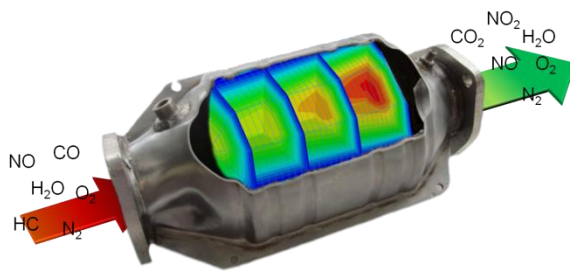


4th International Symposium on Modeling of Exhaust-Gas After-Treatment



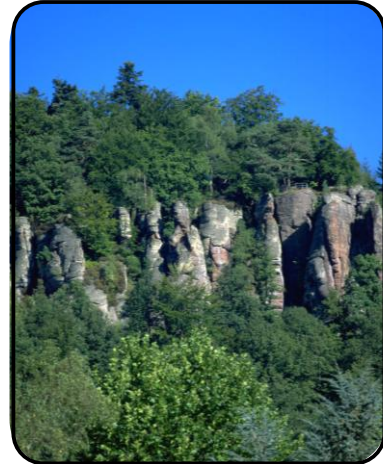
MODEGAT IV

13th - 15th September 2015
Bad Herrenalb/Karlsruhe
Germany

Book of Abstracts

Welcome to Bad Herrenalb!

Welcome to the 4th International Symposium on Modeling of Exhaust-Gas After-Treatment. This is the fourth symposium in Europe that specifically focuses on modeling and numerical simulation in automobile exhaust-gas after-treatment. The purpose of this workshop is to support the exchange of state-of-the-art modeling and simulation techniques and new approaches among researchers, scientists, and engineers from industry and academia.



The meeting has over 100 registered participants, about 40 % from academia and about 60 % from industry. These numbers show the large interest of both academia and industry in the simulation of exhaust-gas after-treatment.

We warmly welcome you to Bad Herrenalb and wish you a pleasant and successful symposium.

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Local Organization

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Monday, 14.09.2015

08:45	Welcome	
09:00	Toops	Tutorial Modeling SCR
10:00	Olsson	
10:25	Coffee Break	
10:55	Tronconi	
11:20	Bendrich	
11:45	Tamm	
12:10	Lunch	
13:15	Birkhold	Tutorial Urea Injection
14:15	Koltsakis	
14:40	Posters with Coffee	
16:00	Kočí	Tutorial modeling NO_x storage and Three way catalysts
17:00	Walting	
17:25	End	
19:00	Dinner with social get-together afterwards on-site	

Tuesday, 15.09.2015

09:00	Auckenthaler	Tutorial Models for Engine Control
10:00	Papadimitriou	
10:25	Posters with Coffee	
11:20	Arvajová	
11:45	Gremminger	
12:10	Lunch	
13:30	Sappok	Tutorial DPF
14:30	Vidal	
14:55	Coffee Break	
15:25	Maletic	
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16:15	Hayes	
16:40	Poster Award and Concluding remarks	
16:50	Coffee and farewell	

Symposium Program

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10:00	A kinetic model for sulfur poisoning and regeneration of Cu/SSZ-13 used for NH₃-SCR L. Olsson*, K. Wijayanti, K. Leistner, Chalmers University of Technology, Göteborg, Sweden A. Kumar, S. Joshi, K. Kamasamudram, N. W. Currier, A. Yezerets, Cummins Inc., Columbus, USA
10:25	Coffee break
10:55	Enhanced-SCR reaction: experimental and modeling study over a commercial Fe-zeolite catalyst F. Marchitti, I. Nova, P. Forzatti, E. Tronconi, Politecnico di Milano, Milano, Italy S. Adelberg, V. Strots, IAV GmbH, Berlin, Germany
11:20	Simulation of SCR/ASC systems with automatically optimized NH₃ dosing strategies M. Bendrich, B. Opitz, J. Rink, A. Scheuer, M. Votsmeier*, Umicore AG & Co. KG, Hanau, Germany J.F. Forbes, R.E. Hayes, University of Alberta, Edmonton, Canada
11:45	Detailed kinetic model of the hydrogen effect during the selective catalytic reduction of NO with ammonia over Ag/Al₂O₃ S. Tamm*, Chalmers University of Technology, Göteborg, Sweden
12:10	Lunch
	Session NO_x storage and TWC chaired by M. Votsmeier
13:15	From the injection point to the SCR catalyst: Analysis and modeling of the AdBlue preparation F. Birkhold, Robert Bosch GmbH, Stuttgart, Germany
14:15	3-way catalyst modeling and applications for system design and control D. Karamitros, A. Khatke, Exothermia SA, Thessaloniki, Greece G. Koltsakis*, Aristotle University Thessaloniki, Thessaloniki, Greece A.-F. Villegas, P. Barrillon, Renault SA, Lardy, France
14:40	Posters with Coffee
16:00	NO_x reduction dynamics and selectivity in lean NO_x traps and three-way catalysts P. Kočí, University of Chemistry and Technology Prague, Prague, Czech Republic
17:00	The Effect of NO and O₂ Concentration on the Rate of NO_x Storage on a Lean NO_x Trap: An Experimental and Modelling Study T. C. Watling*, Johnson Matthey Technology Centre, Reading, UK P. D. Bolton, D. Swallow, Johnson Matthey Emission Control Technologies, Royston, UK
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10:00	Methodology for Derivation of ECU Capable Models from Detailed Models of a SCR Reactor S. R. Gundlapally, I. Papadimitriou, S. Wahiduzzaman*, Gamma Technologies, Inc., Westmont, USA. T. Gu, University of Houston, Houston, USA.
10:25	Posters with Coffee
11:20	Modeling of platinum oxide formation and reduction by CO and C₃H₆ pulses during NO oxidation <u>A. Arvajová</u> , P. Kočí*, University of Chemical Technology, Prague, Czech Republic V. Schmeißer, M. Weibel, Daimler AG, Stuttgart, Germany
11:45	Influence of gas composition on bimetallic catalysts for exhaust gas after treatment of gas engines A. Gremminger, H. W. P. Carvalho, R. Popescu, J.-D. Grunwaldt*, O. Deutschmann*, Karlsruhe Institute of Technology, Karlsruhe, Germany
12:10	Lunch
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14:30	Simulation of the impact of thermophoresis on the capture efficiency of diesel particulate filters <u>D. Vidal</u> , G. Matte-Deschênes, F. Bertrand*, Polytechnique Montréal, Montréal, Canada R. E. Hayes, University of Alberta Edmonton, Edmonton, Canada
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15:25	Modeling of NO_x reduction and soot oxidation in a DPF with SCR coating <u>B. Maletic*</u> , N. Markert, D. Chatterjee, MTU Friedrichshafen GMBH, Friedrichshafen, Germany E. Tronconi, I. Nova, F. Marchitti, Politecnico di Milano, Milano, Italy G. Koltsakis, LAT Thessaloniki, Thessaloniki, Greece D. Karamitros, Exothermia SA Thessaloniki, Thessaloniki, Greece
15:50	Modeling of the loading in partially damaged DPFs <u>O. Haralampous*</u> , Technological Educational Institute of Thessaly, Larissa, Greece C. Dritselis, University of Thessaly, Volos, Greece
16:15	Modelling the Combined DOC/DPF System using a Multi-Scale Approach <u>R.E. Hayes*</u> , R. Litto, J.P Mmbaga, University of Alberta, Alberta, Canada T. Atmakidis, Exothermia, Thessaloniki, Greece G. Koltsakis, Aristotle University Thessaloniki, Thessaloniki, Greece
16:40	Poster Award and Concluding remarks
16:50	Coffee and farewell

Underlined: First Author/Presenting Author
 Asterisk*: Corresponding Author

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www.modegat.org.

A kinetic model for sulfur poisoning and regeneration of Cu/SSZ-13 used for NH₃-SCR

Louise Olsson^{*1)}, Kurnia Wijayanti¹⁾, Kirsten Leistner¹⁾, Ashok Kumar²⁾, Saurabh Joshi²⁾, Krishna Kamasamudram²⁾, Neal W. Currier²⁾, Aleksey Yezerets²⁾

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Introduction

Ammonia SCR is a widely practiced technology for reducing NO_x emissions from diesel and lean burn engines. Copper-zeolites and silicoaluminophosphates with chabazite (CHA) structure, like Cu-SSZ-13 and Cu-SAPO-34, were commercialized because of their hydro-thermal durability and hydrocarbon resistance. These catalysts are susceptible to sulfur poisoning and it is therefore important to study the sulfur poisoning and regeneration of copper-zeolites. However, there are to our knowledge no kinetic models available that can describe the sulfur poisoning during NH₃-SCR. The objective of this work is to develop a kinetic model that can describe the sulfur poisoning and gradual regeneration during NH₃-SCR using a Cu-SSZ-13 catalyst.

Materials and Methods

We have synthesized Cu/SSZ-13 (3.1 wt-% Cu and Si/Al ratio of 3.56) and the prepared material was characterized with XRD, BET, and ICP-SFMS. The Cu/SSZ-13 monolith sample was poisoned at 300°C using 30 ppm SO₂ in presence of 400ppm NH₃, 400ppm NO, 8% O₂, 5% H₂O for 90 min. Thereafter, the temperature was decreased to 100°C and SCR experiments were conducted, where the temperature was increased step wise to 400°C while exposing the catalyst to 400ppm NH₃, 400ppm NO, 8% O₂, 5% H₂O. The SCR experiments were repeated eight times in order to examine the gradual removal of sulfur (denoted SCR1, SCR2, etc). After the repeated SCR experiments, several other reactions were conducted. The kinetic modeling was done in AVL BOOST 2013.

Results and Discussion

First, a kinetic model for NH₃-SCR over Cu/SSZ-13 was developed over a broad temperature interval. This model was used as a base for developing a sulfur poisoning mechanism including gradual sulfur removal. Figure 1 shows the NO_x conversion versus temperature for both the model as well as experiment during SCR experiments; for fresh catalyst and after sulfur poisoning (SCR1) and after repeated sulfur regeneration experiments (SCR3 and SCR8). The conversion is decreasing significantly after the sulfur poisoning (SCR1) which shows that sulfur is attached to copper sites. After SCR experiments to 400°C, some of the sulfur species are removed and the activity is increased. However, after repeated experiments a stable activity level is reached, which is significantly lower than the initial activity. In addition, ammonia oxidation and ammonia storage before and after poisoning was simulated. The model can describe the experimental features well.

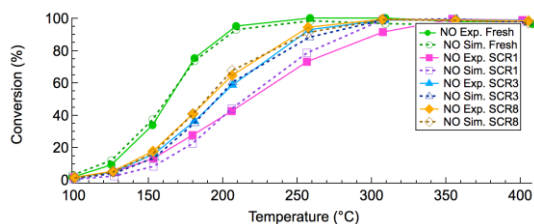


Figure 1. Experiment and kinetic model for sulfur poisoning and regeneration during SCR conditions.

Significance

Sulfur poisoning is one of the critical degradation mechanisms for NH₃-SCR catalysts and it is therefore essential to examine the sulfur poisoning and regeneration. Kinetic models are important both for the understanding as well as for prediction. This is, to our knowledge, the first kinetic model presented, for sulfur poisoning and regeneration of Cu/zeolites used for NH₃-SCR.

Acknowledgements

Cummins Inc. and the Swedish Research Council are gratefully acknowledged for the financial support.

