Modeling and Simulation of NO_x Abatement with Storage/Reduction Catalysts for Lean Burn and Diesel Engines

Jan Koop and Olaf Deutschmann

Institute for Chemical Technology and Polymer Chemistry
University of Karlsruhe, Germany

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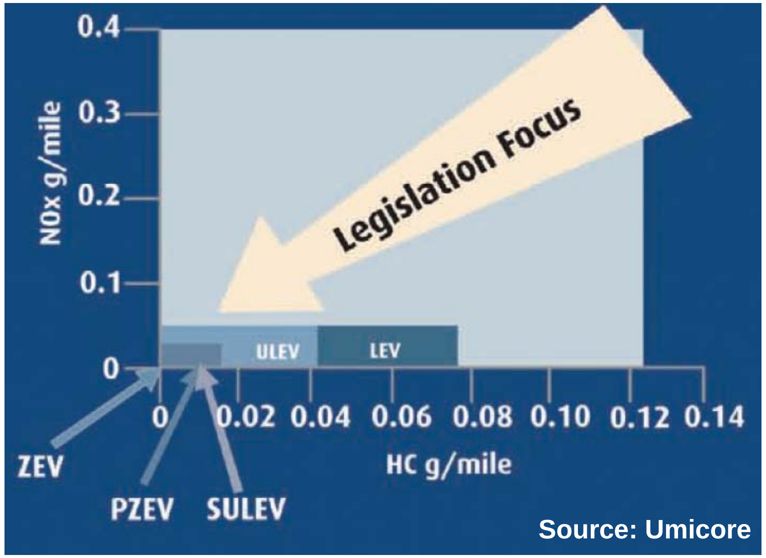
Introduction



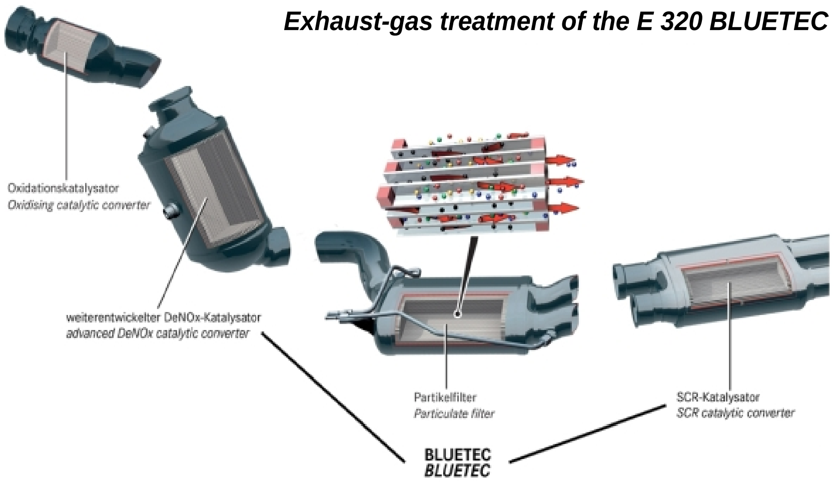
- ❑ Increasing number of vehicles
- ❑ More stringent Emission Regulations (specially in Europe and California)

➡ ***Solution:*** **Lean operated engines**
→ less fuel consumption

➡ **demand for new types of catalytic exhaust-gas aftertreatment, e.g.**

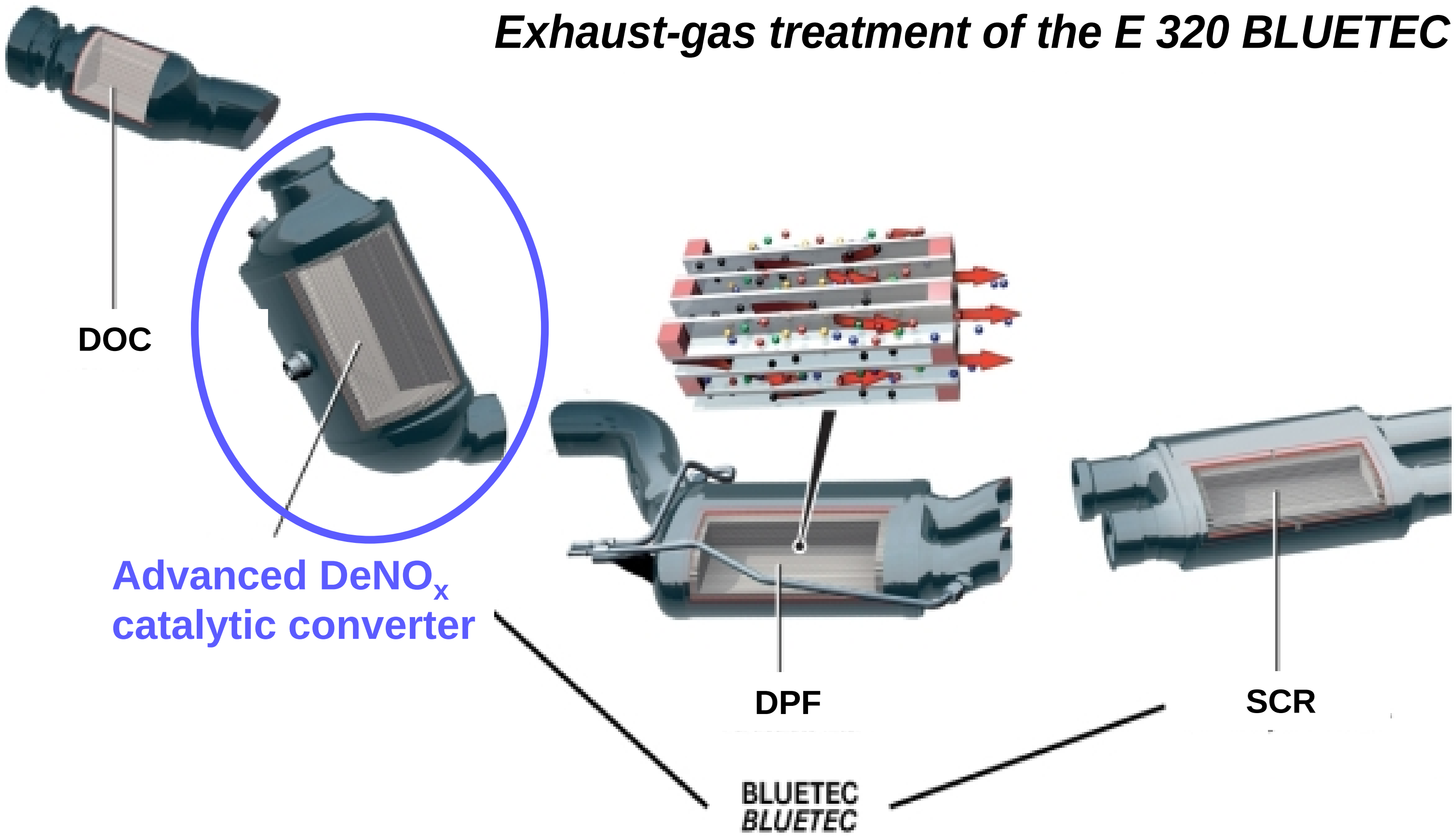
- ❑ Diesel Particle Filter (DPF)
- ❑ Urea-SCR
- ❑ NO_x-storage catalyst (NSC)

