

5th International Symposium on Modeling of Exhaust-Gas After-Treatment (MODEGAT V)

The latest developments in computer simulation of vehicle emissions control catalysts and systems

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This symposium held in Bad Harrenalb, Germany, from 3rd–5th September, 2017, specifically focused on modelling and numerical simulation in automobile exhaust-gas aftertreatment. The purpose of the workshop was to support the exchange of state-of-the-art modelling and simulation techniques and new approaches among researchers, scientists and engineers from industry and academia. The meeting had over 100 registered participants, about 45% from academia and 55% from industry. The scientific programme was composed of four tutorials, plus oral and poster presentations.

This report gives a summary of the oral presentations, which will be divided into five sessions: selective catalytic reduction (SCR), methane oxidation, diesel oxidation catalyst (DOC), diesel particulate filter (DPF) and modelling and performance.

Selective Catalytic Reduction Session

“Tutorial: Peculiarities of SCR Kinetics, and their Practical Implications” was delivered by A. Yezerets (Cummins Inc, Columbus, USA). This tutorial covered different aspects of SCR catalysis:

1. Hierarchy of active sites: this was described on the basis of their proximity (isolated

copper, adjacent copper or copper sharing a cage), copper site coordination (single aluminium or two aluminiums) and nature of the Brønsted acid sites (unexchanged or formed upon reduction). The different sites have been characterised by *operando* extended X-ray absorption fine structure (EXAFS), hydrogen temperature-programmed reduction (H₂-TPR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and modelled using density functional theory (DFT). It was concluded that both ZCuOH and Z₂Cu sites exist, but they show similar activities. However, their different behaviour towards sulfur poisoning and N₂O selectivity makes it important to distinguish between them when modelling an SCR system. Also, the site distribution changes after mild ageing (750°C), with some of the ZCuOH turning into Z₂Cu, although the total ammonia storage remains the same.

2. Reactivity pathway: the focus was on the low temperature (T<200°C) mechanism, proceeding through ammonium nitrate formation, sublimation and decomposition. The reaction rate is limited by the accumulation of ammonium nitrate, which inhibits the SCR reactions. For temperatures above 170°C, ammonium nitrate can melt and sublime, a process which can be improved by using large pore zeolites.
3. Reaction engineering aspects: the example of the abnormal behaviour of Cu/SSZ-13 was reported. This catalyst shows an apparent negative activation energy at high temperatures after ageing. It was shown how

studying the effect of varying the washcoat thickness and the cell density can help discern between kinetic and mass transfer regimes. In the particular example given, the reaction was shown to be kinetically controlled at both low and high temperatures ($T > 500^\circ\text{C}$), whereas a mixed regime was observed in the mid-temperature range.

"A Detailed Transient Kinetic Model of the NO-NO₂-NH₃/O₂ SCR Reactivity over Cu-Zeolites" by S. Liu, W. Hu, I. Nova, E. Tronconi (Laboratory of Catalysis and Catalytic Processes, Department of Energy, Politecnico di Milano, Italy) described the dynamics associated with the unsteady reactivity of the NO-NO₂-NH₃/O₂ SCR system by a micro-kinetic model. In particular, it was shown how the nitrate decomposition reaction occurs through the reverse of nitrate formation, with consumption of nitric oxide and release of nitrogen dioxide. The model also predicts a hysteresis of the N₂O concentration trace, which is associated with storage/decomposition of ammonium nitrate on the catalyst. Finally, a physical mixture of barium oxide/alumina and Cu-CHA was studied: the idea is that the unstable species on Cu-CHA can be trapped by barium and then identified by infrared (IR) spectroscopy. Results show that the two systems alone have very little storage, but this is strongly enhanced when using the physical mixture, confirming that the unstable species formed on Cu-CHA were then trapped by barium. IR shows the formation of nitrite species on barium, decomposing to NO and NO₂. It is suggested that a similar mechanism should occur with stored NH₃ as active site instead of barium.

