

23.8.2010

Final report of the NEADS (Next Generation Exhaust Aftertreatment for Diesel Propulsion Systems) Project

Executive summary

The impact of NEADS in the scientific landscape is reflected by its quite impressive publication list included in this report. NEADS enabled not only some scientific work with interesting results for academia, technology and industry. It is not incidental that some of the efforts achieved additional funding as well as industrial interest and have spawned some, smaller scaled application projects. In addition a patent has been applied for.

Nevertheless the impact of NEADS has additional components: It provided some educational opportunities for young academics and technicians, apart from the pressure on the older ones to keep up with newest developments. It provided also a unique platform where scientist of different skills, institutions and interests met and, at least in the beginning, knew they had to find a common language. This imperative, however, very soon, was replaced by mutual curiosity and interest. This led to collaborations as well as to a fruitful competitive atmosphere.

The scopes of each project partner, the main breakthroughs as well as the major interactions among the partners are summarized below.

Project I activities have focussed on the development of zeolithe SCR catalysts with high activity at low and good stability at high exhaust temperatures. While understanding low temperature behaviour required detailed description of the underlying processes on the molecular level, high temperature characteristics implied research of the aging mechanisms. The acquired knowledge enabled not only the formulation of a new catalyst and the preparation of first prototypes, it provided important insights on the operational modes of SCR catalysts leading to important parameters for the numerical simulation of such systems for Task II of this project consortium. Prototypes are now tested by industrial partner and a product application is feasible.

Main new insights can be summarised as

- Catalytic performance variations of a zeolithe are due to the different catalytic activity of monomeric, dimeric, clustered and oligomeric Fe-sites over exhaust temperature. Thus, purposeful zeolithe formulation can improve properties over the entire temperature range.
- The Brønsted-acidity of the catalyst is not a crucial factor for high activity, but is necessary to bind and disperse the metal ions.
- Main reason for hydrothermal aging is the Fe migration, which leads to the formation of FeO_x clusters, increasing in size during aging. The stability is thereby rather a question of the stability of the active iron species in the ion exchange site than of the framework stability itself.

The development of a new catalyst based on ceramic foam substrates was the scope of Project II. The goal was to develop a catalyst with low precious metal requirements and excellent conversion behaviour.

This included the study of the flow field and the mass transfer properties through and inside such a structure. This implied some modelling which extended from the surface characteris-



tics to an analytical solution of the mass transfer perpendicular to a cylindrical foam strut and further to a Kelvin cell up to some 1-d numerical simulation. Two promising applications emerged (instead of one as initially anticipated):

- Three Way Catalyst application for CNG powertrains
- Diesel Oxidation Catalyst (DOC) upstream of the Diesel Particulate Filter (DPF)

Both applications are currently under vehicle testing. The DOC application required some additional prestudies aiming in analysing and deep understanding of the DOC during operation in active and passive regeneration modes as well as understanding soot and ash distribution in the DPF downstream. Soot micro and nanostructure analysis was performed in close collaboration with the Task A and C.

Project III has further developed the soot emission model and compared the predictions with in-cylinder and exhaust gas measurements. The capabilities of the model are very good for stationary engine operation while the accuracy during transients also impressive. Apart from this, further main achievements can be summarized as follows:

- Soot emission quantification by leading edge measurement technology, i.e. micro soot sensor and filter smoke number in the exhaust and two-colour pyrometry in cylinder
- Prediction and measurement of the soot emission of different Diesel fuels

The success of the model is best underlined by the additional funding that this project received throughout its duration.

The focus of Task A was the development of advanced diagnostic techniques for analysis and quantification of particle emissions and particle behaviour in the atmosphere.

- Development of a microreactor exposing individual soot particles to a defined environment and usage at the Pollux X-ray scanning transmission microscope beam line of the Swiss Light Source
- Spectroscopic and microscopic characterization of individual particles from a vehicle DPF (Project II of this consortium) and from the smog chamber (Task C of this consortium)
- Successful application of the high resolution time-of-flight aerosol mass spectrometer (also called W-ToF-AMS) in test bench, smog chamber and field experiments
- FHNW has continued to improve the developed MiniDiSC device as a mobile soot quantification device for the low soot emissions in modern exhaust

Activities in Task B have successfully developed a numerical tool for simulating the momentum, heat and mass transfer as well as wash coat diffusion and chemical reactions in one representative channel of an SCR catalyst. The tool was successfully tuned by experimental data from Project I of this consortium. Further achievements can be summarized as follows:

- Successful simulations with wide variations of the most relevant operating parameters like Gas Hourly Space Velocities, temperatures, NO/NO₂ feed ratios as well as NH₃ feed quantities
- Successful simulation of transient operations
- Fundamental numerical investigation of the urea-water solution injection, droplet formation and evaporation

The topic of Task C was the description of primary emissions from vehicles at different operating conditions and with different fuels but also of the traffic as a whole. Thereby the focus was the mass spectral signature of the particulate matter in the exhaust but also in the air of heavy traffic tunnels. Based on the primary emission and their behaviour in the smog cham-

ber the secondary aerosol formation under sun light was a further focus. The main achievements can be summarized:

- Emission factor characterisation of different vehicle categories (from trucks to scooters) on various cycles and with different fuels
- Correlation of vehicle type emission factors with road tunnel air quality measurements
- Secondary organic aerosol forming potential of different vehicle emissions under various climatic conditions

Task C had intensive interaction with Task A as well as with Project II of this consortium.

The fact that the NEADS consortium with only minor variations decided to move on with a new project is the best proof that the involved parties regard this platform as inspiring, fruitful and efficient.

From my part, of the project leader, as well as from the part of all persons involved in the one or the other way in NEADS we would like to thank CCEM for all their efforts and endeavours.



Project I: New generation of zeolite SCR catalysts for passenger cars (as well as medium and heavy-duty vehicles), to be combined with Diesel particulate filters, by O. Kröcher

Scope of activities

The scope of this project was to develop improved zeolite-based SCR catalysts that are both active at low temperatures and stable at high temperatures without the production of undesired side-products.

Starting point was a commercial Fe-ZSM-5 material, provided by the project partner Süd-Chemie AG, which is currently used for the production of SCR catalysts in industry. In order to achieve the project goal, it was tried to gain a fundamental understanding of Fe-ZSM-5 and related materials in order to suggest suitable improvements in the next step. An important milestone to be reached was the identification of the active iron sites and to elucidate the contribution of the Brønsted-acid sites in the SCR reaction. Furthermore, the mechanism of hydrothermal aging and key factors for high stability and activity should be clarified.

On basis of the gained knowledge our industrial partner should be enabled to explain observations from real-world SCR systems and to prepare better iron-exchanged zeolite materials with higher activity as well as higher hydrothermal stability.

Current state of projects compared to the proposal's aims/milestones

Significant progress has been achieved in the understanding of iron-exchanged zeolites and their deactivation behaviour. Based on these results, new promising metal-exchanged zeolites and zeolite-like materials have been prepared for the Süd-Chemie AG.

In addition to the R&D activities on the development of new materials, a cordierite monolith was coated with Fe-BEA, which is beside Fe-ZSM-5 the second usually applied metal-exchanged zeolite material in SCR applications, and measured in our lab over a broad variety of parameters as input for the CFD model currently developed at the ETH in the group of Prof. K. Boulouchos.

Main achievements of the overall project

The clear identification of the active sites in Fe-ZSM-5 was primarily impeded by the absence of a suitable method for characterizing the nuclearity of the iron centres. To overcome this analytical problem, in this work a calculation method was developed, by which the concentration of isolated and clustered iron species were estimated by calculating the statistical distribution of isolated and neighbouring iron sites as a function of the iron loading (Fe/Al) and the Si/Al ratio of the zeolite employed. Under the assumption of uniformly distributed iron, the probability with which Fe-O-Fe bridged and higher nuclear Fe-species are formed in a Fe-ZSM-5 sample may be calculated based on a simple Poisson distribution. The results of these calculations were proved with DR-UV/VIS and DRIFT spectroscopy measurements on a variety of Fe-ZSM-5 samples with different Fe/Al ratios. Moreover, the calculated concentration profiles were checked with literature data from other studies.

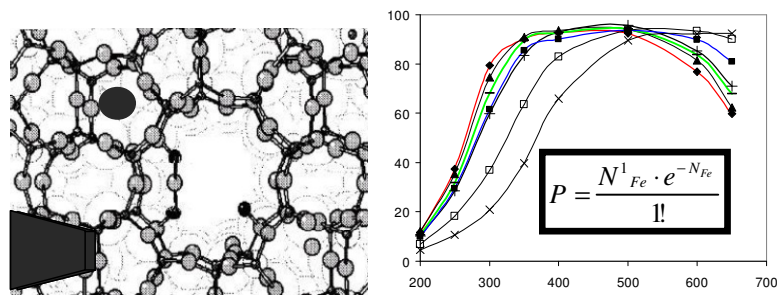
It was shown that the fractions of different iron species in Fe-ZSM-5 can be estimated by this calculation method with satisfactory accuracy, provided that the metal-exchange process resulted in a uniform distribution of iron in the zeolite. The method proved to be useful for verifying of analytical results, understanding of observed activity patterns and the identification of activity-structure relationships.

