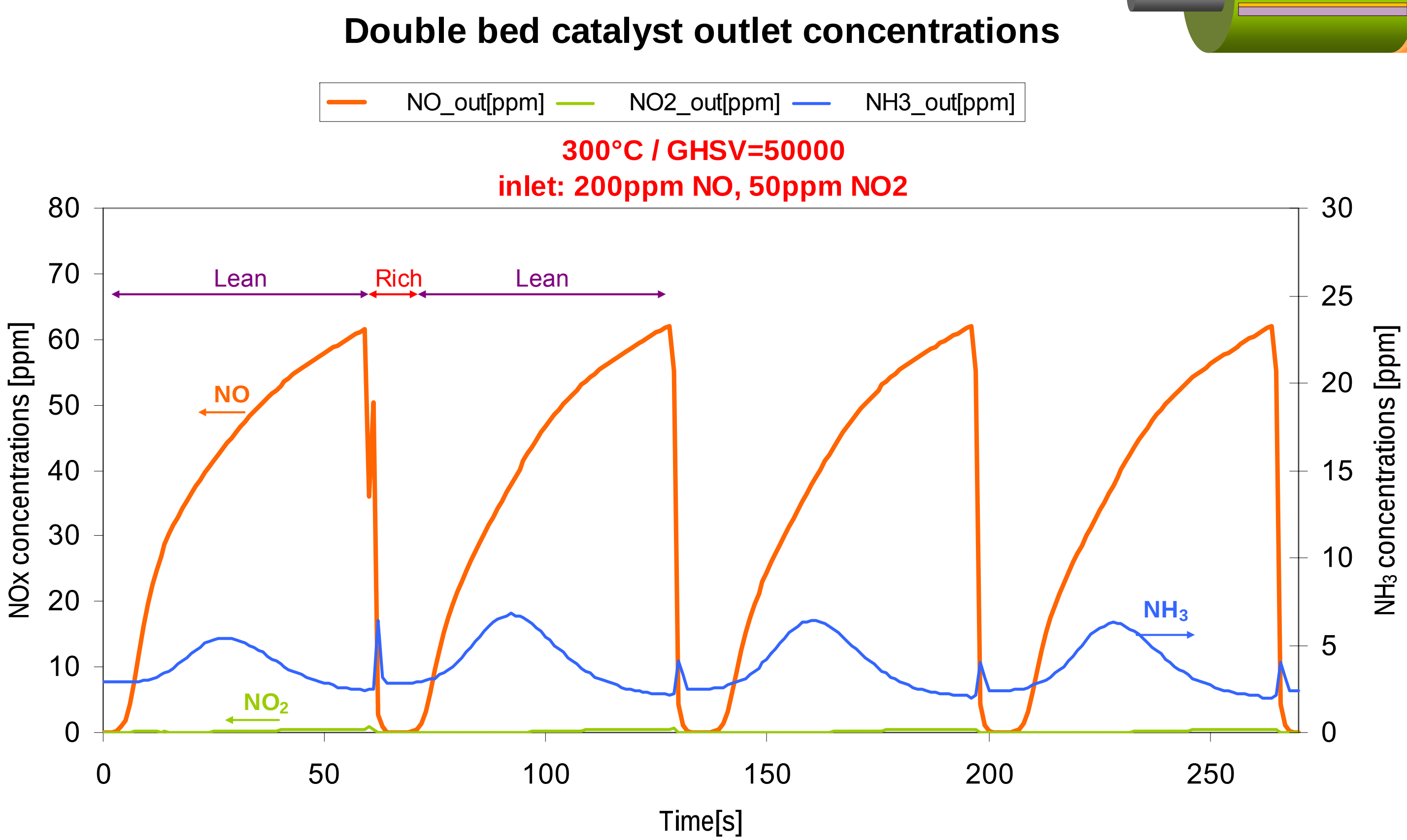

All NO_2 disappears downstream the SCR
Less NH_3 slip compared to 200 C.
Almost no NO breakthrough during rich mode

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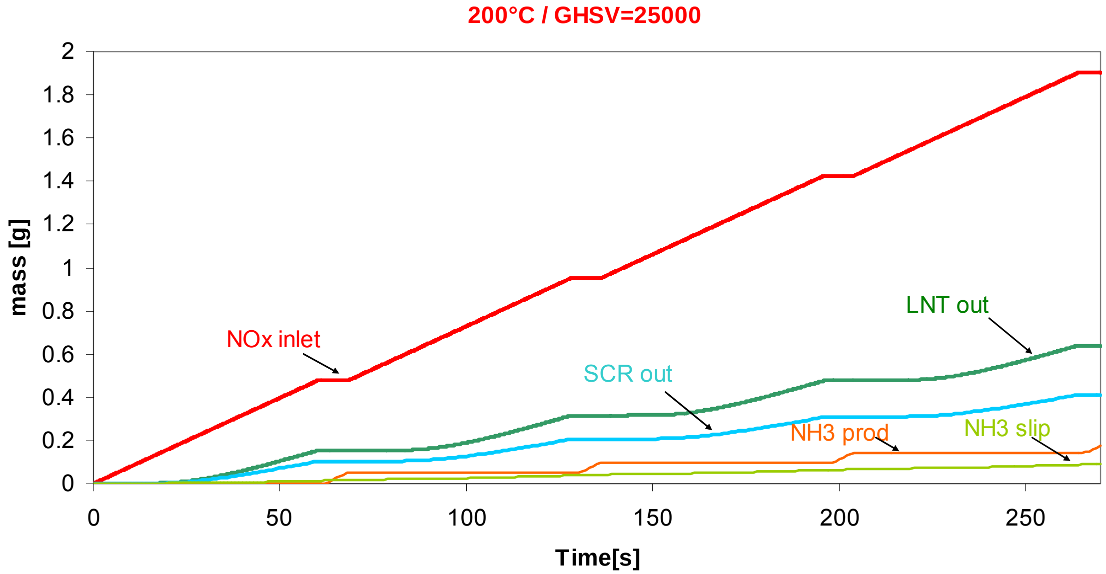
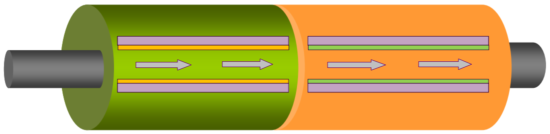
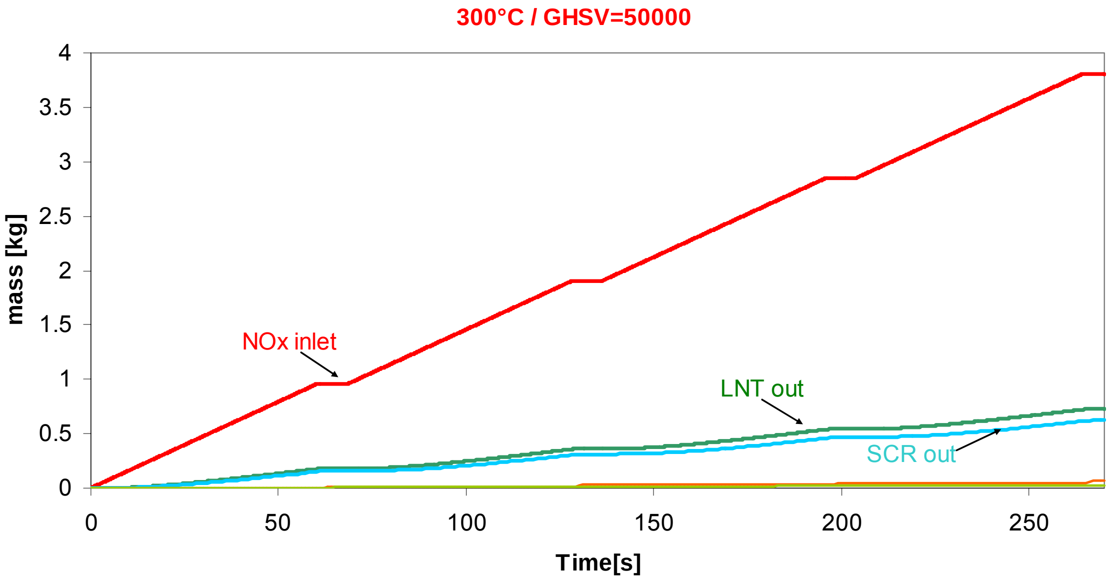
Double bed LNT-SCR catalyst
Comparative cumulative emissions