Enhanced-SCR reaction: experimental and modeling study over a commercial Fe-zeolite catalyst

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It has been demonstrated [1,2] that addition of aqueous solutions of NH_4NO_3 (AN) to a NO-NH_3 containing feed results in the “Enhanced SCR” (E-SCR) reaction, that is associated with high DeNOx efficiencies in the 180-350°C T-range without upstream oxidation of NO to NO_2 . The aim of the present work is to clarify both fundamental and practical aspects of the E-SCR reactivity, with particular focus on the key mechanistic steps responsible for the improvement of the DeNOx activity. Further, a simulation model is developed to quantitatively describe the E-SCR chemistry and to assess its practical potential for EAT systems.

Both NH_3 -SCR and E-SCR reactions were investigated over core samples drilled from a commercial Fe-Zeolite washcoated monolith catalyst supplied by Umicore. Isothermal steady-state and transient runs were carried out in the $T=150\text{--}500^\circ\text{C}$ and $\text{GHSV} = 35000\text{--}100000 \text{ h}^{-1}$ ranges. Typical feed concentrations of NOx ($\text{NO}_2/\text{NOx} = 0\text{--}0.5$) and NH_3 were 500 ppm, with 8% O_2 , 5% H_2O v/v and N_2 as balance gas. In E-SCR runs an aqueous solution of AN (100-350ppm) was also dosed upstream of the SCR catalyst.

The DeNOx activity was greatly boosted by the AN additive in the low-T range. The enhancement was maximum at 180°C, with NO conversion going from about 10% without additive to over 90% upon addition of

250ppm of AN, which is very close to the Fast-SCR activity at the same conditions.

Based on the analysis of the experimental results and the related mechanistic findings, a simplified model of the AN reactions was built and used to analyze the potential improvement of the performance of a heavy-duty SCR system comprising a diesel oxidation catalyst, a coated particulate filter, injection of aqueous solution of urea, SCR and ammonia oxidation catalysts. The model enabled simulation of different architectures, including independent injection of urea and AN solutions from two separate tanks, and injection of an aqueous mixture of urea and AN from a single tank. The system simulation results showed that the separate injection of AN resulted in $\text{NO}_2:\text{NO}$ ratio of 1:1 at the SCR catalyst inlet during most of the transient operating cycle, which produced ~30 % reduction of NOx emissions at the system outlet. Simulations of injection of urea-AN mixtures with molar ratios of 0.3, 0.6, and 0.9 indicated existence of an optimum ratio with slightly higher NOx emission levels.

Acknowledgments

Financial support from the EU FP7-284909 Project “CORE – CO_2 reduction for long distance transport” is gratefully acknowledged.

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Simulation of SCR/ASC systems with automatically optimized NH₃ dosing strategy

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The purpose of the ammonia slip catalyst (ASC) is to improve the robustness of the SCR system towards NH₃ dosing tolerances. Ultimately, the hope is to increase the NO_x conversion by enabling a more aggressive NH₃ dosing. Given the strong relation between ASC performance and NH₃ dosing, it is clear, that a meaningful comparison of different SCR-ASC systems requires an individually optimized dosing strategy for each system.

We have recently developed a method to automatically optimize the NH₃ dosing profiles for a given catalyst system [1]. The method is simple enough to be implemented in a standard simulator and to be executed routinely as part of the model based system design process.

In this contribution, we apply the automated NH₃ dosing optimization towards a study of the SCR-ASC system. The studied system consists of an iron-zeolite SCR catalyst followed by a dual layer ASC catalyst [2], all simulations are performed using the WHTC test cycle. Numerically efficient simulation of the ASC catalyst is achieved using a low dimensional model based on internal mass transfer coefficients [3].

It is investigated, in how far the addition of an ASC allows to increase the NO_x conversion or the robustness of the SCR system. In particular, we study the effect of the size of the ASC catalyst and the thickness of the ASC catalyst's upper layer on the system performance during a WHTC test cycle. The performance of the different SCR-ASC systems is compared to an SCR only system with the same total volume.

References

- [1] B. Opitz, M. Bendrich, A. Drochner, H. Vogel, R. E. Hayes, J. F. Forbes and M. Votsmeier, "Simulation study of SCR catalysts with individually adjusted ammonia dosing strategies," *J. Chem. Eng.* 264, 936-944 (2015).
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Detailed kinetic model of the hydrogen effect during the selective catalytic reduction of NO with ammonia over Ag/Al₂O₃

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A detailed kinetic model was developed that is able to explain the hydrogen effect during H₂-assisted NH₃-SCR over an Ag/Al₂O₃ catalyst. Silver/alumina is active for NO_x reduction with NH₃ and H₂ as reducing agents, however, the activity is very limited with only one of the reducing agents present [1]. Moreover, the presence of only H₂ as reductant dramatically increases the activity for NO oxidation [1]. In the model, we explain the H₂-effect by H₂ creating special sites (S1*) for oxidation, probably on silver. Only on these special S1* sites, NO can be oxidized to NO₂. Moreover, NH₃ can adsorb on these S1* sites. The reduction of NO occurs via a reaction of adsorbed NO₂, and NH₃ adsorbed on S1* sites. This reaction mechanism ensures a molar stoichiometry between NO, NH₃ and H₂ of 1:1:2 for the SCR reaction and a molar stoichiometry of 1:1 for the H₂ assisted oxidation of NO as observed previously [2]. In addition, this proposed reaction mechanism can also explain phenomena observed during H₂-assisted hydrocarbon-SCR over Ag/Al₂O₃ catalysts, as increased oxidation of hydrocarbons, which is not included in the present model. During the modelling, different ways were tested to describe the hydrogen effect. In a previous model we included H₂ in a global SCR-reaction. In the present model hydrogen creates special sites on silver to describe the effect by less than 1000 ppm of hydrogen in an atmosphere with 10 % of oxygen. Without these specific reactions for hydrogen, the addition of hydrogen did not give any effect in the model.

During the development of the model, first, the NH₃ storage and release was modelled on two different storage sites using NH₃ temperature programmed desorption. Moreover, the adsorption and release of NO₂ was studied. Large amounts of NO₂ were adsorbed on the catalyst. However, during SCR conditions, the release of NO₂ was very limited. That is why in the model only adsorption of NO₂ on silver sites is included. Further reactions included in the model are the oxidation of NH₃ to N₂ and NO, and the unselective oxidation of H₂ to water. The model was fitted to the results of several NH₃-TPD and NH₃ oxidation experiments with different concentrations of H₂ and O₂, and a series of H₂-assisted NH₃-SCR steady-state experiments. The model predicts the conversion of NO_x well even during transient experiments.

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3-way catalyst modeling and applications for system design and control

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In response to the tougher market and legislative requirements for fuel efficiency, the gasoline engine technology is changing rapidly with increased introduction of downsized, turbocharged concepts and direct fuel injection. In combination with electric hybridization, the engine operating conditions will generally shift to higher specific loads which is expected to change the exhaust gas properties as well. In addition, the legislative requirements for new driving cycles and real-driving emissions compliance are expected to pose additional challenges for the design and control of highly efficient 3-way catalysts.

This work presents the methodology of developing and calibrating reaction models for 3-way catalysts based primarily on synthetic gas tests. Particular emphasis is given to the oxygen storage (OSC) phenomena [1, 2] that are modelled using a two-site approach and employing a reversible reaction mechanism involving re-oxidation of the OSC sites by H₂O and CO₂. The reaction models are developed for different catalyst coatings featuring substantially different PGM loadings. Modeling and simulation is supported by a comprehensive multi-dimensional commercial software platform (axisuite®).

The validation of the model in fully transient driving cycles is performed step-wise. Originally, transient cycle measurements with uncoated substrates are used to validate the thermal predictions of the model and evaluate the impact of radial temperature and flow non-uniformities. Next, a meticulous input data processing and clean-up is applied in order to meet the high accuracy input data requirements for use in 3-way catalyst modeling. Then, the model is applied to predict CO, THC and NO_x tailpipe emissions in 3 completely different driving cycles using the same catalyst model parameterization. The model results are examined in two modes: (a) ability to predict the onset of catalyst activation after cold-start, (b) ability to predict emissions breakthroughs under highly transient modes in the hot part of the cycles. The good agreement of the predicted vs measured results allows the identification of the physic-chemical phenomena that lead to some non-obvious emissions breakthroughs during the driving cycle. These are attributed either to catalyst activity/oxygen storage related limitations or to the control of the air-to-fuel ratio of the engine. This process provides useful insight towards identifying areas of total system improvement.

The last part of the paper illustrates potential areas of application of the calibrated model as stand-alone or embedded in an integrated vehicle simulation platform for control-oriented purposes. Typical applications include predictions of the effect of engine start-stop on catalyst performance, usage of active heat-up measures for cold-start performance improvements as well as sensitivity analysis with respect to OSC variations.

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The Effect of NO and O₂ Concentration on the Rate of NO_x Storage on a Lean NO_x Trap: An Experimental and Modelling Study

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This study considers the effect of NO and O₂ concentration (as well as temperature) on NO_x storage on a Lean NO_x Trap (LNT). It represents an extension of previous work [1] which looked at the effect of temperature on NO_x storage at constant inlet concentration.

The experimental data consisted of breakthrough curves measured with a laboratory reactor for a series of concentrations and temperatures. The NO_x breakthrough curves were run until the LNT was saturated with NO_x to enable NO oxidation to NO₂ to be studied in the absence of NO_x storage, to enable the effective NO_x capacity as a function of temperature and concentration to be determined, and to provide a more demanding test for potential models.

The inlet concentration affects both the rate of NO_x storage and the amount of NO_x stored at saturation. The rate of NO_x storage is found to increase with both the NO and O₂ concentration, while the effective NO_x storage capacity increases with NO concentration, but is independent of O₂ concentration (Fig. 1).

The data has been modelled and the performance of a number of kinetic models for NO_x storage compared. As with the earlier work [1], two types of storage sites were required: "Fast" sites are responsible for the initial part of the breakthrough curve, which is independent of temperature; both the rate of storage on these sites and the available capacity is independent of temperature. The rate of storage on "slow" sites, on the other hand, is temperature dependant, as is the available storage capacity. Slow sites are more abundant than fast sites. The rate of storage and the available capacity of both types of site are concentration dependent.

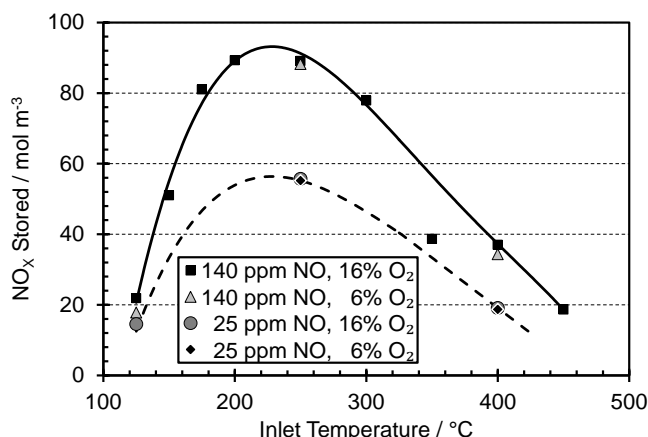


Figure 1. The effect of inlet concentration and temperature on the amount of NO_x stored obtained by integrating the full breakthrough curves (run to saturation). The lines are intended to guide the eye.