On this basis, the activities of monomeric, dimeric, clustered and oligomeric species in Fe-ZSM-5 in the SCR reaction could be expressed in terms of turn over frequencies (TOF values). The results suggest that the SCR of NO by NH₃ is catalyzed by different active sites and that their activation energies are dependent upon the reaction temperature. Isolated spe-

cies are responsible for the SCR activity up to 300 °C, but, with increasing temperature, dimeric and oligomeric species, and even Fe₂O₃ particles, become active. Obviously, the temperature at which the species become active increases with increasing nuclearity of the clusters. Thereby, dimeric species become even more active than the monomeric species at high temperatures.

With respect to the oxidation of ammonia it was found that isolated iron sites and large Fe₂O₃ particles become active at temperatures greater than 500 °C. The activity below this temperature is governed by clustered species, whereas dimers and small oligomers seem to be more active than highly clustered sites.

These results contribute to the understanding of the role of the various iron species in the SCR reaction, and may have important implications on the preparation of metal exchanged zeolites. By preparing zeolites with a maximum quantity of single iron sites, good selectivity at high temperatures and high activity at low temperature is obtained. For Fe-ZSM-5 with a Si/Al ratio of 14 this condition is best fulfilled for an exchange degree of about 0.4. On the basis of the presented correlation the optimum iron concentration in Fe-ZSM-5 SCR catalysts can be predicted also for other Si/Al ratios.




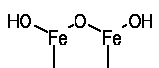
Temperature	Isolated species 	Dimeric species 	Oligomeric species Fe _x O _y	Particles Fe ₂ O ₃
200-300 °C	Active TOF ≈ 14 s ⁻¹ (250 °C)	-	-	-
≈ 350 °C	Active TOF ≈ 46 s ⁻¹ (350 °C)	Active TOF ≈ 120 s ⁻¹ (350 °C)	-	-
≈ 400 °C	Active TOF ≈ 100 s ⁻¹ (400 °C)	Active TOF ≈ 170 s ⁻¹ (400 °C)	Active	-
≥ 500 °C	Active	Active	Active	Active

Fig. I-1: Determination of the SCR activities of different iron sites in Fe-ZSM-5.

The influence of Brønsted-acidity on the SCR activity of Fe-ZSM-5 could also be revealed. The acidity of the catalyst is not a crucial factor for high activity and that Brønsted-acidity may not be required for adsorbing or activating the ammonia, but is necessary to bind and disperse the metal ions. The form in which ammonia is held by the support is not crucial and the support acts mainly as a reservoir for ammonia, which then migrates to the active site in order to undergo a reaction with NO. On the other hand, the oxidation activity of Fe-ZSM-5 was found to be the main factor that controls the high activity. The altered oxidation activity is largely responsible for the decreased SCR activity after hydrothermal aging. The analysis of deactivated samples indicates that under moderately aging conditions dealumination due to hydrolytic attack occur only on that Brønsted-acid sites that still carry a proton. Thereby, the zeolite lattice is locally destabilized due to Brønsted-acid protons but this destabilization does not result in a deactivation. The results show that the direct reason for hydrothermal aging is the Fe migration, which leads to the formation of FeO_x clusters, increasing in size during aging. The stability is thereby rather a question of the stability of the active iron species in the ion exchange site than of the framework stability itself. The results suggest that the remaining activity after hydrothermal aging is given by isolated iron ions, still located in the ion exchange positions. The metal ion has been identified as a key factor for high activity, the influence of the zeolite framework type (MFI, BEA, SAPO-34) is less pronounced. On the other hand the zeolite framework type is the key factor for high stability. Iron is thereby more stable in the BEA framework, whereas for copper the BEA framework is preferable. The results show that Cu-SAPO-34 is very susceptible against hydrothermal aging. The stabilization of Fe-ZSM-5 against hydrothermal aging is a very difficult task and seems only possible with extraordinary expense.

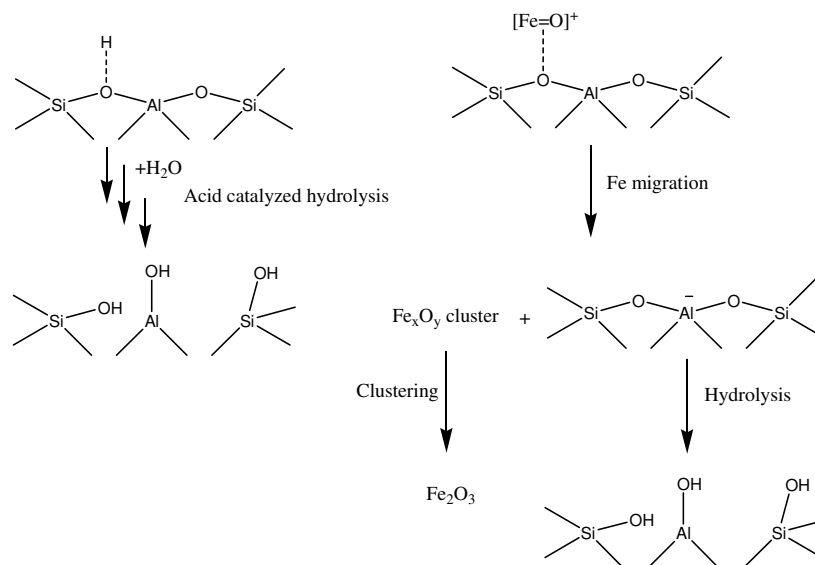


Fig. I-2: Scheme of the mechanism of hydrothermal ageing of Brønsted-acid sites and iron-sites in Fe-ZSM-5.

Publications

S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff, "The state of the art in selective catalytic reduction of NO_x by ammonia using metal-exchanged zeolite catalysts", *Catal. Rev.* 50(4) 2008, 492-531.

S. Brandenberger, O. Kröcher, A. Wokaun, A. Tissler, R. Althoff, "The role of Brønsted-acidity in the selective catalytic reduction of NO with ammonia over Fe-ZSM-5", J. Catal. (2009), in press.

S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff, "Estimation of the fractions of different nuclear iron species in uniformly metal-exchanged Fe-ZSM-5 samples based on a Poisson distribution", Appl. Catal. A, accepted manuscript (2009).

S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff "Determination of the activities of different iron species in Fe-ZSM-5 for NO-SCR", submitted to Appl. Catal. B

Activities within the project such as events, talks, workshops

S. Brandenberger, O. Kröcher, R. Althoff, A. Tissler, "Selective catalytic reduction (SCR) of NO_x with ammonia over Fe-ZSM-5: Influence of ion exchange degree on activity and stability", Talk at the 20. Deutsche Zeolith-Tagung, March 5-7, 2008, Halle-Wittenberg, Germany.

S. Brandenberger, O. Kröcher, R. Althoff, A. Tissler, "Assignment of active sites in Fe-ZSM-5 for the selective catalytic reduction of NO_x with ammonia by catalytic tests and statistical considerations ", Talk at the 42. Jahrestreffen Deutscher Katalytiker, March 11-13, 2009, Weimar, Germany.

O. Kröcher, S. Brandenberger, "Assignment of active sites in Fe-ZSM-5 and the role of Brønsted-acidity for the selective catalytic reduction of NO_x with ammonia", Invited talk for the Technical Chemistry seminar at the Ruhr-Universität Bochum, Germany, June 24, 2009.

Industrial partner

Süd-Chemie AG, Waldheimer Str. 15, 83052 Bruckmühl, Germany.

Project II: Exhaust Microreactor, by P. Dimopoulos Eggenschwiler

Scope of activities

The development of a new catalyst based on ceramic foam substrates was the scope of the activities. The main goal was to develop a catalyst with low precious metal requirements and excellent conversion behaviour.

This included the study of the flow field and the mass transfer properties through and inside such a structure. This implied some modelling which extended from the surface characteristics to an analytical solution of the mass transfer perpendicular to a cylindrical foam strut and further to a Kelvin cell up to some 1-d numerical simulation. Two promising applications emerged (instead of one as initially anticipated):

- Three Way Catalyst application for CNG powertrains
- Diesel Oxidation Catalyst (DOC) upstream of the Diesel Particulate Filter (DPF)

In a next step reactivity studies have been performed. The CNG application is currently under way since two vehicles are equipped with optimized ceramic foam catalysts aiming to obtain some first results concerning every day use and behaviour of such systems.

The DOC application required some additional prestudies aiming in analysing and deep understanding of the DOC during operation in active and passive regeneration modes as well as understanding soot and ash distribution in the DPF downstream. Soot micro and nanos-tructure analysis was performed in close collaboration with the Task A and C.