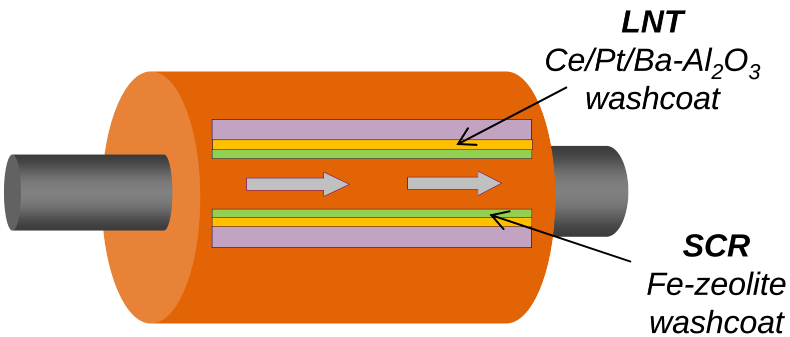


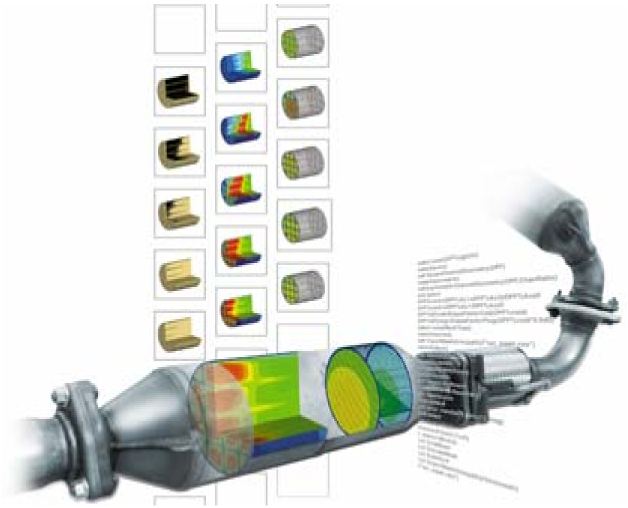
At 200 C the deNO$_x$ efficiency is significantly improved. Some NH_3 is still slipping.



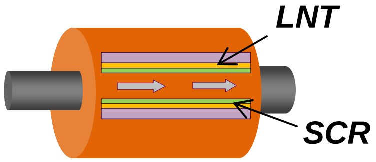
At 300 C the deNO$_x$ efficiency is slightly improved. The NH_3 slip is drastically reduced.