Exhaust-gas treatment of the E 320 BLUETEC



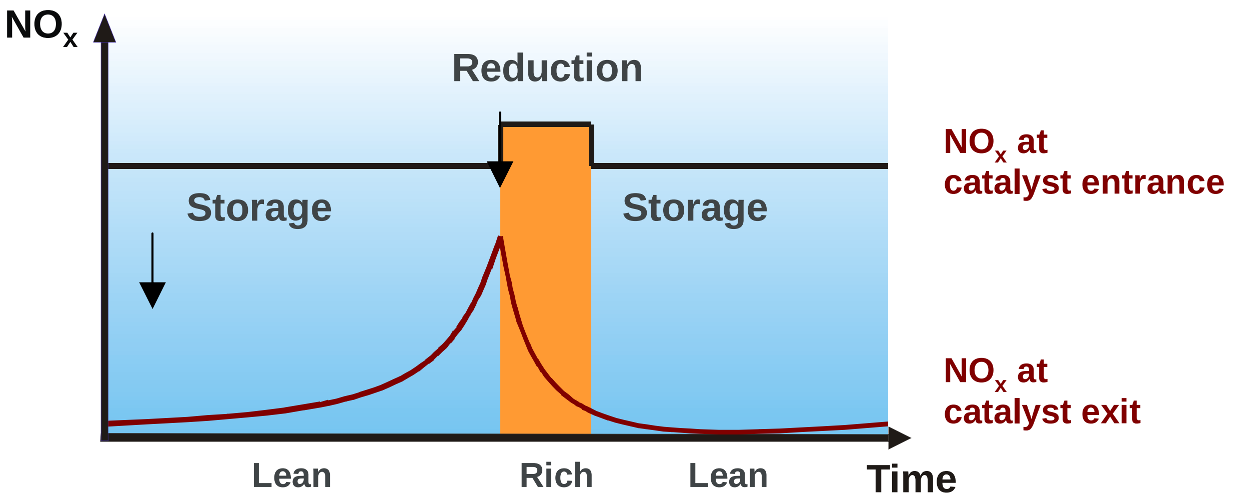
Introduction

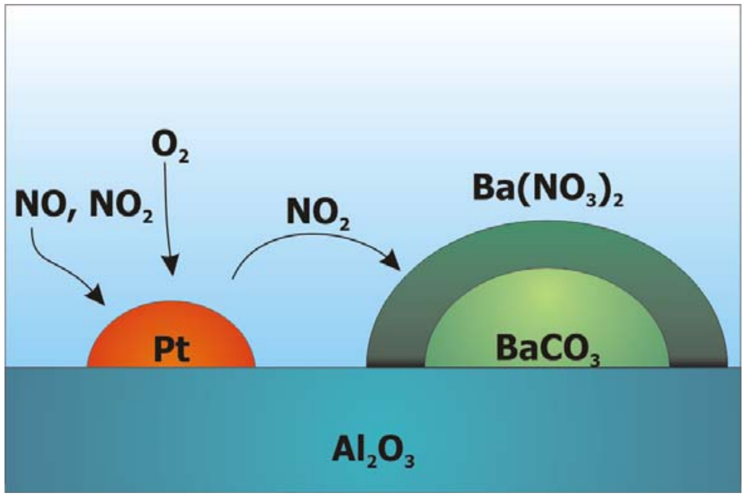
Exhaust-gas treatment of the E 320 BLUETEC



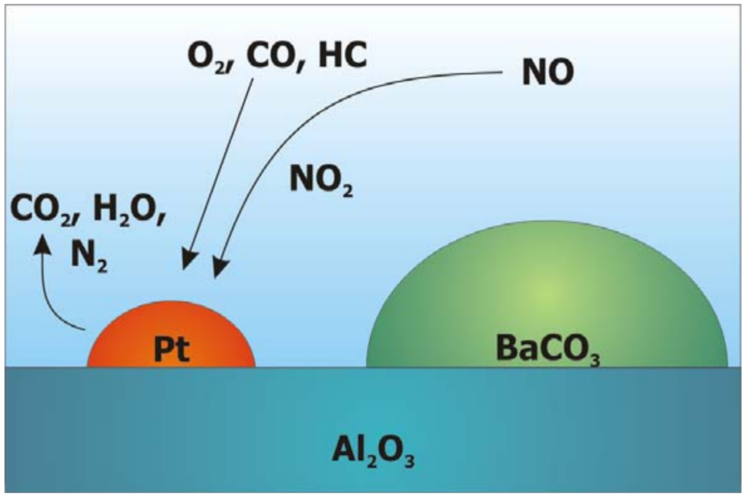
Source: DaimlerChrysler

Function of the NO_x Storage and Reduction Catalyst





Lean phase – O_2 rich



Rich phase – O_2 deficit

Model Specifications

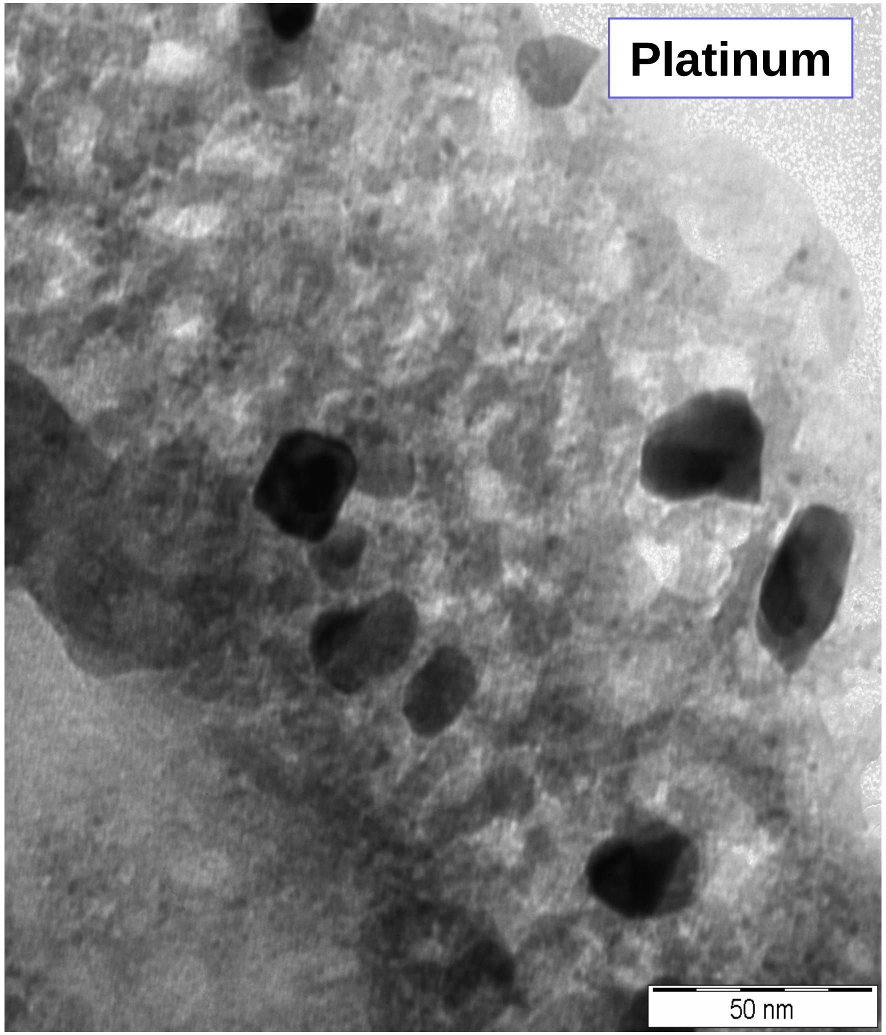
- **Well-defined Model Catalysts: Pt/Al_2O_3 and Pt/Ba/Al_2O_3**
- **Dimension: *3 cm* (Width), *20 cm* (Length)**
- **Realistic Exhaust-gas Composition:**