Fig. II-1: Vehicle for Diesel Oxidation Catalyst (DOC) application on the chassis dynamometer with the specifically designed exhaust aftertreatment housing (recognisable behind the right front wheel of the vehicle)

We were able to demonstrate comparable conversion properties with foam catalysts having half of the overall volume in respect to extruded production catalysts. This result is impressive, however we do not possess all necessary composition details of the wash coat in order to make the correct assessment. The industrial partner performing the coating has promised some more information as we enter the product development phase. Nevertheless our studies have shown that a specific wash-coat composition for foams has the potential to drastically improve the foam's characteristics and thus is considered necessary.

Current state of projects compared to the proposal's aims/milestones

Both applications are currently under testing in real vehicles. It is possible that a further product pre development phase will be added.

Main achievements of the overall project

The main aspect in the flow field investigations was the effect of the catalyst substrate on the flow uniformity. Our study confirmed previous studies suggesting that the flow downstream of honeycomb monoliths becomes less uniform with increasing mean flow velocity, but demonstrated that this is not the case with ceramic foam substrates, where the flow uniformity is practically not affected by the mean flow velocity. Moreover, ceramic foam substrates result in higher flow uniformity compared to honeycomb monoliths. The best flow uniformity was achieved downstream of 10ppi foams. Foams with higher pore size (8ppi) resulted in less uniform velocity profiles, while smaller pore size (15ppi) increased pressure drop without improving flow uniformity (see Fig. II-2).

Velocity field downstream of catalyst substrate:
a) honeycomb b) foam

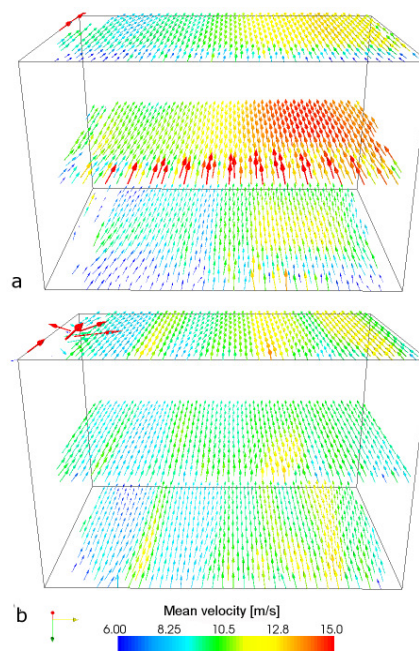


Fig. II-2: Results of the experimental fluid dynamic work comparing the flow field in the downstream of a conventional honeycomb catalyst and of a ceramic foam based catalyst at otherwise identical flow conditions.

Fig. II-3a shows the soot emission time series shortly before, during and shortly after the active regeneration of the DPF, while Fig. II-3b shows the number of particles upstream the DOC (=engine out) as well as downstream the DPF (=tail pipe). The comparison of the latter two leads to the DPF filtration efficiency (Fig. II-3c). Fig. II-3d shows the duration of the active regeneration, i.e. the time during which the engine combustion characteristics are deliberately changed in order to achieve high exhaust temperatures and promote soot combustion.

Most striking is the drop of the filtration efficiency of the DPF during the active regeneration. During the longest part of the regeneration filtration efficiency drops to around 90% (Fig. II-3c). In the same time tail pipe particle number emission (post DPF) increases for more than three orders of magnitude (Fig. II-3b) in respect to the tailpipe emission under normal operation, while the increase of the soot sensor signal (Fig. II-3a) is lower. The higher particle number in combination with the modest soot increase raises the question concerning the composition of the “counted” particles during active regeneration.

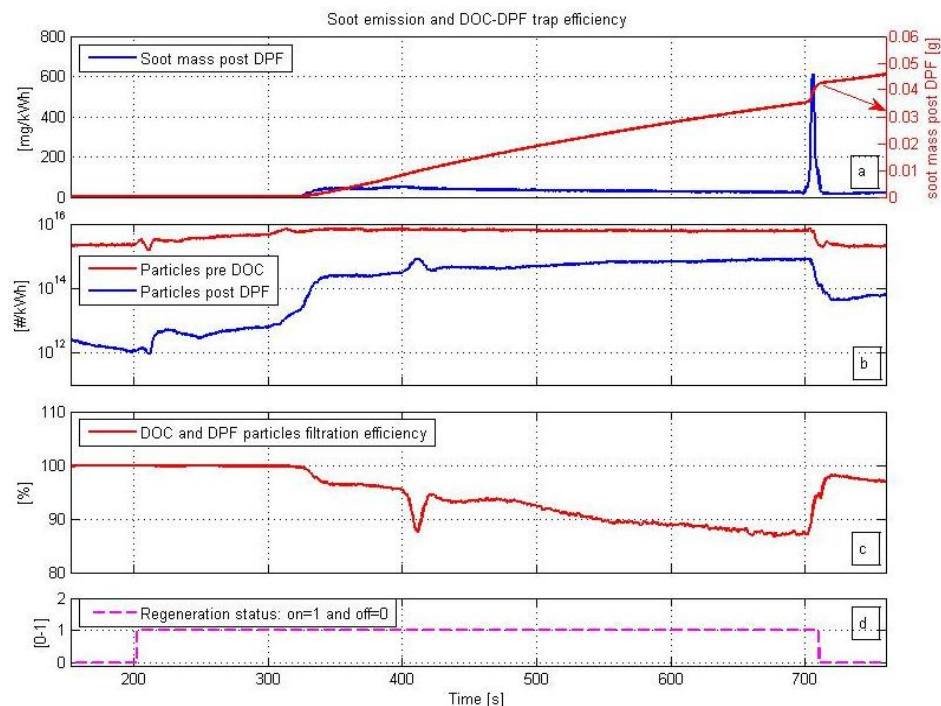


Fig. II-3: Soot emission (a), Engine out particle number, and tail pipe particle number emission (b), Filtration efficiency of the DPF (c) shortly before, during and shortly after DPF active regeneration (d).

The soot nanostructure investigations have incorporated Raman Spectra measurements complementary to the measurements performed under Task A in the SLS at PSI. The results of the Raman measurements of soot samples from the studied DPF reveal a G and a D band in all spectra. The G band of all examined spectra lied in average at 1600cm^{-1} , having a very narrow distribution (standard deviation of 3cm^{-1}) indicating some degree of ordering of the carbon atoms. In agreement with this is also the D band, which is not only strongly pronounced, at an average of 1342cm^{-1} (and even lower standard deviation), it leads to a relatively high I_D/I_G ratio of (in average) 3.32. Interestingly though, the full widths of the bands at half maximum are rather small. In comparison to carbon black values the DPF soot values are closest to carbon with low average surface (as characterised by BET) but high structure (as characterised by dibutyl phthalate, DBP, adsorption).

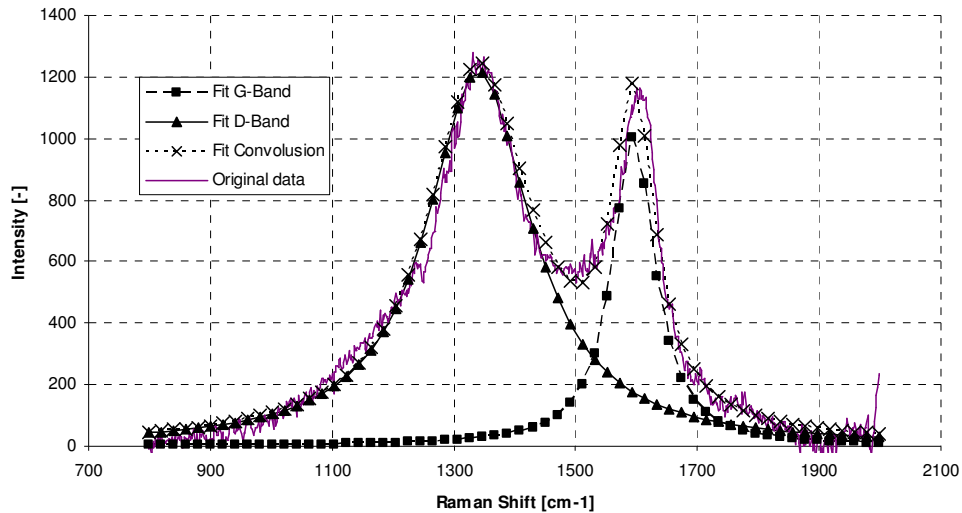


Fig. II-4: Typical Raman Spectra of soot collected from central DPF channels

Comparison of results from the SLS with the Raman spectra and further measurements from the Project II and Task A are item of a publication currently under preparation. Also under preparation is the publication of the full comparison of the two DOCs, the new and the conventional one, and their impact on the DPF loading and regeneration.

