System Simulation of Advanced SCR-Systems

11th CLEERS Workshop

15.03.2008

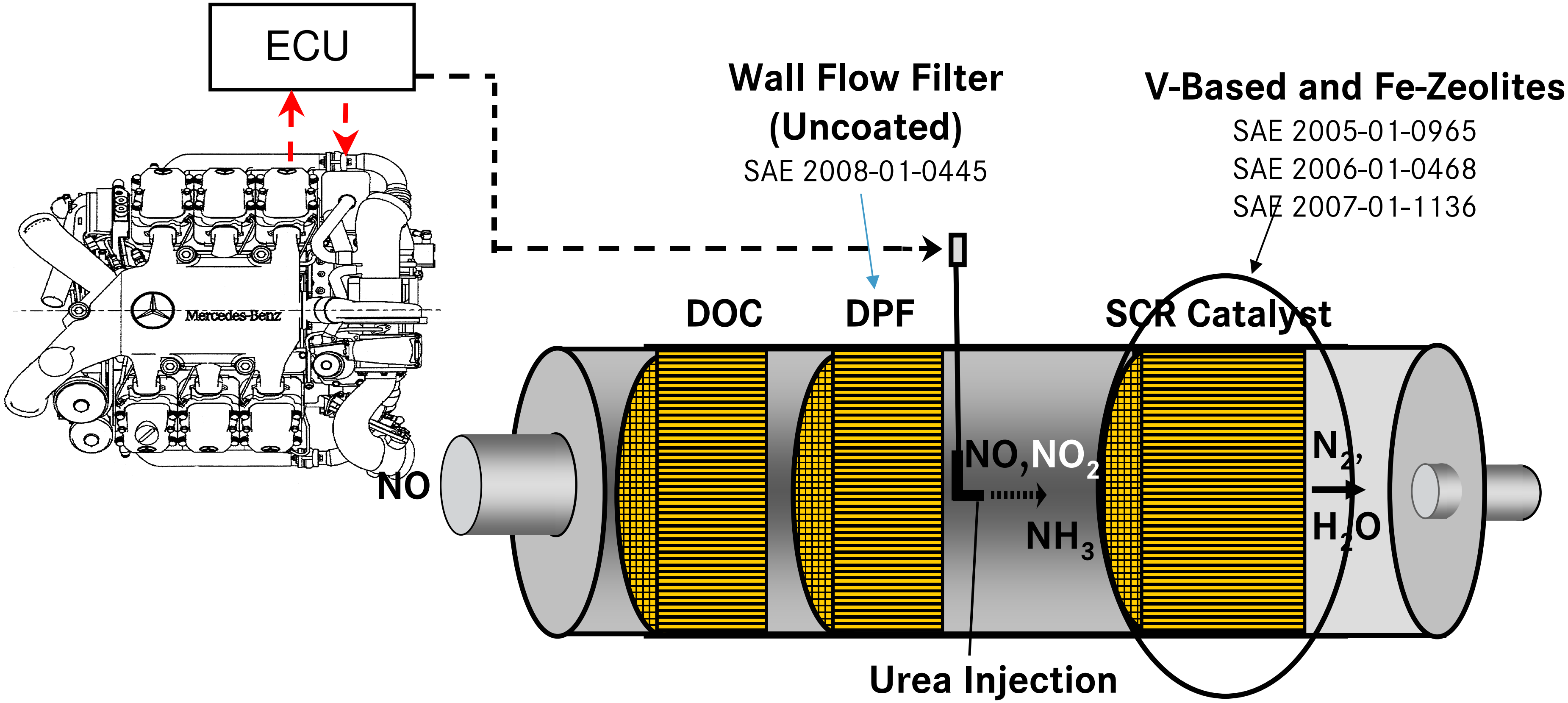
Daniel Chatterjee, Thomas Burkhardt, Stefan Schöffel

and Michel Weibel

Outline

- Advanced SCR-System Setup (DOC+DPF+SCR)
- Simulation Concept
- Modeling SCR Converters
- Modeling DOC Converters
- DOC: Kinetic Correlations
- Simulation Based System Optimization: DOC Impact on SCR
- Modeling of Urea Processing
- Conclusions

Advanced SCR-System: DOC+DPF+SCR



- **NO_2** increases NO_x reduction efficiency and complexity of the system.
- High thermal mass in front of the SCR delays NO_x reduction lightoff.
- Adaptation of the DOC+DPF+SCR-System to the individual application is required.
- Optimization target: High NO_x conversion efficiency without NH_3 slip.

DAIMLER

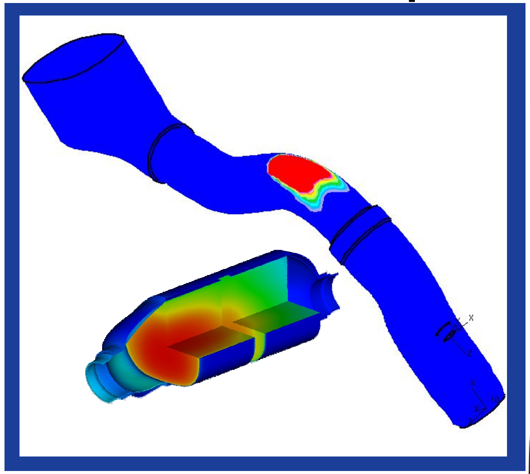
Outline

- Advanced SCR-System Setup (DOC+DPF+SCR)
- Simulation Concept
- Modeling SCR Converters
- Modeling DOC Converters
- DOC: Kinetic Correlations
- Simulation Based System Optimization: DOC Impact on SCR
- Modeling of Urea Processing
- Conclusions

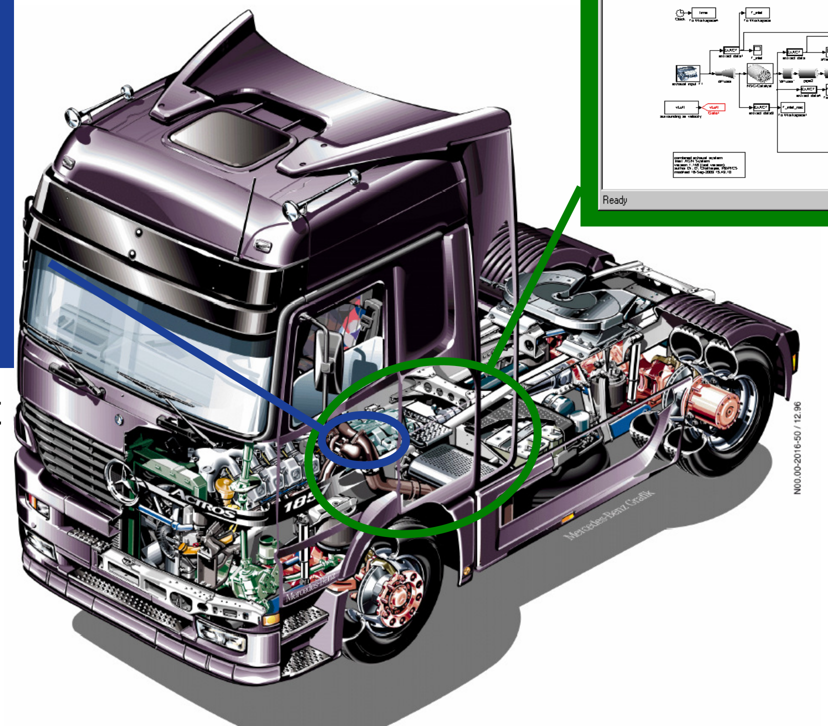
Exhaust Gas Aftertreatment Simulation

3D-Simulation:

Optimization of Geometry for Individual Components



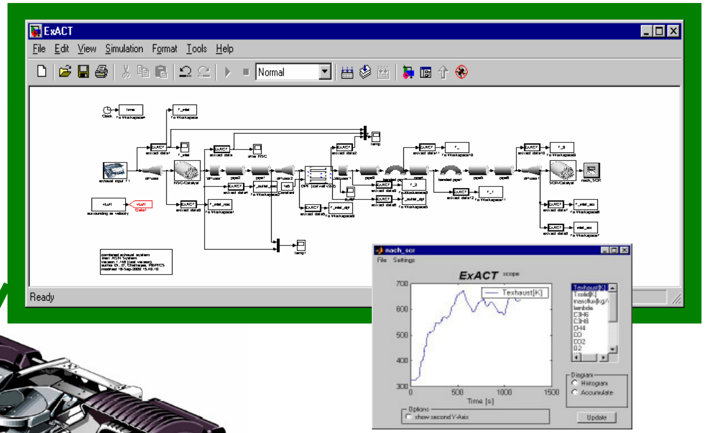
- Effect of non uniform inlet conditions
- Urea Processing



Mercedes - Benz 1857 LS

ExACT:

1D Simulation of Combined Exhaust Aftertreatment Systems

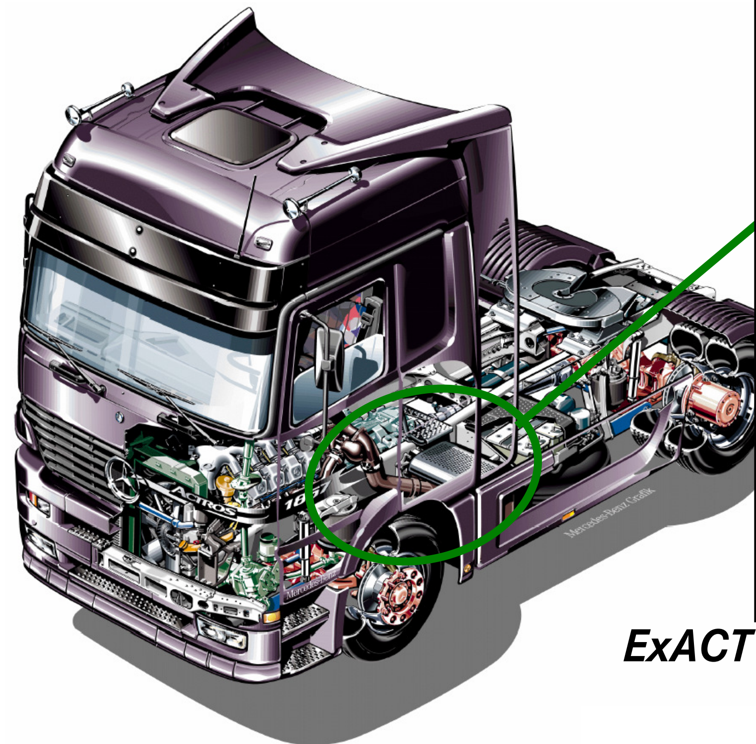


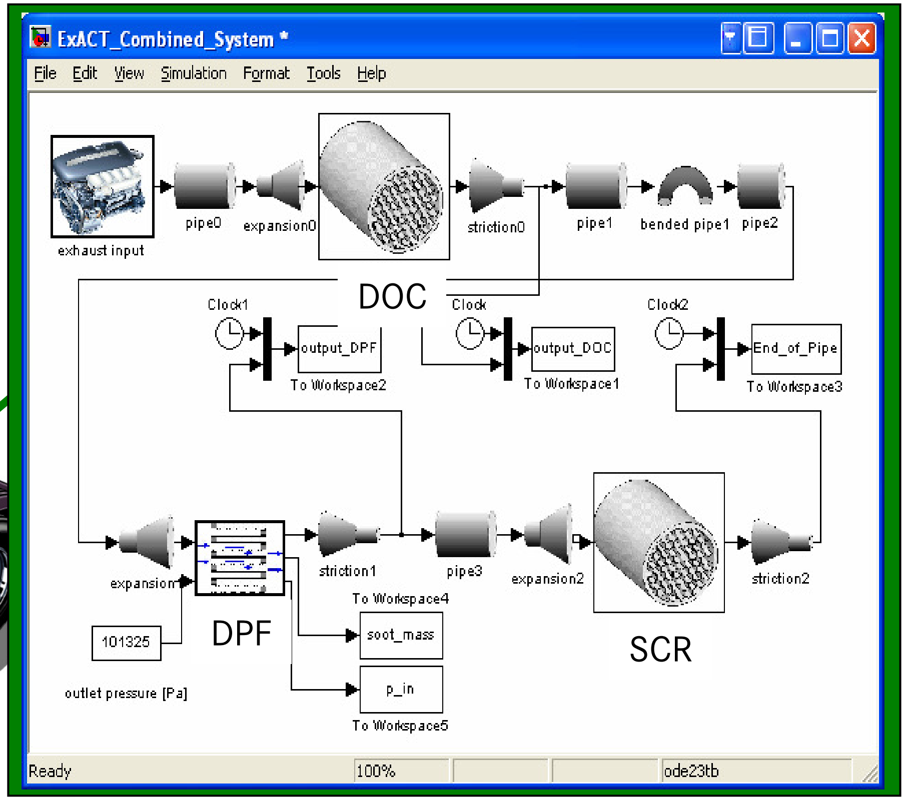
Testcycle Performance

System-design

Operating strategies

Simulation Toolbox *ExACT*





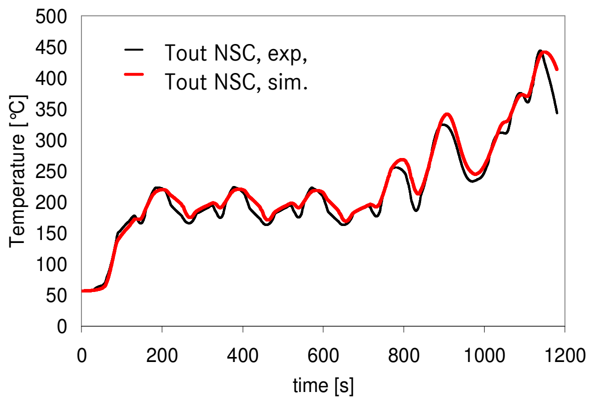
ExACT = ***Ex***haust Gas ***A***ftertreatment ***C***omponents ***T***oolbox

- ExACT toolbox consists of 1D models for SCR, ASC, DOC, DPF, LNT, TWC.
- Model generation by drag&drop.
- Focus: Testcycle simulation, system design, operating strategies.

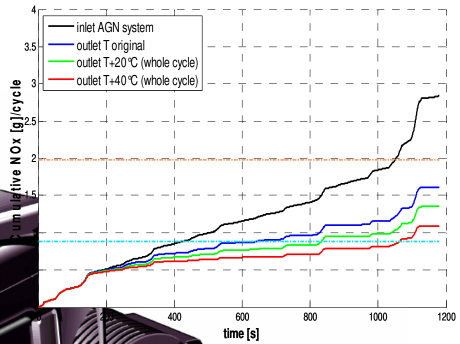
DAIMLER

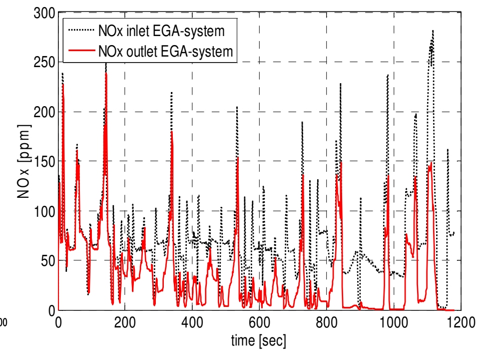
ExACT Exhaust Aftertreatment System Modeling: Application Examples

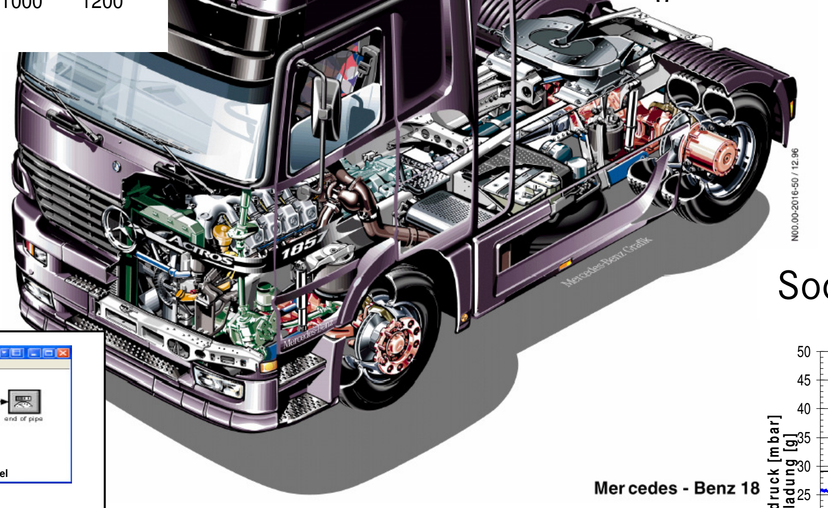
Temperatures



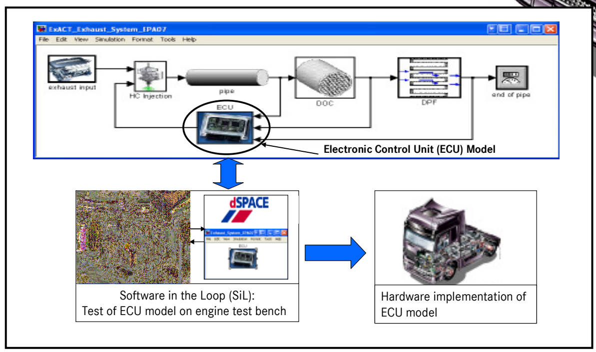
Prediction of Soot, NOx, CO, HC Conversion