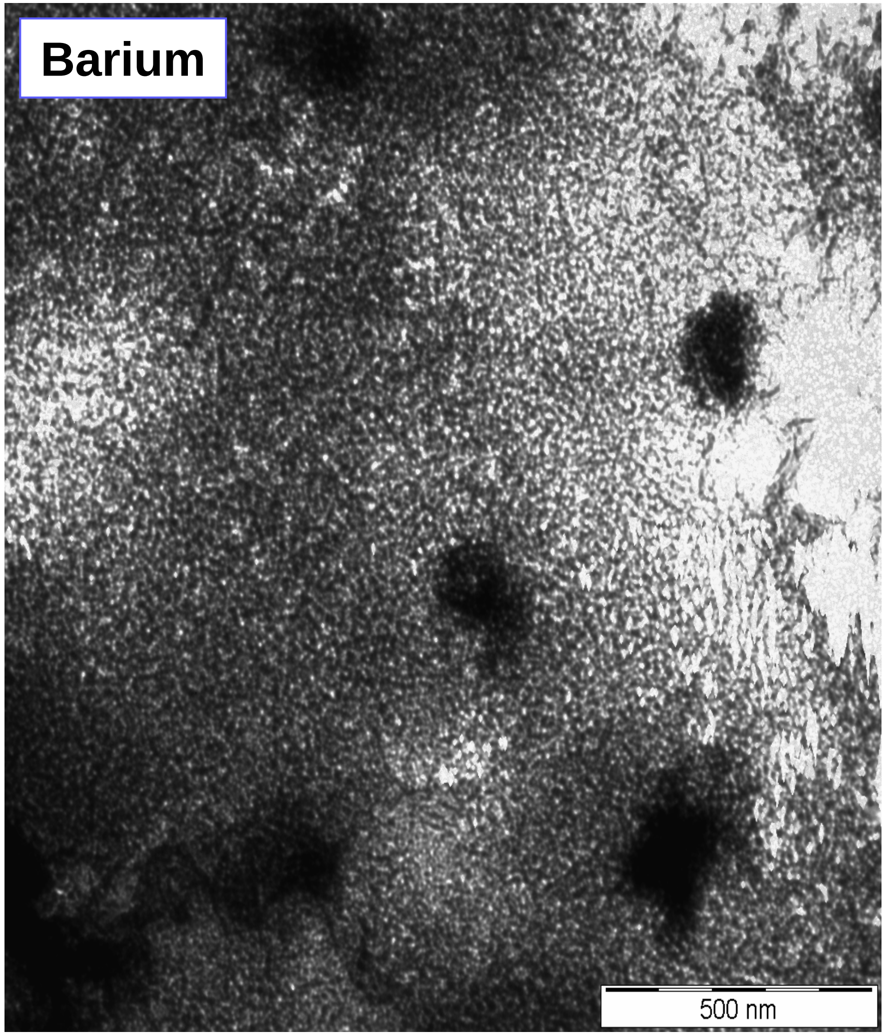
	NO [ppm]	NO_2 [ppm]	O_2 [Vol.-%]	C_3H_6 [ppm]	CO [Vol.-%]	CO_2 [Vol.-%]	H_2O [Vol.-%]	H_2 [Vol.-%]
Lean	200	40	12	60	0,04	7	10	0
Rich	200	40	0,9	60	2,1	7	10	0,7

- **Isothermal Flatbed Reactor**
- **NO_x Long-Term Storage Experiments**
- **Lean/Rich Cycling 300s/15s and 60s/5s *(realistic time scale)***
- ***SV= 40000 h^{-1}***
- ***T= 250 - 450°C***

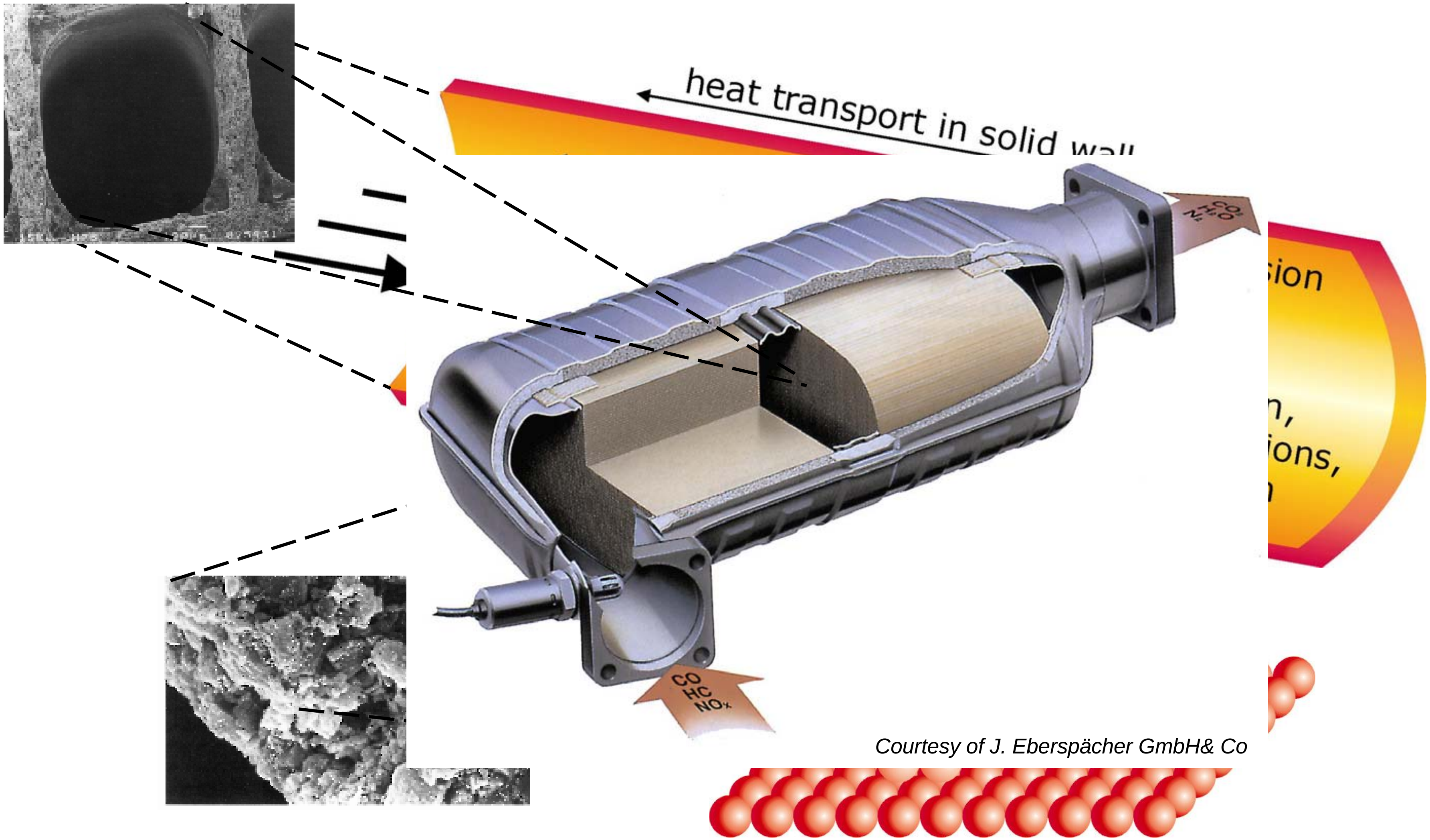
TEM-Images of Platinum and Barium Particles

Pt/Ba/Al_2O_3 Catalyst (aged: 4h, 700°C, 10% H_2O)