Publications/Patents

International Patent Application filed by the end of 2006: PCT/CH2006/000679. The patent researching revealed only 5 contradictory claims, which have been officially confuted from our side. Current status: Pending

Dimopoulos P., Bach C., Vogt U. F., Herrmann K.. Ceramic Foams as Catalyst Substrates: Pre-catalyst application homogenising the Exhaust Flow upstream of Aftertreatment Devices, SAE Paper 2007-24-0097

Winkler A., Hauert R., Dimopoulos P., Bach C., Aguirre M.. Catalytic activity and aging phenomena of three-way catalysts in a compressed natural gas/gasoline powered passenger car, Applied Catalysis B: Environmental, 10.2008, Vol. 84, Nr. 1-2, pp162-169

P. Dimopoulos, C. Bach : Ceramic Foams for Automotive Catalyst Substrate Applications EET-2008 European Ele-Drive Conference, International Advanced Mobility Forum, Geneva, Switzerland, 2008

P. Dimopoulos, T. Thurnheer, C. Bach : High efficiency exhaust aftertreatment: Purposeful application of ceramic foams MTZ-Konferenz, "Der Antrieb von morgen", Proceedings, München, 2008, eingeladener Vortrag

P. Dimopoulos Eggenschwiler, D. N. Tsinoglou, J. Seyfert, C Bach, U. F. Vogt, M. Gorbar : Ceramic foam substrates for automotive catalyst applications. Fluid mechanic analysis Experiments in Fluids, Springer Berlin/Heidelberg, (2009), 47, 2, 209-222

D.N. Tsinoglou, P. Dimopoulos Eggenschwiler, T. Thurnheer, P. Hofer : A simplified transient model for 3-way catalysts with honeycomb and foam substrates Proc. IMechE (2009), Part D Vol. 223: J. Automobile Engineering, 2009

A. Liati, P. Dimopoulos Eggenschwiler : Characterisation of particulate matter captured in diesel particulate filters. Geochimica Cosmochimica Acta, 73/13, Supplement 1, A761, 2009

A. Liati, P. Dimopoulos Eggenschwiler: Characterisation of particulate matter deposited in diesel particulate filters: visual and analytical approach in macro-, micro- and nano-scales, Combustion and Flame, 157 1658-1670, 2010

S. Weimer, R. Richter, C. Mohr, D. Schreiber, A.S.H. Prevot, M. Mohr, and P. Dimopoulos Eggenschwiler: Particles emitted by 2- and 4-stroke engines: Aspects from chasing and test bench experiments, Proceedings of the 18th International Symposium Transport and Air Pollution, Switzerland, 62-67, 2010

A. Karpf, D. Schreiber, P. Dimopoulos Eggenschwiler and R. Wachter: Passive and active regeneration modes and their characteristics on a modern diesel Particulate filter system, Proceedings of the 18th International Symposium Transport and Air Pollution, Switzerland, 2010

P. Dimopoulos Eggenschwiler, A. Liati, A. Winkler: Soot layer evolution, as well as ash accumulation phenomena in Diesel Particulate Filters, Proceedings of the 10th Stuttgart International Symposium, Automotive and Engine Technology, 373-385, 2010

P. Dimopoulos Eggenschwiler, A. Liati: Soot and Ash Layer Characteristics in Ceramic Diesel Particulate Filters, Proceedings of the 12th International Ceramics Congress, CIMTEC, 2010, including invited lecture

U. F. Vogt, G. Wagner, A. Broenstrup, P. Dimopoulos Eggenschwiler, M. Gorbar und P. Colombo: Improving the Properties of Ceramic Foams by a Vacuum Infiltration Process, Journal European Ceramic Society, J. Eur. Ceram. Soc. doi:10.1016/j.jeurceramsoc.2010.06.003, 2010

Activities within the project such as events, talks, workshops

Presentation of the fluid dynamic investigation results by P. Dimopoulos in the SAE Conference in Napoli, September 2007

Presentation by P. Dimopoulos in the CCEM General Assembly, June 2007

The EU-FP7 Research Project Submission: Catalytic Exhaust Gas Diffuser for Diesel Engines in Activity 7.2.1, Area 7.2.1.1, SST.2008.1.1.1 Clean and energy efficient gasoline and diesel power trains (Level 1) has received 11 points by the evaluators, this was over the threshold of 10points, but not enough for receiving funds (best possible score 15points)

NEADS Workshop, 11.12.2007, EMPA Dübendorf

NEADS Workshop, 4.11.2008, ETH Zürich

NEADS Workshop, 7.7.2009, PSI, Würenlingen

Industrial partners



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Additional Funding

BAFU has contributed additional funds (100kCHF) for the diesel project while Novatlantis has contributed additional funds (140kCHF) for the CNG catalyst project. The additional funding was necessary given that two separate applications are in focus (instead of one as in the initial project outline) with higher equipment and manpower requirements.

Project III: Combination of SCR systems with DPF systems: Combustion Interface, by Prof. K. Boulouchos

Scope of activities

The Mean Value Soot Model (MVSM) has been further developed and validated by a comprehensive set of experimental data. Improvements were carried out in particular in the area of transient engine operation predictions. These investigations have revealed that during a rapid change in the engine load, the lag in turbocharger boost pressure, a finite duration required to close the exhaust gas recirculation (EGR) valve combined with the rapid increase in fuel quantity lead to a short term oxygen deficit. This results in an inhibition of the soot oxidation process during a few select engine cycles only, while the formation remains largely unaffected; see

Fig. . These five to ten engine cycles however account for the majority of the soot emissions of the entire transient.

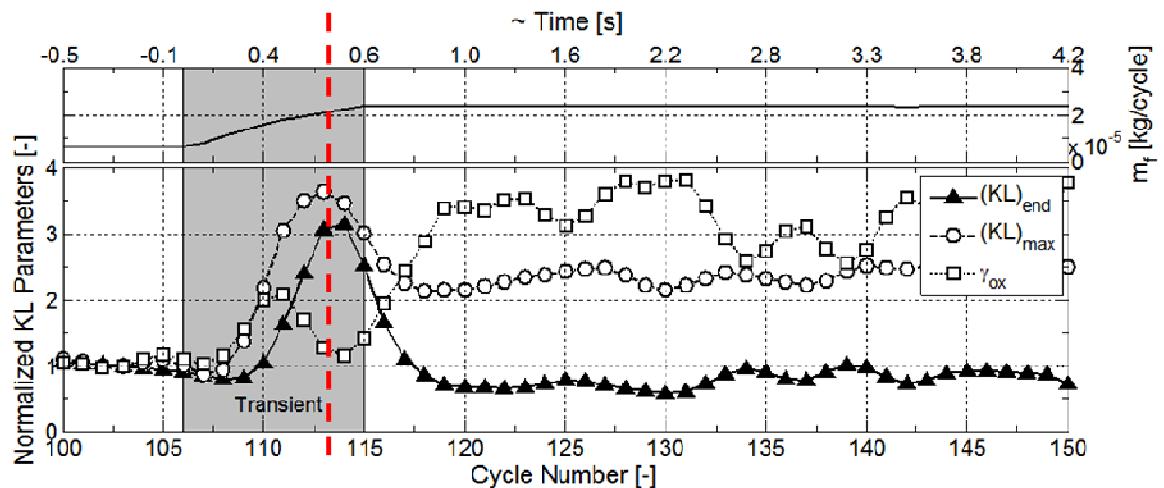


Fig. III-1: Transient Diesel engine operation: Evolution of KL parameters representing soot formation (KL_{max}), oxidation (γ_{ox}) and net soot emission (KL_{end})

The model also revealed that an accurate estimation of the intake air temperature is extremely important, since it is used to calculate the temperature used in the computation of the soot formation rate expression.

Further efforts were directed at measuring on a light-duty common-rail Diesel engine the soot emissions in the exhaust-stream by means of a micro soot sensor and filter smoke number and in-cylinder by means of two-colour pyrometry. Correlations have been developed between the different techniques for a synthetic Diesel fuel with low aromatic content and lower cetane number as well as for 'standard' reference Diesel fuel, see

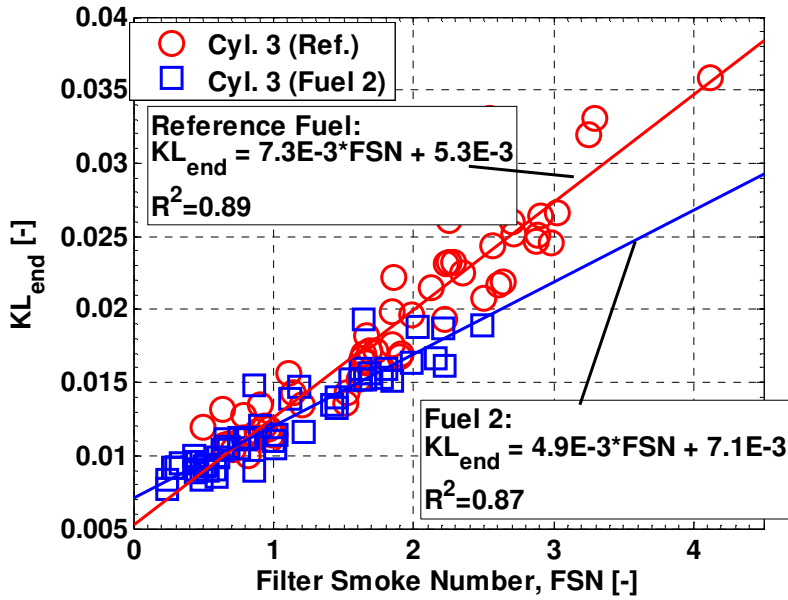


Fig. .