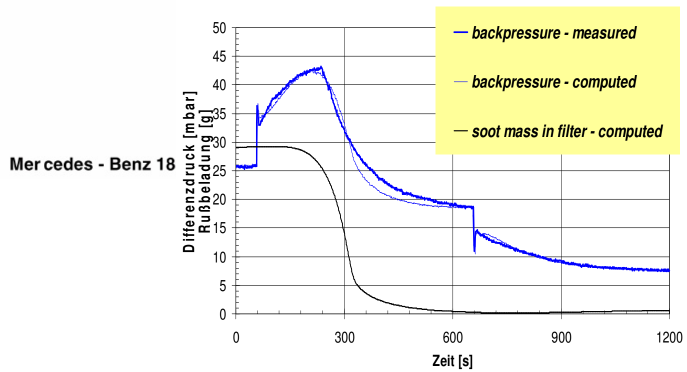




ECU-Development „Virtual Testbench“



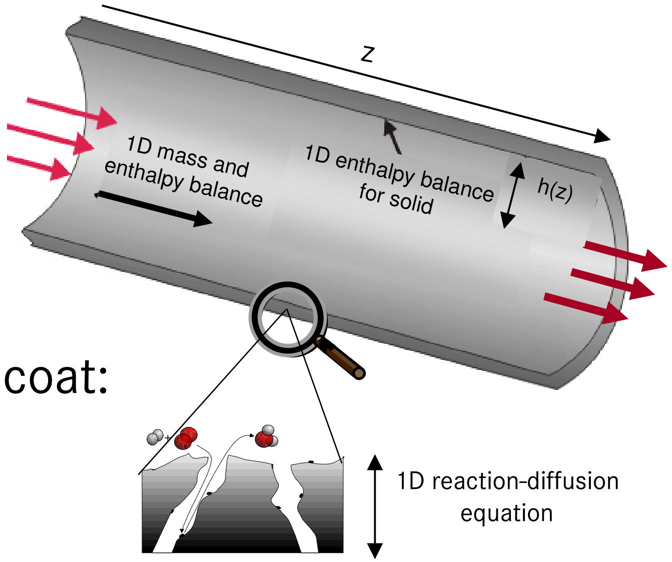
Soot Loading/Pressure Loss



Modeling SCR and DOC Catalytic Converters

Transport Processes:

- Modeling of one representative channel.
- 1D mass and enthalpy balances for gas and solid.
- Gas-solid mass and heat transport by means of transfer coefficients, h(z).
- SCR :1D reaction-diffusion equation to account for diffusional limitation within the catalytic wall/washcoat:



$$0 = D_{eff,j} \frac{\partial^2 C_j^*}{\partial x^2} + S_W^2 R_j$$

- DOC: Effectiveness factor/Thiele modulus

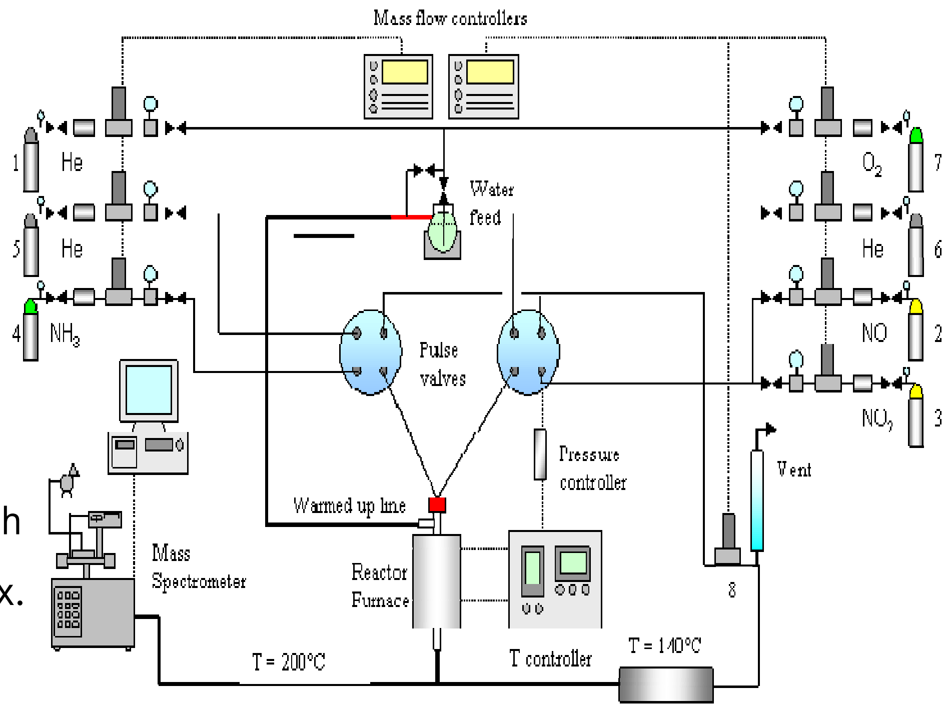
$$\eta = \frac{\tanh(\phi)}{\phi} \qquad \phi = L\sqrt{\frac{R_4}{D_{eff}\, c_{NO}}}$$

Outline

- Advanced SCR-System Setup (DOC+DPF+SCR)
- Simulation Concept
- Modeling SCR Converters
- Modeling DOC Converters
- DOC: Kinetic Correlations
- Simulation Based System Optimization: DOC Impact on SCR
- Modeling of Urea Processing
- Conclusions

Modeling SCR-Catalytic Converters:
Intrinsic Transient SCR Kinetics

- Catalyst samples taken from commercial SCR catalysts.
- Kinetic investigations with TRM experiments in a flow-microreactor with powdered catalyst.
- Typical concentrations: 1000ppm NO_x and NH_3, $0 \leq NO_2/NO_x \leq 1$, 2% O_2 and 1% H_2O.
- Temperature range: 50-450°C (NH_3 ads./des., NH_3 ox.),160-450°C (SCR react.)
- Kinetic parameter estimation of subsystems with the respective TRM runs.(NH_3 ads./des., NH_3 ox. NO-SCR react., NO+NO_2 react.)

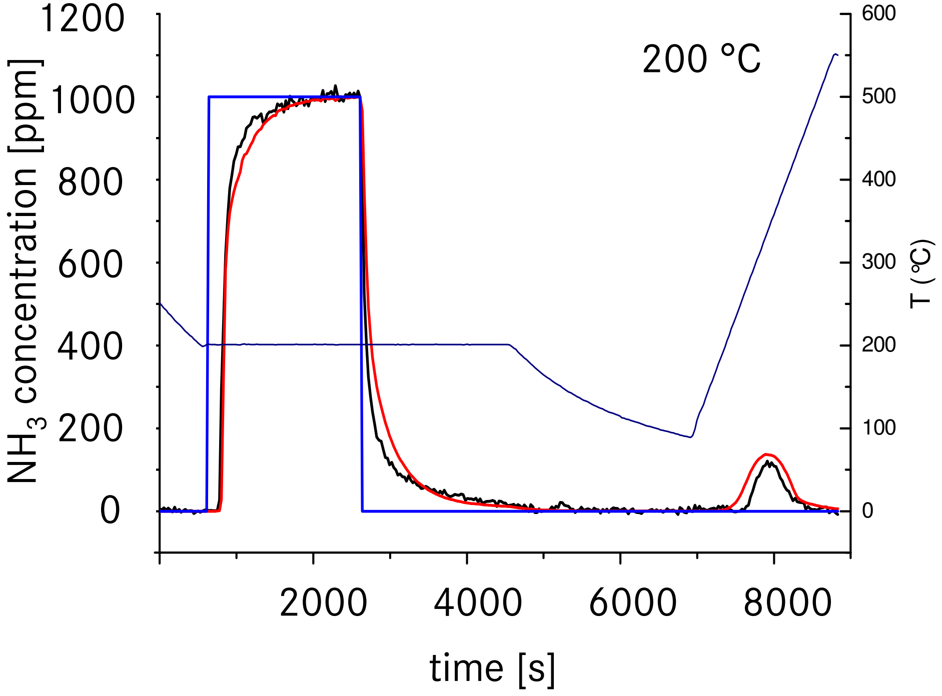


- Experimental set up avoids the influence of transport effects on kinetic measurements.
- Sequential fitting of kinetic subsystems minimizes parameter correlations.

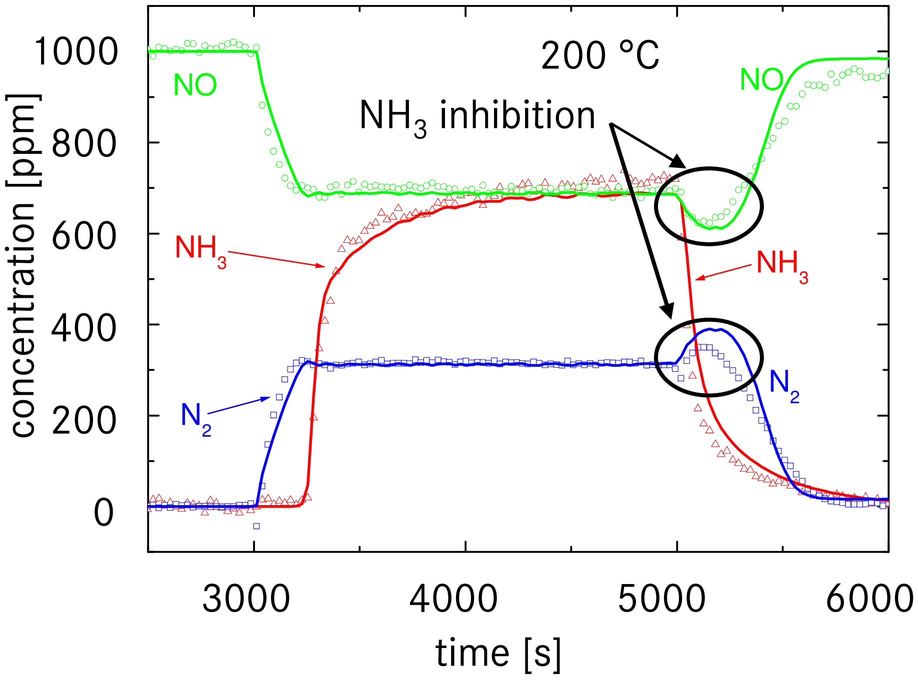
DAIMLER

Modeling SCR-Catalytic Converters:
Calibration of Reaction Kinetics by TRM Experiments

NH_3 TRM run



NO + NH_3 and NO + NO_2 + NH_3 TRM



Parameters for NH_3 Adsorption/Desorption, NH_3-Oxidation

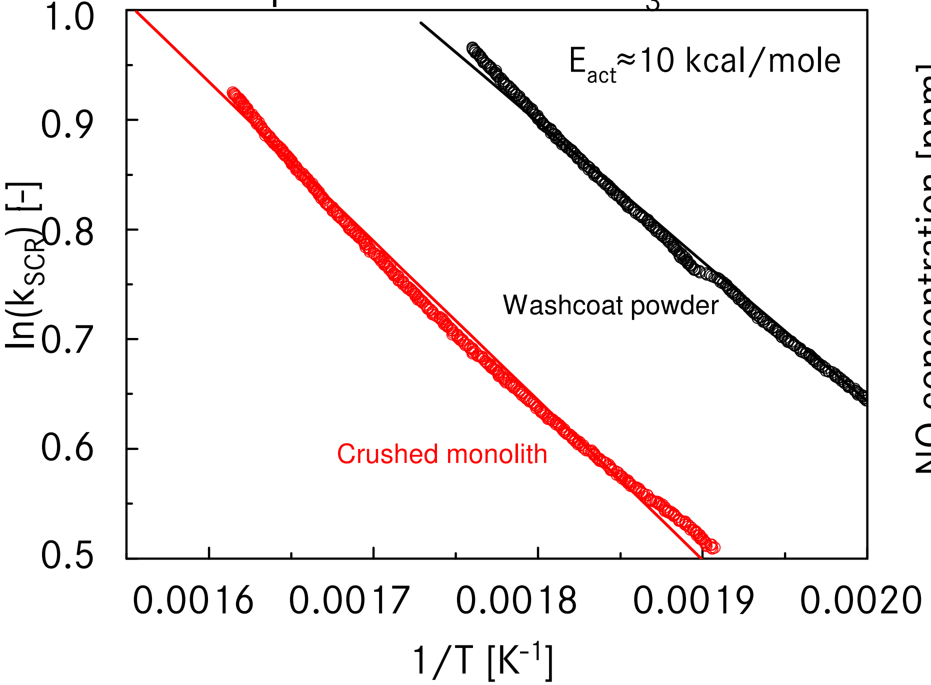
Parameters for NO-SCR Reaction

DAIMLER

SCR Kinetic Measurements:

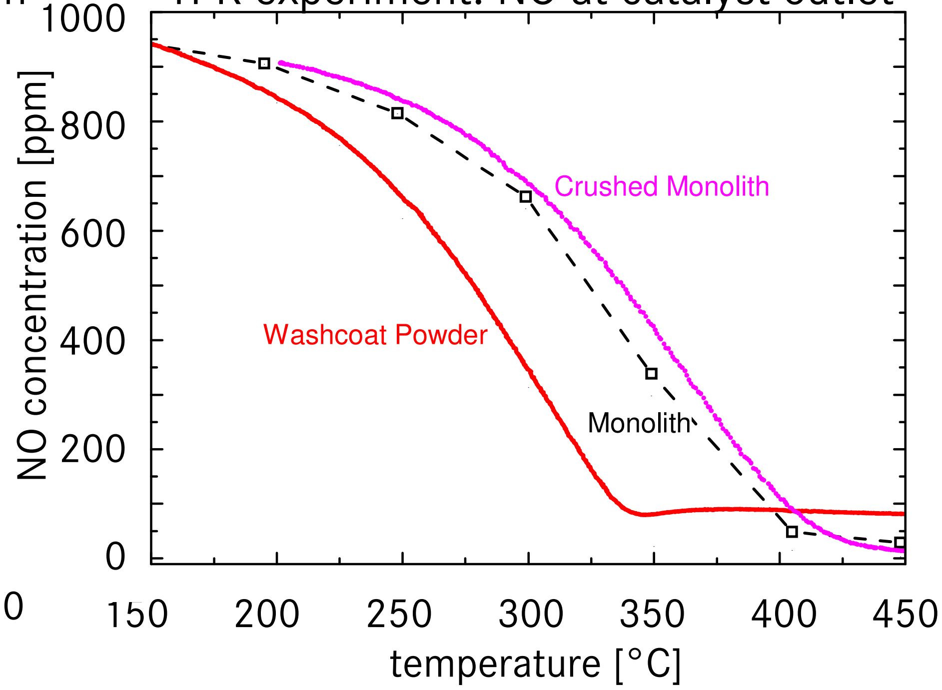
Zeolith Washcoat Powder vs. Crushed Monolith

Arrhenius plot for the $NO+NH_3$ SCR reaction



Feed: 1000 ppm NH_3, 1000 ppm NO, 1% H_2O, 2% O_2, balance N_2,
same catalytic active mass GHSV 170000 $Ncm^3(gh)^{-1}$

TPR experiment: NO at catalyst outlet



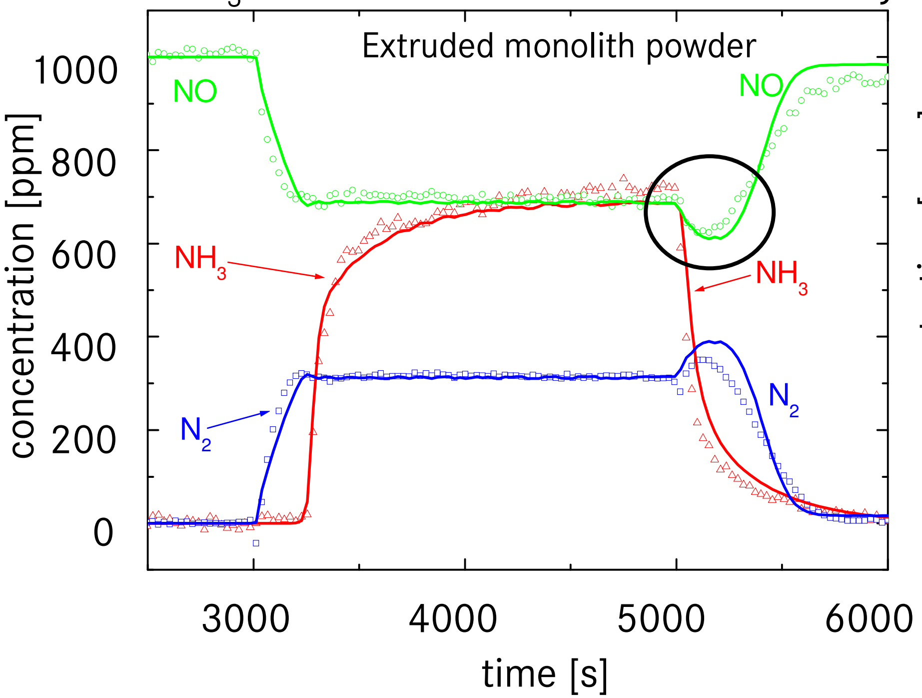
Feed: 1000 ppm NH_3, 1000 ppm NO, 1% H2O, 2% O2, balance N2,
same catalytic active mass GHSV 177000 Ncm3(gh)-1

- Washcoat powder reveals a higher SCR activity compared to the monolith.
- NH_3 storage and NH_3 oxidation are more efficient on powder.
- Experiments on crushed monoliths are quantitatively more representative.