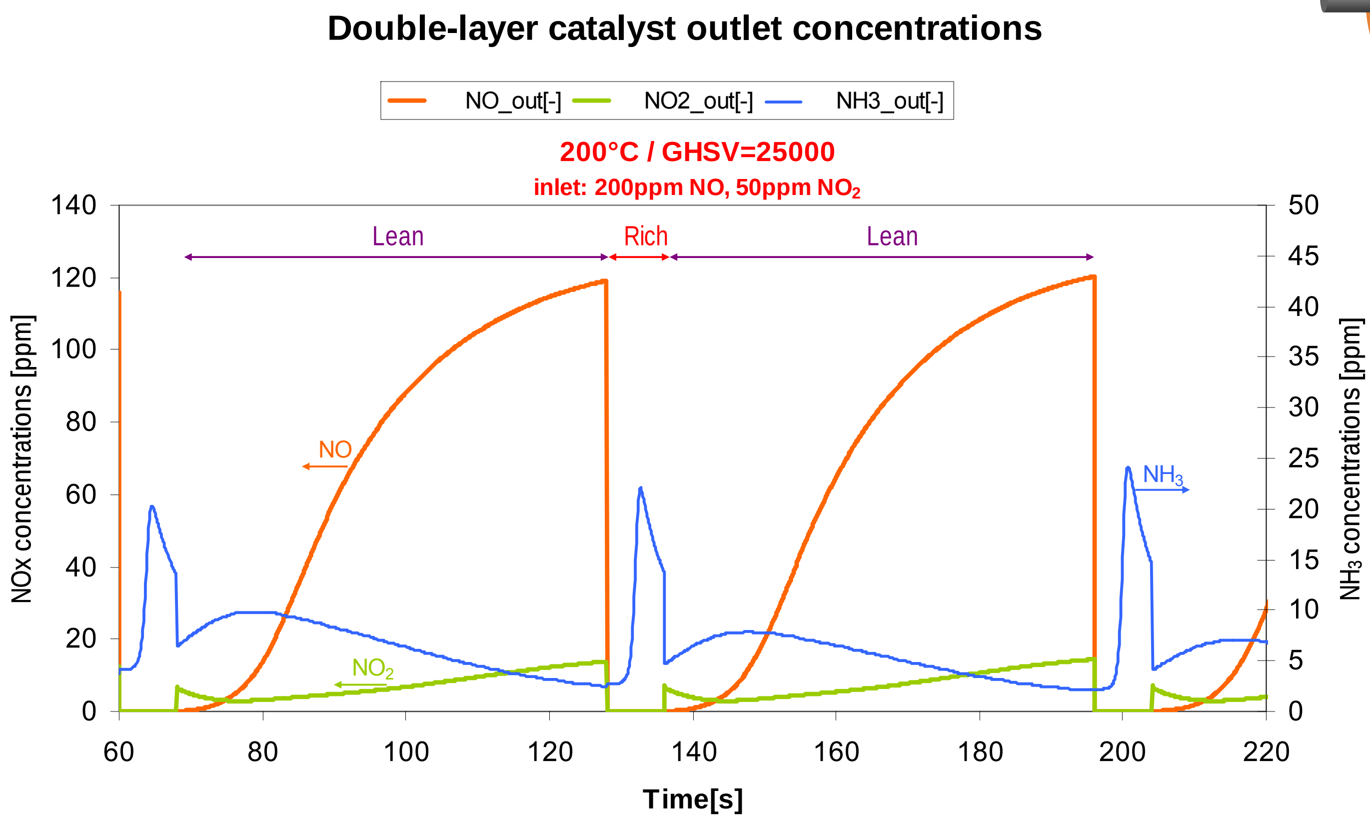
Double layer LNT-SCR catalyst





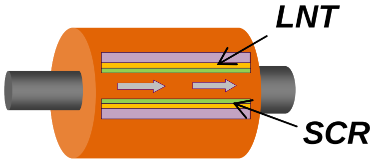
Double layer LNT-SCR catalyst
Results @ 200°C



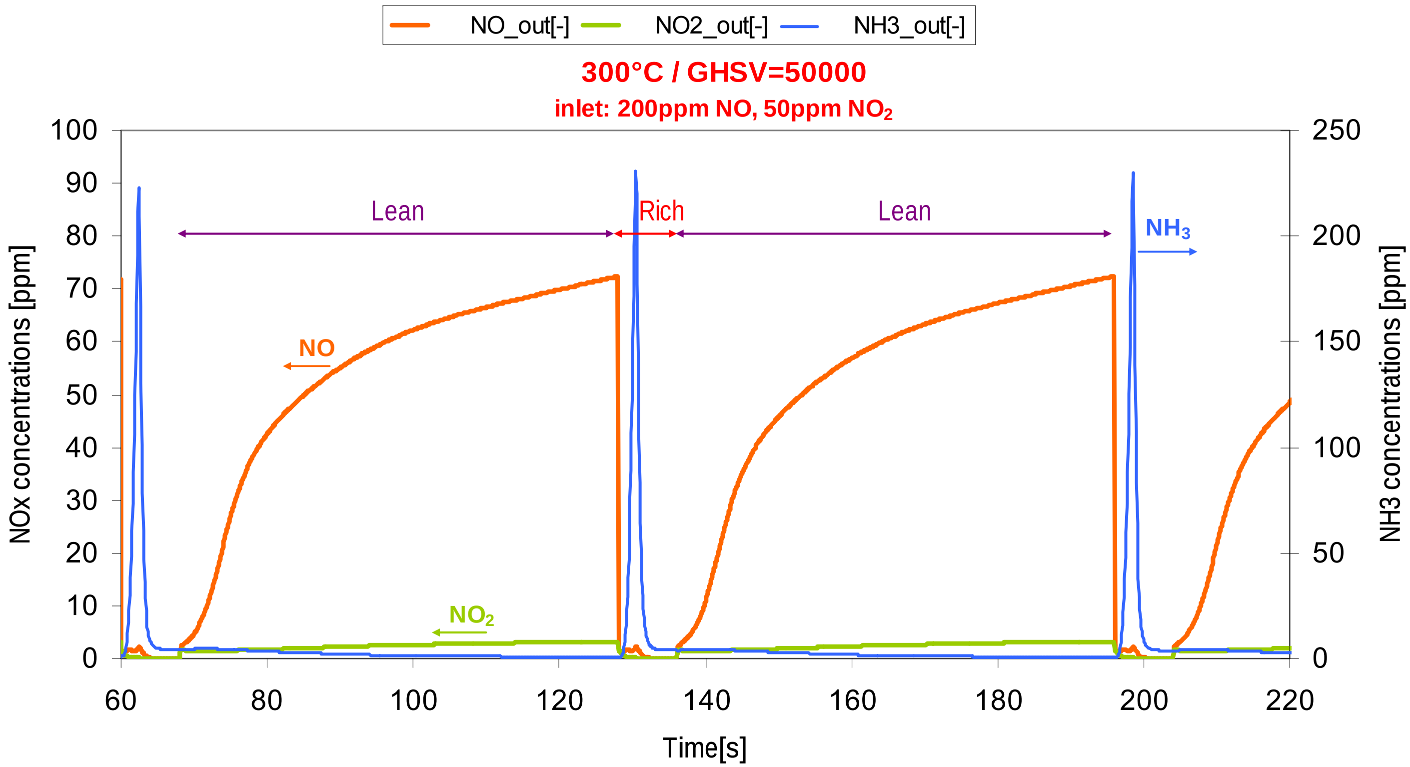


Qualitatively similar to the double bed system.
Less NH_3 slip compared to double bed.
Some NO_2 is breaking through.

Double layer LNT-SCR catalyst
Results @ 300°C



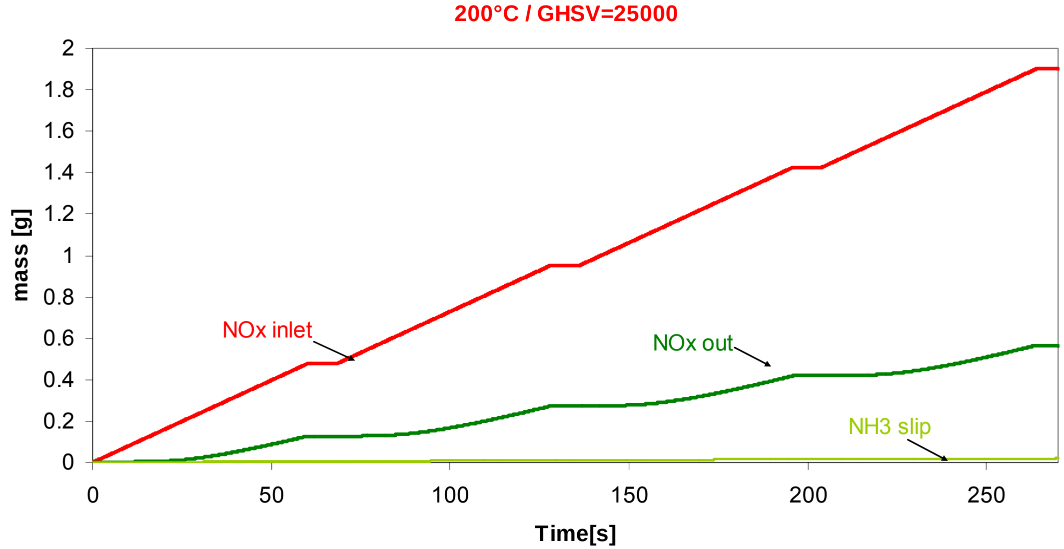
Double-layer catalyst outlet concentrations

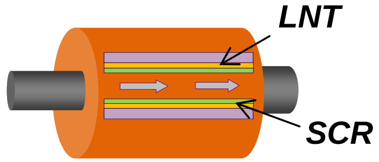


Almost zero NH_3 slip during lean mode.
Little NO_2 is breaking through.