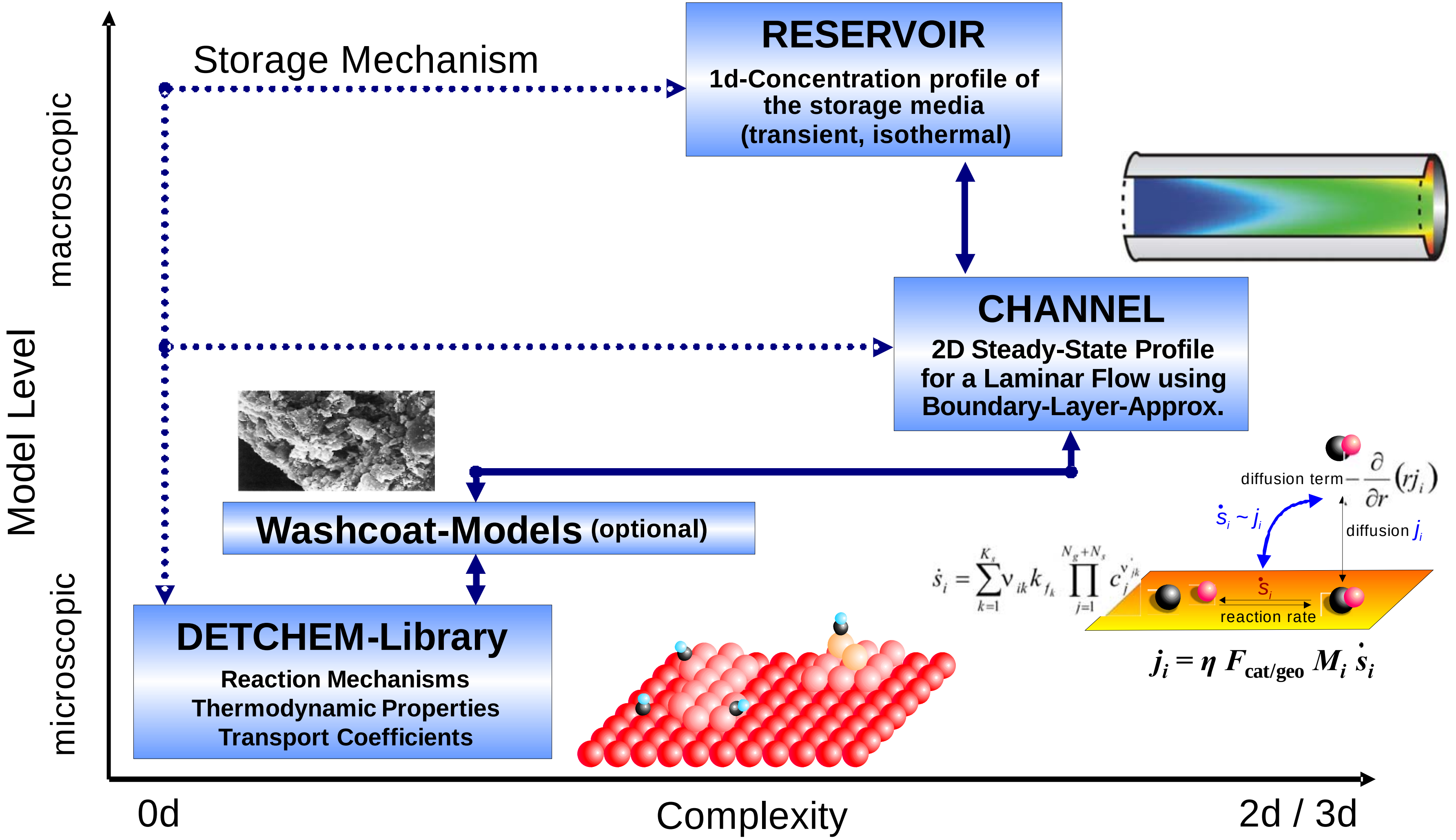


Hierarchical Modeling of a NSC



Courtesy of J. Eberspächer GmbH& Co

Simulation Program DETCHEM^{RESERVOIR}



Tischer, S. and O. Deutschmann (2005). Catalysis Today 105(3-4): 407-413

Elementary-step Mechanism on Platinum

HC-decomposition:

$C_3H_6 + 2\,* \leftrightarrow C_3H_6*$

$C_3H_6* \leftrightarrow C_3H_5* + H*$

$C_3H_5* + * \leftrightarrow C_2H_3* + CH_2*$

$CH_3* + * \leftrightarrow CH_2* + H*$

$CH_2* + * \leftrightarrow$ C…

$CH* + * \leftrightarrow$ C…

$C_2H_3* + O* \leftrightarrow$ …

$CH_3CO* + * \leftrightarrow CH_3* + CO*$

$CH_3* + O* \leftrightarrow OH* + CH_2*$

$CH_2* + O* \leftrightarrow OH* + CH*$

$CH* + O* \leftrightarrow OH* + C*$

$C_3H_6 + * + O* \leftrightarrow C_3H_5^+ + OH*$

$C_3H_5^+ + O* \rightarrow C_3H_4^+ + OH*$

$C_3H_4^+ + 4\,O* + 2\,* \rightarrow 3\,C* + 4\,OH*$

C-O-Reaction:

$CO + * \leftrightarrow CO*$

$CO_2 + * \leftrightarrow CO_2*$

$CO* + O* \leftrightarrow CO_2* + *$

$C* + O* \leftrightarrow CO* + *$

N-O-Reaction:

…

$NO + O* \leftrightarrow NO_2*$

$NO* + O* \leftrightarrow NO_2*$

$NO* + N* \leftrightarrow N_2O*$

$NO* + H* \leftrightarrow N* + OH*$

$NO_2* + H* \leftrightarrow NO* + OH*$

…on:

… $\leftrightarrow 2\,O*$

$H_2 + 2\,* \leftrightarrow 2\,H*$

$H_2O + * \leftrightarrow H_2O*$

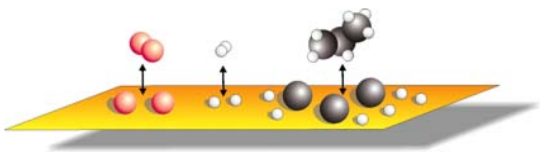
$H* + O* \leftrightarrow OH* + *$

$OH* + H* \leftrightarrow H_2O* + *$

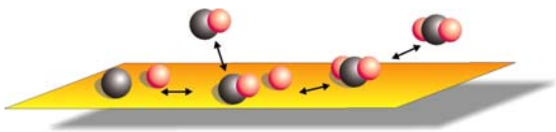
$2\,OH* \leftrightarrow H_2O* + O*$

70 Elementary-step Reactions with 35 surface species and 10 gas-phase species

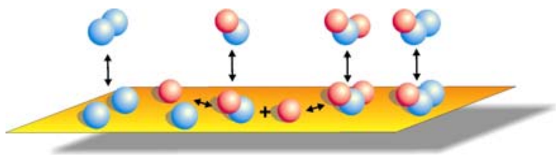
D. Chatterjee, O. Deutschmann and J. Warnatz (2001). Faraday Discussions 119 :371-384