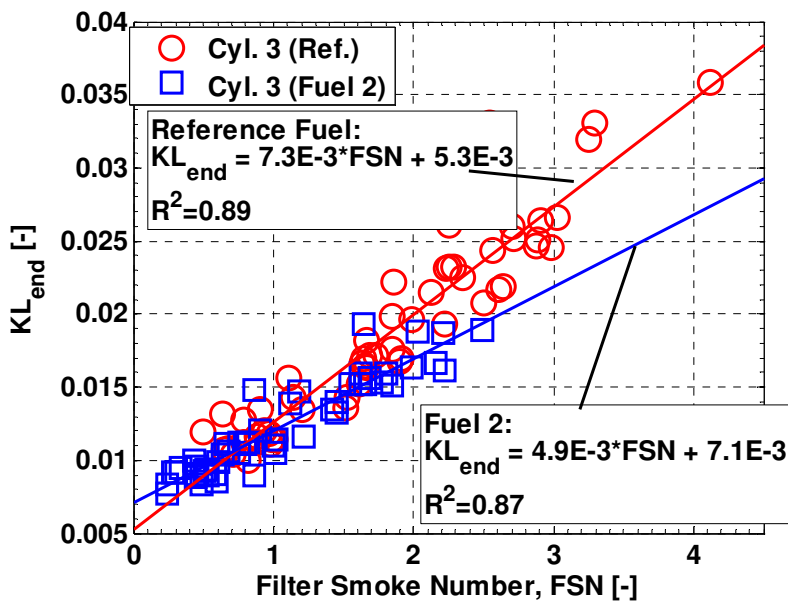


Fig. III–2: correlation between in-cylinder measurement of soot emissions (KL_{end} factor) and the exhaust stream measured filter smoke number (FSN) for two different fuels

Current state of project compared to proposal's aims/milestones

As outlined in the annual report 2008, the focus has been placed exclusively on engine-out particle emission and all activities relating to DPF state characterisation have been dropped. Main reason therefore is the high level of success in the soot model developments which manifests itself in a large number of publications and very successful fundraising, as can be seen from the following sections.

Main achievements of the overall project

- Results for MVSM published in SAE (2009-01-1277) and presented at the SAE World congress, Detroit, April 2009.
- Focus on further development and validation of the MVSM for transient engine operation, published in SAE (2009-01-1904). Identified importance of temperature estimation in the intake manifold on predicted engine-out soot emissions.
- Application of the MVSM to synthetic diesel fuel with low aromatic content and lower cetane number; comparison with std. Diesel (ASME ICEF proceedings)

Additional Funding

The funding proposal submitted to the Swiss Federal Office of Energy end of 2008 has been approved (BfE grant no. 102859).

Joint public and third party funding has also been approved by the Swiss Innovation Promotion Agency (KTI) and Kistler Instruments; the projects aims at further developing miniaturised, in-cylinder pyrometers (KTI grant no. KTI10604_1_PFMN_NM).

Further funding has been granted by the Swiss Federal Office for the Environment (BAFU grant no. 07.0086.PJ/1252-1882).

Publications/Patents

Kirchen P. et al.: Correlation and Analysis of In-Cylinder and Engine-Out Soot Emission Measurements from a Multi-Cylinder Diesel Engine. in 8. Internationales Stuttgarter Symposium. 2008. Stuttgart, Germany. Vol.2, p. 129-145.

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Activities within the project (seminars, workshops etc.)

NEADS Workshop, 11.12.2007. EMPA Dübendorf
LAV Scientific Seminar Series. 14.03.2008, ETH Zürich
NEADS Workshop, 4.11.2008, ETH Zürich
NEADS Workshop, 7.7.2009, PSI, Würenlingen

Task A: New Instrumentation for Particle Characterisation, by M. Ammann

The following part is structured along the following topics:

- a) synchrotron based microspectroscopy
- b) high resolution time-of-flight aerosol mass spectrometry
- c) electrical and optical methods for emission studies

Scope of activities

a) The overall aim of this subtask was to develop synchrotron based X-ray microscopy and absorption spectroscopy as a tool to obtain spatially resolved chemical information from individual soot particles under ambient conditions mimicking diesel exhaust soot particles in the atmosphere. Therefore, a small microreactor was developed allowing exposing soot particles to a well defined gas environment with respect to temperature and humidity. The new development should then be applied to characterize individual soot particles from smog chamber experiments (see Task C) related to investigating the atmospheric fate of exhaust particles for different diesel exhaust aftertreatment technology. Finally, particles from various places within a diesel exhaust aftertreatment device (see Project II) should be characterized with respect to their carbon functional group composition.

b) High Res-ToF-AMS

The high resolution time-of-flight aerosol mass spectrometer (sometimes called W-ToF-AMS) was the instrument of choice on the market to measure quantitatively the organic aerosol including elemental composition at 1 Hertz. The high time resolution is important in the investigation of highly transient signals at the vehicle test bench or in ambient air very close to an emission source. The higher mass resolution of the time-of-flight mass spectrometer compared to the quadrupole instrument enables the determination of the elemental composition of each fragment after the electron impact ionization.

c) The focus of the activities is the investigation of new techniques for field measurement of particle emissions, which take into account the changed requirements of modern low emission engines. Conventional techniques as opacimeters can no longer be applied there. Methods based on electrical charging and optical techniques are investigated. This work performed by FHNW was attached to the NEADS consortium up to the final year. Therefore the state of art reported here corresponds to the one of the 4th annual report.

Current state of projects compared to the proposal's aims/milestones

a) After having undergone several design revisions, the microreactor concept has evolved into a mature tool ready to use in beamtimes at the Pollux X-ray scanning transmission microscope beam line of the Swiss Light Source. Two papers have been submitted to renowned journals describing its design, performance tests and first applications. The PhD student involved in this development has participated in several diesel soot aging experiments in the PSI smog chamber performed within Task C, and a manuscript gathering the results of this activity is currently in preparation. Finally, soot particles from a diesel particulate filter from experiments performed within Project II have been analyzed with X-ray absorption spectroscopy, analysis and reporting of which is underway. Therefore, all tasks intended were completed successfully.

b) The AMS was successfully applied during test bench, smogchamber and field experiments and all results are presented in Task C, Atmospheric Implications.

c) Based on the 'Diffusion Size Classifier DiSC', the MiniDiSC has been developed, which is small enough to be used as personal monitor for ambient air measurements. Together with a new dilution system, which is presently being built, a robust tool for field monitoring of particle emissions will be available.

Main achievements of the overall project

a) Particulate matter emissions from exhaust processes are of significant concern to humans, ecosystems and climate. Chemical composition and the distribution of chemicals within particles, as well as their evolution under ambient conditions are at the core of these issues. Establishing the combination of submicron scale spatial resolution with spectroscopic information is at the forefront of research in this area. The microreactor developed within this project is a complete de-novo and major step forward (Huthwelker et al., 2010). Its design is strongly constrained by X-ray optics requirements as well as significant absorption of materials in the soft X-ray range. However, these challenges were overcome and the current design has been proven in a range of applications (Zelenay et al., 2010). This development and the specific requirements for X-ray spectroscopy at the carbon edge have also contributed to the further development of the Pollux beamline at SLS.

The chemical characterization of individual soot particles demonstrated differences with varying exhaust aftertreatment technology, changes with aging under simulated atmospheric conditions (Figure A-1, left) and also significant particle to particle variability. Parallel to that, the chemical changes are also reflected in water uptake behavior – a key aspect in the climate effect of soot particles – as shown for one individual soot particle in Figure A-1. The quantitative analysis of such images significantly extends information from aerosol based methods with unprecedented sensitivity for the small amounts of water associated with the particles.

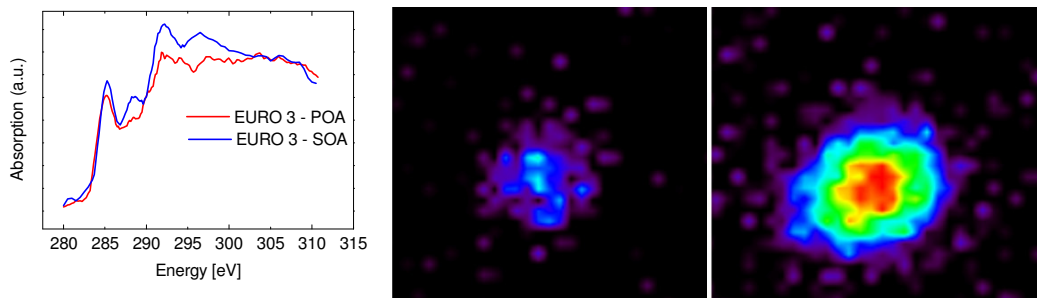


Fig. A-1: Carbon K edge NEXAFS spectra of individual soot particles in samples taken immediately after injection into the smog chamber (POA) and after processing by simulated sunlight (SOA) from a Euro-3 diesel vehicle (left). The main features of interest are peaks at 285 eV (aromatic hydrocarbon), at 288 eV (carboxylic functional groups) and 292 eV (aliphatic hydrocarbon). The relative contribution of these features can be related to the water uptake behaviour demonstrated by the middle and right, scanning transmission X-ray images of a soot particle 200nm in diameter at 30 and 88 % relative humidity taken in the microreactor developed in this project for the Pollux microscope at the Swiss Light Source. The pictures were taken at 538 eV, where oxygen absorbs due to a resonant transition. The particle stemmed from a diesel passenger car and was exposed to photo-oxidation for several hours in the PSI smog chamber. The absorption is a direct and in situ probe of the increasing amount of water absorbed by the soot particle with increasing humidity.

b)

c) The above mentioned MiniDiSC has been developed and tested.