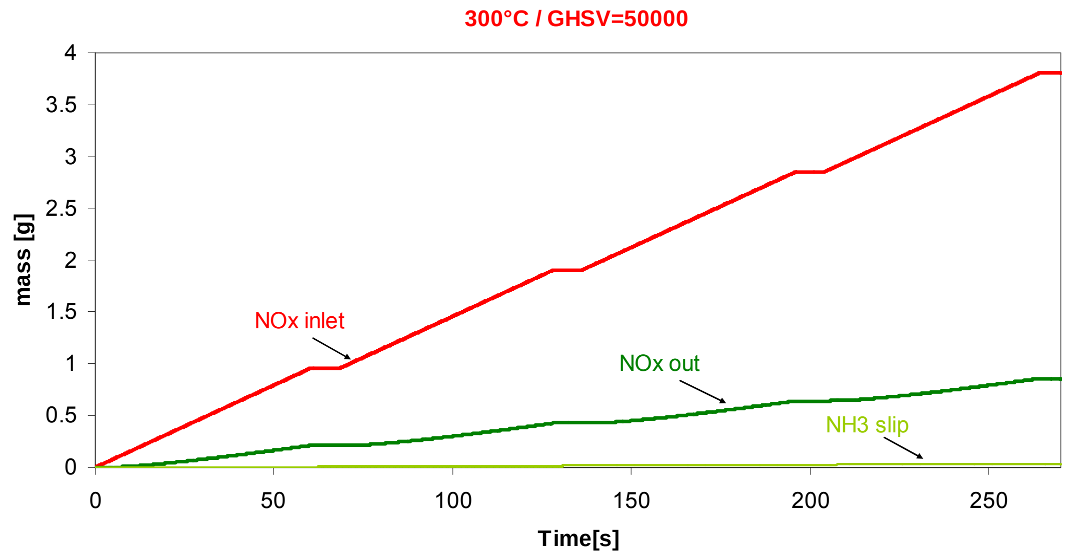
Double layer LNT-SCR catalyst
Comparative cumulative emissions

Exothermia



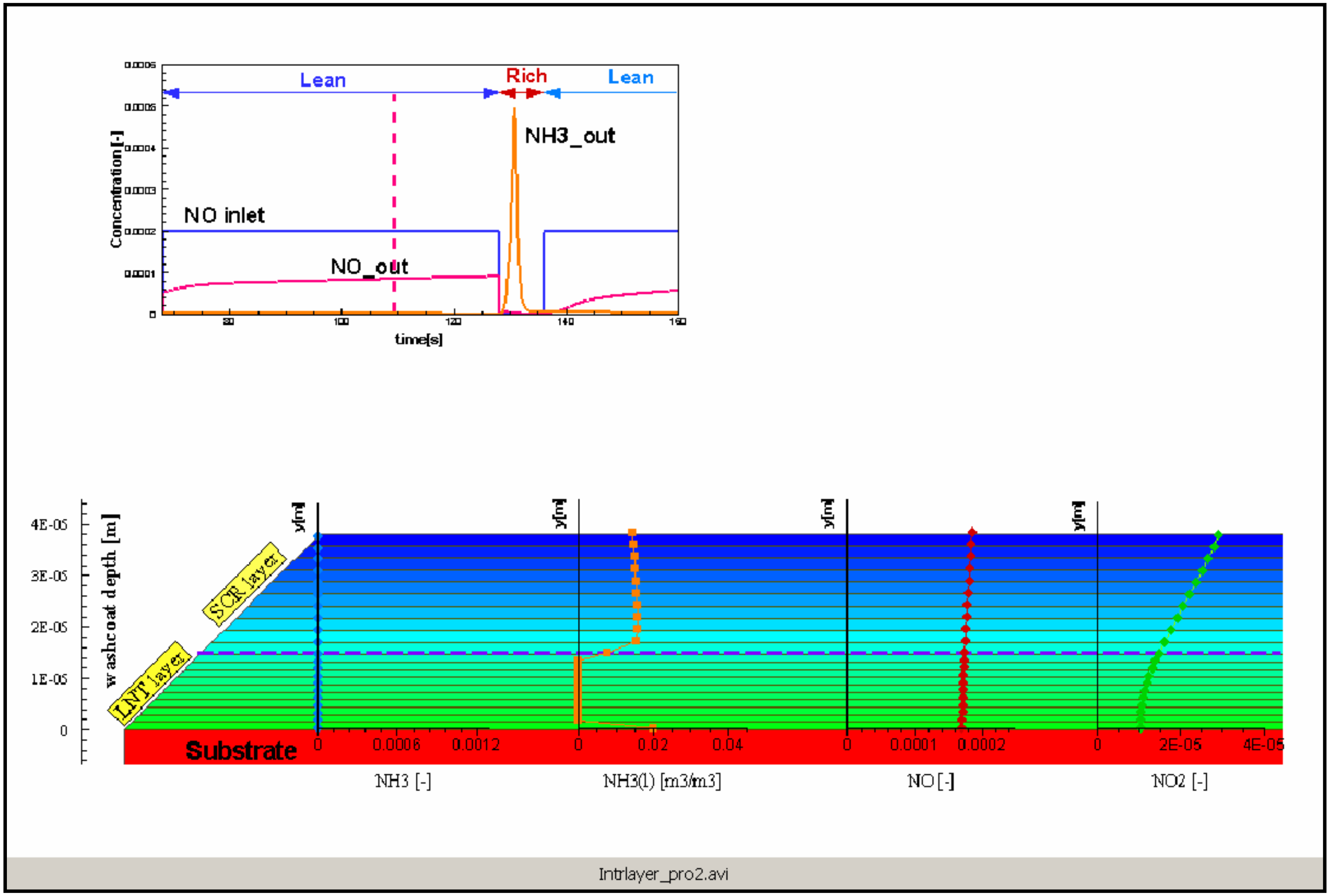


NH$_3$ slip is well controlled in both temperatures.