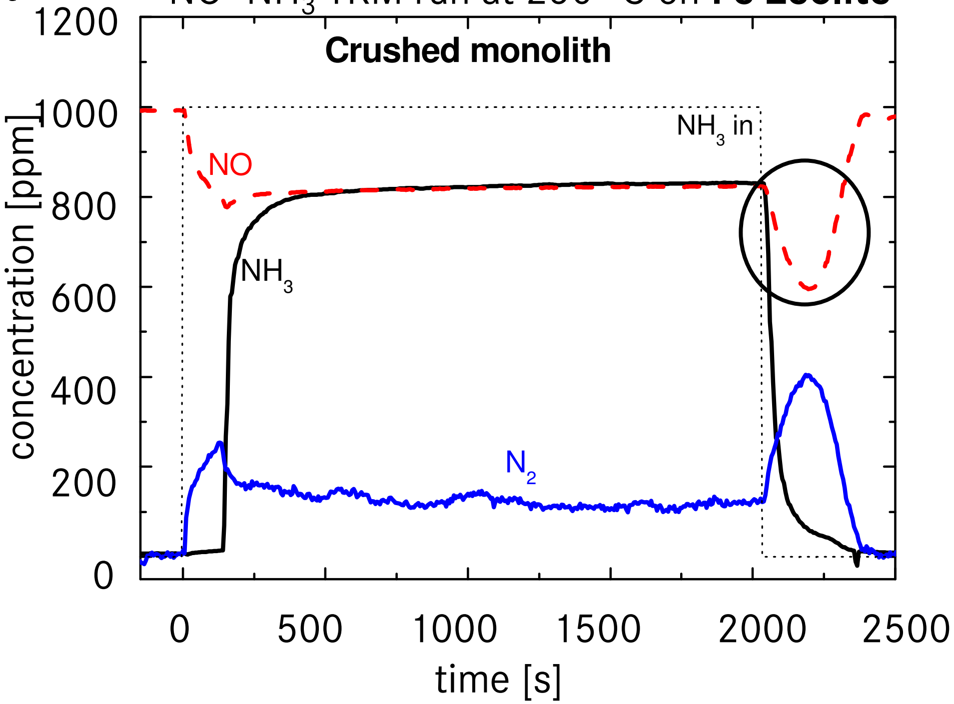
DAIMLER

SCR Kinetic Measurements:
Zeolite vs. V-Based Catalyst

NO + NH_3 TRM run at 250 °C on **V-based** catalyst



NO+NH_3 TRM run at 250 °C on **Fe-Zeolite**

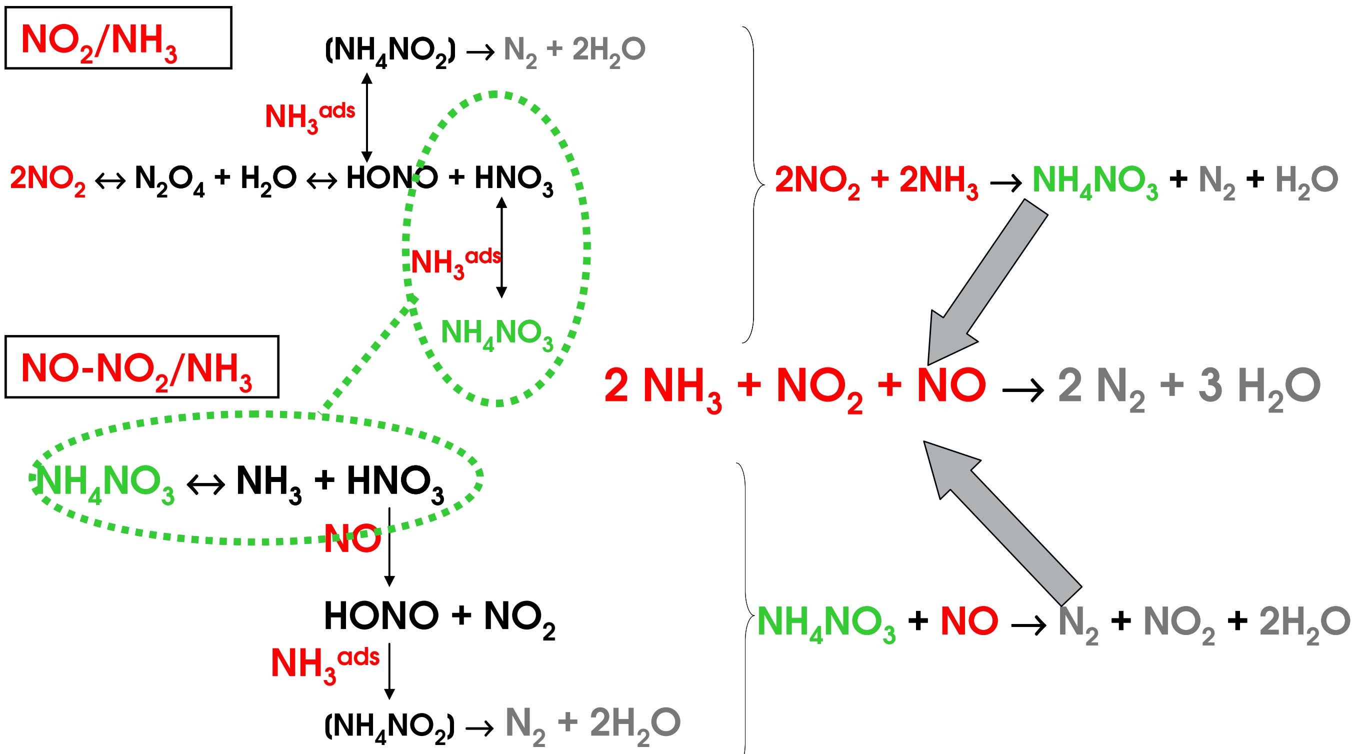


- Kinetic experiments reveal similar features on V-based an Fe-Zeolite SCR catalysts.
- NH_3 inhibition effect is more pronounced on Fe-Zeolite.
- Experimental results suggest the use of similar global reaction rate expressions.

DAIMLER

Modeling SCR-Catalytic Converters:

Proposed Reaction Mechanism for NO_2+NO+NH_3
on **V-Based** and **Fe-Zeolites** SCR Catalysts:



C. Ciardelli, I. Nova, E. Tronconi, D. Chatterjee, B. Bandl-Konrad, *Chem. Commun.* **23** (2004), 2718,
D. Chatterjee, T. Burkhardt, M. Weibel, E. Tronconi, I. Nova, C. Ciradelli, SAE 2006-01-0468,
I. Nova, C. Ciardelli, E. Tronconi, D. Chatterjee, B. Bandl-Konrad, *Catal. Today*, 114 (2006), 3,
A.Gossale, I. Nova, E. Tronconi, D. Chatterjee, M. Weibel, *J. of Catalysis* (submitted)
O. Kröcher, 1st Conference MinNO$_x$, Feb. 2007 Berlin (Germany).

Data analysis and literature supports the assumption of a similar reaction mechanism on V-based and Fe-Zeolites SCR catalysts.

DAIMLER

Modeling SCR-Catalytic Converters

Chemical Reactions: NO+NH_3*

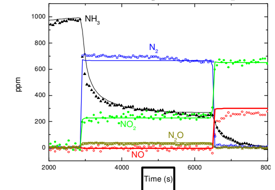
- **NH_3 adsorption:** $NH_3 \rightarrow NH_3^*$
- **NH_3 desorption:** $NH_3^* \rightarrow NH_3$
- **NH_3 oxidation:** $4NH_3^*+3O_2 \rightarrow 2N_2+6H_2O$
- **NO-SCR reaction:** $4NH_3^*+4NO+O_2 \rightarrow 4N_2+6H_2O$

Chemical Reactions: NO+NO_2+NH_3**

- **Fast-SCR reaction:** $2NH_3^*+ NO_2 + NO \rightarrow 2N_2 + 3H_2O$
- **NO_2- SCR reaction:** $4NH_3^*+ 3NO_2 \rightarrow 3.5N_2 + 6H_2O$
- **N_2O formation:** $2NH_3^*+2NO_2 \rightarrow N_2O+3H_2O+N_2$

* SAE 2005-01-0965, **SAE 2006-01-0468+SAE 2007-01-1136+SAE 2008-01-0867

Microreactor experiments with catalyst powder



Reaction mechanism

Rate equations/parameter

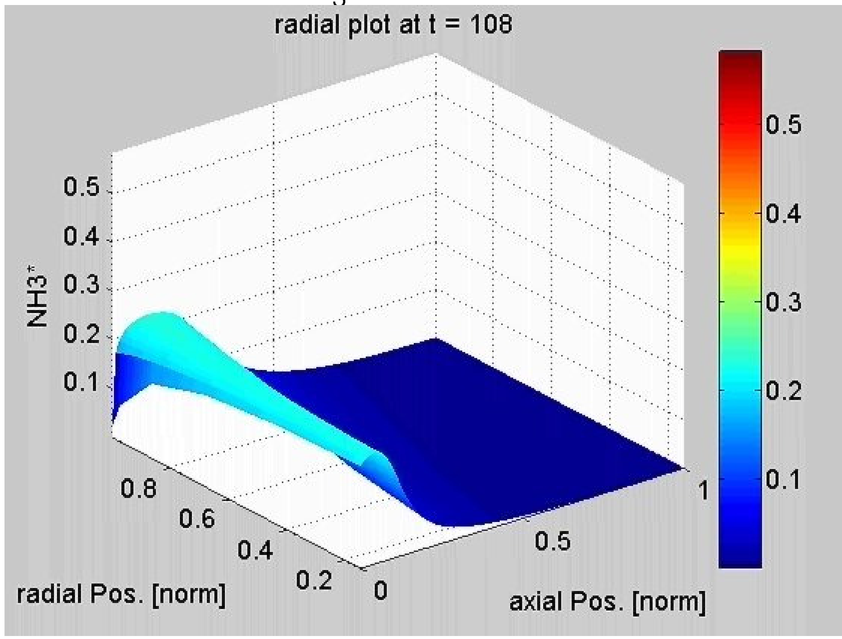
$$r_{NO} = k_{NO}^{\circ} \exp\left(-\frac{E_{NO}}{RT}\right) \frac{C_{NO}\vartheta}{1+K_{LH}\frac{\vartheta}{1-\vartheta}} \left(\frac{P_{O_2}}{0.02}\right)^{\beta}$$

- No NH_3 adsorption/desorption equilibrium is assumed.
- Two-sites L.-H. expression accounts for NH_3 inhibition of the SCR reaction.
- Higher O_2 concentration increases SCR reaction and NH_3 oxidation rates.
- Simplified reaction scheme for the fast SCR reaction (NH_4NO_3 formation neglected)

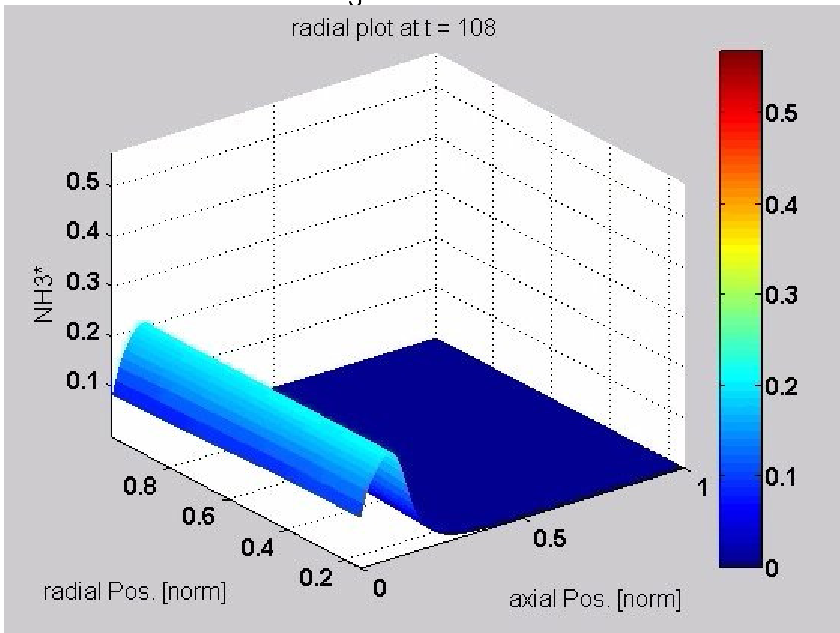
Modeling SCR-Catalytic Converters:
Zeolite vs. V-Based Catalyst: NH_3 Gradients within Catalytic Walls/Washcoat

ETC-Simulation

V-based extruded catalyst
Stored NH_3^* within monolith wall



Fe-Zeolite coated catalyst
Stored NH_3^* within monolith wall



⇨ Washcoat diffusion seems to be of minor importance on Zeolite.

α=1, Catalyst: 18L, 400cpsi

Outline

- Advanced SCR-System Setup (DOC+DPF+SCR)
- Simulation Concept
- Modeling SCR Converters
- Modeling DOC Converters
- DOC: Kinetic Correlations
- Simulation Based System Optimization: DOC Impact on SCR
- Modeling of Urea Processing
- Conclusions

DOC Modeling: Reaction Kinetics

Chemical Reactions: Oxidation Reactions

Reaction		Rate Equations*
• $CO + 1/2\ O_2$	$\rightarrow CO_2$	$R_1 = k_1 \frac{y_{CO}\, y_{O_2}}{G_1}$
• $H_2 + 1/2\ O_2$	$\rightarrow H_2O$	$R_2 = k_2 \frac{y_{H_2}\, y_{O_2}}{G_1}$
• $C_3H_6 + 9/2\ O_2$	$\rightarrow 3\ H_2O + 3\ CO_2$	$R_3 = k_3 \frac{y_{C_3H_6}\, y_{O_2}}{G_1}$
• **$NO + 1/2\ O_2$**	**$\leftrightarrow NO_2$**	$R_4 = k_9 (y_{NO}\, y_{O_2}^{0.5} - \frac{y_{NO_2}}{K_{y,9}^{eq}}) \frac{1}{G_2}$
• $H_2O + CO$	$\leftrightarrow H_2 + CO_2$	$R_5 = k_4 (y_{CO}\, y_{H_2O} - \frac{y_{CO_2}\, y_{H_2}}{K_{y,4}^{eq}})$

G_x = *L.H. Inhibition Term*

Chemical Reactions: NO-Reduction

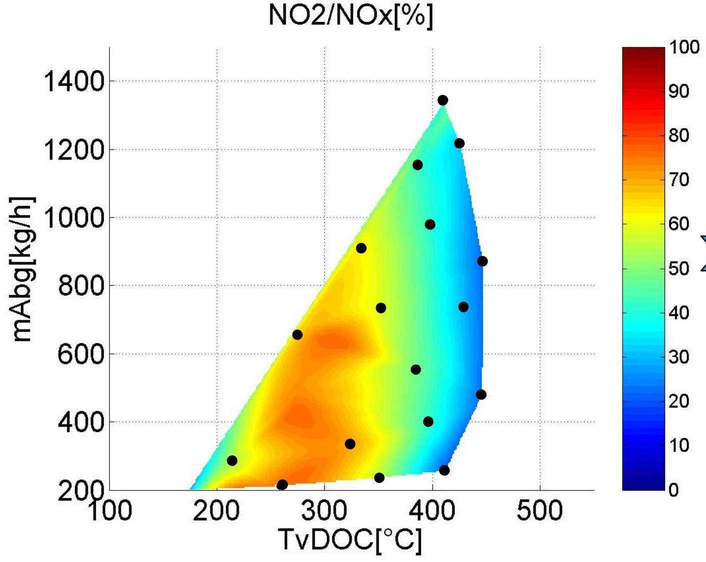
Reaction		Rate Equations*
• $NO + CO$	$\rightarrow CO_2 + 1/2\ N_2$	$R_6 = k_6\, y_{CO}\, y_{NO}^{0.5}$
• $NO + H_2$	$\rightarrow H_2O + 1/2\ N_2$	$R_7 = k_7\, y_{H_2}\, y_{NO}^{0.5}$
• $9\ NO + C_3H_6$	$\rightarrow 3\ CO_2 + 9/2\ N_2 + 3\ H_2O$	$R_8 = k_8\, y_{C_3H_6}\, y_{NO}^{0.5}$

- Global reaction kinetics for CO, H_2,C_3H_6 oxidation and NO reduction.
- Backward reaction/thermal equilibrium included for NO-Oxidation
- Inhibition effects are considered.