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Methodology for Derivation of ECU Capable Models from Detailed Models of a SCR Reactor

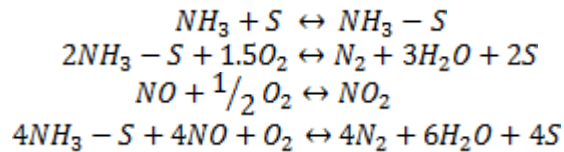
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Selective catalytic reduction (SCR) of NO_x with NH₃ is a widely used after-treatment technology for reducing the NO_x emissions from heavy-duty diesel engines. Detailed mathematical models of SCR reactors consist of large number of coupled differential algebraic equations, which can only be solved numerically. In recent years, model based control is getting more traction in the control community and for this purpose simple and yet reasonably accurate model that runs faster than real time is required. Hardware in loop (HIL) systems and Engine control units (ECU) have not only low frequency processor but also small memory size. Integrating dynamic models consisting of large number of coupled differential algebraic equations is not practical on these systems and hence there is need for a simple and fast running model (FRM). We developed FRM by systematically reducing the detailed model. This FRM is still fundamentals-based, the model parameters are directly related to physical and chemical properties of the catalyst, and can be used on HIL and ECU systems due to its faster run time and small memory footprint. Initially, the following set of reactions are included in the model:



The above reaction set can be easily extended to include fast and NO₂ SCR reactions when necessary. Assuming isothermal system and considering NH₃ and NO are the only trace species that we are interested in, commonly used 1+1D (axial direction in both phases and radial direction in the washcoat) model consists of five PDEs. If we assume quasi-steady state for species balances and no diffusional limitations in the washcoat, there are still three ODEs and two algebraic equations that need to be solved. Large space velocities in monolith channels allow us to axially lump the model which results in one ODE (for site balance) and four algebraic equations. This assumption can be easily relaxed by using several lumped blocks in sequence to capture spatial dynamics. We will discuss the implications of these assumptions in detail in the presentation. These four algebraic equations can be solved analytically and can be expressed as a function of fractional coverage (θ). This simplified one ODE model is computationally efficient and easier to solve. The previously calibrated detailed model is used to generate the data required for system identification process. Finally, we will compare the FRM predictions with the recently published experimental data for Cu-chabazite and Fe-zeolite catalysts and show that the FRM results are accurate for all practical purposes.

Modeling of platinum oxide formation and reduction by CO and C₃H₆ pulses during NO oxidation

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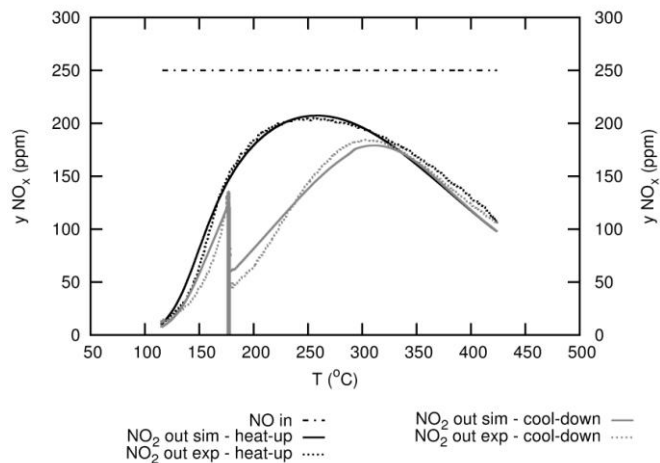
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NO oxidation in diesel oxidation catalyst (DOC) located in front of a deNO_x catalysts significantly affects the overall function of the combined aftertreatment system, as the NO_x reduction efficiency in SCR and NO_x storage catalysts depends on NO₂/NO_x ratio in the exhaust gas. NO conversion varies during NO oxidation under lean conditions due to a gradual Pt oxidation caused by NO₂ and O₂ [1,2]. It is known that platinum oxide (PtO_x) can be reduced by NO at lower temperatures or thermally decomposed at high temperatures. In this study, we present experimental and modeling results showing that PtO_x can be reduced also by CO and C₃H₆ pulses in the oxidative atmosphere. A commercial diesel oxidation catalyst containing Pt was used in experiments.

Temperature ramps from 120 to 420 and back to 120 °C and isothermal experiments at different temperatures were performed with a constant inlet gas composition (250 ppm NO, 8 % O₂, 8 % CO₂, 8 % H₂O), or with the pulses of increased CO (1000 ppm) and C₃H₆ (111 ppm) concentration while still keeping lean conditions. The restoration of NO oxidation activity by pulses with an increased CO and C₃H₆ concentration under lean conditions was newly studied during the cool-down ramp as well as during the reactivation phase of the isothermal experiments. The maximum effect of regeneration pulses was observed around the light-off temperature for CO and C₃H₆ oxidation, see example with CO pulses at 180 °C in Figure 1. At higher temperatures, the reductant was consumed in a short zone at the catalyst inlet and the major part of the catalyst remained unaffected.

Based on the above described experimental observations, a global kinetic model was developed.

The model considers the slow oxidation of Pt by NO₂ and O₂, PtO_x thermal decomposition, PtO_x reduction by NO, and PtO_x reduction by CO and C₃H₆ pulses. **Figure 1:** Simulation and experimental results of NO oxidation during the temperature ramp with 250 ppm NO, 8 % O₂, 8 % CO₂ and 8 % H₂O and CO reactivation pulses at 180 °C.



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Influence of gas composition on bimetallic catalysts for exhaust gas after treatment of gas engines

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Lean burn gas engines enjoy growing popularity due to growing supply of natural gas and high power with respect to CO₂ emissions. However, gas engines suffer from methane slippage, i.e. the emission of unburned methane into the exhaust pipe. The strong greenhouse activity of methane and tightening legislation makes it necessary to lower the emissions. Noble metal based catalysts are widely reported to be the most efficient for total oxidation of methane [1].

This study focuses on the influence of typical exhaust gas components on the activity and durability of a Pd-Pt/Al₂O₃ model catalyst [2]. Experiments were performed on commercial monolithic samples on test benches using synthetic gases. The catalysts were characterized by CO-chemisorption, N₂-physisorption, XRD, TEM and XAS in the fresh as well as in the deactivated state.

Figure 1 summarizes the results of 100 h long-term experiments at 450°C and a GHSV of 30000 h⁻¹. Under lean conditions containing 12% H₂O, 10% O₂ and 3200 ppm CH₄ in N₂ (curve I) the catalyst continuously deactivates

and methane conversion decreases from 98 to 68% in 100 hours. Characterization of the catalyst showed that neither pronounced sintering nor reduction of PdO causes the deactivation. Slight changes in the noble metal particles morphology leading to segregation of Pd and Pt forming core-shell particles could be observed. Surprisingly, the addition of 150 ppm NO_x and 500 ppm CO completely suppressed the deactivation process and stabilized a high methane oxidation activity (curve II). However, small amounts of SO₂ (4 ppm) present in the gas mixture caused rapid deactivation of the Pd-Pt-catalyst (curve III). In this case, a loss in dispersion caused by blockage of the noble metal sites was found to be responsible for the strong decrease of activity.

The study nicely shows how sensitive the methane oxidation activity of the catalyst depends on the reaction mixture. The results can be used to improve the adjustment between engine and catalyst to optimize the overall efficiency with regard to methane emissions.

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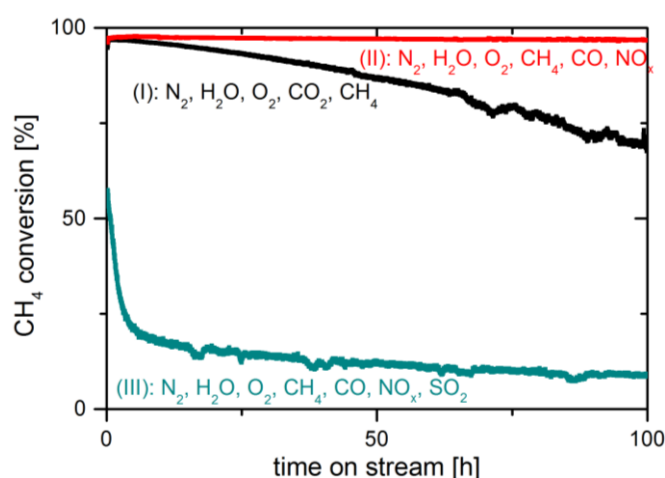


Fig. 1: methane conversion under different gas compositions as function of time on stream at 450°C and a GHSV of 30000 h⁻¹.

Simulation of the impact of thermophoresis on the capture efficiency of diesel particulate filters

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A three-step numerical model has been developed to shed light on the impact of thermophoresis on soot capture in the cordierite porous walls of a clean diesel particulate filter (DPF). It consists of: (1) the numerical reconstruction of a representative volume of the cordierite porous wall using either a simulated annealing (SA) procedure or X-ray tomography (CT) data, (2) the computation of gas flow through the reconstructed porous wall by means of the lattice Boltzmann method (LBM), and (3) the prediction of the DPF capture efficiency by solving a modified Langevin equation that includes the thermophoretic force. Permeability predictions of SA and CT reconstructions of cordierite porous walls computed using the LBM are first compared to data from the literature. From the computed flow field through these cordierite porous walls, we then present the trajectories and the resulting capture efficiencies of soot particles of various sizes, obtained for different operating conditions and various orientations and magnitudes of the thermophoretic force. In particular, we show that this force can affect soot capture efficiency in the presence of particle and flow inertia. A dimensionless criterion defined as the product of Stokes and Reynolds numbers is proposed to predict the onset of what can be called thermophoresis-enhanced inertial impaction. While similar results have been reported by others using simple flow geometries, this is the first time, to our knowledge, that this phenomenon is reported for complex cordierite porous walls.

Modeling of NO_x reduction and soot oxidation in a DPF with SCR coating

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The combination of SCR and DPF in one system (so called SDPF) enables a very compact design and has already found its way into commercial application for passenger cars. In the case of heavy-duty and non-road applications, the design and control of the SDPF heavily depends on the interaction between NO_x reduction and soot oxidation reactions taking place in close vicinity. The governing phenomena are described and studied in the present work by means of multi-scale experimental testing and mathematical modeling. Detailed kinetic studies at a micro-scale laboratory test rig are used to acquire the intrinsic reaction rates of the NH₃ - SCR reactions over a Cu-based catalyst, as well as to obtain qualitative trends of the role of soot presence. The above reaction kinetics are then directly implemented in a physico-chemical model of the transport and reaction processes in a wall-flow catalyzed filter. This model is validated against medium-scale engine tests revealing the competitive effects of SCR and passive soot oxidation, by a simple superposition of SCR chemistry and soot oxidation chemistry. This indicates that proper modeling of the species diffusion processes in the channels, the soot layer and the wall is sufficient to describe the inhibiting effect of NH₃-SCR on soot oxidation. This allows for a straightforward decoupled model calibration process which can be used to develop efficient system design and dosing control methodologies. Finally, the model is applied to a much different SDPF scale relevant for large non-road engines. The necessary adaptations to the model parameters are discussed as well as a methodology to apply predictive simulation tools when the boundary conditions are changed.

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Modeling of the loading in partially damaged DPFs

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One of the latest developments in automotive emissions control is the adoption of new stringent On-Board Diagnosis (OBD) threshold limits for particulate mass. As a result, novel soot sensors are actively under development and extensive failure studies are underway aiming at the development of reliable exhaust systems. In this frame, modeling tools can provide insight into the behavior of partially damaged filters, facilitate the interpretation of the experimental measurements and support the calibration of OBD systems.