LAT

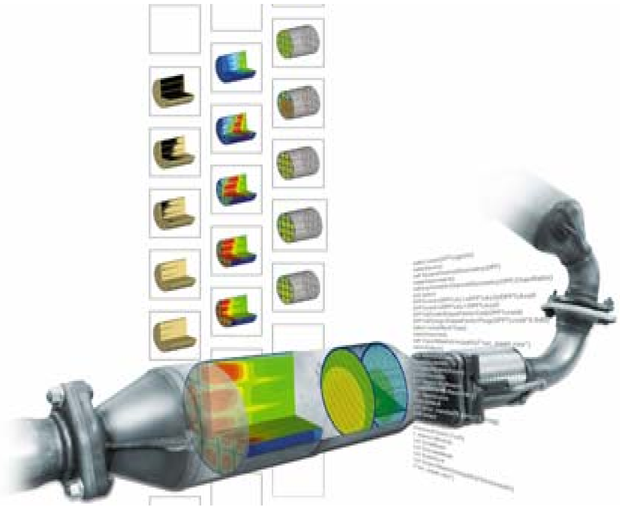
Calculated concentration profiles in the double-layer washcoat



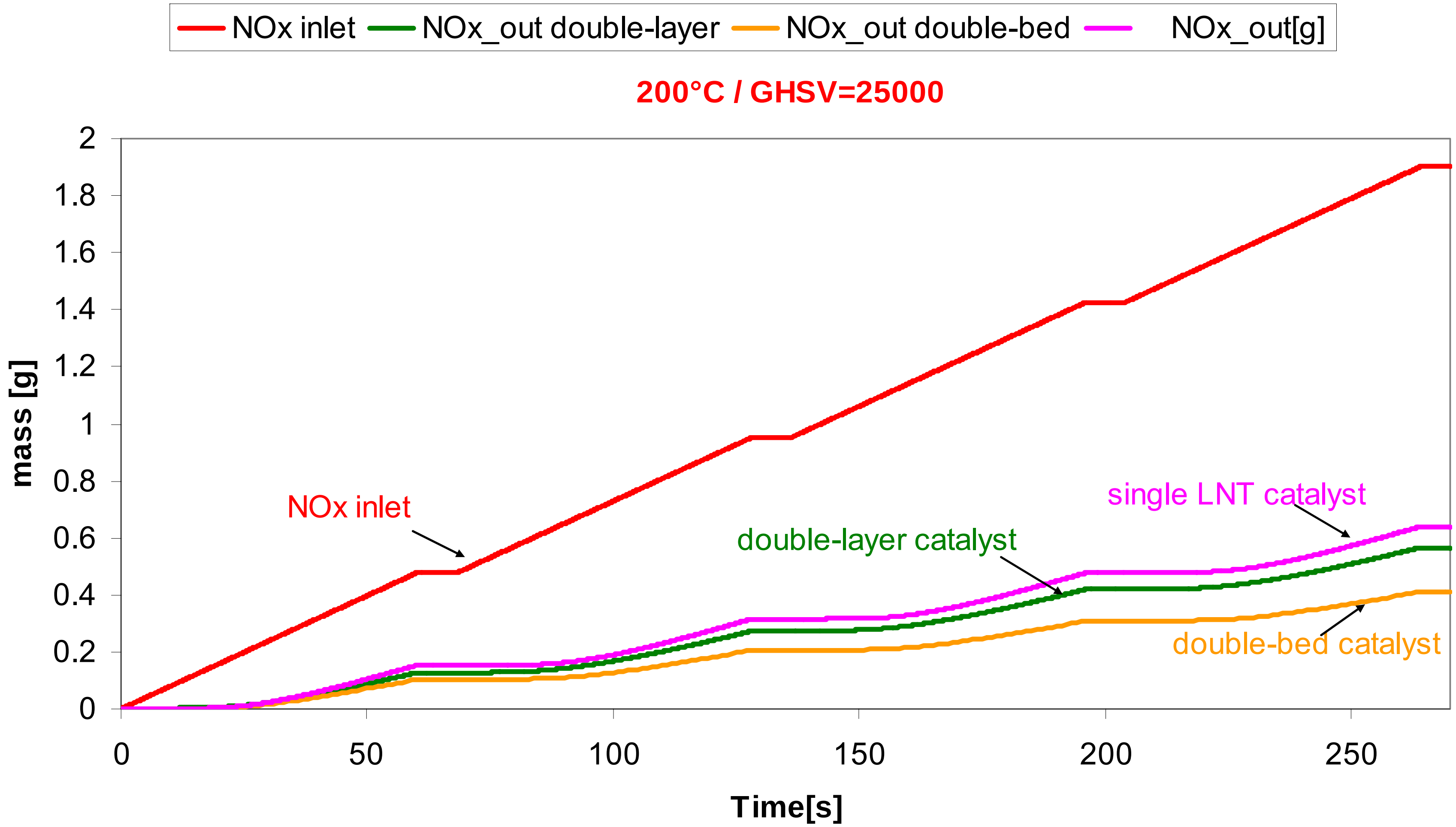
Profiles shown 1cm from inlet face

Exothermia
modeling efficiency

Numerical benchmarking summary

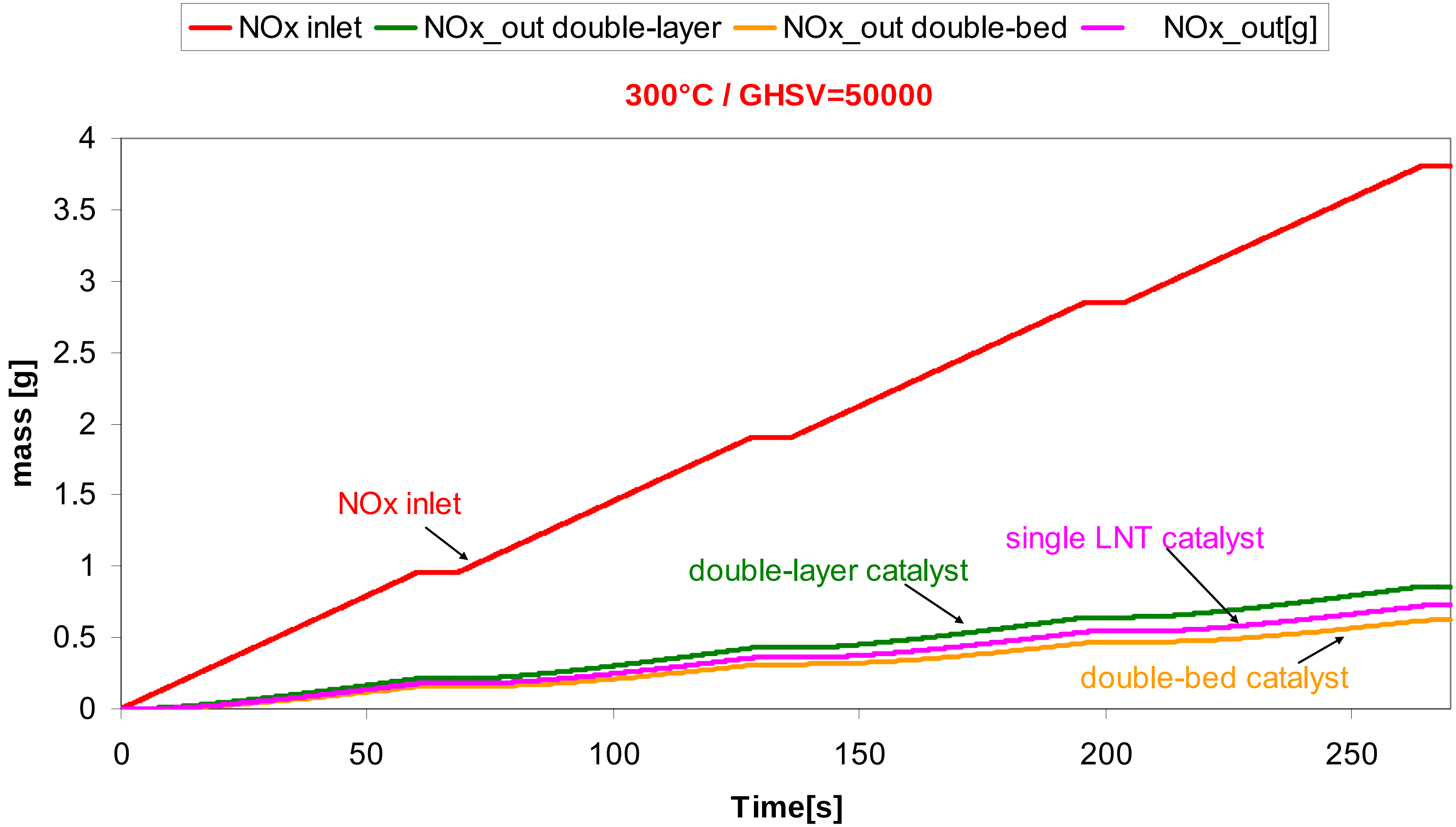