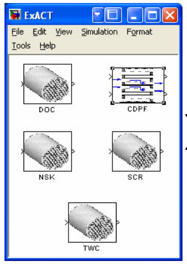
* SAE 2008-01-0867

DOC Modeling: Model Calibration Strategy

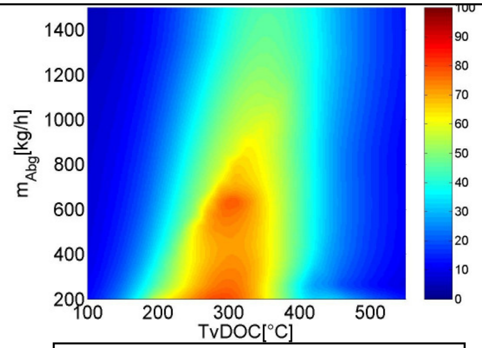
Measurement of Selected Operating Points (Engine Test Bench)



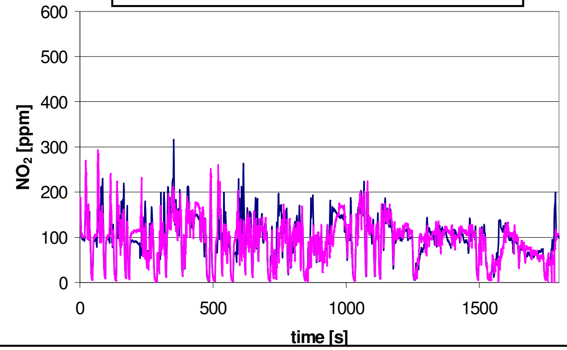
Calibration



Extrapolation to Complete Engine Map



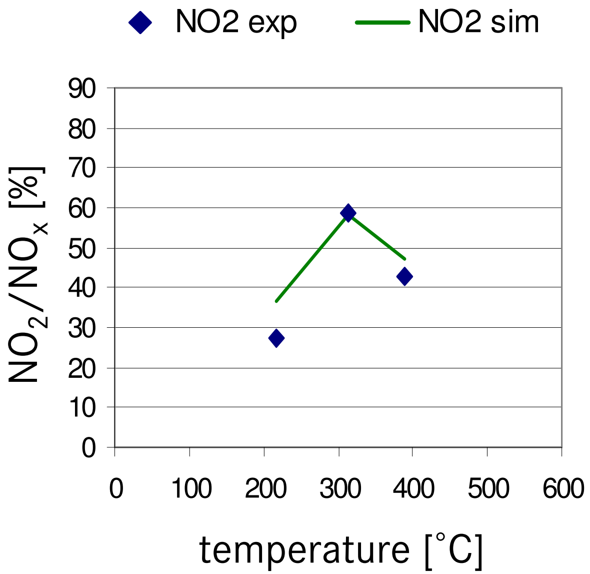
Transient Simulations



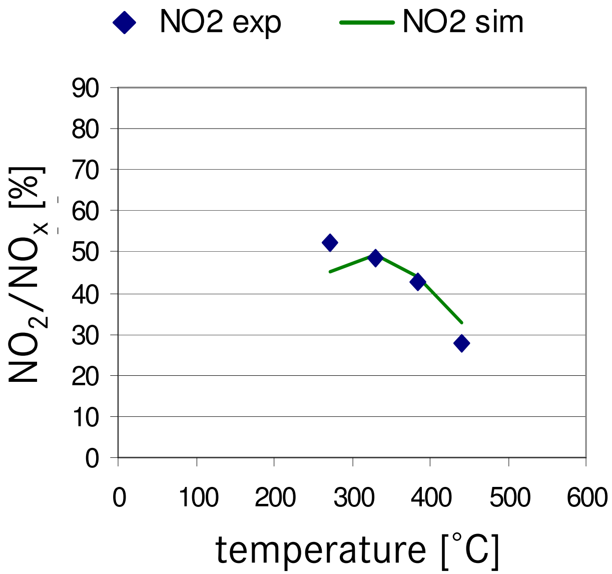
- Development of standard calibration procedures.
  (stready state test bench data sufficient for NO-oxidation)
- Model based map generation for ECUs + Assessment of transient performance.

DAIMLER

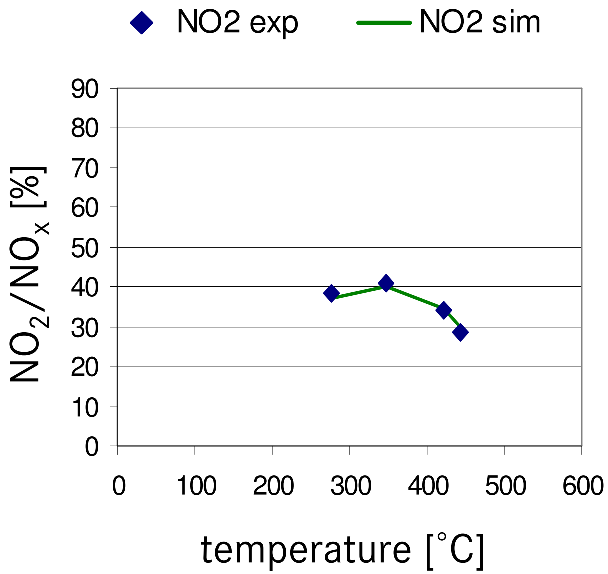
DOC Modeling:
NO-Oxidation – Calibration of Reaction Kinetics



NO_2-Ratio at approx. 400kg/h m_{Exh}



NO_2-Ratio at approx. 500kg/h m_{Exh}



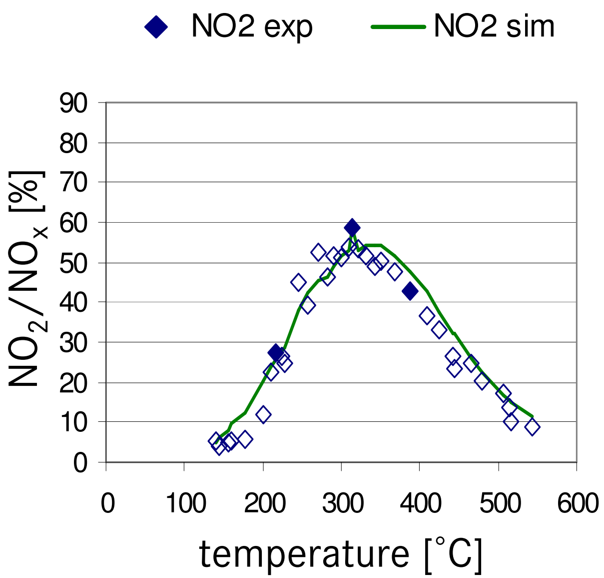
NO_2-Ratio at approx. 700kg/h m_{Exh}

Measurements taken from test bench experiments (catalyst 1)

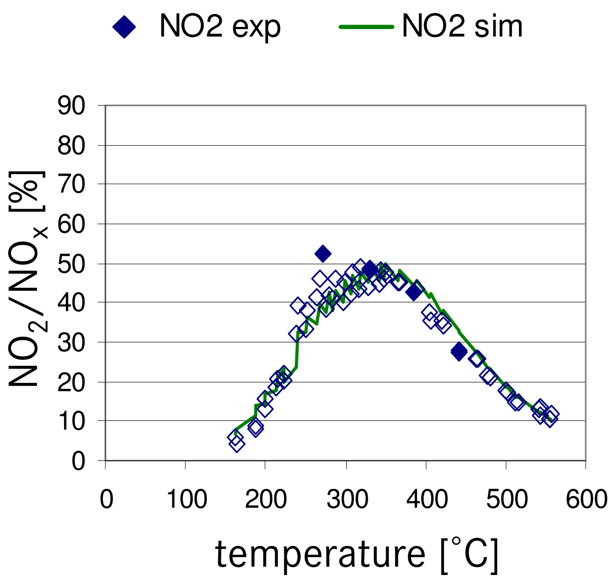
- Objective: Development of a simple calibration procedure
- Model calibration to new DOC technology:
- Keep E_{act} fixed, only preexponetial factor k_0 is changed

DAIMLER

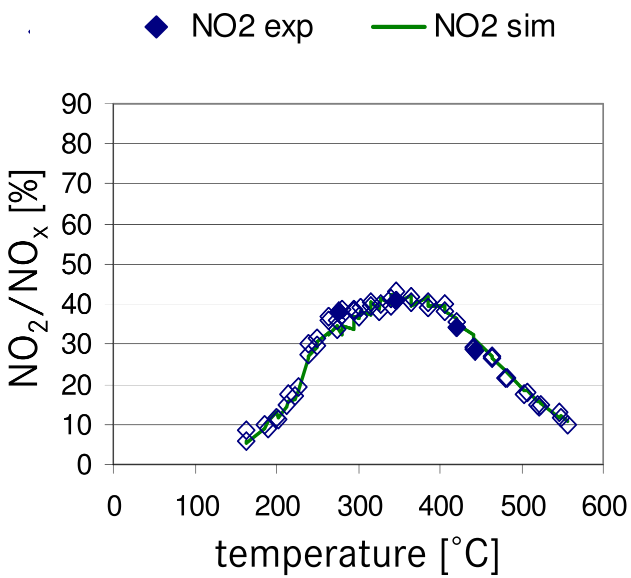
DOC Modeling:
NO-Oxidation – Steady State Validation



NO_2-Ratio at approx. 400kg/h m_{Exh}



NO_2-Ratio at approx. 500kg/h m_{Exh}



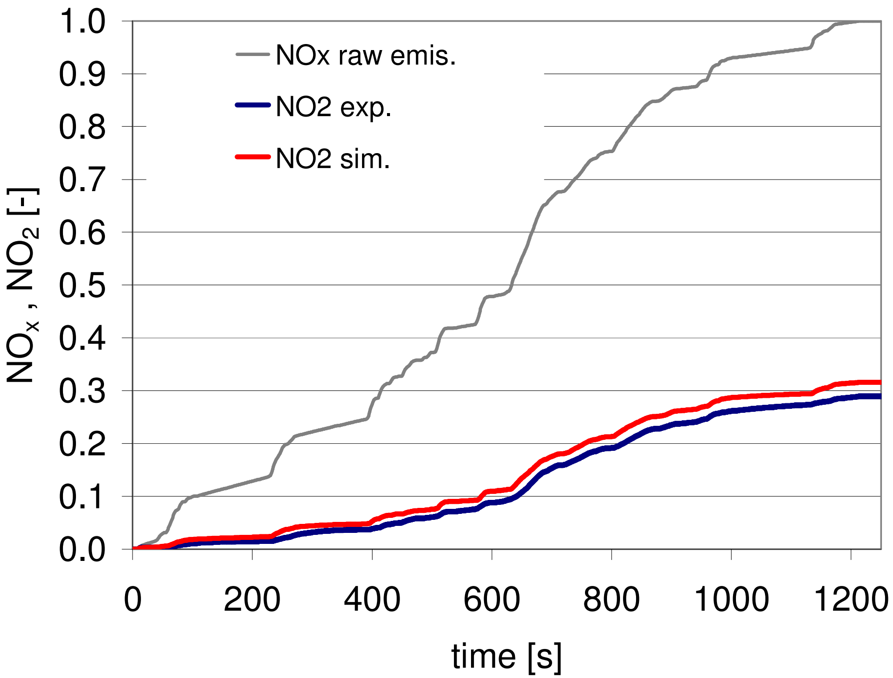
NO_2-Ratio at approx. 700kg/h m_{Exh}

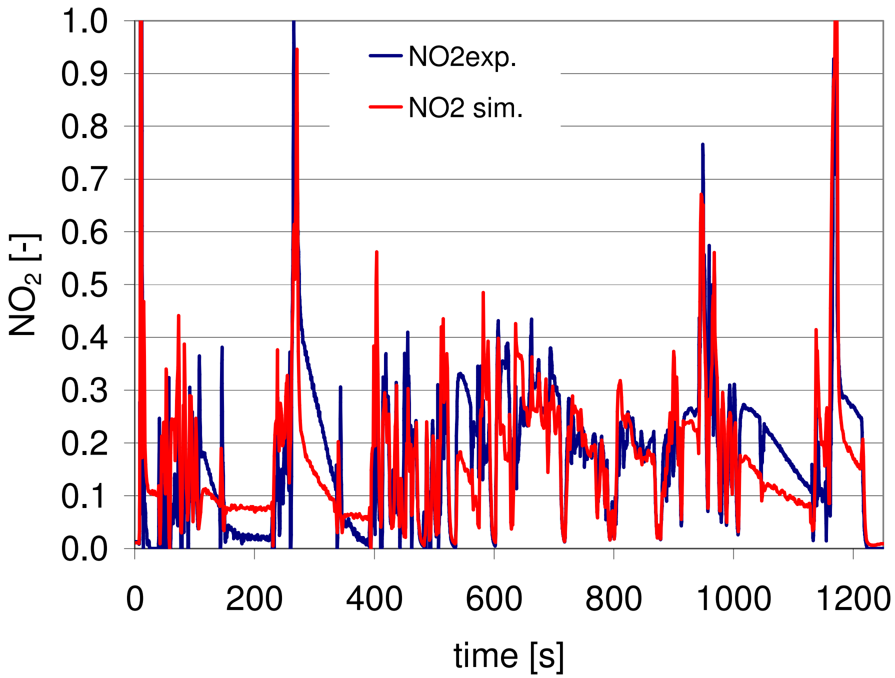
Measurements taken from test bench experiments (catalyst 1)

- Only a few measurements at different mass flows are required for calibration.
- Excellent prediction quality for steady state conditions.

DOC Modeling:
NO-Oxidation - Transient Validation

FTP-Testcycle





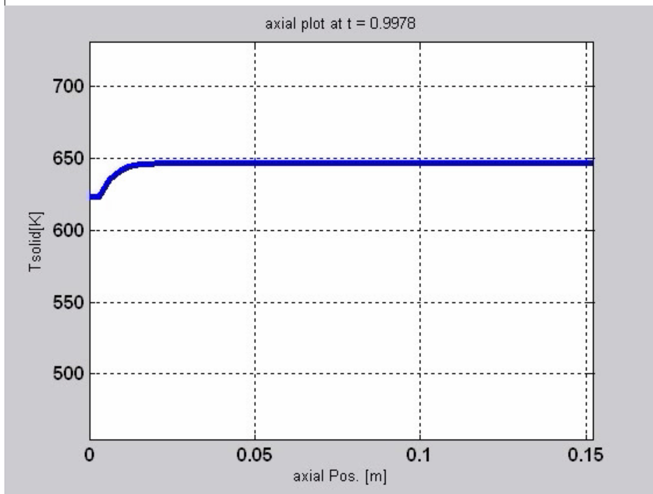
- Excellent prediction quality (error<2.3%) also for transient conditions.
- Deviations at idle speed conditions.

DAIMLER

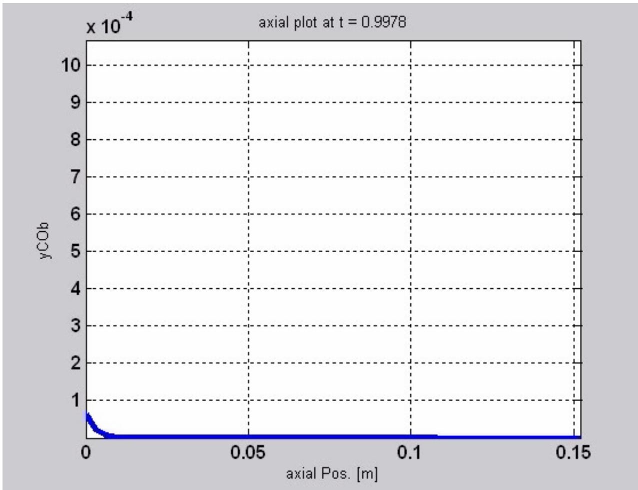
DOC Modeling:
Axial Profiles within DOC Catalyst

ETC Simulation

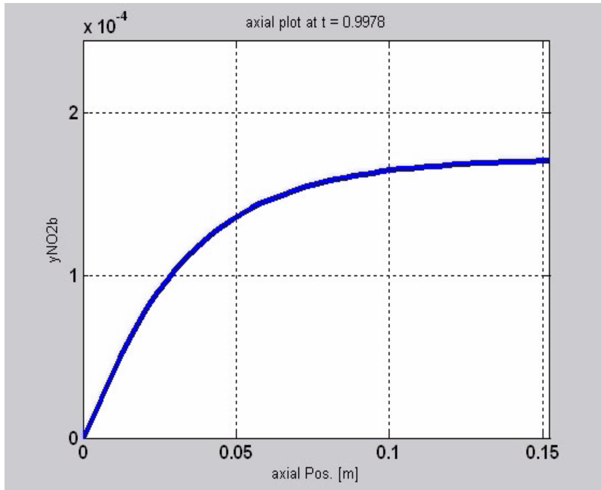
T_{solid} [K]



CO molefrac. [-]



ΔNO_2 molefrac. [-]



- Significant axial temperature and concentration gradients within monlith.
- CO/HC-oxidation located at catalyst entrance. NO_2 formation only after CO and HC depletion.
- Slow NO oxidation rate compared to CO and HC oxidation.