The current work presents a transient multi-channel mathematical model for partially damaged Diesel Particulate Filters (DPF), combining conventional wall-flow filter modeling and recent developments in semi-open channel modeling [1]. The latter is used to approximate the damaged region with channels missing rear plugs, as shown in Fig. 1. Equivalent resistance circuits are employed to solve numerically the transient flow distribution both inside the channel and at the filter entrance. Multiple particle classes are used to account for the inlet particle distribution, while the necessary collection mechanisms are included in the particle and deposit mass balances along the channel axis. This way, the local flow rate, filtration efficiency and deposit loading are calculated as a function of time for both the intact and damaged region.

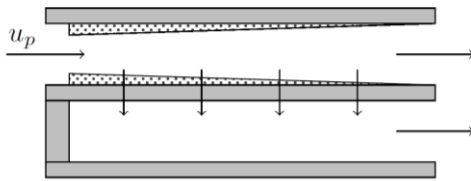


Fig.1: Schematic of a damaged DPF channel

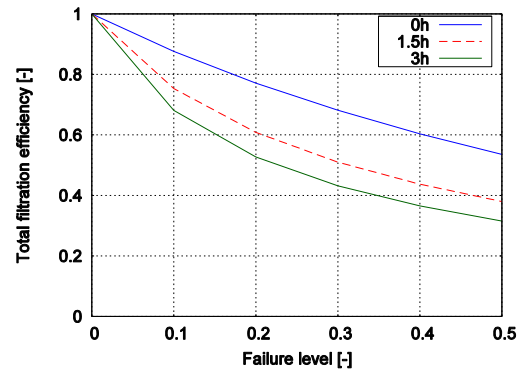


Fig.2: Filtration efficiency as a function of failure level and loading duration

Next, the loading mechanism in the compromised DPF is explained using the detailed computational results, while the overall performance is discussed in conjunction with experimental measurements available in the literature [2]. The evolution of pressure drop and deposit loading during a loading phase is compared between damaged and intact filters. Finally useful trends are identified with reference to the failure level. Indicatively Fig.2 depicts the negative effect of the damage on filtration efficiency and how this is enlarged with time.

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Modelling the Combined DOC/DPF System using a Multi-Scale Approach

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Modelling the exhaust gas after treatment system can be considered as an exercise in multi-scale modelling. Scales range from nanometres at the catalyst level, microns at the washcoat and cell wall level, to centimetres and larger at the full reactor scale. Depending on the required accuracy, various approximations can be made when modelling a full scale system. In this work, we consider a combined DOC and DPF unit, with an emphasis on the effect on the DOC performance of the DPF. To model the performance of the DPF requires a detailed model, which correctly captures the small scale phenomena such as the flow patterns in the channels, the particle deposition and filtration effects. To include such a detailed model in a standard CFD type software package would result in a large problem to solve.

The purpose of this work is to show how a customized DPF model that includes the detail can be coupled with a commercial CFD package to develop a model for the whole system. We model the DPF using the Axisuite package from Exothermia, specifically the Axitrap module. Axitrap deals with all aspects of the DPF, including the soot loading and regeneration. The DPF is contained within a single can with the DOC, and the entire system includes the inlet and outlet diffusers and the pipework. All of these components are modelled using Ansys Fluent software. The two packages must be coupled to ensure continuity of flow and mass in the system. This coupling is provided by means of a User Defined Function (UDF). The DOC is modelled using a continuum porous medium model.

This presentation will explain (1) the basic model equations for the overall system, including the turbulence model and treatment of the DOC (2) the coupling methodology used for Fluent and Axitrap and (3) present some results for the coupled systems under loading and regeneration conditions. The influence of the DPF on the flow patterns in the DOC will be shown for both the baseline DOC and a modified versions.

Abstracts

Poster Presentations

(in alphabetical order of 1st author's last name)

Model Based Evaluation of Control Algorithms for the Automotive SCR Catalyst

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Diesel engine exhaust gases contain amongst other things nitrous gases such as NO and NO₂ (together NO_x). Reducing the amount of these gases is of great importance due to new legislation, and because of the effect they have on urban air quality [1, 2]. A promising and widely used technology for this is based on selective catalytic reduction (SCR) of the gases, with ammonia as a reducing agent [3, 4]. Challenges with this technology include dosing the right amount of urea to reach the required NO_x conversion, but at the same time keeping the ammonia slip below the legislative limit. This requires efficient dosing algorithms, and to this end, model-based control is a promising strategy. Little work has been done to develop a standardized way of evaluating controllers for the automotive SCR catalyst. The evaluation is non-trivial because of the complicated nature of the SCR catalyst, where an increased urea dosing will reduce NO_x emissions, but increase ammonia slip. A standardized way of evaluating controllers based on current regulation would help in the development and selection of controllers for the exhaust gas treatment system. To reduce experimental effort, a simulation model that can be used for testing controllers will have to be developed. An objective function for evaluation of controller performance will also have to be developed.

A first principle model has been developed and coupled with a kinetic model. The kinetic parameters have been estimated using steady-state data from reactor tests with bench-scale equipment under isothermal conditions. The model has been validated with transient data from a full-scale monolith and a real engine following the European Transient Cycle (ETC). An objective function based on current legislation for the automotive system has been developed. The objective function punishes NO_x conversion below the required, average ammonia slip above the allowed, and also ammonia slip peaks above the regulations. The objective function can be used as a standardized way of evaluating control algorithms for the automotive exhaust gas cleaning system. A simplified form of the objective function can be used for online optimization in for example and model predictive controller. Three different controllers, a feedforward, a feedback and a combined feedforward/feedback have been implemented and tried with the derived model. The controllers have been evaluated with the objective function.

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Effect of Reversible Activation/Deactivation Processes on the Cold Start Performance of a Three-Way Catalyst

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Research on three way catalysts has shown that activation and deactivation processes play an important role in TWC performance [1]. Considering the major role of cold start emissions in TWC (~75% of total CO [2]), this study investigates reversible activation/deactivation processes occurring before and during cold start and shows their effect on catalyst performance.

Methods

A test procedure has been designed to reproduce engine cold start in an idealized laboratory scale experiment. A preheated exhaust mixture is suddenly directed towards an initially cold monolithic catalyst (Pd/Al₂O₃). This allows the hot exhaust gas stream to transiently heat the cold catalyst sample. Within seconds, a temperature gradient develops within the catalyst, eventually leading to an ignition of the catalytic reactions.

The exhaust gas composition represents a typical mixture of cold start motor exhausts. It consists of CO, C₃H₆, C₃H₈, H₂, NO, O₂, H₂O, CO₂ and N₂ for balance. A/F-ratio was set via the oxygen concentration. Gas analysis was done using FID for hydrocarbons and IR for CO/CO₂.

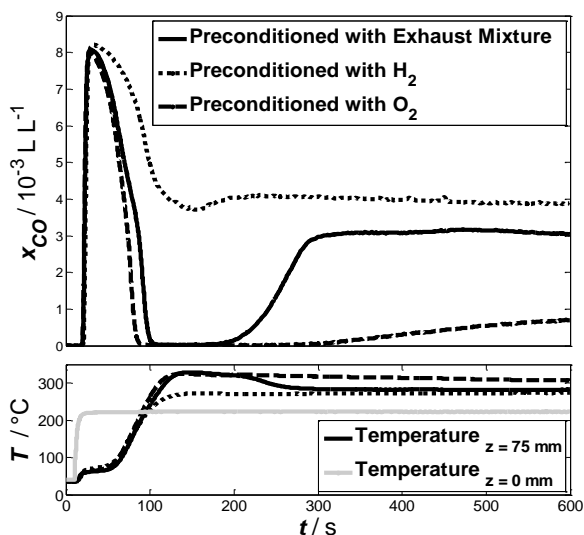
Prior to each test run, the catalyst was preconditioned for 2-10 min at varying temperatures (300 to 600 °C) with different gas environments. An oxidizing (O₂), a reducing (H₂) and a slightly lean real exhaust gas mixture each have been used for preconditioning. Furthermore, the length of heating and gas exposure during preconditioning was varied.

Results and Discussion

Figure 1 shows the measured CO tailpipe signals during the first 10 minutes after gas dosage for different methods of catalyst preconditioning. It stands out that exhaust conversion during cold start varies strongly, depending on the applied preconditioning.

An oxidized Pd-surface tends to be more active for CO and HC conversion. This process is reversible, since the CO-tailpipe concentration once again increases with time. Higher temperatures during preconditioning further promote the activation effect.

Also, it has been shown that activation/deactivation processes become less pronounced with increased aging of the catalyst.



While the influence of the catalyst's oxidation state on the catalytic activity has been known for a long time, this study shows that activation/deactivation is relevant on the time-scale of a typical cold start [3]. This suggests that by taking into account activation/deactivation processes, the accuracy of TWC models can be further improved; either by developing a standard preconditioning routine for test runs or by accounting for the catalyst surface state at $t=0$ in the model.

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Application of system simulation for the development of urea injection strategies for EU6c

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In order to comply with the level of nitrogen oxides (NO_x) and soot required with the upcoming Euro 6c emissions regulation, the enhancement of Diesel exhaust line after-treatment systems is mandatory. Various architectures need to be tested to achieve an overall high NO_x conversion efficiency. In addition to the oxidation catalyst (DOC), a possible solution is the combination of a close-coupled SCR (ammonia selective catalytic reduction coated on a particulate filter) with an under-floor SCR. The benefits of this layout are the early light-off and higher temperatures that allow higher NO_x conversions. A key point to reach the maximum efficiency of the system is the optimization of the urea injection control. Engineers need to develop advanced control laws in order to manage the distribution between NH₃ stored in the SCR and NH₃ slip used for the passive SCR device, while the emission of tailpipe NH₃ slip shall remain below the regulations limits under any driving condition. In that context, model-based systems engineering approaches enable to create virtual exhaust lines and run a large number of tests over a wide range of operating conditions, while keeping development times and costs under control.

This project introduces a methodology for building a complete exhaust line model for the design of the control law. This methodology is developed by IFP Energies nouvelles and Siemens PLM Software using the LMS Imagine.Lab Amesim platform. The level of detail of the exhaust devices model needs to be well adapted to offer a good compromise between accuracy and CPU time. Some variables like temperatures of catalyst devices, NH₃ or NO_x concentrations are particularly targeted by the control design and only slight deviations from experimental results are acceptable. The model calibration is done for each device, using the results of specific reactor bench tests. The model is then extended to the real exhaust line architecture and validated on driving cycle, integrating catalyst size variations and thermal aspects. The injection controller can be designed and tested in early stages when both the control and the model are connected with a feedback loop. To evaluate the control in a more realistic setting, the model is then adapted to be embedded in a hardware-in-the-loop (HiL) platform.

This methodology has demonstrated its efficiency for the modeling of the SCR catalysts behavior, taking into account the deNO_x results and NH₃ storage in exhaust line simulation. It provides a usable simulation platform for the development of complex control laws.

Hysteresis Phenomena on Platinum and Palladium based Diesel Oxidation Catalysts (DOCs)

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The Diesel Oxidation Catalyst (DOC) plays a key role in diesel exhaust treatment systems. Typical noble metals used as active components are platinum (Pt), palladium (Pd), or a combination of these (Pt/Pd, e.g. alloyed, multilayered). During lightoff/lightout experiments, hysteresis phenomena of CO, NO, and HC conversion have repeatedly been reported and attributed to noble metal oxidation [1] or surface coverage effects.