Benchmarking @ 200°C



Double-bed system is superior

Benchmarking @ 300°C

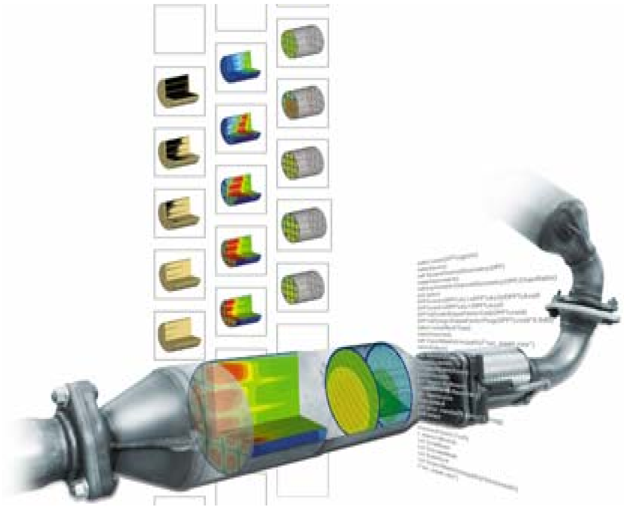


Double-layer system shows lower deNO$_x$ efficiency compared to single bed LNT. The explanation is related to washcoat diffusion effects.