Hydrocarbons

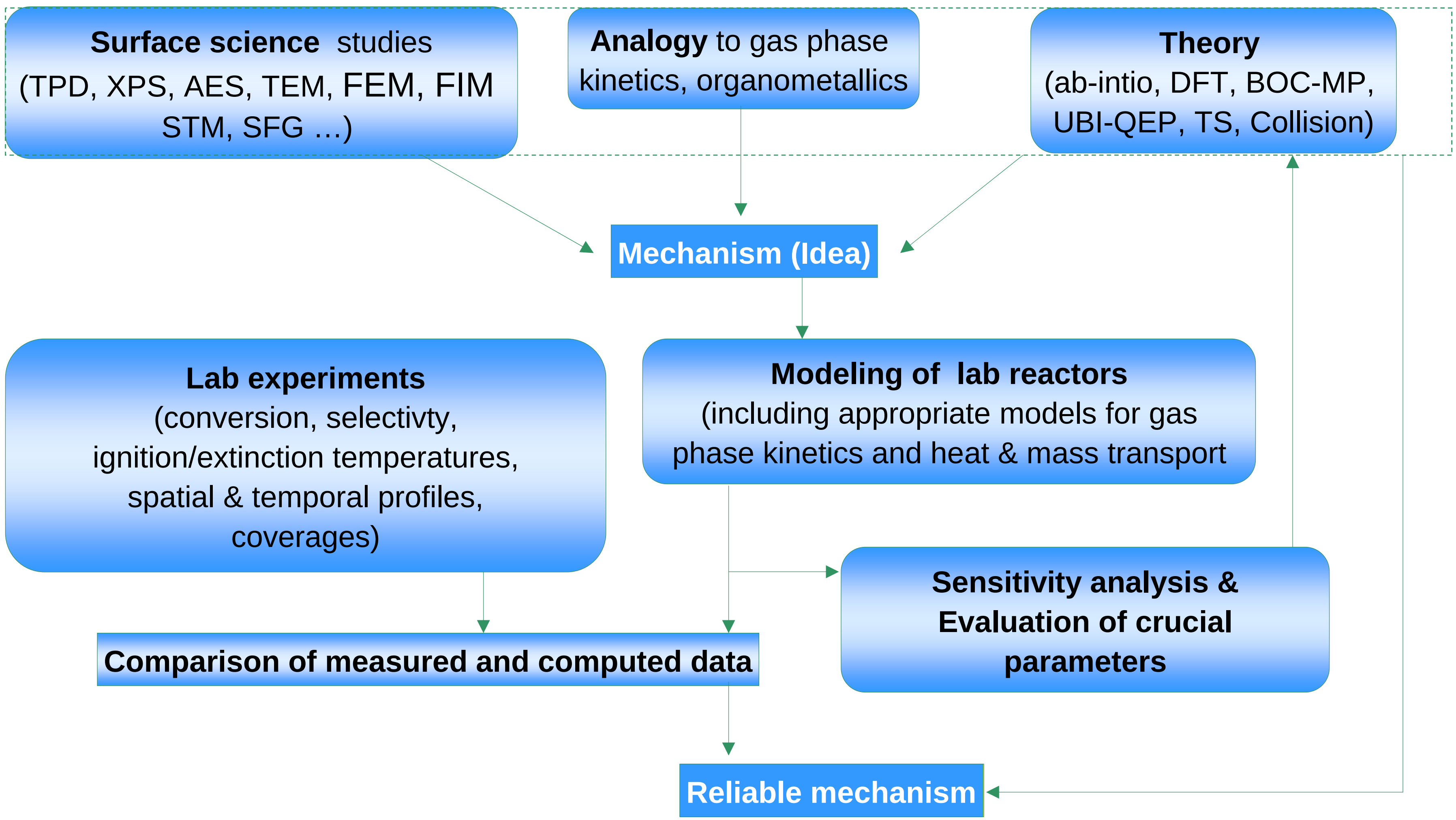


Carbon monoxide

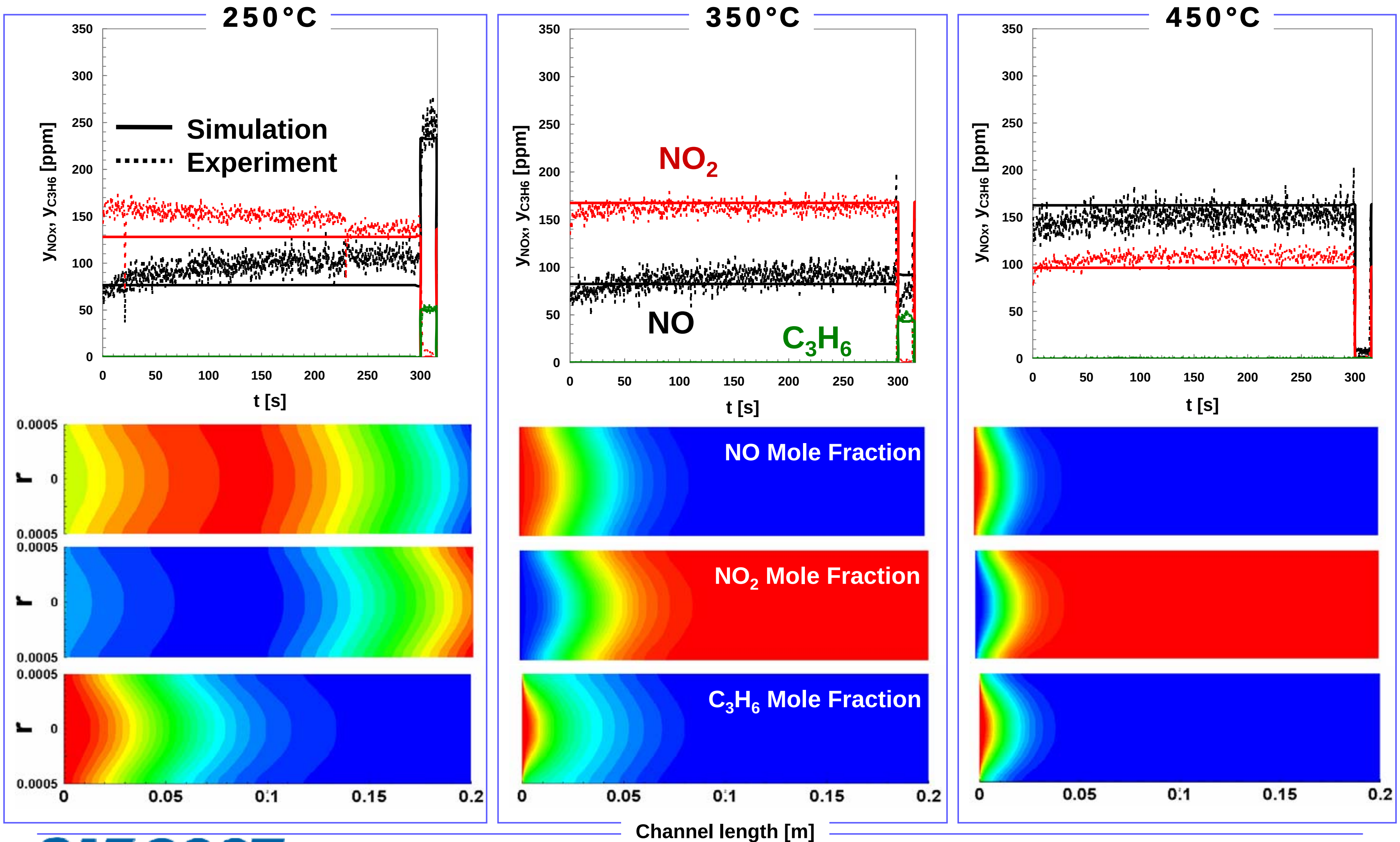


Nitric oxide

Development of heterogeneous reaction mechanisms

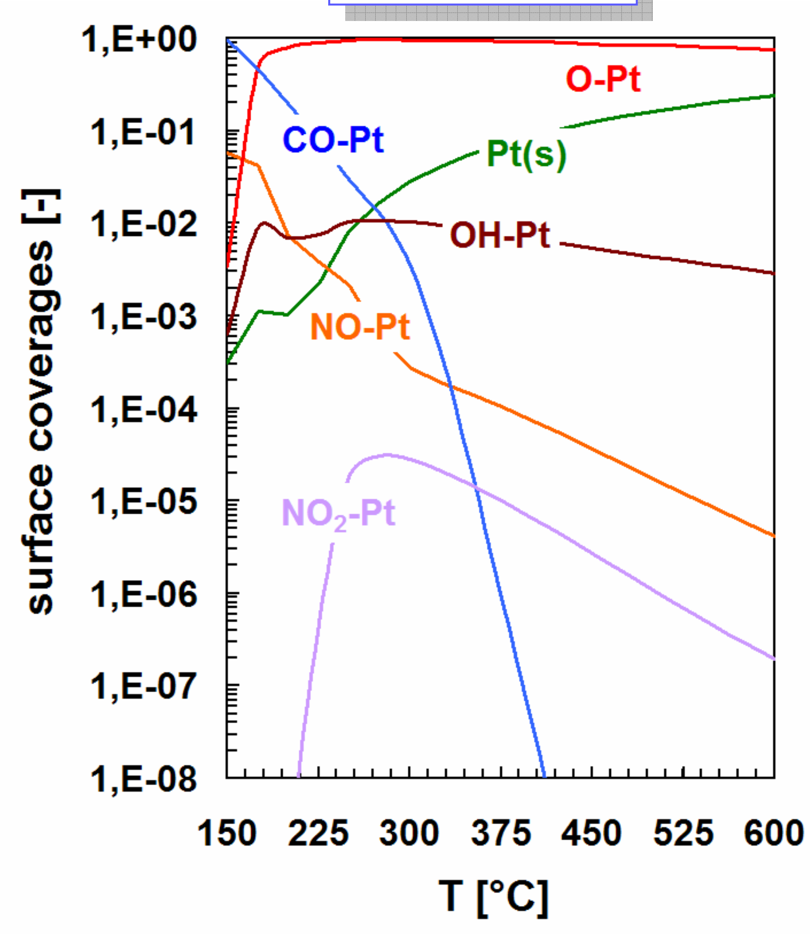


Lean/Rich Cycle (300s/15s) and Axial Profiles for Pt/Al_2O_3

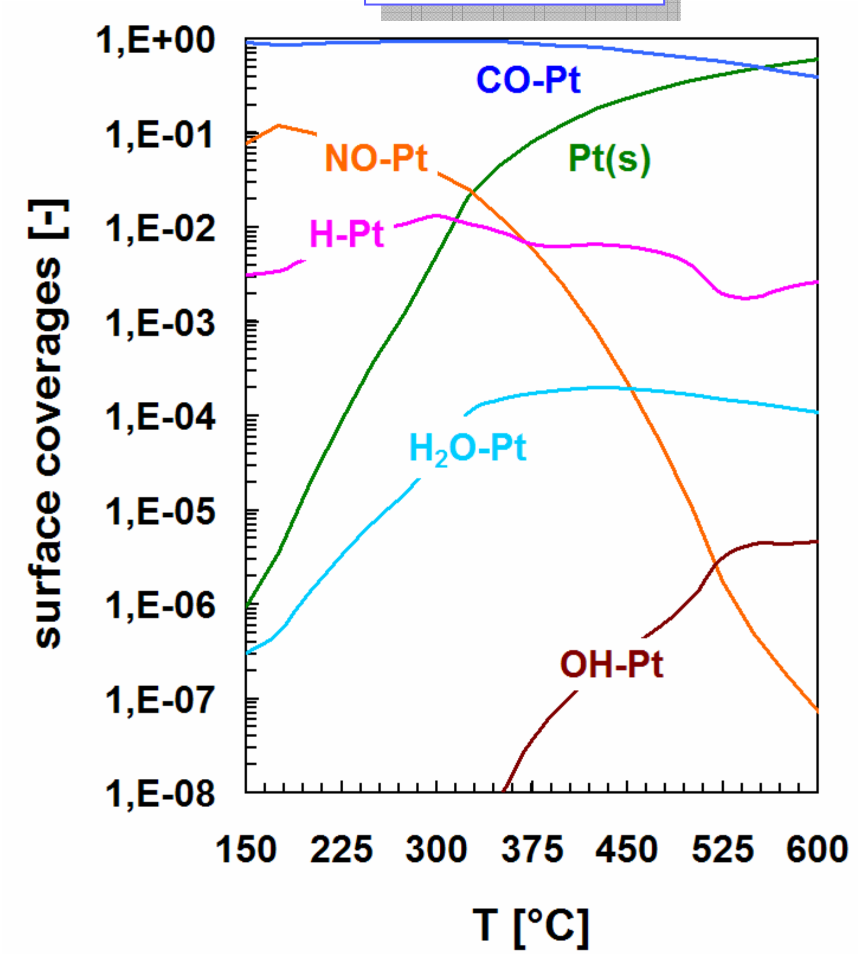


Simulated Surface Coverages on Platinum

Lean Phase



Rich Phase



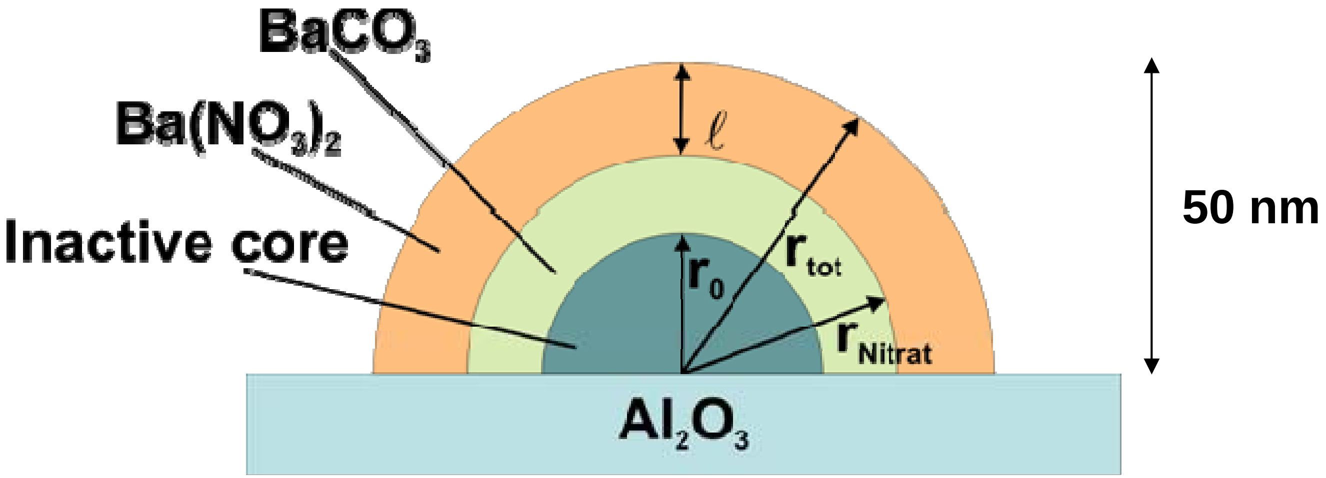
→ Model enables the prediction of the concentration profiles along the channel length and gives detailed insight into the surface coverages of the lean/rich phase

Storage Reactions on Barium

- **$BaCO_3 + 2NO_2 + ½O_2 \leftrightarrows Ba(NO_3)_2 + CO_2$**
- **$BaCO_3 + 2NO + ½O_2 \leftrightarrows Ba(NO_2)_2 + CO_2$**
  $Ba(NO_2)_2 + O_2 \rightarrow Ba(NO_3)_2$
- **$BaCO_3 + 3NO_2 \leftrightarrows Ba(NO_3)_2 + NO + CO_2$**

Modeled as Global Reactions <u>with</u> Shrinking Core Model, due to Diffusion Limitation during Storage Process