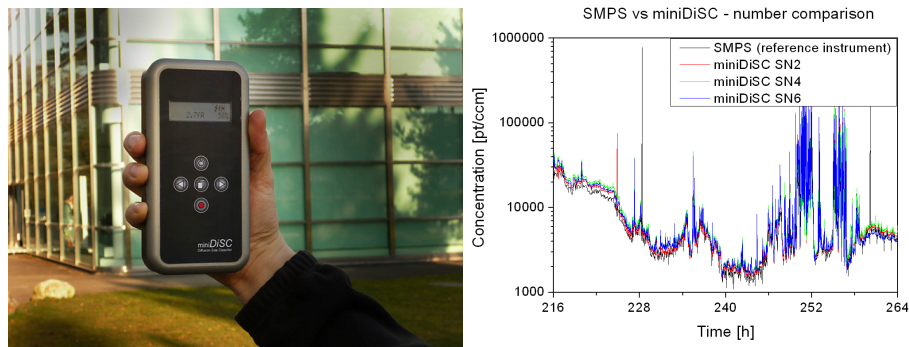


Fig. A-2: MiniDiSC and comparison of the number concentration measured with 3 MiniDiscs and an SMPS

Publications/Patents

a) Zelenay V., A. Křepelová, M. Ammann, M. G.C. Vernooij, M. Birrer, G. Tzvetkov, J. Raabe, and T. Huthwelker: A new device for the study of water uptake and release in aerosol particles using X-ray microspectroscopy. Proc. European Aerosol Conference, Thessaloniki, Aug. 2008.

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c) Fierz M., Keller A., and Burtcher H.: Charge-based personal aerosol samplers. *Inhalation Toxicology*, 2009; 21(S1): 30–34.

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Fierz M., S. Weimer, and H. Burtcher: Miniaturized electrical diffusion battery compares well with TSI FMPS. Proc. European Aerosol Conference, Thessaloniki, Aug. 2008.

Activities within the project such as events, talks, workshops

a) Presentation of first results at the PhD Symposium at Empa, November 2007 by Veronika Zelenay.

Zelenay, V., A. Křepelová, M. Ammann, M. G.C. Vernooij, M. Birrer, G. Tzvetkov, J. Raabe, and T. Huthwelker: Water uptake on aerosol particles studied by X-ray microspectroscopy. X-ray Absorption Spectroscopy Workshop, Paul Scherrer Institute, Villigen, Oct 7-8, 2008.

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Zelenay, V., T. Huthwelker, A. Křepelová, M. Ammann,
Observations of water uptake in ammonium sulphate particles using x-ray microspectroscopy, INTRON conference, April 14 – 17, 2009, Portoroz, Slovenia

Ammann, M., V. Zelenay, T. Huthwelker, A. Křepelová, J. Raabe, and B. Watts, The climate effect of atmospheric particles caught in act, Joint PSI User Meeting, October 12 – 13, 2009, Villigen, Switzerland

Ammann, M., A. Rouvière, Y. Sosedova, C. George, B. D'Anna, V. Zelenay, A. Křepelová, T. Huthwelker, Photochemistry and microstructure of organic particles, EUCAARI Annual Meeting, November 17-20, 2009, Stockholm, Sweden

b) Presentation of first results in the LAC seminar series, PSI, on 29 October 2007 by Roberto Chirico

c) Presentation of results at the annual meeting of the 'Arbeitskreis Partikelfilter AKPF'

Task B: Numerical Simulation, by K. Boulouchos

Scope of activities

A numerical tool has been successfully developed to simulate one representative channel of an SCR converter. The model accounts for 1D convective mass transfer through the channel and 1D diffusion within the catalytically washcoated wall, which are coupled via a mass transfer boundary condition at the wall. Several surface reactions have been considered in the layer according to the literature and the related parameters have been calibrated according to experimental data for a Fe-BEA zeolite catalyst obtained from the Paul Scherrer Institute (PSI).

Current state of projects compared to the proposal's aims/milestones

A comprehensive set of data collected by the Exhaust Gas Aftertreatment Laboratory of PSI has been used to fit the model parameters. Variations include the Gas Hourly Space Velocities (GHSV 30000, 50000, 70000), a broad range of temperatures (200, 250, 300, 350, 450 °C), different NO/NO₂ feed ratios (0, 25, 50, 75, 100 %) as well as different levels of NH₃ feed at the channel inlet. The parameters have been fitted by employing an optimisation procedure based on genetic algorithms, which has seen very successful application at LAV in the past.

Following this, some remaining shortcomings of the model have been further investigated. To this end, in a first step, the ammonia adsorption/desorption has been studied in great detail. The ammonia adsorption capacity of the catalyst and four rate parameters including the desorption activation energy have been determined in a calibration procedure based on the available experimental data. The adsorption capacity of the catalyst decreases when the temperature increases as is shown in Fig. B- 1, which is also in agreement with findings which have previously been reported in literature.

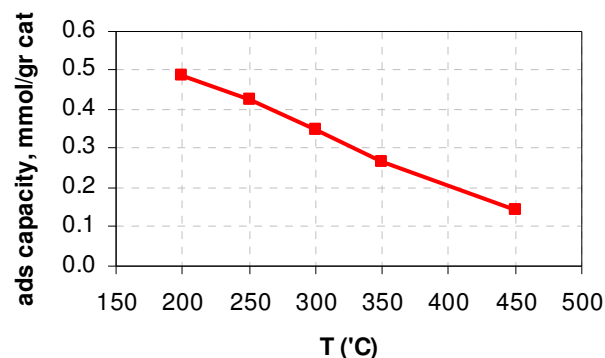


Fig. B- 1. Ammonia adsorption capacity

New findings allowed for more detailed modeling of the SCR reactions. This new mechanism comprises a total of 10 reactions describing NH₃ adsorption/desorption/spill-over, NO_x reduction and oxidation of components as well as production of some minor species, cf. table B-1. This allows for improved predictions, in particular with respect to the inhibition phase following the shut-off in the ammonia inlet feed.

1,2	Ammonia ads/desorption	$\text{NH}_3 \leftrightarrow \text{NH}_3^*$
3	Standard SCR	$4 \text{NH}_3^* + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$
4	Fast SCR	$4 \text{NH}_3^* + 2 \text{NO} + 2 \text{NO}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$
5	Ammonia spill-over	$\text{NH}_3^* \leftrightarrow \text{NH}_3\text{X}$
6	NO oxidation	$2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$
7	Ammonia oxidation	$4 \text{NH}_3^* + 3 \text{O}_2 \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O}$
8	Direct NO ₂ reduction	$2 \text{NH}_3^* + 3/2 \text{NO}_2 \rightarrow 7/4 \text{N}_2 + 3 \text{H}_2\text{O}$
9	Ammonium nitrate formation	$2 \text{NH}_3^* + 2 \text{NO}_2 \rightarrow \text{NH}_4\text{NO}_3 + \text{N}_2 + \text{H}_2\text{O}$
10	Nitrous oxide formation	$2 \text{NH}_3^* + 2 \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{N}_2 + 3 \text{H}_2\text{O}$

Table B-1. Comprehensive mechanism for SCR surface reactions

Main achievements of the overall project

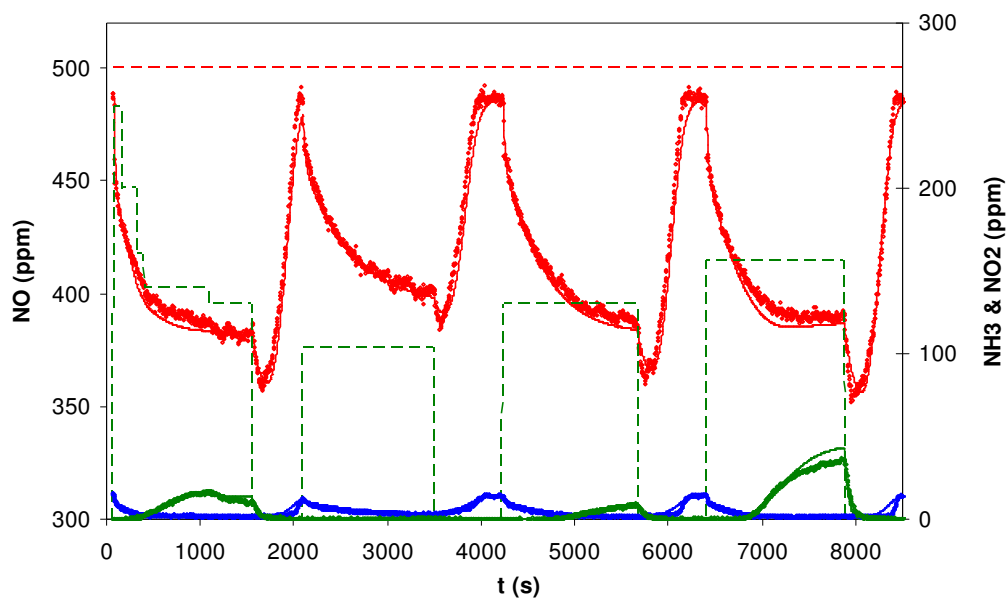


Fig. B- 2. Conversion rate of NO, NO₂ and NH₃ for a single channel of an SCR converter: GHSV = 50000 h⁻¹, inlet temperature = 200 °C, inlet NO_x = 500 ppm (100% NO)
Symbols: experiment, line: simulation, dashed line: inlet, red: NO, blue: NO₂, green: NH₃