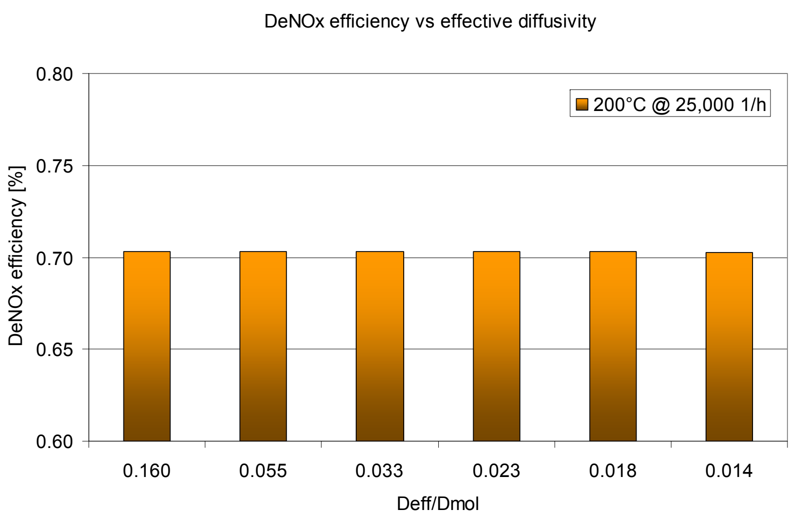
Washcoat diffusion

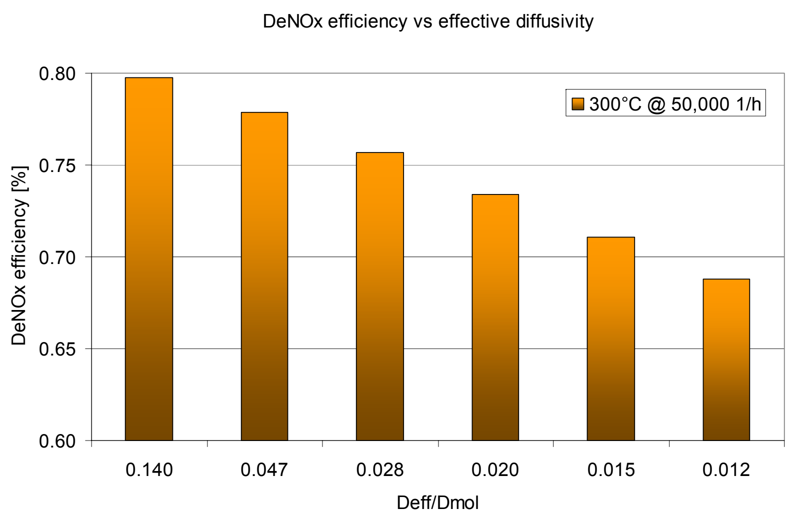
Effects on system performance

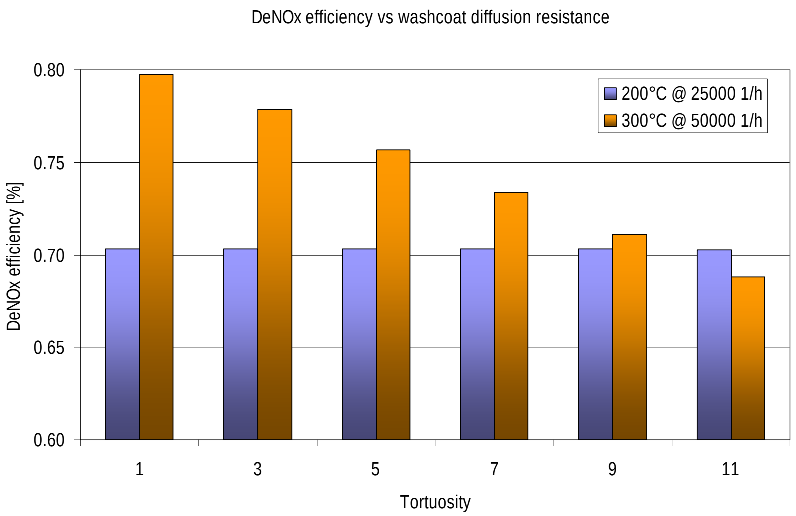
Sensitivity analysis



Washcoat limitation



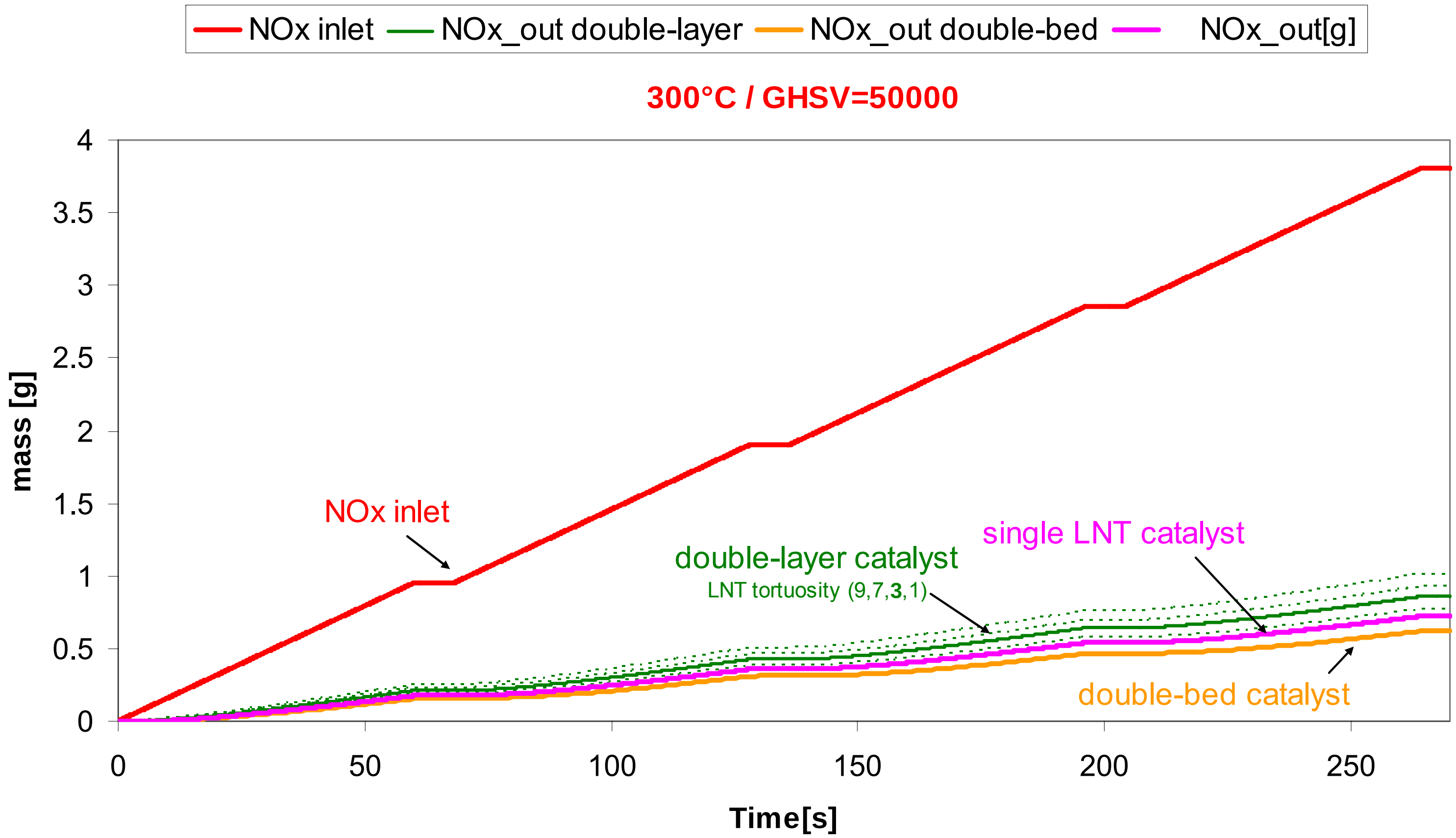




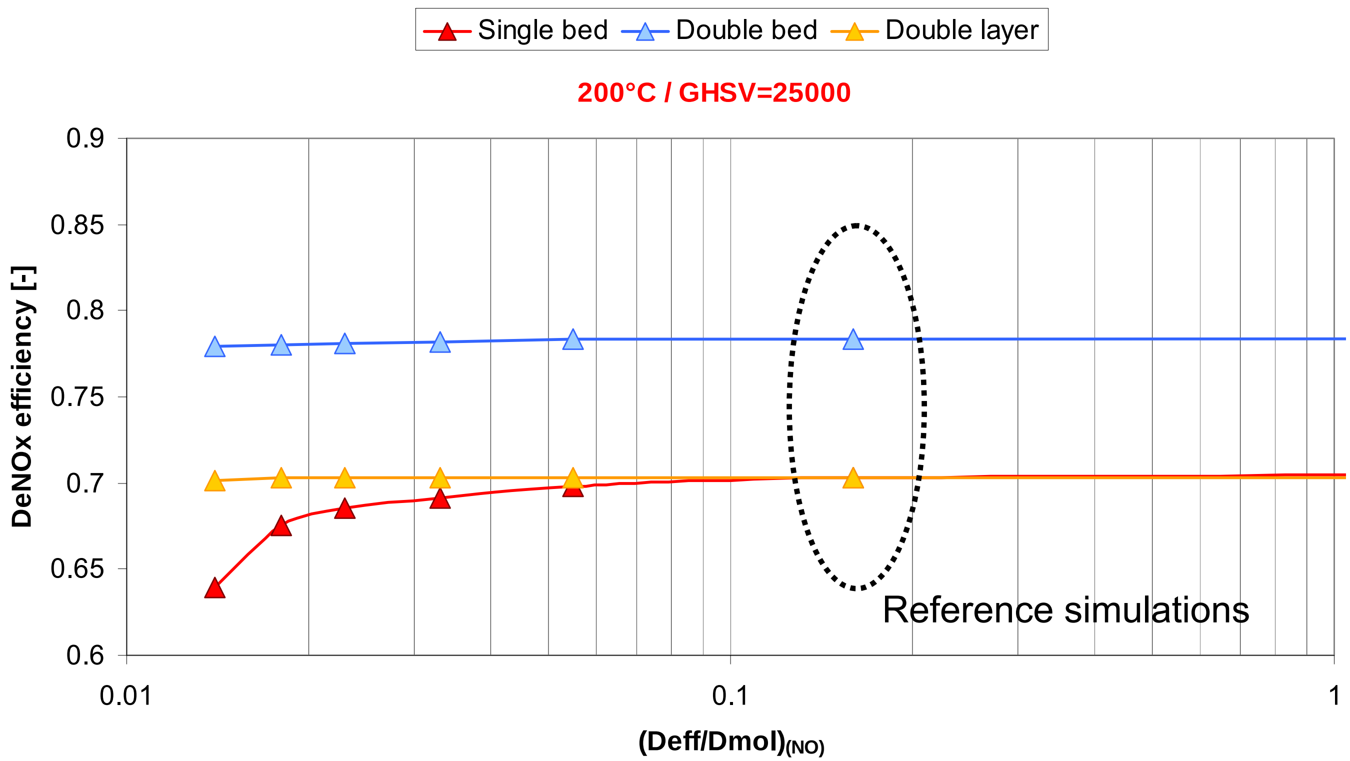
Washcoat properties:
porosity=0.57
Tortuosity= 1 - 11
Mean pore size = 70nm

Washcoat limitation

Double-layer versus double-bed catalyst

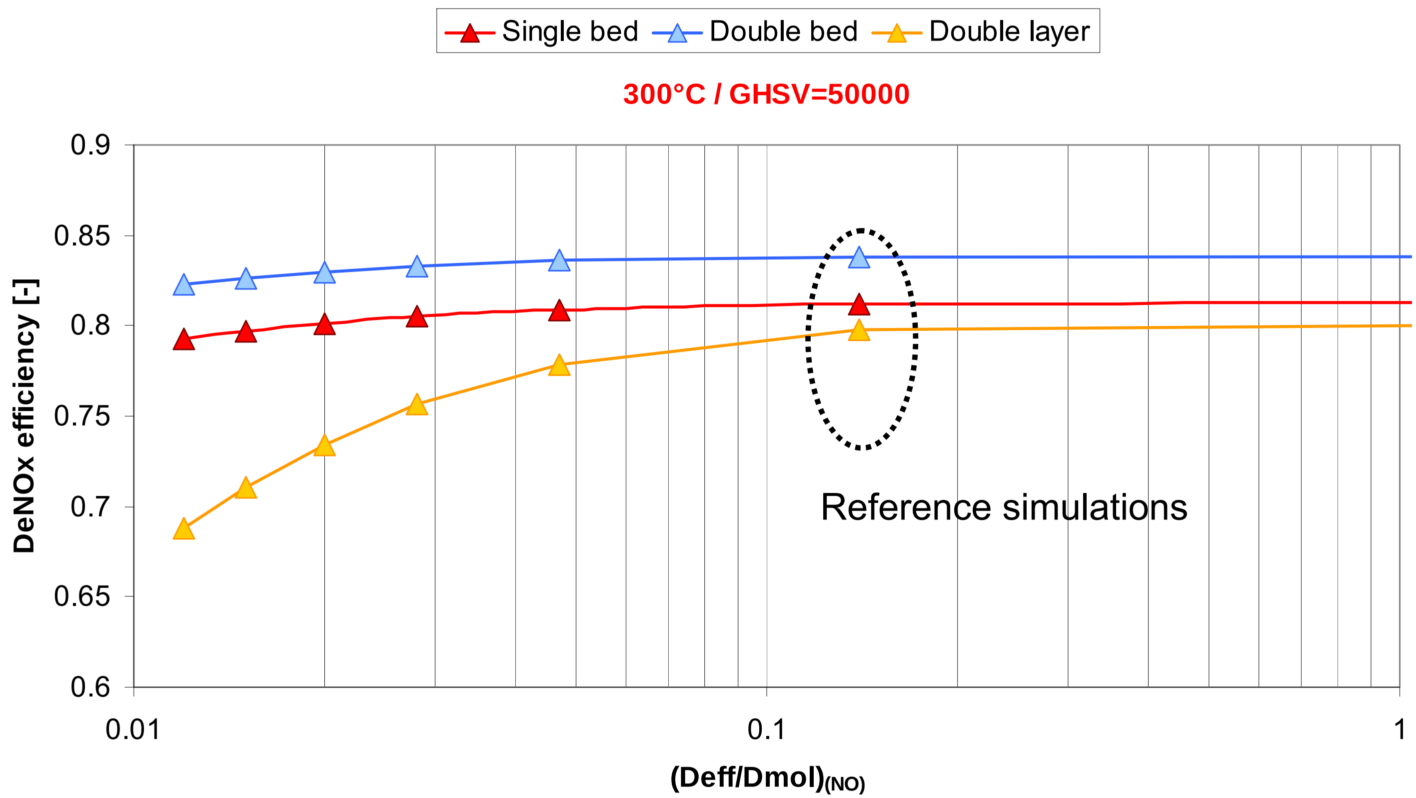


Washcoat diffusion limitation effects @ 200°C/25000 h^{-1}



At low temperature low GHSV
- the double-bed and double-layer systems are not affected by diffusion limitations
- the single bed LNT is affected for Deff values about 10 times lower than the reference value.

Washcoat diffusion limitation effects @ 300°C/50000 h^{-1}



At high temperature, high GHSV
- the double-layer system is most severely affected due to its thick layer

Conclusions

- Washcoat diffusion modeling is important under certain conditions
  - Thick/low-diffusivity washcoats
  - Extruded catalysts
  - Multiple layer catalysts
- LNT and SCR technologies can be combined towards optimizing deNO_x efficiency and minimizing NH_3 slip.
- Simulation based on calibrated models could provide insight in the governing physico-chemical mechanisms
- The present non-exhaustive study illustrated that the performance of the combined LNT-SCR systems is a non-trivial function of temperature, flow-rate, composition, L/R cycling and washcoat properties
- Future work should focus on realistic assessments of washcoat properties and experimental validations in combined LNT-SCR systems.

Thank you very much for your attention!

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www.exothermia.com