Shrinking Core Model with an Inactive Core



$$R_{diff} = 4\pi r^2 * D_S * \frac{\partial c}{\partial r}$$

At the interface Nitrate-Carbonate: $r = r_{Nitrate}$

$$\dot{r}_{NO2-O2-Ba} * A_{Particle} = R_{diff}$$

Olsson, L., R. J. Blint, et al. (2005) Industrial & Engineering Chemistry Research 44(9): 3021-3032.
Tuttlies, U., V. Schmeisser, et al. (2004) Chemical Engineering Science 59(22-23): 4731-4738.

Shrinking Core Model with an Inactive Core

$$\tfrac{1}{2}BaCO_3 + NO_2 + \tfrac{1}{4}O_2 \leftrightarrows \tfrac{1}{2}Ba(NO_3)_2 + \tfrac{1}{2}CO_2$$

$$\dot{r}_{NO2-O2-Ba} = \tilde{k}_f * c_{NO2} * c_{O2}^{1/4} * \Theta_{BaCO3} - \tilde{k}_b * c_{CO2}^{1/2} * \Theta_{Ba(NO3)2}$$

Rate coefficients

$$\tilde{k}_f = \frac{k_f}{1 + k_f * \tau} \qquad \tilde{k}_b = \frac{k_b}{1 + k_f * \tau}$$

$$k_f = A_f * T^{\beta} * e^{-\frac{Ea,f}{RT}}$$

$$k_b = \frac{k_f}{K^{eq}_{NO2-O2-Ba}} = \frac{k_f}{\exp\left(-\frac{\Delta_R H}{RT} + \frac{\Delta_R S}{R}\right)}$$