DAIMLER

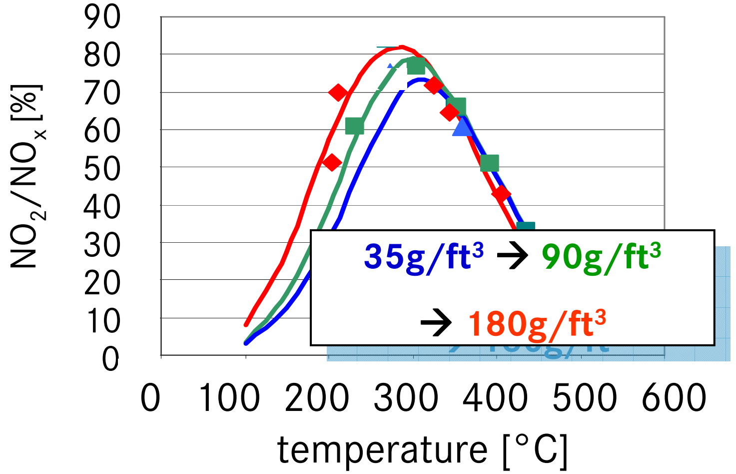
Outline

- Advanced SCR-System Setup (DOC+DPF+SCR)
- Simulation Concept
- Modeling SCR Converters
- Modeling DOC Converters
- DOC: Kinetic Correlations
- Simulation Based System Optimization: DOC Impact on SCR
- Modeling of Urea Processing
- Conclusions

DOC Modeling:
Correlation PGM-Loading – Kinetic Parameters

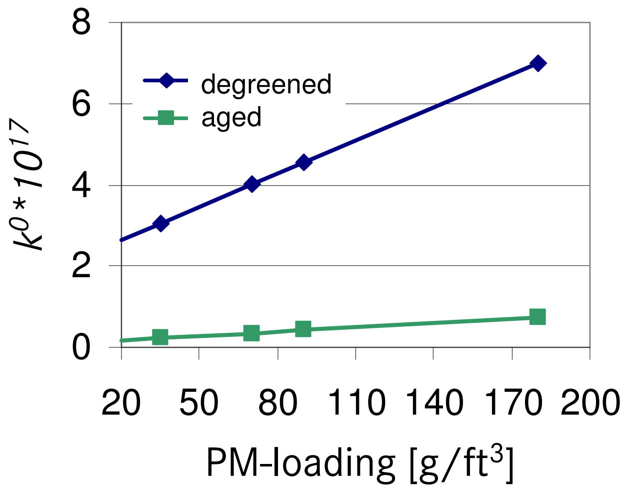
e.g.: NO-oxidation: *$NO + 1/2\ O_2 \leftrightarrow NO_2$*

Steady State Measurements:



Parameterization: k^0

$$R_4 = k_0^0 e^{-\frac{E_a}{RT}} \left(y_{NO}\, y_{O_2}^{0.5} - \frac{y_{NO_2}}{K_{y,9}^{eq}} \right) \frac{1}{G_2}$$



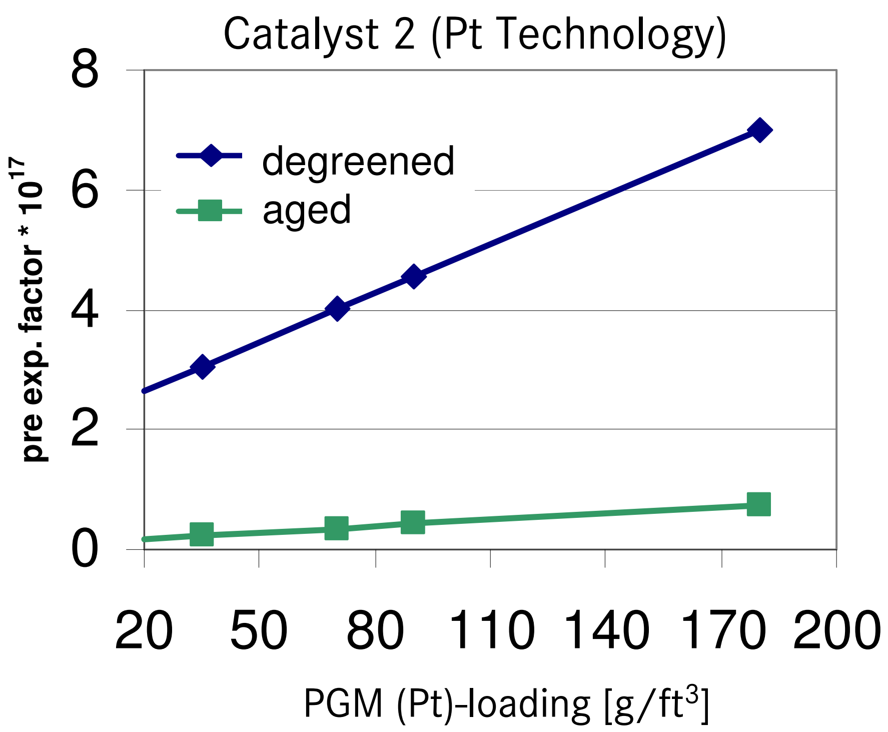
Correlation:

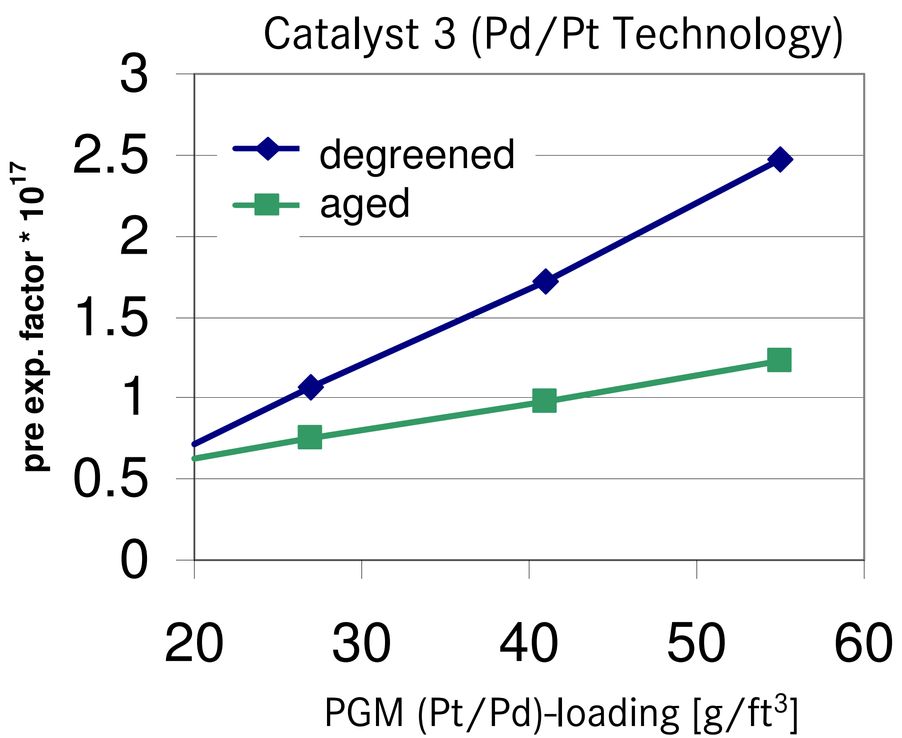
$$\frac{k^0}{k_{max}^0} = a\,\rho_{EM}^b + c$$

Kinetic-parameter

PM-loading

DOC Modeling:
Kinetic Correlation for NO-Oxidation





Degreened: 600°C, 5h real exhaust, Aged: 700 °C, 200h hydrothermal oven aged

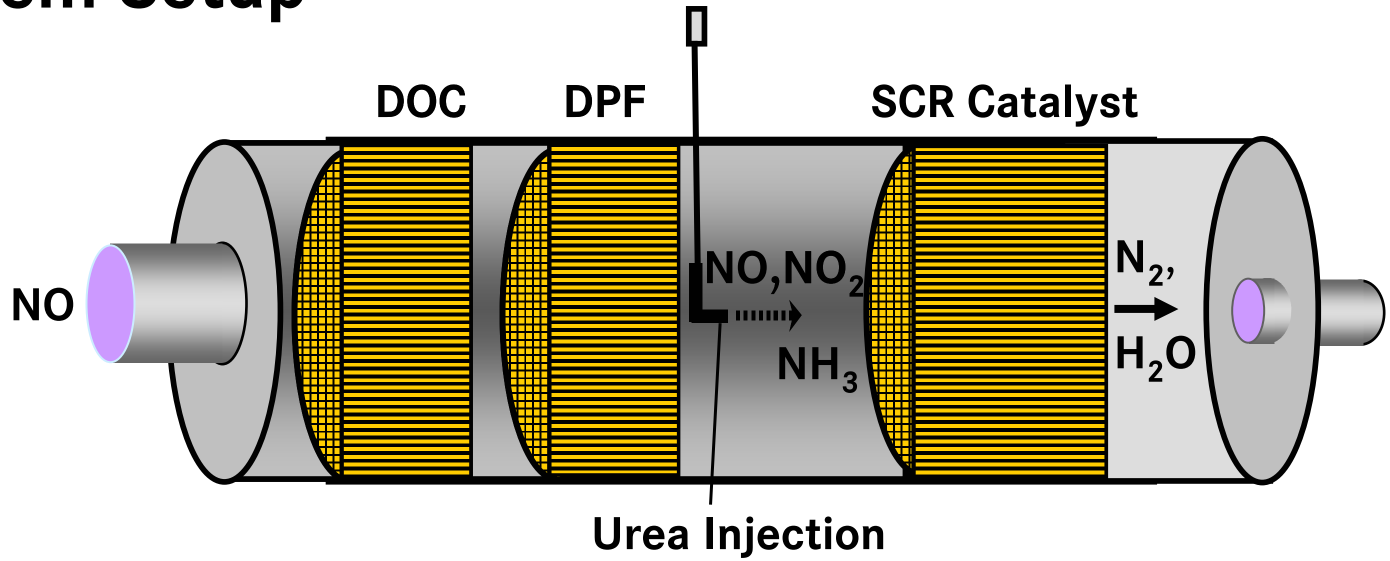
- A linear correlation is revealed within the studied range of PGM loadings.
- Linear correlation is valid also for degreened and aged state.
- Stronger deterioration by aging at higher PGM loading.
- Pd/Pt technology reveals lower intrinsic activity, but more aging resistance.

DAIMLER

Outline

- Advanced SCR-System Setup (DOC+DPF+SCR)
- Simulation Concept
- Modeling SCR Converters
- Modeling DOC Converters
- DOC: Kinetic Correlations
- Simulation Based System Optimization: DOC Impact on SCR
- Modeling of Urea Processing
- Conclusions

Simulation Study: DOC+DPF+SCR:
System Setup

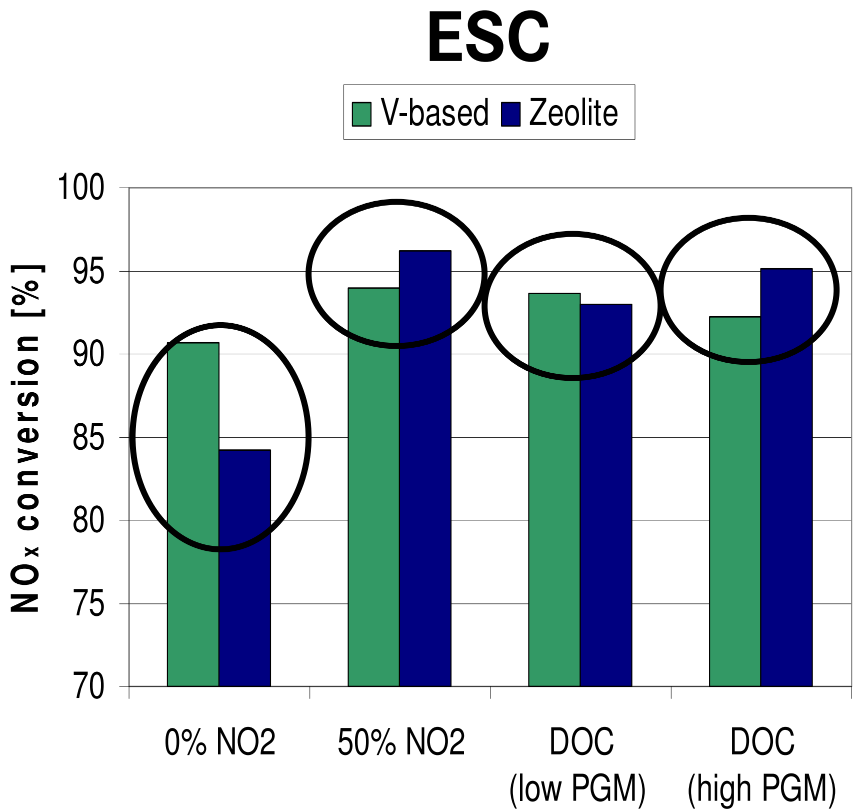


	DOC	DPF	SCR
Noble Metal	Pt/Pd	uncoated	-
Loading [g/ft^3]	varied	uncoated	Fe-Zeolite
Volume*	0.5	0.7	1

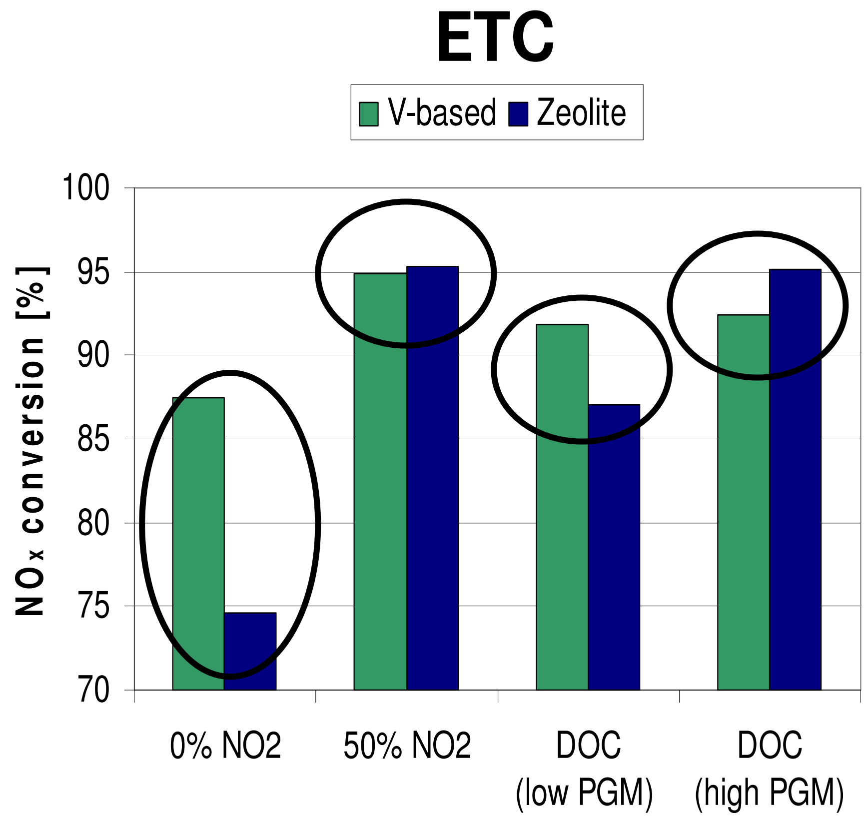
Design Target 80% NOx conversion within the combined FTP
(1/7 cold FTP + 6/7 hot FTP)

DAIMLER

Model Application: Total NOx Conversion Efficiencies: Fe-Zeolite vs. V-Based Catalyst*



yst: 18

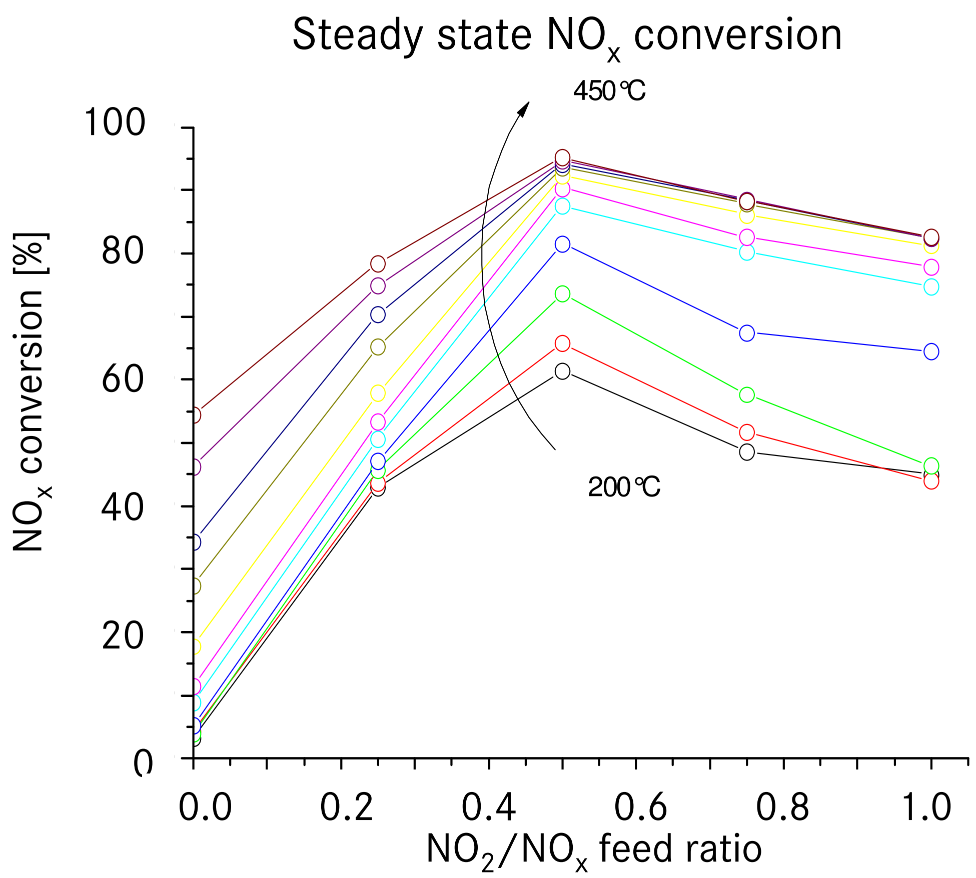


- V-based catalyst has higher efficiency for low NO_2 input concentrations.
- Fe-Zeolite catalyst has higher efficiency for optimized NO_2/NO_x ratios.