Hauff et. al. have developed a kinetic model that is able to account for the hysteresis effects observed in NO conversion on Pt-only catalysts due to noble metal oxidation neglecting surface phenomena [2]. Validness, however, has only been proven for temperature ramp experiments with one single concentration of NO.

In this current work, further experiments on Pt-only will be presented for more diverse concentrations of NO. By addition of CO and propene to the feed, further hysteresis phenomena are observed that can either be attributed to surface effects or to oxygen storage. A phenomenological model is then derived from those experiments in which NO hysteresis phenomena are regarded as solely dependent on the catalyst oxidation state. A clear distinction between surface effects as known from CO-only oxidation and the noble metal formation under O₂/NO₂ containing atmosphere is being made.

In addition, the transferability of the phenomenological noble metal oxidation model to palladium catalysts (Pd-only) is examined. Low NO conversion is obtained here. Besides, results indicate that under lean exhaust conditions, the noble metal is completely oxidized after one lightoff. For real life application this indicates that classic Lagmuir-Hinshelwood kinetics may be applied neglecting the reduced state of the catalyst in most cases. However, some small hysteresis phenomena still occur in the presence of CO which may be caused by surface coverage effects. For more detailed studies it shows the simple transferability of the known noble metal oxidation model to Pd-only catalysts by solely omitting the reactivation rate.

Finally, experiments with NO and/or CO/propene on a Pt/Pd alloyed catalyst are shown, also revealing inverse hysteresis occurrence as found on the Pt- and Pd-only catalysts. Surprisingly, however, after repeated lightoff/lightout cycles, an increase in activity is observed. The effect is partly reversible by reducing treatment of the catalyst. This indicates that on the alloyed catalyst noble metal oxide formation also plays a key role in explaining hysteresis in NO conversion. Furthermore, it emphasizes that additional effects have to be accounted for in order to adequately describe the catalyst behavior. Consequently, it is impossible to sufficiently describe the alloyed catalyst by superposition of the single metal catalyst kinetics.

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Influence of maldistribution and substrate material properties on the cumulative emission of a three-way-converter

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In order to cope with the increasing demands on internal combustion engines, with respect to emissions, engine performance and fuel consumption, it is essential that experimental methods of research are combined with advanced methods of simulation. Because of the increasingly stringent regulations on emissions, optimization of three-way-catalytic-converters (TWC) by means of 3D-CFD methods has become extremely important in the development process of catalytic-converters. The 3D-CFD simulation flow is a powerful tool to investigate the influence of maldistribution on the TWC intake and the influence of substrate material properties on the performance of the TWC, in a systematic fashion [1, 2]. This poster presents a numerical investigation of maldistribution on the TWC intake for a ceramic and a metallic substrate comparing the cumulative emission during cold-start. The study is based on the assumption that the substrates possess the same catalyst loading. A simplified curved cone geometry is used to obtain homogeneous and inhomogeneous flow conditions. The metallic substrate and ceramic substrate are characterized by assigning the thermal conductivities (1 [W/(m K)] - 50 [W/(m K)]) and the specific heat capacities (400 [J/(kg K)] - 1400 [J/(kg K)]). The selected mass flow corresponds to realistic engine operating points of a 4 stroke gasoline engine.

The developed 3D-CFD methodology is implemented in ANSYS CFX and is based on a thermodynamic coupling between representative numbers of channels and the catalyst substrate [2]. Channels with approximately the same inlet conditions with respect to temperature and velocity are grouped and represented by one channel. The gas-phase of these representative channels is fully discretized three-dimensional as well as the whole solid-phase (substrate).

It is of significant importance to model the surface reactions, when the gas-phase reactions are negligible. The surface reactions take place on the lateral surface of the representative channels. Hence the washcoat-diffusion effect is modeled using the effectiveness factor approach [3]. Therefore Brunauer, Emmett and Teller (BET) measurements [4] as well as CO-chemisorption measurements [5] are performed to determine the entire surface area, the average pore diameter and the active catalytic surface. In order to reduce the model depth a simple global Langmuir-Hinshelwood surface mechanism is used neglecting oxygen storage capacity of cerium [6, 7]. Associated kinetic parameters are determined by DETCHEM [8] in combination with a global evolutionary optimization Algorithm [9].

Using the simulation methodology, the results show the positive effect of a homogeneous inflow condition in case of pressure drop and cumulative emission. Besides, it proves the behavior of faster light-off (lower cumulative emission) using metallic substrate within the range of realistic engine operating points.

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Total oxidation of methane on Pd-Pt/Al₂O₃ catalysts – De- and reactivation

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The catalytic combustion of methane to form CO₂ and H₂O is a process of general interest. Especially in exhaust gas catalysis the reaction becomes more and more interesting due to the growing application of lean burn gas engines. The removal of unburned methane emitted by Natural Gas Vehicles, trucks, ships or stationary applications running on methane based fuel is necessary because of tightening environmental legislation. Palladium-based catalysts are reported to be the most active materials for the total oxidation of methane [1]. The activity and thermal stability of such Pd based catalysts can further be improved by the addition of small amounts of Pt [2-3]. However, these catalysts suffer from constant deactivation depending on external parameters such as temperature, GHSV or gas composition. In this study different parameters are varied to investigate their impact on the activity of a commercial Pd-Pt/Al₂O₃ model catalyst provided by Heraeus. Additionally, their impact is investigated with spatially resolution along a monolithic channel using a very thin adjustable capillary [4].

The results obtained show a shift of light-off temperature in case GHSV is raised by factor 2.5 to higher temperatures under a lean burn gas composition (12% H₂O, 10% O₂, 3200 ppm CH₄ in N₂). Regarding the long-term activity of the catalysts, experiments using the same gas composition showed a constant deactivation at 450°C resulting in a loss of methane oxidation activity from 98 % in the beginning to 68 % after 100 h. Different methods are found to reactivate the catalyst under operation at 450°C. The addition of small amounts of NO (120 ppm) as well as NO₂ (30 ppm) constantly increased the methane oxidation activity of the deactivated catalyst. Furthermore, short reductive treatments such as reduction of the catalyst by H₂ or CH₄ in N₂/H₂O at 450°C reactivated the catalyst completely.

To investigate the deactivation more deeply, water concentration and temperature were varied during long-term experiments of 15 to 40 hours. The velocity of catalyst deactivation is directly connected to the concentration of water in the feed gas at 450°C e.g. deactivation is faster the higher the water concentration in the gas mixture is. Concerning temperature, the deactivation is completely suppressed at 500°C while deactivation at 400°C is very rapid.

This study expands the knowledge about the deactivation of Pd-Pt catalysts under different conditions and shows first promising possibilities of reactivation.

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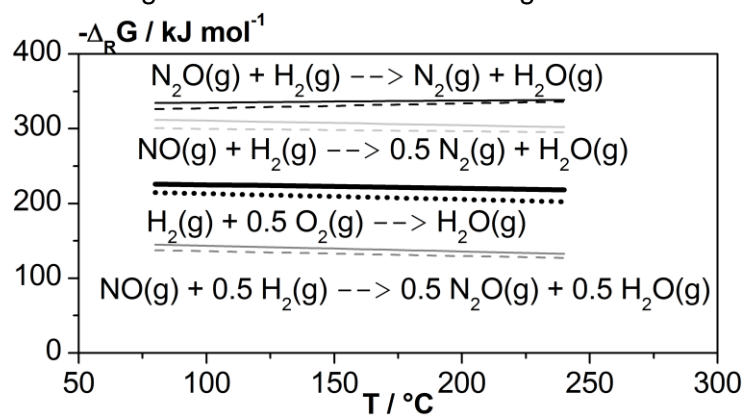
Kinetic mean field modelling of the NO_x reduction by H₂ on Pt/WO₃/ZrO₂ catalyst in excess of O₂

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This work addresses the elementary kinetic mean field modelling of the NO_x reduction by H₂ on Pt/WO₃/ZrO₂ under oxygen-rich conditions. Pt/WO₃/ZrO₂ was recently shown to reveal substantial low-temperature deNO_x activity with enhanced N₂ selectivity referred to traditional Pt catalysts [1]. The model was developed based on a postulated reaction mechanism as well as kinetic examinations conducted in a gradient-free loop reactor and implied a network of 48 reaction steps described by Arrhenius-based rate expressions. Kinetic parameters were taken from literature [2] and by fitting calculations, while pre-exponential factors of adsorption were estimated from kinetic gas theory. Also, the kinetic parameters for adsorption and desorption of O₂ were deduced from independent TPD study. For validation, experiments were simulated and thermodynamic consistency was proven by checking the Gibbs free enthalpy of the catalytic surface reactions (Figure 1) [3]. The elementary kinetic model also provided simulation of the coverage of the Pt surface showing that the active sites are predominantly covered by NO below 200°C. The improved N₂ selectivity of Pt/WO₃/ZrO₂ was found to be associated with the relatively high surface coverage by N originated from NO dissociation. Also, the recombination of chemisorbed N to yield N₂ is faster than the reaction of chemisorbed N and NO forming N₂O. However, above 200°C the catalytic H₂-deNO_x performance is drastically decreased by growing oxygen coverage. As a result of the elementary kinetic mean field model, we conclude that the marked performance and high N₂ selectivity of Pt/WO₃/ZrO₂ is related to the significantly lower energy barrier of the dissociation of chemisorbed NO as compared to traditional Pt/Al₂O₃ [2]. This results in an increased Pt coverage by N predominately evoking N₂ instead of N₂O [3]. These findings are in line with our recent in situ DRIFT spectroscopic studies [1] and allow the rational catalyst design in future work.



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Modelling of Dual Layer Ammonia Slip Catalyst for Diesel Exhaust Aftertreatment

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The diesel exhaust ammonia slip catalyst (ASC) selectively catalyzes the oxidation of excess NH_3 to N_2 and H_2O . The ASC commonly uses a dual layer structure, consisting of an ammonia oxidation (AMOX) catalyst below a SCR catalyst. The AMOX catalyst oxidizes NH_3 to N_2 and NO_x , while the SCR catalyst converts the NO_x formed to N_2 using NH_3 . The dual layer structure benefits from an increased selectivity of ammonia conversion to N_2 .

To better understand the dual layer ASC, a 1D-1D model using a tank-in-series model in the axial direction was developed for a single monolith channel of the dual layer ASC (steady state and isothermal conditions). For each tank, the model considers gas flow entering and leaving, mass transfer across a stagnant gas film to the washcoat, and diffusion and reaction throughout the porous catalytic washcoat. Mass transfer between the gas and solid phases was modeled with film resistance and a position dependent Sherwood number. Diffusion through the catalytic layers was modelled using an effective diffusion coefficient with contributions from bulk diffusion and Knudsen diffusion. Kinetic models for a 0.25 wt.% Pt/TiO₂-SiO₂ AMOX catalyst and a 3.5 wt.% Cu-BEA zeolite SCR catalyst were applied.

Validation of the ASC model against experimental data for three small monolith samples (an AMOX sample, a SCR sample, and a dual layer sample) shows a general good agreement (Figure 1). The assumption of an ideal washcoat distribution may explain the overestimation of NH_3 conversion between 275-400°C for AMOX and dual layer simulations. Other significant variations include an underestimation of NH_3 conversion above 400°C for SCR and dual layer simulations, an underestimation of NO_x yield for SCR simulations above 400°C, and an overestimation of NO_x yield above 400°C for AMOX simulations.