Inhibition term: $$\tau = \frac{\ell}{D_S} * \frac{r_{Nitrat}}{r_{tot}}$$

→ Increasing inhibition term gives rise to a decreased rate coefficient

Reduction Reactions on Barium

- ***Carbon Monoxide CO***

  $Ba(NO_3)_2 + 3\ CO \rightarrow BaCO_3 + 2\ NO + 2\ CO_2$

- ***Hydrogen H_2***

  $Ba(NO_3)_2 + 3H_2 + CO_2 \rightarrow BaCO_3 + 2NO + 3H_2O$

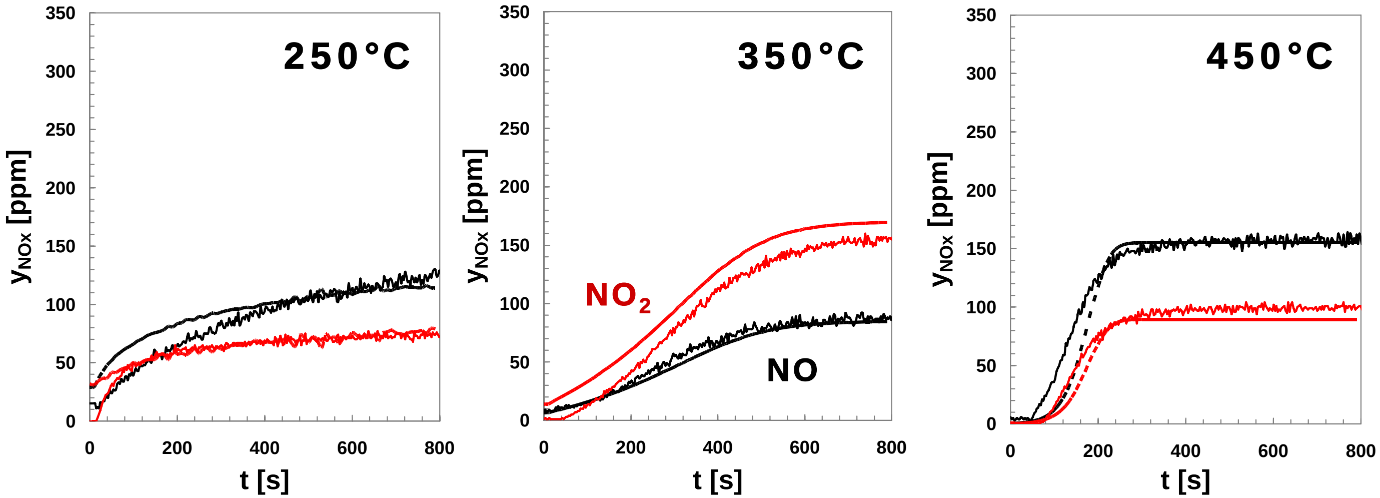
- ***Propylene C_3H_6***

  $Ba(NO_3)_2 + {}^1/_3 C_3H_6 \rightarrow BaCO_3 + 2NO + H_2O$

Modeled <u>without</u> Shrinking Core Model, no Diffusion Limitation during Regeneration