*SAE 2007-01-1136

DAIMLER

SCR NO_x Conversion Efficiency:
Influence of NO_2

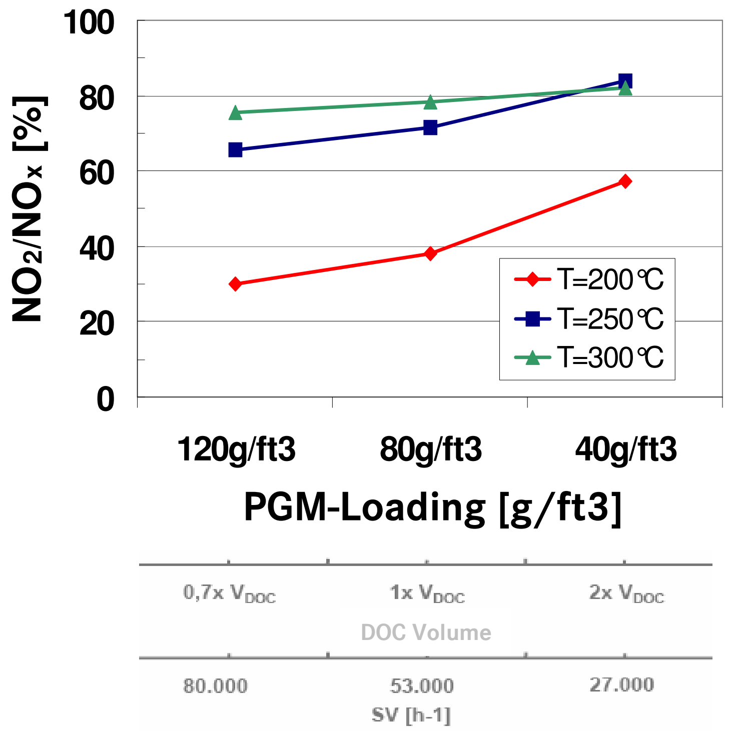


Microreactor sim./exp. with Fe-Zeolite SCR:
Feed S.V. 172.000 1/h, 1000ppm NO_x and 1000ppm NH_3, 2 Vol-% O_2, 10 Vol-% H_2O

- SCR conversion efficiency and product selectivity is influenced by the NO_2/NO_x feed ratio.
- Fe-Zeolites are more sensitive to NO_2/NO_x ratios lower than 50%,

DOC Modeling: Steady State NO-Oxidation
PGM-Loading vs. Catalyst Volume – Steady State

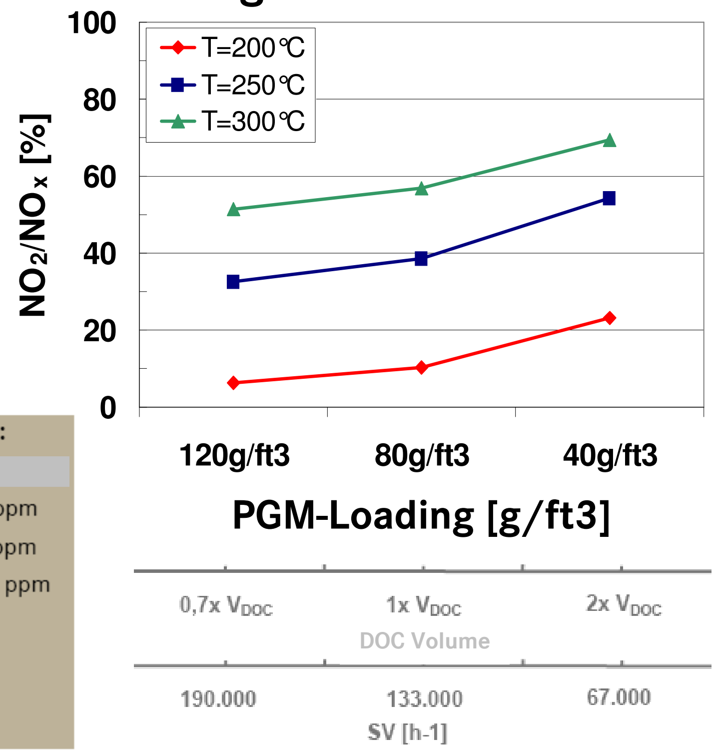
Constant Total PGM-Loading



*NO_2-Ratio [%] with **low** S.V. [h^{-1}]*

Gasmatrix:

NO = 200 ppm
CO = 100 ppm
C3H6 = 20 ppm
O2 = 8 %
CO2 = 8 %
H2O = 8 %
N2 = Rest



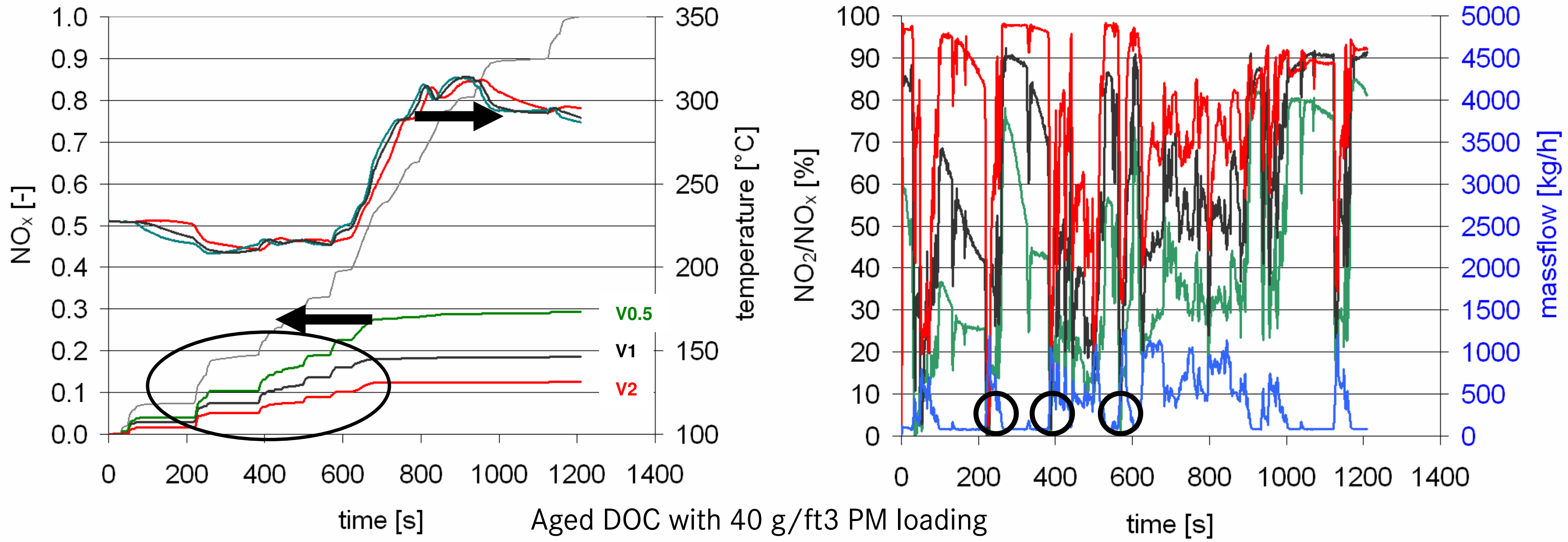
*NO_2-Ratio [%] with **high** S.V[h^{-1}]*

- Simulation reveals higher performance for low specific PGM-loading.
- Conversion efficiency at high S.V. is limited by residence time.

DOC+DPF+SCR Simulation:
DOC Optimization: Detailed Analysis Hot Start FTP

Cumulative NO_x (End of Pipe) and SCR Temperature

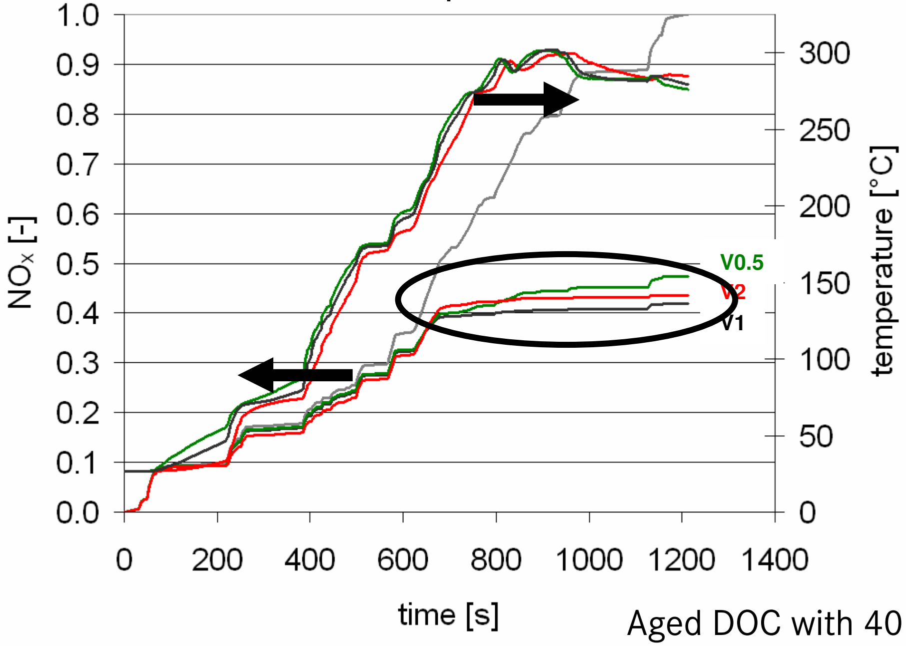
NO_2/NO_x at DOC Outlet and Exhaust Mass Flow



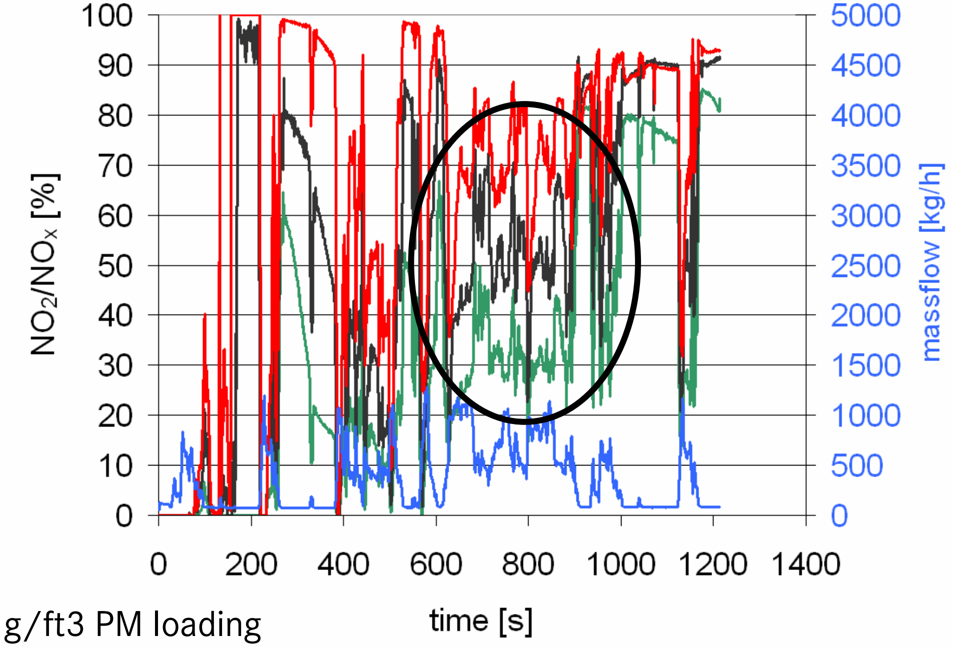
- Total NO_x conversion determined by first 650s of the FTP.
- Low NO_2/NO_x ratios after DOC during acceleration peaks in the first 650s.
- System performance limited by DOC performance under low temperature and high mass flow operating conditions.

DOC+DPF+SCR Simulation:
DOC Optimization: Detailed Analysis Cold Start FTP

Cumulative NO_x (End of Pipe) and SCR Temperature



NO_2/NO_x at DOC Outlet and Exhaust Mass Flow



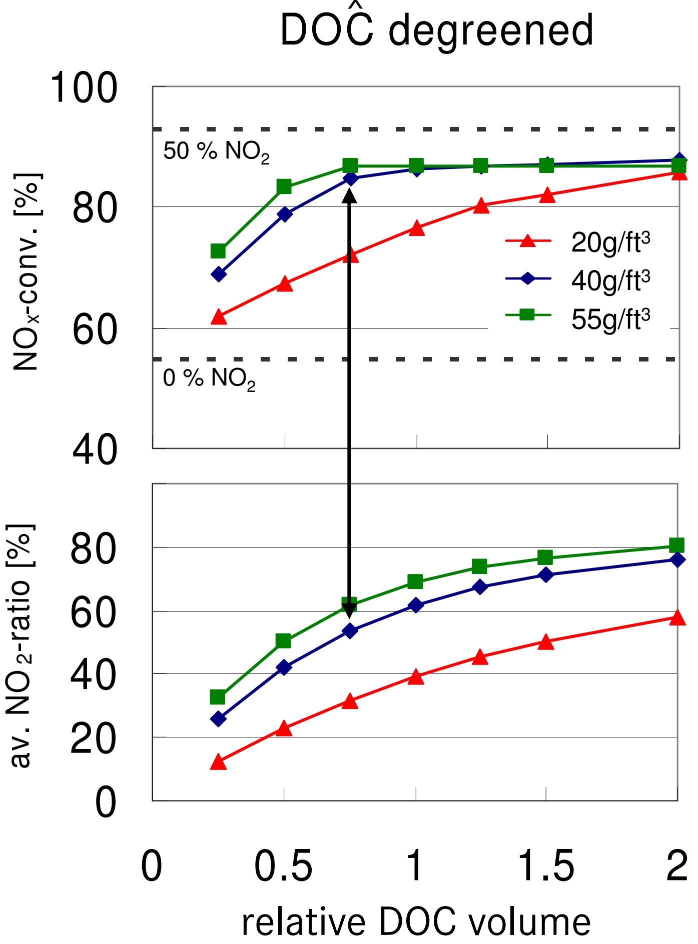
Aged DOC with 40 g/ft3 PM loading

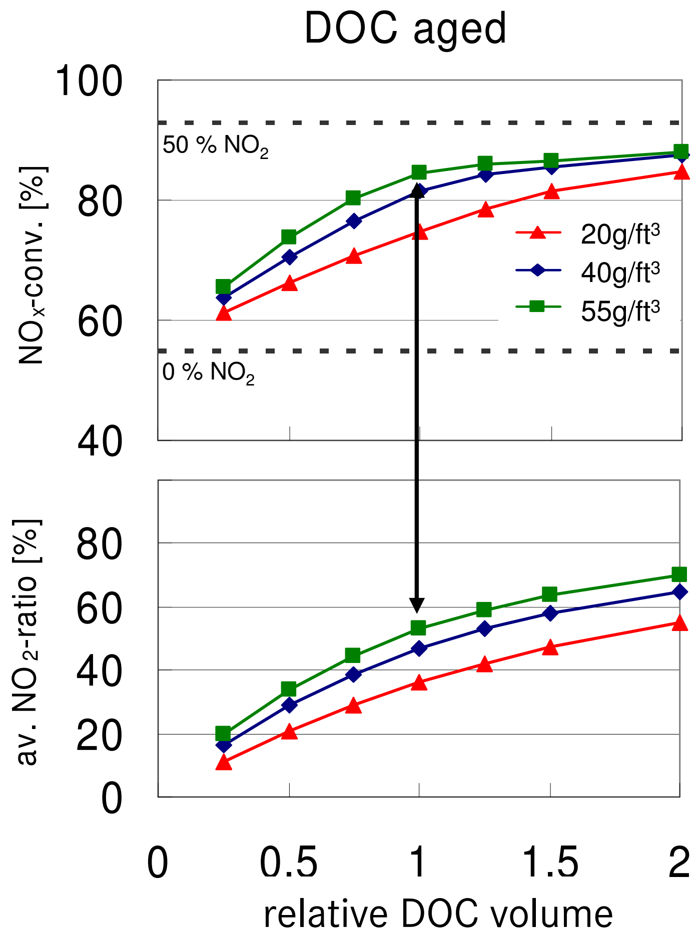
Total NO_x conversion determined by the second part of the FTP (600s-1200s)