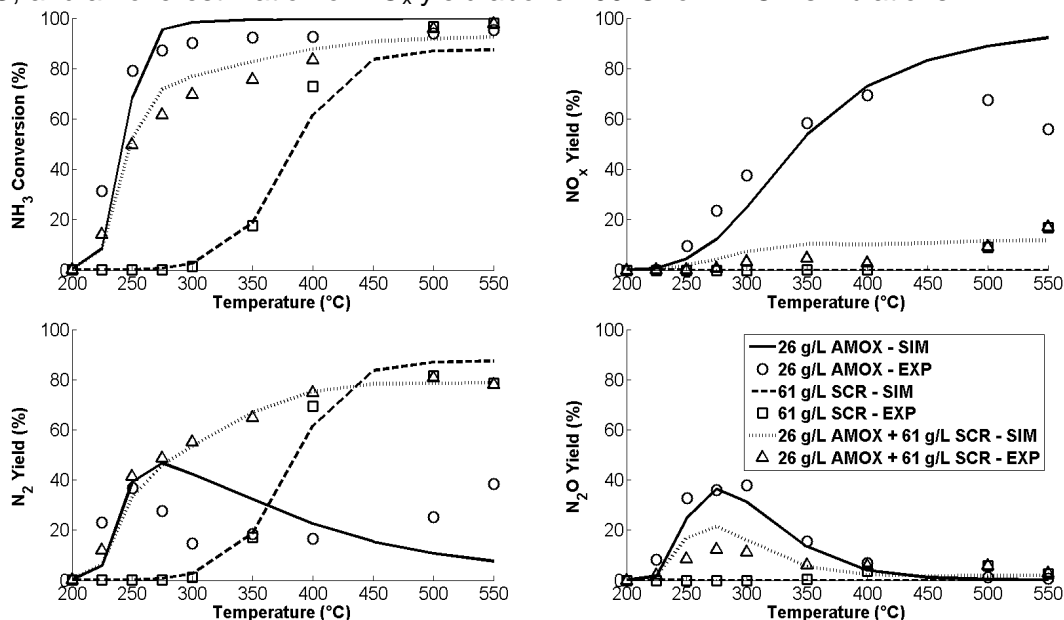


Figure 1: Comparison of experimental data and simulations: 26 g/L AMOX, 61 g/L SCR, and 26 g/L AMOX + 54 g/L SCR (300 cpsi/5 mil, Ø 5 cm x L 3.7 cm). Test conditions: 200 ppm NH_3 , 12.3 vol.% O_2 , 3.3 vol.% H_2O , balance N_2 , and GHSV 250,000 hr^{-1} .

Study on NH₃ and N₂O Formation Mechanisms in Commercial TWC Pd/Rh-catalysts

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Three-way catalysts, which are effectively converting the major pollutants CO, hydrocarbons (HCs) and NO_x, are the state-of-the-art aftertreatment technology for modern gasoline engines. Besides the conversion of CO, HCs and NO_x there are proceeding side reactions within the complex reaction network of the converter leading to NH₃ and N₂O [1-3]. Both gases are as-yet unregulated but are strongly effecting our environment, N₂O is a greenhouse gas while NH₃ contributes to formation of particulates [4].

To set up a model capable of predicting the NH₃ and N₂O formation and dynamic catalyst behavior, lambda-sweep and light-off experiments were performed using an engine-aged commercial Pd/Rh catalyst (600 cells/in²). The concentrations of O₂, H₂, CO, CO₂, NO, HCs, H₂O and N₂ used for the experiments lie in the range of engine-exhaust gas compositions. For lambda-sweep tests a lambda interval between 0.990 and 1.009 was screened using 0.001 steps. For light-off performance tests a static lambda value was set while the temperature is ramped from 75 °C to 550 °C using a 20 °C/min heating rate. The experiments show that significant amounts of NH₃ and N₂O are formed during light-off and lambda-sweep tests. A great part of NO is transformed into NH₃ and N₂O.

To investigate the mechanism of this encountered formation of N₂O and NH₃ kinetic models are set up. Mechanisms of differing complexity are used in this modeling study in order to identify the underlying mechanisms of the observed formations. First a sensitivity analysis setting the range for the optimization of the different mechanisms is done. Then the mechanisms are parameterized using an automated algorithm. The optimized mechanisms are used to predict the formation of N₂O and NH₃ as well as the catalyst performance and efficiency.

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Activation and Deactivation Effects in Diesel Oxidation Catalysts

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It is well known that conversion hysteresis can occur during the ignition and extinction process on a platinum catalyst due to several investigated effects such as thermal inertia or multiple steady states. Hauptmann et al. reported an inverse hysteresis in NO and CO oxidation and attributed the effect to the reversible oxidation of the platinum surface by NO₂ and its reduction by NO.^[1] Abedi et al. observed that the addition of C₃H₆ can lead to an inverse hysteresis in the oxidation of CO. The effect was attributed to the formation of HC intermediates competing with CO for active sites on the catalyst's surface.^[2]

In this work we investigate the conversion during several consecutive light-off experiments. It is shown that the hysteresis behavior observed by Abedi et al. is due to a permanent deactivation of the catalyst which can be revoked by a temperature ramp up to 350 °C in the absence of pollutants. Therefore light-off / light-down experiments were performed in a stainless tubular steel reactor with a hydrothermal aged (600 °C for 10 h) monolithic (400cpsi, 4,33 mil) Pt/Al₂O₃ diesel oxidation catalyst.

Figure 1 shows the CO conversion as a function of temperature in an experiment where the inlet temperature was ramped twice from 80 °C up to 350 °C and back to 80 °C. The conversion of CO to CO₂ shifts approximately 20 °C to higher temperatures after the first ignition. A deactivation takes place after the first light-off.

The ignition and extinction temperature remains constant for the deactivated catalyst during all following light-off / light-down cycles. If a temperature ramp up to 350 °C is applied in the absence of pollutants the deactivation can be revoked (see figure 2).

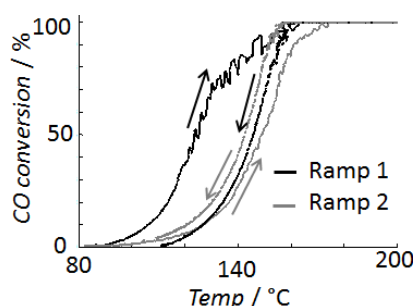


Figure 1: Light-off and Light-down curves of CO in the presence of C₃H₆ for two ramps on a Pt/Al₂O₃ catalyst pretreated with a mixture of N₂, O₂, CO₂.

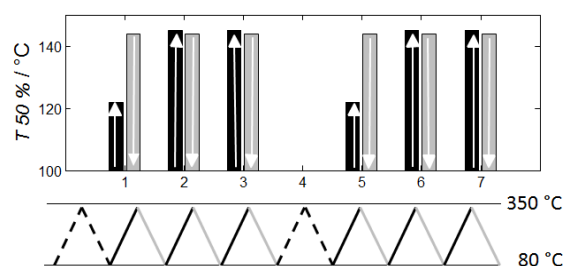


Figure 2: Required Temperature for 50 % CO conversion in the presence of C₃H₆ during ignition (black) and extinction (gray) for the first, second and third ramp after a pretreatment with N₂, O₂, CO₂ (dashed).

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Deactivation of Cu/SAPO-34 During Low-Temperature NH₃-SCR

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A major issue in catalyst development is catalyst stability and resistance to deactivation. Despite their excellent high-temperature stability, there have been some early reports of poor low-temperature stability in SAPO-n materials [1,2]. These studies found an often reversible loss of crystallinity and porosity upon low-temperature hydration of SAPO-34 powders and membranes. SAPO-34 is also known to be prone to hydrolysis when under-going aqueous ion exchange. However, the low temperature hydrostability of copper-exchanged SAPO-34 in conditions relevant to NH₃-SCR (smaller relative humidity, temperature between room temperature and 100 °C) has, to our knowledge, not been extensively studied. The objective of this study has therefore been to examine the effect of a low-temperature SCR atmosphere (including water vapour) on the performance of Cu/SAPO-34 with 1.27 and 2.60 wt.% Cu.

After a few hours of exposure to a feed containing water vapour at temperatures below 100 °C, the two catalysts experienced severe loss of activity (Fig. 1). After only 3 h at 70 °C, the NO_x conversion at 200 °C decreases from an initial 87% to 66%, after another 9 h to 6%. The deactivation was not reversible upon attempted regeneration in a dry atmosphere at 600 °C for 35 min.

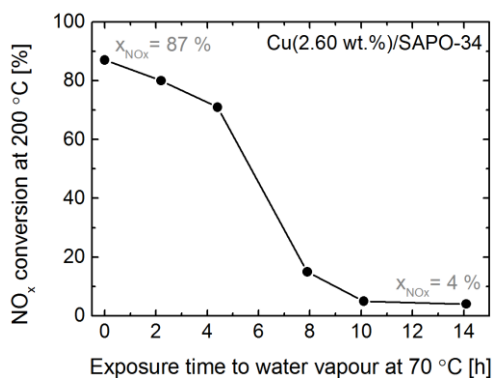


Fig.1. NO_x conversion during NH₃-SCR at 200 °C. Feed: 400 ppm NH₃, 400 ppm NO, 8% O₂, 5 % H₂O. Source: [3]

This observation was accompanied by only a small loss of microporous volume and XRD showed that the crystalline structure of both catalysts is similar before and after deactivation. Thus, the dominating mechanism for the deactivation does not appear to be the breakage of the crystalline SAPO-34 framework. Further, ammonia storage was unaffected. There was a decrease in H₂ consumption during TPR, indicating that fewer copper sites are available for the redox cycle, and this likely contributes to the deactivation. However, the magnitude of the decrease in TPR signals did not exceed 38%. It therefore seems likely that this is not the only reason for the deactivation, given its severity. We postulate that in addition a large number of the copper sites are transformed into an inactive form, and that this transformation is responsible for the loss of SCR activity.

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Modeling of NO_x reduction dynamics in LNT catalyst during lean-to-rich and rich-to-lean exhaust gas transients

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In this contribution we present reaction kinetics model of lean NO_x trap (LNT) catalyst for automotive exhaust gas aftertreatment, focusing on N₂O formation during lean-to-rich and rich-to lean transients. N₂O is an undesired by-product with a high global warming potential.

The LNT is designed to work in two phases – a relatively long lean period characterized by the excess of oxygen and NO_x adsorption (storage), and a short (few seconds) rich period when the stored NO_x are reduction under the excess of CO, H₂ and unburned hydrocarbons. The NO_x reduction leads in ideal case to N₂, however, in reality there may appear also NH₃ and N₂O by-products. N₂ and N₂O products are formed concurrently in two peaks. The primary peaks appear immediately after the rich-phase inception, and tail off with breakthrough of the reductant front (accompanied by NH₃ product). Secondary N₂ and N₂O peaks appear at the rich-to-lean transition as a result of reactions between surface-deposited reductants/intermediates (CO, HC, NH₃, -NCO) and residual stored NO_x (Figure 1).