The large number of parameters which need to be calibrated calls for a highly efficient and structured optimization procedure. Parameters of the reactions are hence determined group by group depending on temperature and the ratio of NO/NO_x in the inlet feed. The experimental condition at low temperature (200 °C) with 100% NO in the feed has the minimum number of effective parameters, allowing for surface reactions 1-6 to be calibrated. Fig. B-2 shows good agreement between the numerical results and the measurements.

Since the real operating condition of an engine is highly transient, the fast transient (dynamic) condition has also been tested to verify the model. Fig. B-3 presents the results in this case which agrees also well with the measurements.

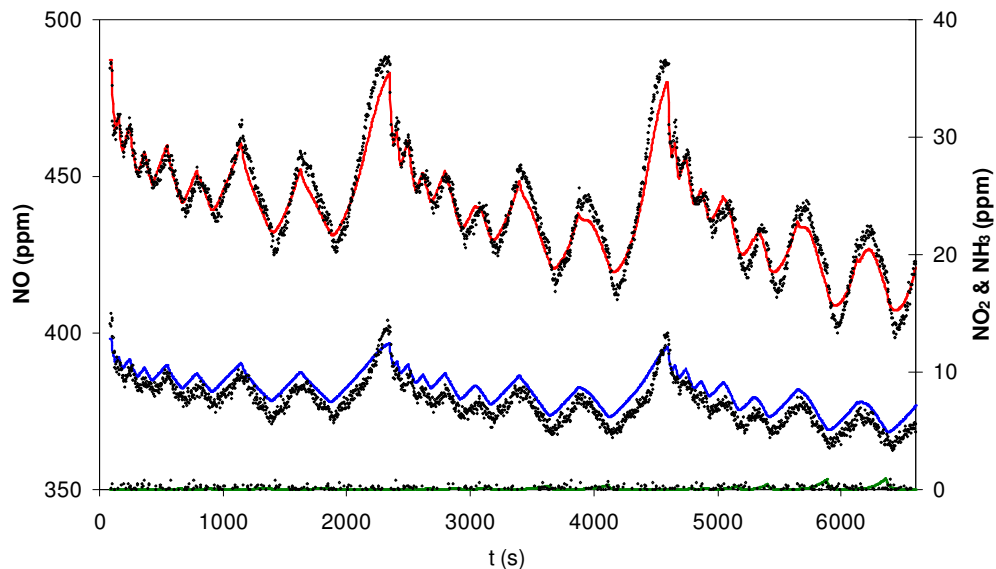


Fig. B- 3. Conversion rate of NO, NO₂ and NH₃ at highly transient inlet ammonia feed: GHSV = 50000 h⁻¹, inlet temperature = 200 °C, inlet NO_x = 500 ppm (100% NO)
Symbols: experiment, line: simulation, red: NO, blue: NO₂, green: NH₃

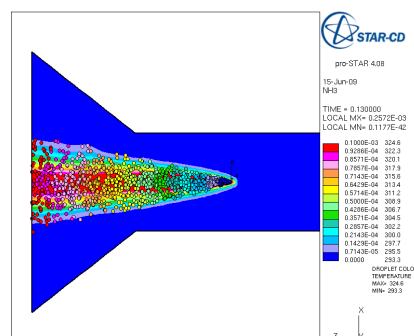


Fig. B- 4. Simulation of urea injection in the exhaust stream: Distribution of ammonia vapour overlaid with liquid droplets

Further progress has been made in the field of the upstream processes. First calculations have been carried out in the framework of a MSc thesis for the urea injection process in the hot exhaust stream, since the knowledge of the urea distribution at the channel entry is of great importance. Fig. B-4 depicts the distribution of liquid droplet and formed ammonia after the injector. The influence of the injector location and orientation, orifice diameter, spray cone angle, droplets initial size and concentration distribution has been examined. The obtained

results suggest that increasing the injector distance and the spray cone angle leads to an increase in yield and uniformity of the spatial distribution of the reducing agent (ammonia). The injection orientation also plays an important role: injection performed in radial or up-stream directions lead to improvements in the ammonia production and homogeneity, a finding which also applies when using multi-stream injectors.

Fig. B- 5 shows the ammonia distribution in a system with 4 injectors. Due to the symmetry reason, simulation is done for half of the real system. The computations also show improved ammonia production and uniformity if a constant initial size for the droplets is imposed. Wall impingement of the spray showed similar benefits, but more work is necessary in the latter two fields before clear conclusions can be drawn.

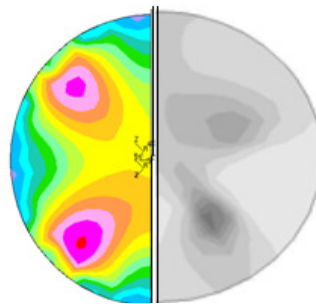


Fig. B- 5. Simulation of urea injection and mixture formation. Comparison of predictions (left) with data from the literature

The findings demonstrate the capability of the models employed to qualitatively predict variations to the injection configuration. More elaborate experimental data such as vapour phase and/or species spatial distributions, droplet sizes and velocities are required for in-depth validation and further model development/improvements.

Additional Funding

Additional funding by the Swiss Federal Office of Energy is gratefully acknowledged (BfE project “Entwicklung schneller Mess- und Rechenverfahren für die Charakterisierung energieeffizienter Diesel-Brennverfahren an der Nahtstelle zur Abgasnachbehandlung”, Grant no. 102859)

Publications/Patents

Sharifian L., Wright Y.M., Boulouchos K., Elsener M., Kröcher O.: “Simulation of NO_x reduction in an Ammonia-SCR system with a Fe-Zeolite catalyst and calibration of related parameters”, submitted for publication in ASME Conference 2010, paper no. IMECE2010-40431

Activities within the project (seminars, workshops etc.)

NEADS Workshop, 11.12.2007. EMPA Dübendorf
NEADS Workshop, 4.11.2008, ETH Zürich
LAV Scientific Seminar Series. 28.04.2009, ETH Zürich
NEADS Workshop, 7.7.2009, PSI, Würenlingen
LAV Scientific Seminar Series, 9.06.2010, ETH Zürich

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CCEM-NEADS final meeting, 18.06.2010, EMPA Dübendorf
CCEM-NADiP kick-off meeting, 18.06.2010, EMPA Dübendorf



Task C: Atmospheric Interactions, by U. Baltensperger

The following part is structured along the following topics:

- a) chasing and dynamometer experiments
- b) smog chamber studies

Scope of activities

a) Test bench studies were chosen to study the emissions from various types of vehicles under varying operating conditions and fuels. To study the current fleet in Switzerland and not only individual cars, a tunnel experiment was performed to assess the average emissions of heavy-duty and light-duty vehicles on the highway.

b) The test bench studies yield the primary emissions, i.e. the aerosol that is emitted directly in particulate form into the atmosphere. However, vehicle emissions contain also trace gases that can contribute to secondary formation of aerosol after oxidation in the atmosphere. The PSI smogchamber was used to study the full impact of the emissions on particulate matter by assessing both the primary emissions and the secondary production potential of the trace gases. Different diesel car technologies were used as an emission source and the mass spectral signature of primary organic aerosol (POA) and secondary organic aerosol (SOA) as a function of time were characterized.

Current state of projects compared to the proposal's aims/milestones

a) The test bench experiments were analyzed in detail. An overview paper including the emission factors of regulated and non-regulated particulate and trace gas compounds is in preparation. Several papers are published or in preparation (see below).

b) The analyses of the large number of the diesel exhaust aging experiments performed at the PSI smogchamber were recently published in Atmospheric Chemistry and Physics Discussions.