DAIMLER

DOC+DPF+SCR Simulation: DOC Influence on SCR

Total NO_x SCR Conversion Efficiencies Within **Hot Start FTP**



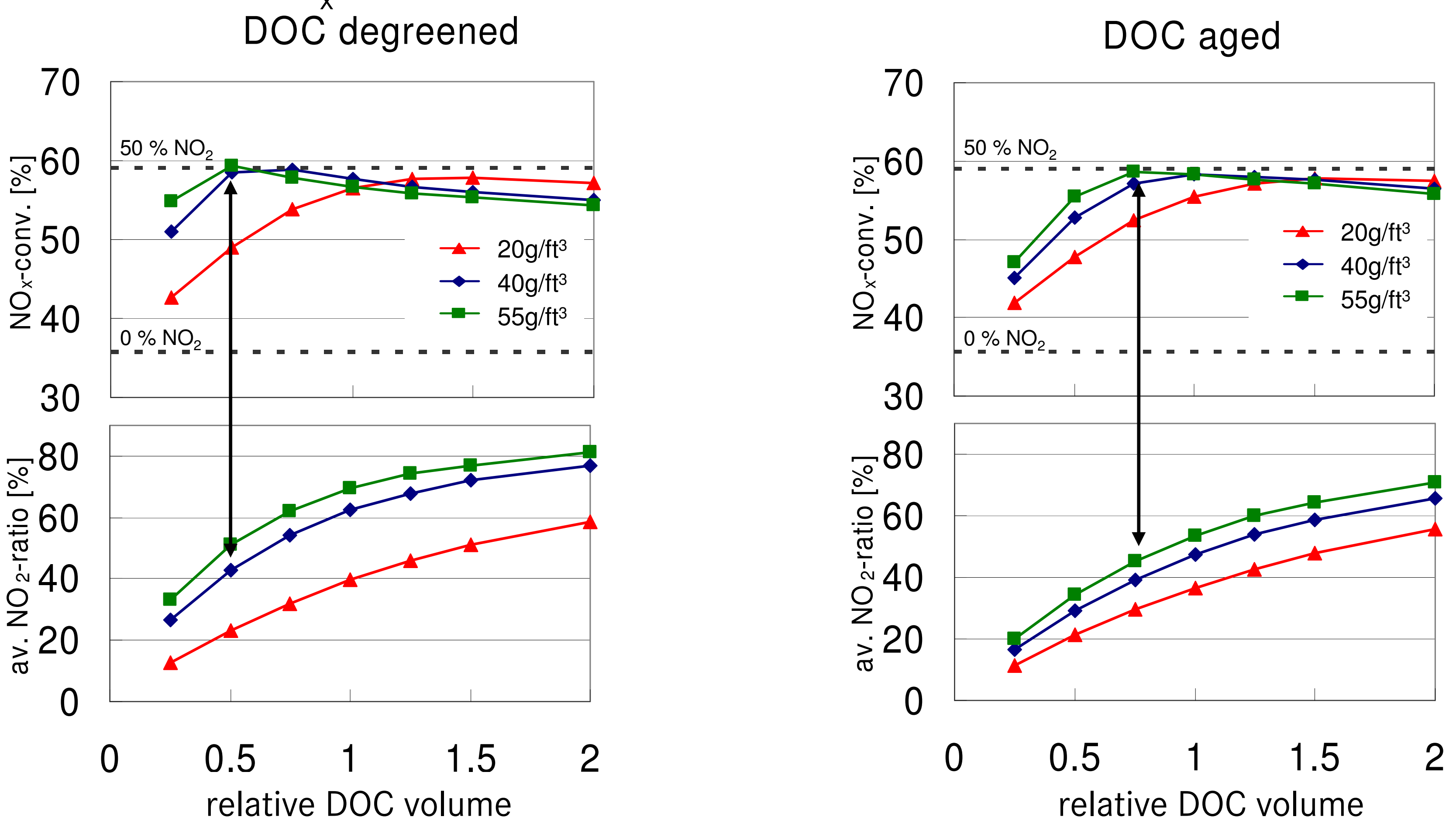


- Significant drop of SCR efficiency below a critical DOC volume.
- Best case NO_x reduction efficiency of 92% is not obtained.
- NO_x conversion efficiency is DOC residence time limited.

DAIMLER

DOC+DPF+SCR Simulation: DOC Influence on SCR

Total NO_x SCR Conversion Efficiencies Within **Cold Start FTP**



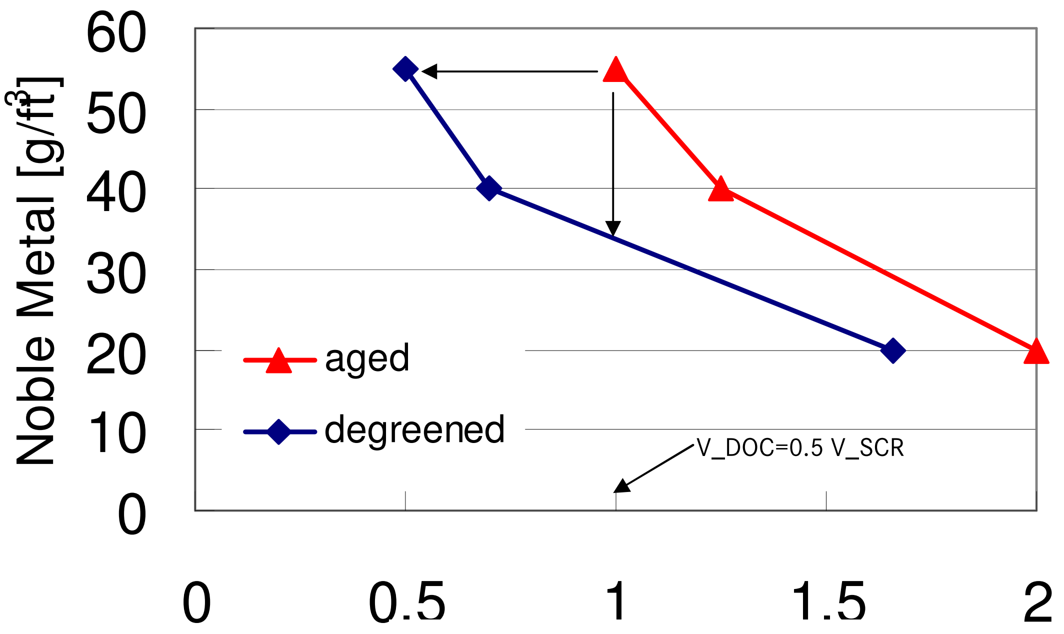
- Depending on PGM loading a optimum DOC volume is revealed.
- Noble metal loading higher than 40 g/ft³ required for max. efficiency.
- Significant volume reduction possible of degreened state could be stabilized.

DAIMLER

DOC+DPF+SCR Simulation:

Impact of DOC Volume vs. Noble Metal Loading on SCR

DOC Parameters for 80% Combined FTP SCR Conversion Efficiency



- 55g/ft3 DOC noble metal loading required with the reference DOC volume at aged state to achieve 80% FTP NO_x Performance.
- Significant volume and noble metal reduction possible if degreened state could be stabilized.
- Volume Reduction requires significant increase in noble metal loading → Residence time limitation.

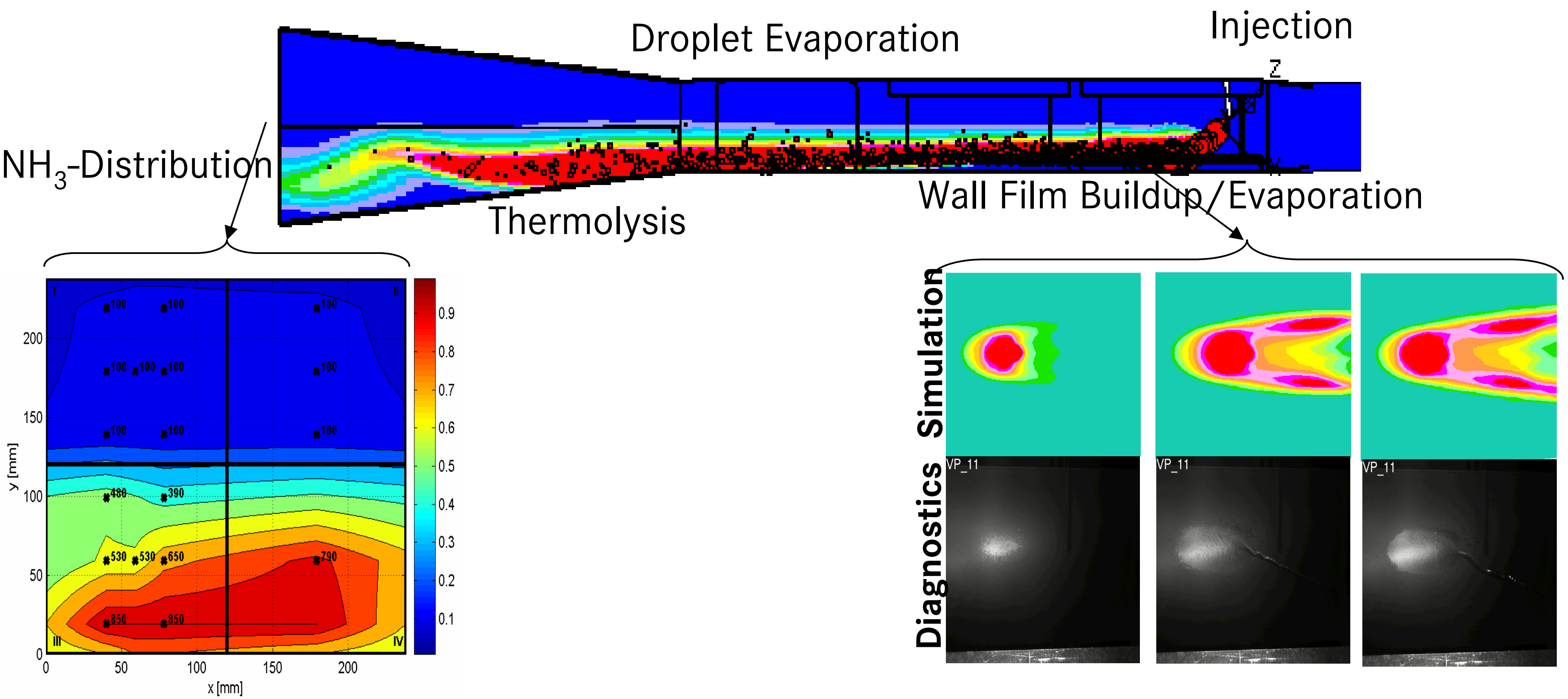
DAIMLER

Outline

- Advanced SCR-System Setup (DOC+DPF+SCR)
- Simulation Concept
- Modeling SCR Converters
- Modeling DOC Converters
- DOC: Kinetic Correlations
- Simulation Based System Optimization: DOC Impact on SCR
- Modeling of Urea Processing
- Conclusions

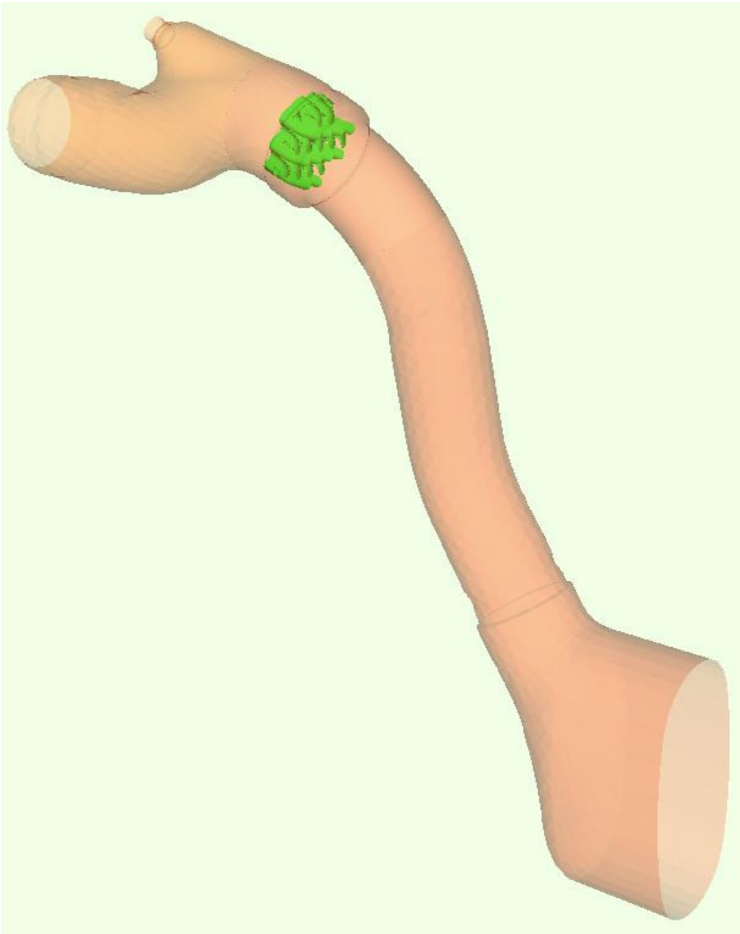
3D Simulation AdBlue Processing:

AdBlue Processing Within the Exhaust Line

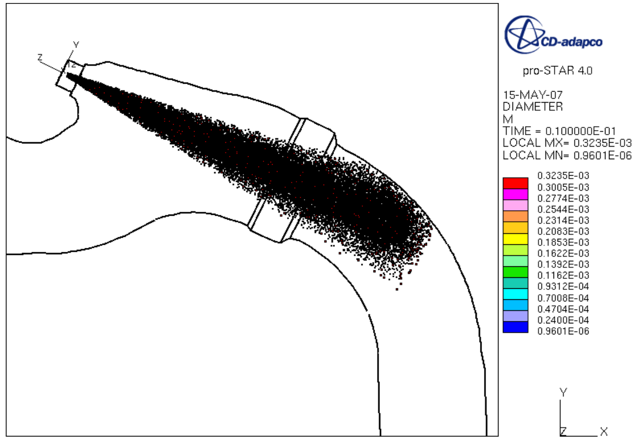


DAIMLER

3D Simulation AdBlue Processing:
Spray Modeling and Influence of Mixing Device



No Mixer



With Mixer

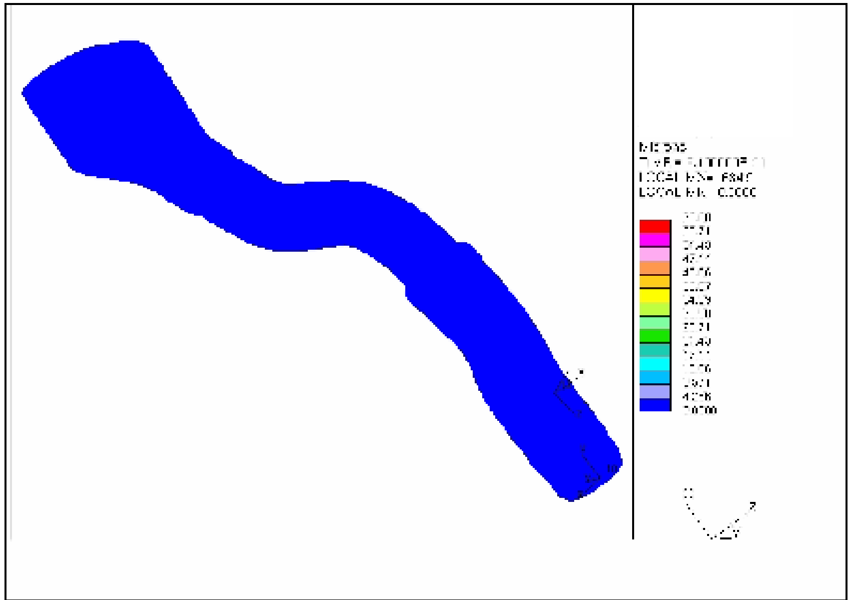
10s after start of injection

Reduction of wall contact, because of spray interception within mixing device.