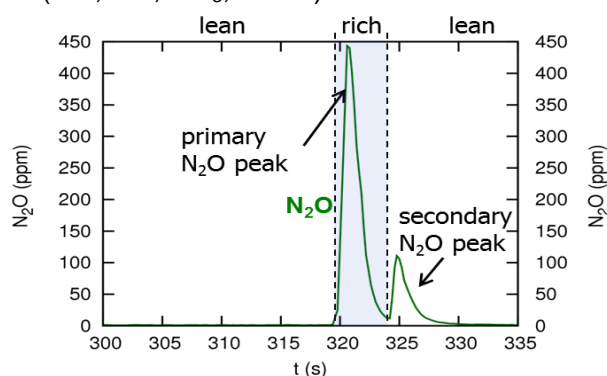


Figure 1. Detail of N₂O formation during the LNT catalyst regeneration.

The developed reaction kinetic model is based on the competitive adsorption and accumulation of reductants on the catalyst surface and their subsequent reaction with stored NO_x. The reaction scheme allows prediction of both primary and secondary peaks of all nitrogen products (N₂O, N₂ and NH₃). The selectivity of NO_x reduction is controlled by actual oxygen coverage on platinum group metal (PGM) sites – high oxygen coverage favors N₂O formation while mainly NH₃ is formed over fully reduced PGM sites. The coverage of PGM sites changes during the lean-to-rich and rich-to-lean transients and this is translated into varying NO_x reduction products selectivity. The developed model agrees well with the experimental data of lean/rich (60s/5s) cycling in temperature range 150-550°C.

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LNT catalyst operating strategy for reduction of N₂O emissions

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During the LNT catalyst regeneration, a variety of gaseous N-products is formed. Ideally, all treated NO_x is converted into harmless nitrogen, but a significant amount of N₂O and NH₃ can be produced, depending on conditions. While NH₃ represents reactive specie that can be used for further NO_x reduction, N₂O is an undesired by-product with very low reactivity, no beneficial catalytic effects and high global warming potential. Once N₂O is formed in the catalyst, it is transported downstream remaining unchanged and released to the environment. Therefore, preventing its formation appears to be the only effective way for N₂O emissions reduction.

The dynamics of all products (N₂, N₂O and NH₃) formation was studied during and after the regeneration of a commercial lean NO_x trap catalyst. To better understand the underlying reaction mechanisms, advanced experimental methods were applied for determining spatiotemporal profiles along the catalyst channel. High-speed FTIR and SpaciMS analyzers were employed together with isotopically-labeled ¹⁵NO and Ar as a carrier gas in order to quantify the N₂ product by mass spectrometry.

Our work [1, 2] suggests that local NO_x reduction selectivity is determined by the mutual ratio between the rates of NO_x release from storage sites and Pt group metal (PGM) reduction. In the performed lean/rich cycling experiments, both N₂ and N₂O were formed concurrently in primary and secondary peaks. The primary peaks appear immediately after the rich phase inception, and tail off with the breakthrough of the reductant front accompanied by NH₃ product. The secondary N₂ and N₂O peaks appeared at the rich-to-lean transition as a result of reactions between surface-deposited reductants/intermediates (CO, HC, NH₃, -NCO) and residual stored NO_x. Up to 30% of N₂ and 50% of N₂O products originated from the secondary peaks. The obtained results indicate that the magnitude of secondary peaks depends on the amount of residual stored NO_x and adsorbed reductants/intermediates.

Based on these findings, a novel strategy is proposed for the minimization of secondary N₂O peaks. It consists of applying a slightly lean (nearly stoichiometric) phase between the rich and fully lean phases. During this inserted transition phase, the adsorbed reductants/intermediates and residual stored NO_x can continue to react over well reduced PGM sites even beyond the rich regeneration phase, preventing N₂O formation. This strategy also allows additional NH₃ formation while minimizing CO or HC breakthrough, which is highly desirable for the coupled LNT-SCR applications.

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Control Oriented Modeling of low temperature NH₃-SCR

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Due to the enforcement of Euro 6 emission regulations, the NH₃/urea Selective Catalytic Reduction of NO_x emitted from Diesel engines will face severe challenges in the upcoming years, especially at low temperature. An effective strategy to improve system performances is the development of Control Oriented Models (COM), i.e. simulation tools suitable for the real-time on-board control of deNO_x system [1]. In current control strategies [1], the NH₃-SCR process is modelled as a Continuous Stirred Tank Reactor (CSTR). In this way, it is possible to reduce energy and mass balances to a system of ODEs that can be solved with minimum computational effort. This is required for on-board implementation of model-based control systems. However, this representation is not able to account correctly for the strong gradients of temperature and reactant concentrations typical of the NH₃-SCR process [2]. Herein we report an innovative COM concept based on a PFR model of the SCR converter with simplified kinetics. The 1D transient model has been derived under the hypothesis of ideal gas properties, isothermal conditions, negligible mass transfer resistances and assuming ammonia as the only species that may adsorb on the catalyst [1]. Resulting PDEs were discretized according to backwards finite differences with a different degree of accuracy (3, 4 and 10 knots). In this way, the effect on the discretization is also investigated. The resulting COM has been used to simulate a World Harmonized Transient Cycle (WHTC) with cold start for heavy-duty diesel engines, normally used to assess deNO_x after-treatment systems performances.

As shown in Figure 1, results have been compared with a state of the art COM from the literature [1] but also with a complete chemical-physical model, already validated [3] and assumed as a reference, with the same kinetics. The proposed approach outperforms state of art COM schemes (based on a CSTR assumption) in terms of accuracy in the evaluation of NH₃ slip and also of emitted NO_x with respect to the reference physical-chemical model (Fig.1a and b). Notably, the proposed COM is significantly faster (fig.1c) with respect to the reference model with simplified kinetics, while exhibiting only a negligible increase in computation time with respect to the CSTR-based COM.

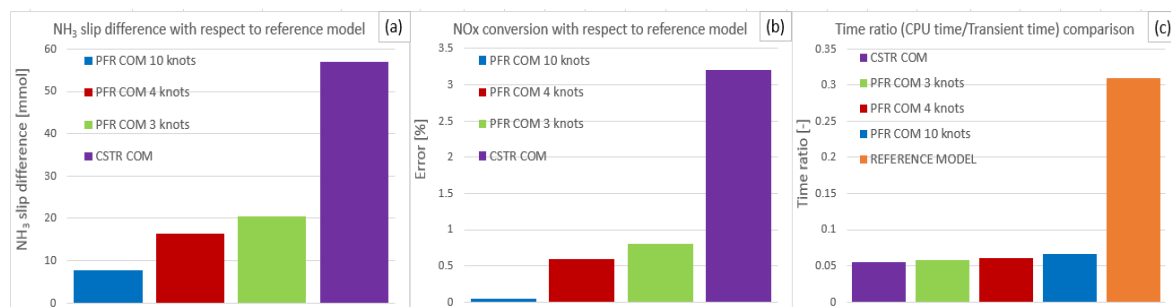


Figure 1 – WHTC simulation: comparison of different models

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B-site dopant effects in La-Co based perovskites

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Abatement of NO_x emissions remains a challenge, especially in fuel-efficient lean-burn engine conditions. The diesel oxidation catalyst promotes the oxidation of NO, CO and remaining hydrocarbons. Currently applied oxidation catalysts are based on supported noble metals with disadvantages of high cost and sintering at elevated temperatures.[1] LaCoO₃ has been proposed as a low price alternative for Pt group metals in oxidation catalysts due to their similar catalytic activities.[2]. Incorporation of dopant ions on either A-site or B-site has significant effects on both physicochemical properties and catalytic activity of such materials. [3] Employing an array of different ions allows to elucidate the origin of the effects of partial substitution on the B-site. For this purpose phase pure LaCo_{0.8}X_{0.2}O₃ (LCX) perovskites were successfully prepared with X representing dopant ions of different stable valence (Zn²⁺, Mg²⁺, Al³⁺, Ge⁴⁺, Zr⁴⁺) or other transition metal ions (Cr, Mn, Fe, Ni).

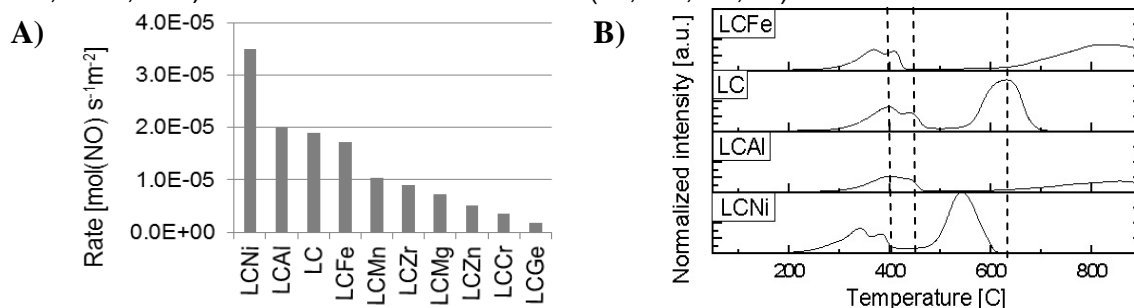


Figure: **A:** Reaction rates for NO oxidation at 250 °C for the LaCo_{0.8}X_{0.2}O₃ (LCX) series normalized to the spec. surface area of the catalyst. Conditions: 800ppm NO, 1% O₂, SV = 80000 h⁻¹.
B: TPR of LC and doped materials. Broken lines highlight maxima of peaks in non-doped LC

The reaction rate in NO oxidation exhibits a significant dependence on the nature of the dopant with an increase by a factor of 2 for LCNi compared to LC. (Fig. 1A). This effect is attributed to the change in Co oxidation state induced by the dopant, which is often accompanied by formation of oxygen vacancies. The effect of the dopant manifests in changes in the reducibility of the material, as evident in temperature programmed reduction experiments (Fig. 1B). Also, stability in reducing atmosphere can be strongly increased through partial substitution with e.g. Al. Additionally the materials are characterized by means of N₂-physisorption, XRD, XRF, TPD of O₂, NO and NO₂, XPS as well as NO and NO+O₂ *in situ* DRIFT-IR measurements.

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Design of chemical models for model-based control of exhaust gas emissions

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Without suitable control systems, efficient exhaust gas treatment would not be possible. Especially three-way-catalysts rely on the use of complex control systems combining feedforward and -backward control. While traditional control systems use PI controllers to stabilize the voltage of the downstream λ sensor [1], new approaches integrate knowledge about the oxygen storage level of the catalyst. The oxygen storage level is not measurable directly and model-based approaches are needed, where chemical models have shown to be quite useful. Due to the required real-time capability of the system, this approach is limited to rather simple models [1]. Furthermore, common control design methods are based on state space models.

Here we present an approach to modify chemical models for the implementation in real-time control systems and to obtain nonlinear state space models. We introduce a new concept, called weight functions, to reduce the mathematical complexity of the model but still capturing all chemical characteristics, allowing for the use of more complex and realistic models.

The process will be demonstrated with the thermodynamically consistent model of [2]. This model consists of the three equilibrium reactions of H_2 , CO and O_2 with cerdioxide. Assuming that the dynamics of the surface species are rate-limiting, numerical integration can be reduced to the oxygen storage level giving all other dimensions analytically. The resulting set of nonlinear differential equations is then transformed into a state space model allowing for the use of common control design and system analysis methods. To derive the state space model, it is utilized that the gas species in the gas phase and in the washcoat enter linearly into all equations resulting in simple matrix multiplications.