Parameterization of Storage/Reduction Reactions on Pt/Ba/Al_2O_3

NO_x Long-Term Storage Experiments

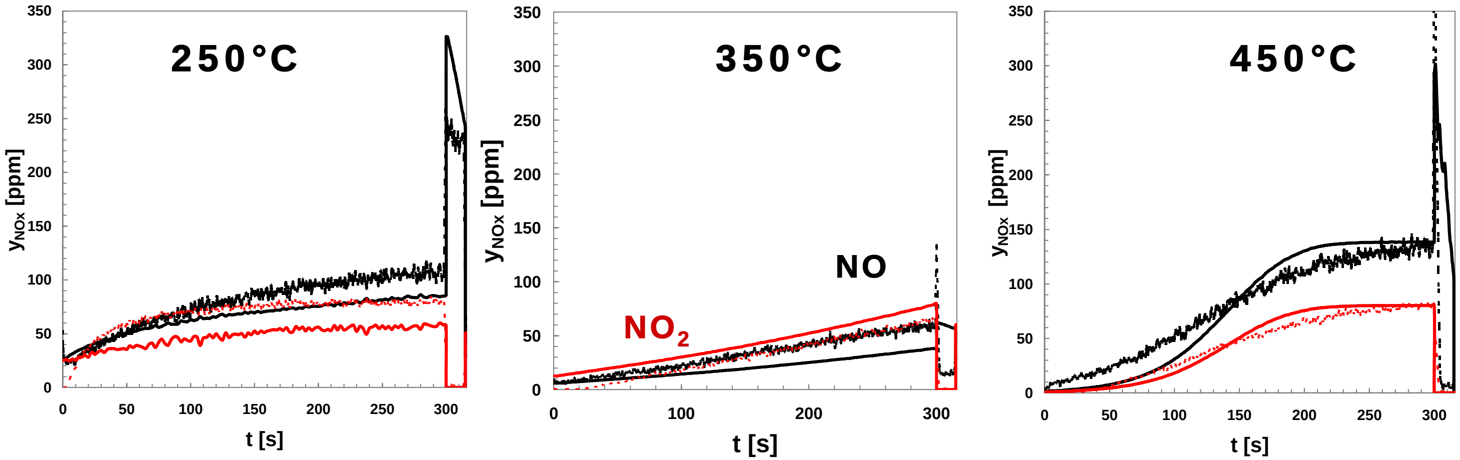


Simulation

Experiment

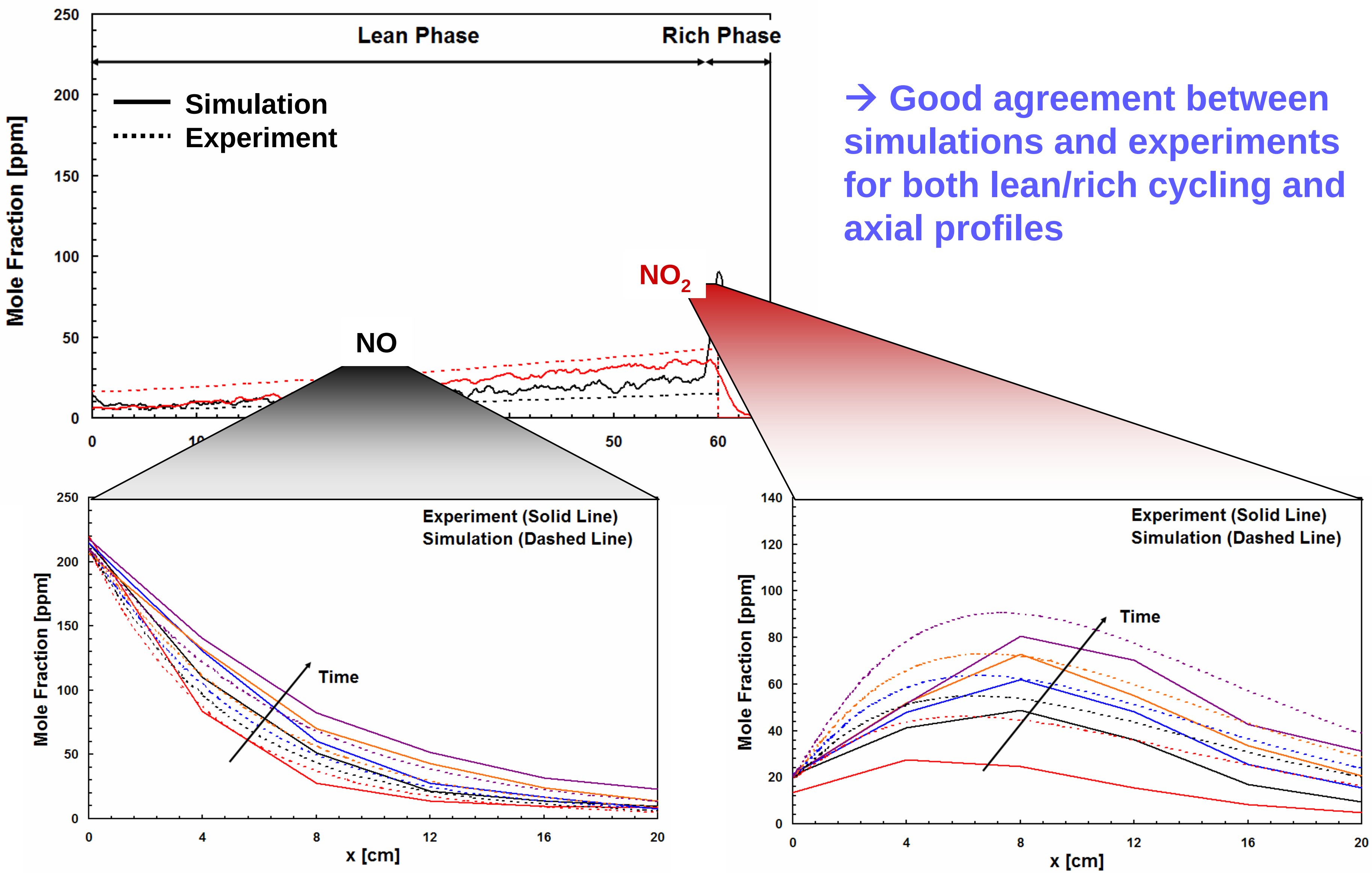
Lean/Rich Cycling

300s/15s



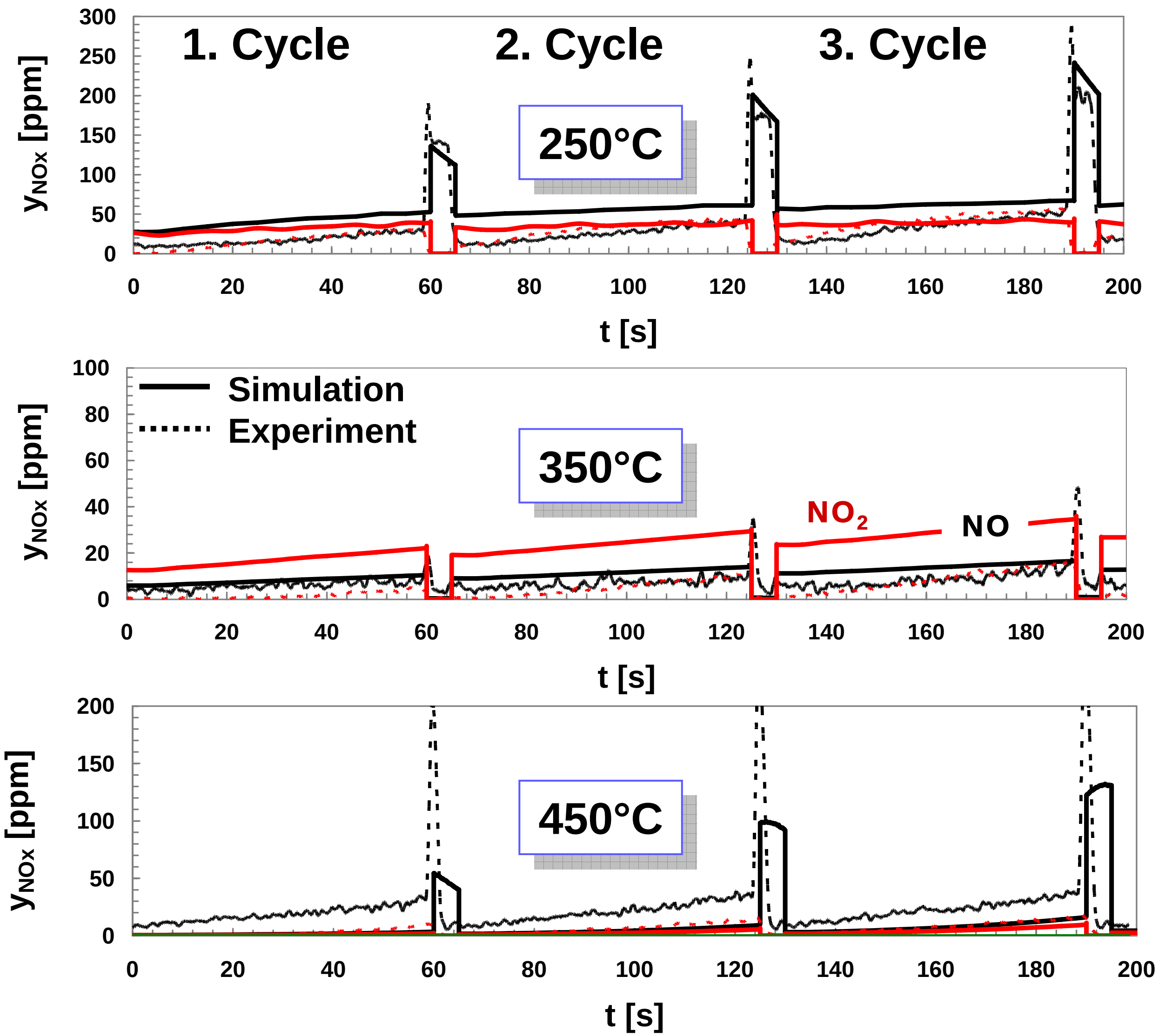
→ Parameterization of the Storage Reactions on LTS Experiments and Parameterization of the Reduction Reaction on Lean/Rich Cycles

Lean/Rich Cycle (60s/5s) for $Pt/Ba/Al_2O_3$ at 350°C



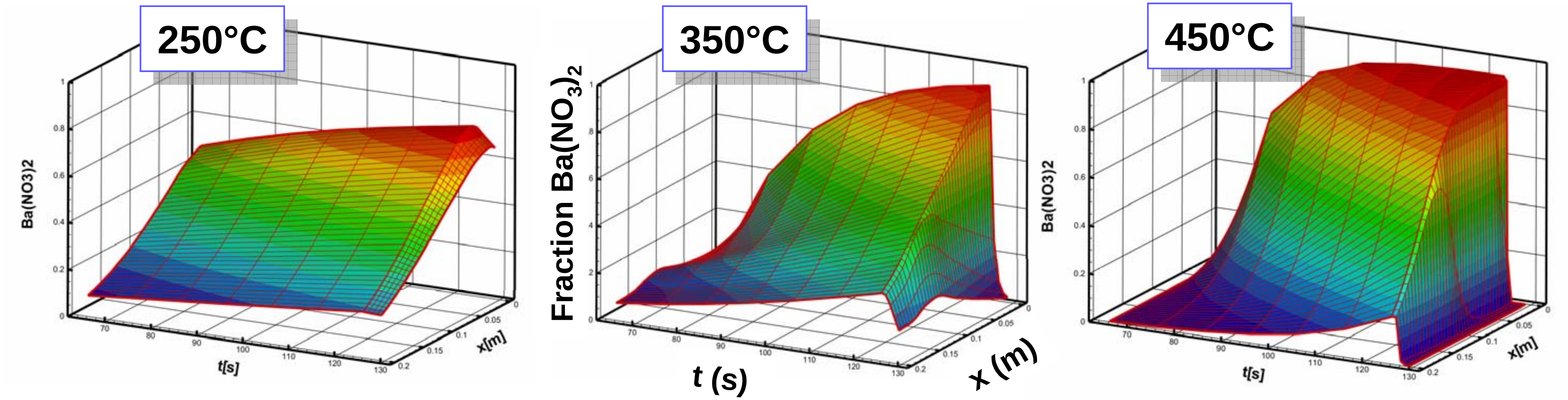
→ Good agreement between simulations and experiments for both lean/rich cycling and axial profiles

Lean/Rich Cycling (60s/5s) for Pt/Ba/Al_2O_3



- First three cycles in a row at different temperatures
- Input conditions of 2nd and 3rd are the surface coverages of the previous cycle
- Model is able to predict concentrations profiles even for incomplete regeneration (250 and 350°C)
- Problems with NO regeneration peak at 450°C

Predicted Fraction with $Ba(NO_3)_2$ on $Pt/Ba/Al_2O_3$ (2. Cycle)



- Predicted fractions during the 2nd lean/rich cycle along the channel length and as a function of cycling time
- Incomplete regeneration at lower temperatures
- Increasing nitrate fraction due to storage reactions
- Non-uniform nitrate distribution along the catalyst length
- Sharp decrease in the nitrate fraction indicates regeneration

→ *Model enables detailed insight into the barium nitrate distribution for a simple NSC at various temperatures*

Summary and Conclusion

Summary:

- **2d and transient Model of a NO_x-Storage Catalyst**
- **Effectiveness Factor Washcoat Model**
- **Realistic Exhaust-gas Composition**
- **Detailed Reaction Mechanism on the Noble Metal**
- **Shrinking Core Model for the Storage of Nitrogen Oxides on Barium**

Outlook:

- **Development and implementation of an Oxygen Storage Model on Ceria**

Acknowledgements:

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Thank You

For your Attention