In "An Experimental and Modeling Study of Sulfur Poisoning in Cu-SSZ-13 for NH₃-SCR Applications" by Y. Jangou, W. S. Epling (Department of Chemical Engineering, University of Virginia, Charlottesville, USA), D. Wang, A. Kumar, J. Li (Cummins Inc, Catalyst Technology, Columbus, USA), Cu/SSZ-13 samples with different silica to alumina ratio (SAR) were studied, having different distributions of Cu²⁺ and [Cu^{II}OH]⁺ species. These were quantified by H₂-TPR and DRIFTS. The results show that the nature of S species formed on Cu/SSZ-13 as well as the poisoning mechanism are site specific. In other words, responses of Cu²⁺ and [Cu^{II}OH]⁺ to sulfur poisoning are different. It was found that S can either be present as ammonium sulfate (decomposing at low temperature, ~380°C) or copper sulfate (decomposing at high temperature, ~580°C) resulting in different poisoning and deSO_x routes. Taking into account this unique

behaviour, kinetic parameters were optimised using a dual-site SCR model to describe S storage and release over Cu²⁺ and [Cu^{II}OH]⁺. The model was able to predict the activity of samples with different SAR by just changing the relative amount of these species and keeping constant the kinetic parameters.

"New Method for Studying Internal Mass Transfer in Wash-Coat, Applied on NH₃-SCR over Cu/SSZ-13" was presented by K. Wijayanti, L. Olsson (Competence Centre for Catalysis, Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden), A. Kumar, K. Kamasamudram (Cummins Inc, Columbus, USA). Cu/SSZ-13 is a very active catalyst for NH₃-SCR (100% NO_x conversion at 200°C, space velocity 30,000 h⁻¹). This makes it difficult to see diffusion effects on this catalyst, a reason why a zeolite with a high SAR of 80 was used in this study in order to decrease the number of exchanged sites for Cu. Varying the washcoat thickness was shown to have an effect only on the standard SCR for $T > 270^\circ\text{C}$. The effect of varying the porosity of the washcoat by including soot in the synthesis, which is afterwards removed by calcination with NO₂ at 600°C, was also studied. Adding 10% porosity was found to be beneficial, although a further increase to 15% caused a partial loss of the benefits. This was explained by an increase in the washcoat thickness with increasing porosity (increased internal mass transfer limitations). Finally, the effect of ageing was studied. Hydrothermal ageing of the powder generally caused a decrease of crystallinity and an increase of dealumination with increasing ageing temperature, and CuO formation for $T > 750^\circ\text{C}$. Since the NH₃-temperature-programmed desorption (TPD) profile changes with ageing, this can be used as a diagnostic method. Cu/SSZ-13 powder was first calcined at 800°C for 24 h before mixing with 20% binder and coating onto monoliths. These monolith samples were then calcined for 4 h at temperatures between 500°C and 800°C to create a series of samples with different mass transfer in the washcoat. Since the catalyst powder had already been calcined for 24 h at 800°C it is likely that only the washcoat was influenced by the calcination of the monoliths, as supported by the similar ammonia storage and desorption of the different samples. The NH₃ conversion during SCR was influenced by the mass-transfer in the washcoat at temperatures above 300°C. The conversion gradually decreased with increased calcination

temperature, probably because the washcoat pores collapsed at higher temperature, resulting in lower activity.

“Nitric Oxide Reduction of Heavy-Duty Diesel Off-Gas by NH_3 -SCR in Front of the Turbocharger (Pre-Turbine SCR)” by T. Rammelt, J. Böhm, R. Gläser (Institute of Chemical Technology, Leipzig University, Germany), B. Torkashvand, C. Hauck, O. Deutschmann (Institute of Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Germany) studied the effect of positioning an NH_3 -SCR and a CH_4 oxidation catalyst in front of the turbocharger. The expected advantages are due to higher temperature and pressure. The effect of pressure was emphasised in this presentation since it can influence:

- Diffusion, the diffusion coefficient being inversely proportional to the pressure
- Residence time, this being inversely proportional to velocity, therefore directly proportional to the pressure
- Kinetics, with the exact pressure dependency depending on the specific reaction and catalyst.