DAIMLER

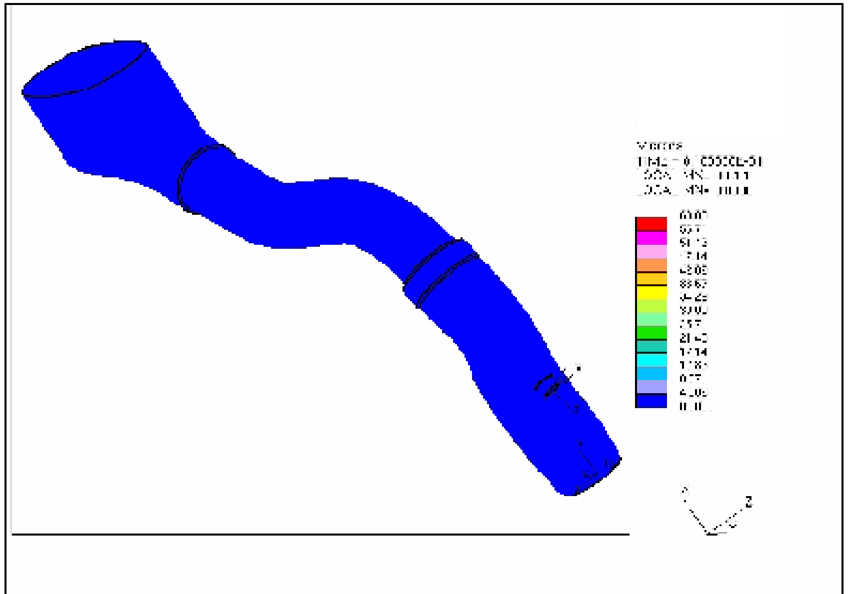
3D Simulation AdBlue Processing:
Mixer Influence on Wall Film Buildup*

With Mixer



mixer-lfthk-sl.avi

No Mixer



nomixer-lfthk-sl.avi

m_{Exh} = 100kg/h, T_{Exh} = 200°C

Spray interception by the mixer yields to reduced wall film formation.

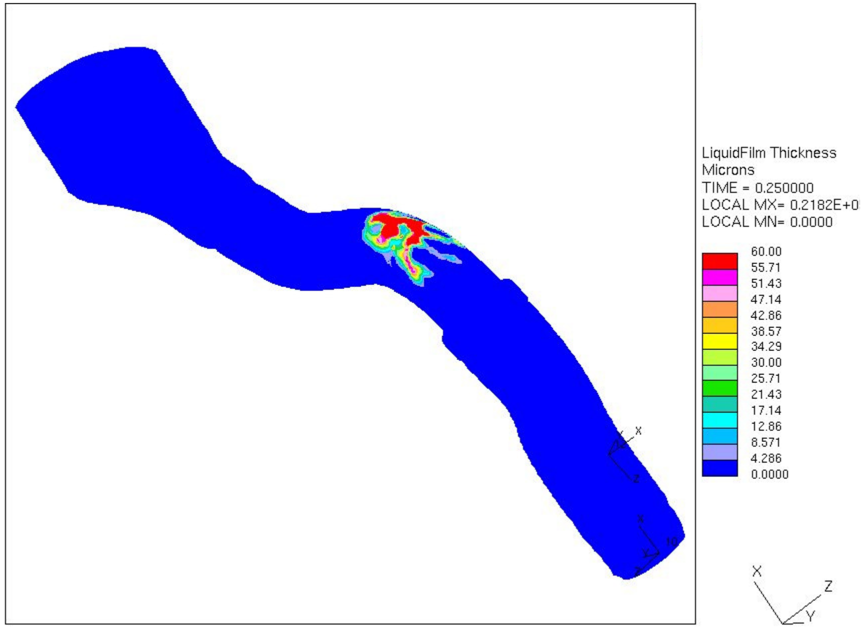
* high AdBlue overdosing

Dr. Schöffel– GR/VPE

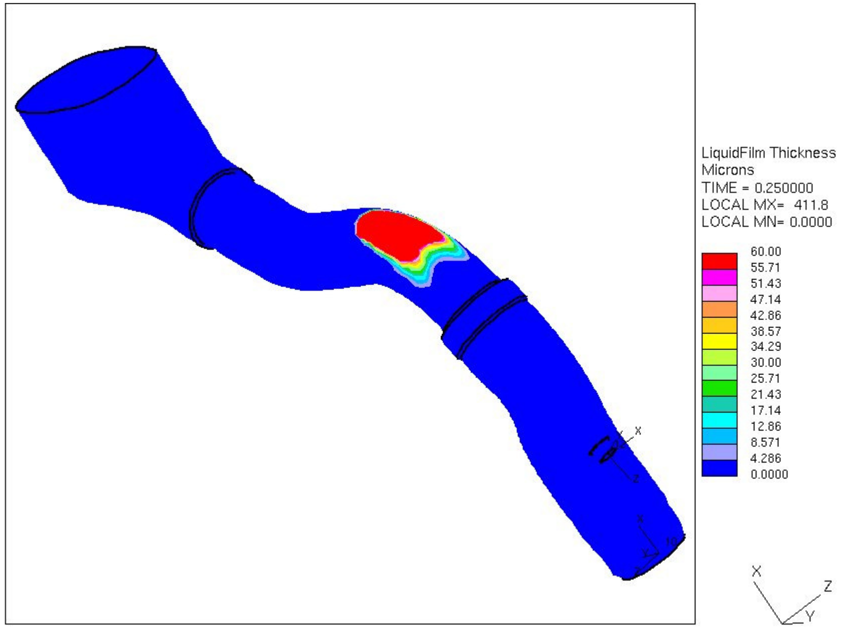
DAIMLER

3D Simulation AdBlue Processing:
Mixer Influence on Wall Film Buildup*

With Mixer



No Mixer



m_{Exh} = 100kg/h, T_{Exh}= 200°C

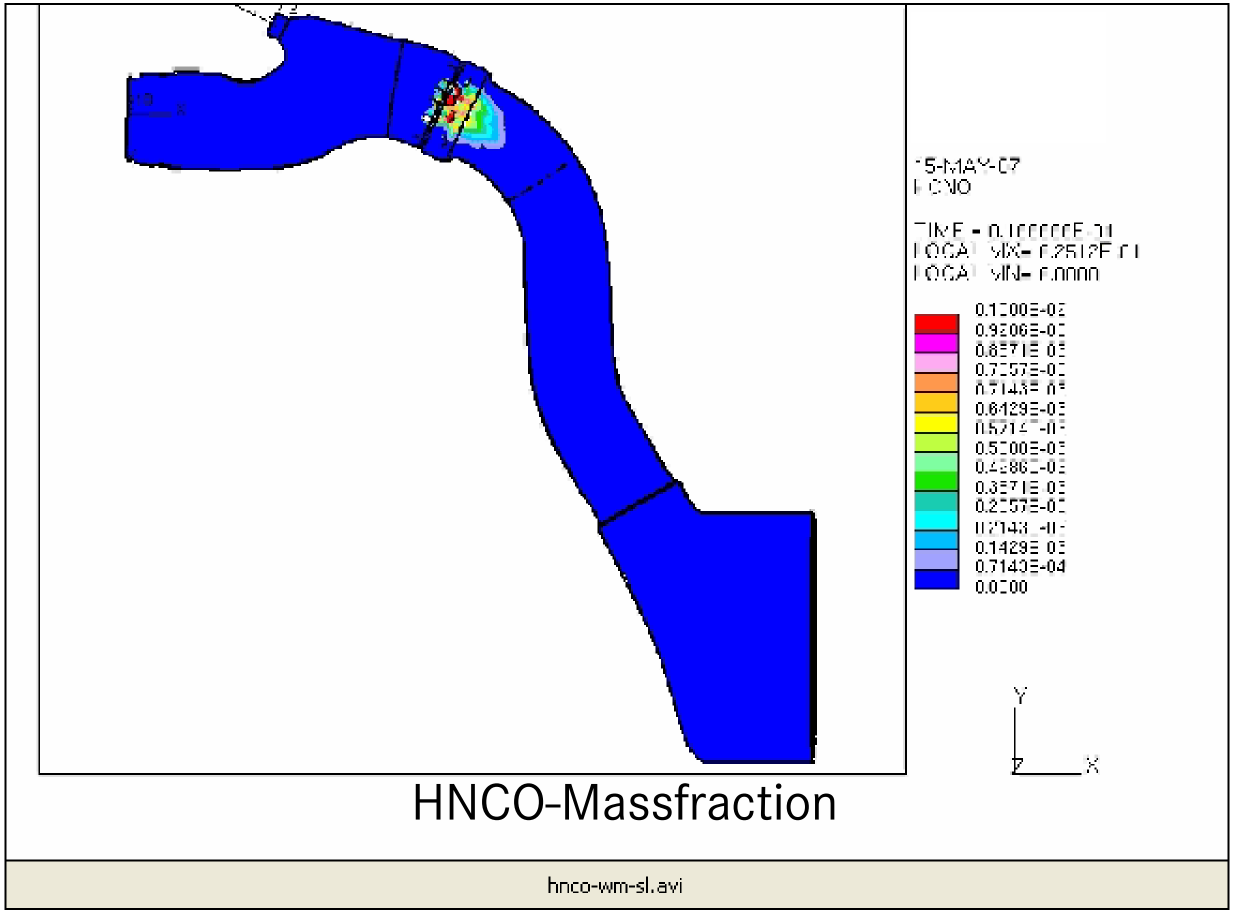
Spray interception by the mixer yields to reduced wall film formation.

* high AdBlue overdosing

Dr. Schöffel– GR/VPE

DAIMLER

3D Simulation AdBlue Processing:
Thermolysis/HNCO-Formation



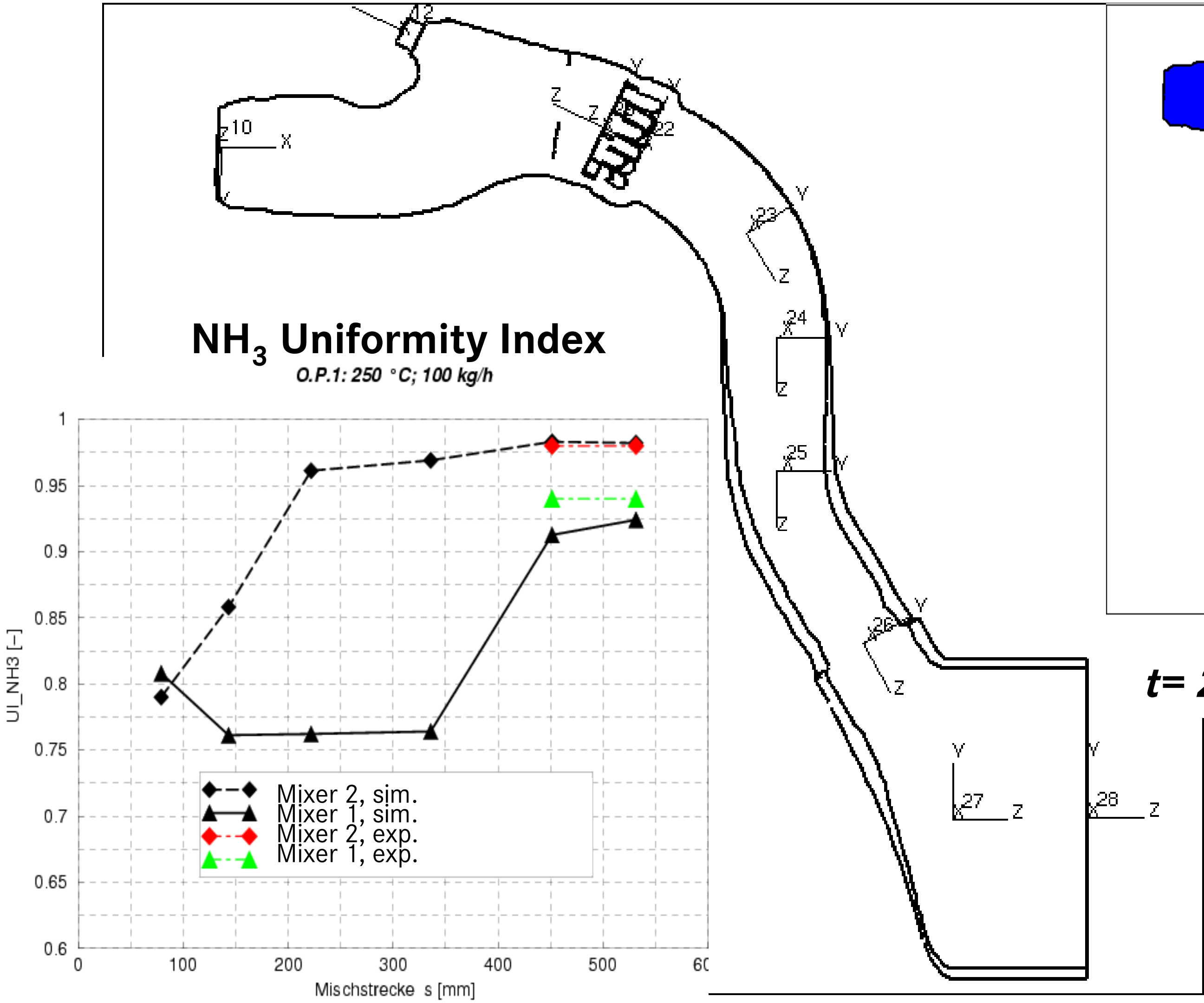
Mixer acts as an efficient evaporation surface within the exhaust flow.

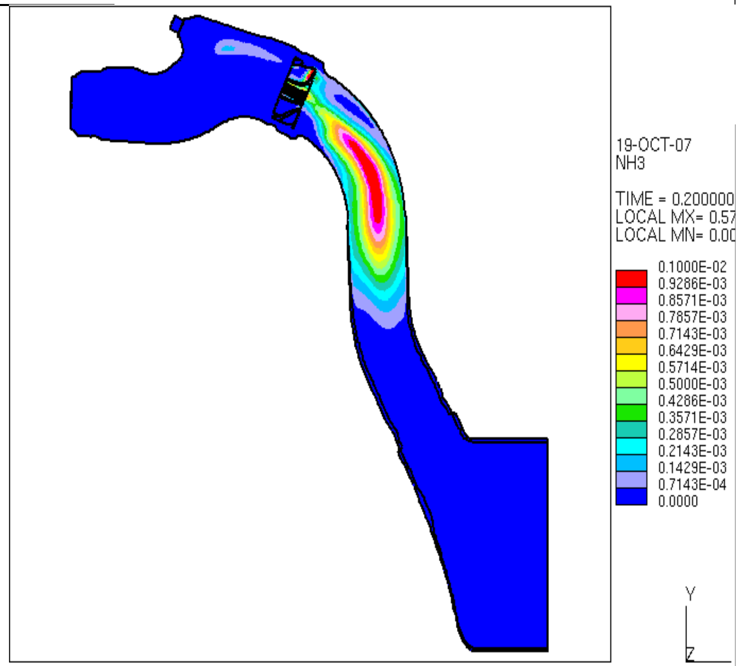
Dr. Schöffel– GR/VPE

3D Simulation AdBlue Processing: NH_3 - Distribution

NH_3 Uniformity Index

O.P.1: 250 °C; 100 kg/h





t= 20 msec after start of dosing

DAIMLER

Outline

- Advanced SCR-System Setup (DOC+DPF+SCR)
- Simulation Concept
- Modeling SCR Converters
- Modeling DOC Converters
- DOC: Kinetic Correlations
- Simulation Based System Optimization: DOC Impact on SCR
- Modeling of Urea Processing
- Conclusions

DAIMLER

Conclusions

- Integrated EGA system modeling has become essential and very efficient tool to assist the design of complex exhaust gas aftertreatment systems.
- Approach: 1D System modeling refined by 3D component modeling.
- Kinetic correlations offers the possibility to include noble metal variations in the system analysis.
- DeNOx efficiency of DOC+DPF+SCR (Fe-Zeolite) systems is limited by the DOC performance at low temperatures and high mass flows.
- New SCR materials may offer the possibility to reduce the critical impact of the DOC performance.
- DOC aging leads to significant “over sizing” of the system.
- Model extensions regarding aging are necessary.

Acknowledgments

Prof. Enrico Tronconi, Prof. Isabella Nova and Antonio Grossale

Dr. Petr Koci, Prof. M. Marek

Prof. G. C. Koltsakis

Jochen Lahr, Alexander Massner and Dr. Bernd Krutzsch