Main achievements of the overall project

- a) A sampling campaign with eight different types of vehicles was conducted in 2009 at the vehicle test facilities of the Joint Research Centre (JRC) in Ispra (Italy). The vehicles chosen were representative of some categories circulating in Europe and were fuelled either with standard gasoline or diesel and eventually some of them were also run with blends of rapeseed methyl ester biodiesel or bioethanol. The aim of this work was to improve the knowledge about the emission factors of gas-phase and particle-associated regulated and unregulated species. The black carbon (BC), the primary organic aerosol (OM) content of particulate matter, the particle number, the monocyclic and polycyclic aromatic hydrocarbons and a selection of unregulated gaseous compounds were measured in real time together with the regulated compounds. Diesel vehicles, without particle filters, featured the highest emissions in particle number, followed by gasoline vehicles and scooters. The particles from diesel and gasoline vehicles comprised of BC with a low fraction of OM, while the particles from the scooters were mainly OM. Scooters were characterized by surprisingly high emission factors for OM, which were orders of magnitude higher than for the other vehicles. The heavy duty diesel vehicle featured the highest NO_x emissions, while the scooters featured the highest emissions for total hydrocarbons and aromatic compounds due to the unburned and partially burned gasoline and lubricant oil mixture. Generally, with biodiesel and bioethanol the emission factors of OA and total aromat-

In the Gubrist tunnel we found emission factors (EF) for organic aerosols (OA) to be heavily influenced by the OA mass loading. To exclude the loading effect, only the organic aerosol interval from $60 \mu\text{g m}^{-3}$ to $90 \mu\text{g m}^{-3}$ was considered and the EF(OA) value for HDV estimated for this OA interval was $33.7 \pm 2.3 \text{ mg km}^{-1}$ for a temperature inside the tunnel of $20\text{-}25^\circ\text{C}$. Using this EF(OA), and considering rush hours with 30 ± 6 HDV and 221 ± 41 LDV every 5 minutes, $45 \pm 7\%$ of the total OA emitted per km driven in the tunnel by all vehicles is from HDV. An overestimate of the EF(OA)HDV value of $47.4 \pm 1.6 \text{ mg km}^{-1}$ was obtained when the linear fit was applied to all data points. Similar to the increasing EF, the OA/BC ratio in the tunnel was also affected by the organic loading and it increased by a factor of ~ 3 over the OA range $10\text{-}120 \mu\text{g m}^{-3}$. For OA concentrations lower than $40 \mu\text{g m}^{-3}$ the OA/BC ratio was below 1, while with an OA concentration of $100\text{-}120 \mu\text{g m}^{-3}$ the OA/BC ratio was ~ 1.5 . The mass spectra (MS) acquired in the tunnel were highly correlated with the POA MS from a EURO 3 diesel vehicle with a speed similar to the average tunnel speed.

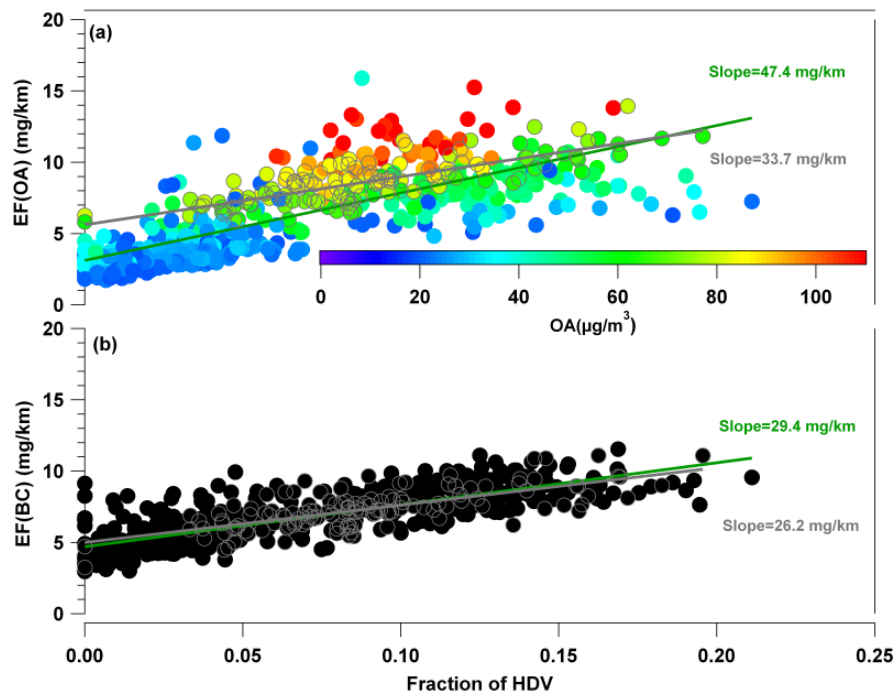


Fig. C-3: Emission factor (EF) for organic aerosol (OA) (a) and black carbon (BC) (b) versus the fraction of heavy duty vehicles (HDV). Two linear fits are shown in part (a) for: all values (green fit) and for the values in the OA interval from $60 \mu\text{g m}^{-3}$ to $90 \mu\text{g m}^{-3}$ only (gray). The slopes correspond to the EF of the heavy duty vehicles (HDV) while the intercepts are equivalent to the EF of the light duty vehicles (LDV).

b) Diesel particulate matter (DPM) is a significant source of aerosol in urban areas and has been linked to adverse health effects. Although newer European directives have introduced increasingly stringent standards for primary PM emissions, gaseous organics emitted from diesel cars can still lead to large amounts of secondary organic aerosol (SOA) in the atmosphere. Here we present results from smog chamber investigations characterizing the primary organic aerosol (POA) and the corresponding SOA formation at atmospherically relevant concentrations for three in-use diesel vehicles with different exhaust aftertreatment systems. One vehicle lacked exhaust aftertreatment devices, one vehicle was equipped with a diesel

oxidation catalyst (DOC) and the final vehicle used both a DOC and diesel particulate filter (DPF). The experiments presented here were obtained from the vehicles at conditions representative of idle mode, and for one car in addition at a speed of 60 km/h. An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was used to measure the organic aerosol (OA) concentration and to obtain information on the chemical composition. For the conditions explored in this paper, primary aerosols from vehicles without a particulate filter consisted mainly of black carbon (BC) with a low fraction of organic matter (OM, OM/BC<0.5), while the subsequent aging by photooxidation resulted in a consistent production of SOA only for the vehicles without a DOC and with a deactivated DOC. After 5h of aging 80% of the total organic aerosol was on average secondary and the estimated "emission factor" for SOA was 0.23–0.56 g/kg fuel burned. In presence of both a DOC and a DPF, primary particles with a mobility diameter above 5nm were $300 \pm 19 \text{ cm}^{-3}$, and only 0.01 g SOA per kg fuel burned was produced within 5h after lights on. The mass spectra indicate that POA was mostly a non-oxidized OA with an oxygen to carbon atomic ratio (O/C) ranging from 0.097 to 0.190. Five hours of oxidation led to a more oxidized OA with an O/C range of 0.208 to 0.369.

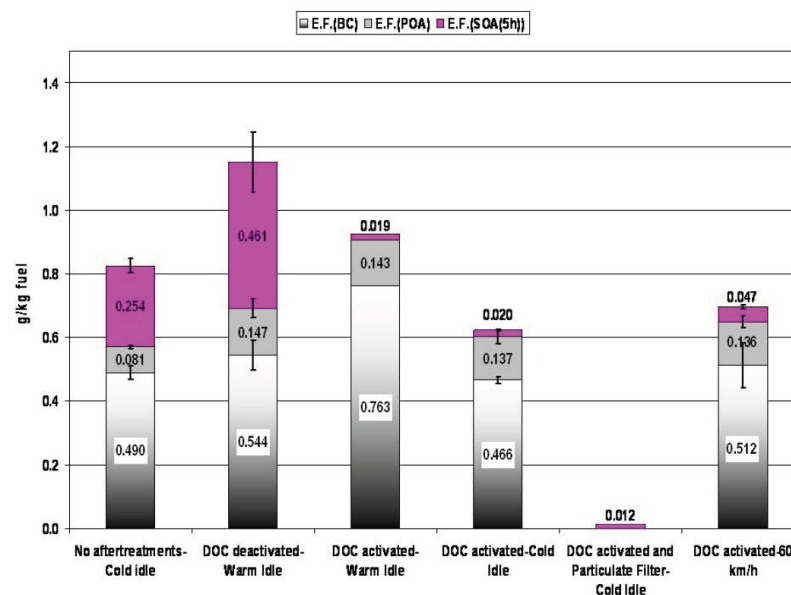


Fig. C-4: Emission factors of black carbon and primary organic aerosol as well as the secondary organic aerosol formation potential (SOA) after 5 hours of aging for different diesel vehicle exhaust technologies and conditions.

Publications/Patents

Adam, T.W., R. Chirico, M. Clairotte, M. Elsasser, U. Manfredi, G. Martini, M. Sklorz, T. Streibel, M.F. Heringa, P.F. DeCarlo, U. Baltensperger, G. De Santi, A. Krasenbrink, R. Zimmermann, A.S.H. Prevot, and C. Astorga, Application of modern on-line instrumentation for chemical analysis of gas phase and particulate phase of heavy duty vehicle exhaust at the novel European Commission test facility, in preparation.



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