In Figure 1, the development of one cell of the nonlinear state space model is illustrated. The entries of the vector f^T are called weight functions and contain all physical-chemical information about the system. The entries of the matrix G can also be expressed by the weight functions and two constants (k , o). The resulting nonlinear state space model can be used for control design and the computation of system values, such as time constants, observability and controllability indices. These system values can be used for quantitative comparison of different catalysts with respect to their control behavior and can support catalyst development. Additionally, the development of controller for individual catalysts becomes more feasible.

$$\left. \begin{aligned} \frac{\partial c_{g_{gas}}}{\partial t} &= -\frac{D}{l}(c_{g_{gas}} - c_{wc}) + u \frac{\partial c_{g_{gas}}}{\partial x} \\ \frac{\partial c_{wc}}{\partial t} &= \frac{D}{l}(c_{g_{gas}} - c_{wc}) + r \\ \frac{\partial c_{surf}}{\partial t} &= r \end{aligned} \right\} \xrightarrow{\text{simplifications}} \begin{aligned} c_{g_{gas}} &= \begin{pmatrix} kf_{CO_2} + o & 0 & 0 & kf_{CO} & 0 \\ 0 & kf_{H_2O} + o & 0 & 0 & kf_{H_2} \\ 0 & 0 & \frac{k}{2}f_{O_2} + o & 0 & 0 \\ -kf_{CO_2} & 0 & 0 & -kf_{CO} + o & 0 \\ 0 & -kf_{H_2O} & 0 & 0 & -kf_{H_2} + o \end{pmatrix} c^{in} \\ \frac{dc_{surf}}{dt} &= \underbrace{(f_{CO_2}, f_{H_2O}, f_{O_2}, f_{CO}, f_{H_2})}_{f^T} c^{in} \end{aligned}$$

Figure 1: Process of development of the state space model for one axial cell.

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An experimental and microkinetic modeling study for the total oxidation of CO over a Pd/Al₂O₃ monolith based DOC.

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Studying the light-off behaviour of the CO oxidation over palladium can give a better understanding of the processes involved on the surface for the palladium catalyzed CO-oxidation. In general it is typically assumed that palladium easily oxidizes under lean conditions. However, is not completely understood if the chemical reduction has a significant influence on the oxidation state of the catalyst particles, especially at low temperatures, eventually leading to a reduced or partially reduced palladium surface. Depending on the extent of the reduction it is suspected that oxidation affects the size of the active palladium particles and thus alters the catalyst dispersion as well [1].

As first steps towards a more detailed investigation, in this study several consecutive temperature ramp-up and cool-down cycles have been performed in a flow reactor setup over a palladium impregnated alumina supported (Pd/Al₂O₃) monolithic honeycomb catalyst as shown in Figure 1. Based on CO conversion light-off measurements the activity of the catalyst has been examined for a GHSV of 80.000 h⁻¹ and reactor feed concentrations of 800ppm CO, 7% CO₂, 5% H₂O, 5% O₂ in balance with N₂.

To further analyse the influence of different aging durations on the light-off activity palladium monoliths with an aging duration of 1, 5 and 16 hours at 750°C and a gas atmosphere of 400ppm CO, 100ppm C₃H₆, 7% CO₂, 12% O₂, 10% H₂O in N₂ balance have been prepared yielding different catalyst dispersions. Additional analogous CO-light-off experiments have been performed.

In order to obtain a better model based understanding of the altered light-off behaviour the study is complemented with CO-light-off simulations. A microkinetic reaction mechanism for the CO-oxidation over the reduced Pd(111) surface has been developed and incorporates the effects of adsorbed CO and O coverage on the surface energetics.

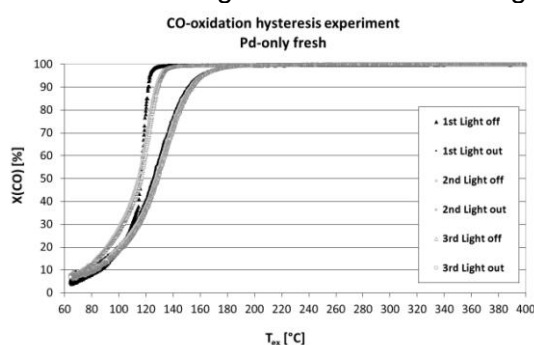


Figure 1. Three consecutive CO-oxidation light-off/ light-out cycles over a fresh Pd/Al₂O₃ monolith.

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Preparation and performance of multi-layer lean NO_x trap catalysts – effect of diffusion limitation

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Lean NO_x trap catalyst (LNT) is an effective tool for removal of nitrogen oxides (NO_x) from automotive exhaust gas – NO_x are periodically adsorbed to the catalyst surface during longer lean phase and reduced within short rich phase that is applied when the NO_x storage capacity is saturated. The LNT is often coupled with other types of catalysts, e.g. a diesel oxidation catalyst (DOC) for conversion of CO and hydrocarbons. Due to spatial and economical reasons there is an effort to combine catalysts with different functions in a single monolith reactor, where the surface of the monolith is coated with multiple catalytic layers. However, the overall efficiency of such converter can be lowered by internal transport limitations. This work is focused on experimental investigation of diffusion limitations in multi-layer catalysts – several combined systems consisting of LNT, DOC and inert layers were studied. The layers of model LNT catalyst (Pt/Ba/γ-Al₂O₃) were overlaid with additional layers (either inert γ-Al₂O₃, or a model DOC catalyst – Pt/CeO₂/γ-Al₂O₃). The samples were characterised and tested in a laboratory reactor for oxidation reactions and NO_x storage and reduction.

Diffusion limitation caused by the inert γ-Al₂O₃ layer (IN) coated on top of LNT layer was observed – it negatively affected both CO/HC oxidation and NO_x removal in comparison to bare LNT layer. Addition of the IN lowered the C₃H₆ conversion by as much as 15 %, which indicates the presence of diffusion limitation (Fig. 1a). The diffusion limitation was not observed in the structurally comparable DOC layer as it was compensated by its catalytic activity. Moreover, the dual-layer LNT+DOC catalyst was superior in all oxidation and NO_x storage experiments – the added DOC layer significantly increased the amount of stored NO_x and the catalyst surface could have been regenerated at lower temperatures. The peak of NH₃ produced during the catalyst regeneration was more delayed in both LNT+IN and LNT+DOC samples (Fig. 1b) which again indicates transport limitation induced by the top layer.

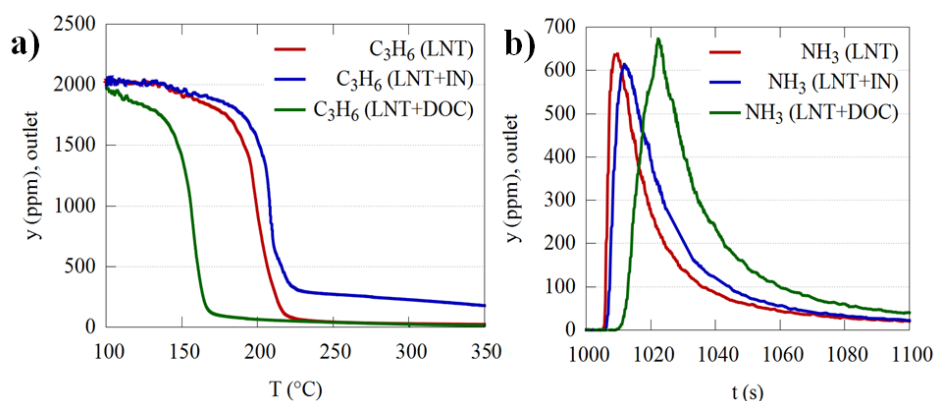


Fig. 1. a) C₃H₆ lean light-off experiment. b) Peaks of NH₃ produced during the reduction of previously stored NO_x.

Ab Initio Computational Study of Soot Deposit Structure

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The structure and properties of soot deposits in Diesel Particulate Filter (DPF) affect significantly the DPF pressure drop, hence the fuel penalty imposed on the vehicle. Attempts to determine soot cake properties from experiments leads to a wide range of values. We have shown ([1],[2],[3]) that during DPF loading the microstructure of the soot cake is determined by the convective-diffusive transport of the soot aggregates towards the deposit and have also demonstrated that soot cake packing density and permeability are related to the local value of the dimensionless mass transfer Peclet number (Pe). In addition, as shown here, cake properties can be related to the fractal-like morphology of the soot particles. Past computational studies of the deposition process (e.g. [4], [5]) have explored the effect of Pe on deposit structure using geometrically restricted and simplified methods. The current work fully accounts for the soot aggregate morphology in a detailed computational study consisting of three parts: a) the generation of appropriate fractal-like aggregate shapes, which are used for b) ballistic deposition simulations and c) ab initio soot particle filtration simulations. The effect of Pe and of soot aggregate structure (number of monomers N , fractal dimension d_f , fractal prefactor k_f) are studied simultaneously by ab initio treatment of filtration with resolved nanostructure representation of soot. The latter is achieved by digital models of fractal-like aggregates (Fig.1) corresponding to a range of likely soot morphologies, the structure of which is fully retained when generating the three-dimensional model deposits (Fig.2). Ballistic deposition simulations give additional information on the effect of soot aggregate morphology and explore limiting conditions ($Pe = 0$, $Pe \rightarrow \infty$). The power law of deposit density as a function of Pe, known to correlate a wide range of experimental soot deposits ([1], [3]) is found to also describe the properties observed in the computed deposits (Fig.3).

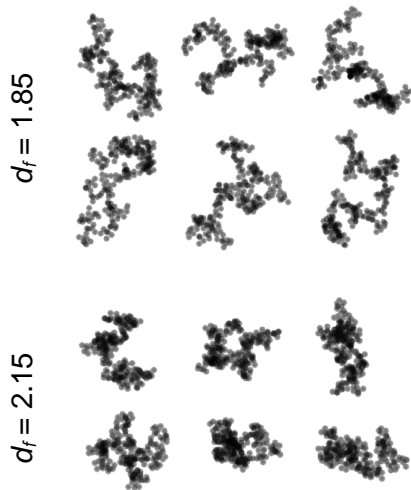


Figure 1. Visualisation of fractal-like aggregates employed in the packing simulations ($N = 212$, $k_f = 2.1$ for all)

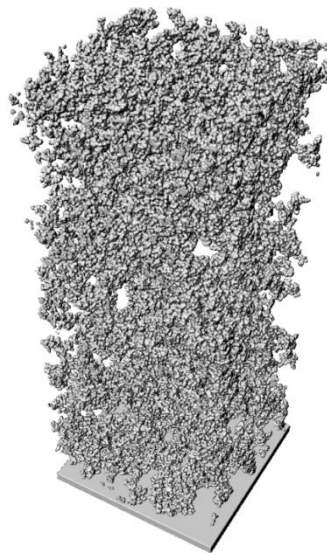


Figure 2. An example model deposit, rendered via 3-D ray-tracing.

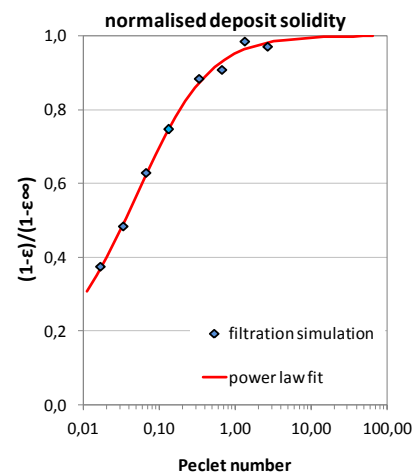


Figure 3. Comparison of current computational deposit properties and past experimental results.

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KIT: Karlsruhe Institute of Technology
 MIT: Massachusetts Institute of Technology

Notes