Increased SCR reactivity was shown with increased pressure, but also increased NH_3 oxidation (and therefore lower NO_x conversion at high temperatures). On the other hand, changing the pressure had no significant impact on the CH_4 oxidation activity as this reaction is ultimately around zero order due to water inhibition, while SCR is effectively first order. The model was able to predict all these effects.

Methane Oxidation Session

“Tutorial: Modeling CH_4 Oxidation” by G. Groppi (Department of Energy, Politecnico di Milano, Italy) covered methane oxidation over palladium-based catalysts under both lean and stoichiometric conditions. The hysteresis observed for methane oxidation in the presence of excess oxygen depending on the direction of the temperature ramp was attributed to the reduction of palladium oxide to metallic palladium when increasing the temperature, and palladium re-oxidation when decreasing the temperature. This hypothesis was supported by temperature programmed oxidation (TPO) experiments, showing at least two positive peaks during ramp up (indicative of PdO reduction with O_2 release) and a negative peak when ramping down (O_2 consumption in the oxidation of Pd to PdO). TPO performed on palladium supported on different oxides showed that only palladium oxidation depends on the support. By

contrast, only PdO reduction was dependent on the O_2 concentration used during TPO. The details of methane oxidation kinetics were then analysed. Three temperature regions showing different kinetics were identified:

1. $T < 400^\circ\text{C}$: reported reaction orders with respect to CH_4 , H_2O and O_2 are 0.7/1, -1 and 0/0.21, respectively. The apparent activation energy is between 120 kJ mol^{-1} and 180 kJ mol^{-1} . A DFT study by Chalmers showed that the most active phase is PdO (101). The activation energy for CH_4 dissociation on this surface was calculated to be 29 kJ mol^{-1} , getting closer to the observed value (95 kJ mol^{-1}) in the presence of H_2O
2. $400 < T < 650^\circ\text{C}$: the activation energy is between 30 kJ mol^{-1} and 75 kJ mol^{-1} . The reaction order with respect to H_2O is bigger than -1 (-0.4/0) and values for the adsorption energy of H_2O are around -80 kJ mol^{-1} to -90 kJ mol^{-1}
3. $T > 650^\circ\text{C}$: the activation energy is between 130 kJ mol^{-1} and 150 kJ mol^{-1} and the reaction is first order on CH_4 .

Iglesia’s group showed that metallic Pd has a better activity compared to Pd covered by stored O, but worse compared to PdO. Under oscillating stoichiometric conditions CH_4 conversion can be enhanced compared to static stoichiometric conditions. Looking at the details of the single rich/lean cycle it becomes clear that the best conversion is obtained under rich condition, which was not expected (all lean studies show PdO as the most active phase). The effect of H_2O under stationary conditions around $\lambda = 1$ was studied and revealed that H_2O inhibits CH_4 oxidation only under lean conditions.

“Kinetic Modelling of Water Inhibited Methane Oxidation Reactions over a Pd/ Al_2O_3 Wash-coated Monolith using Spatially and Temporally Resolved Experimental Data” by C. Coney, A. Goguet, C. Stere, (School of Chemistry and Chemical Engineering, Queen’s University Belfast, UK), A. Raj, D. Thompsett (Johnson Matthey, Sonning Common, UK), S. Wilkinson (Johnson Matthey, Billingham, UK), M. Caracotsios (Chemical Engineering Department, University of Illinois at Chicago, USA), C. Hardacre (School of Chemical Engineering and Analytical Science, University of Manchester, UK) presented a combination of internal, spatially and temporally resolved gas temperature and concentration profiles. These were used to screen a number of hypothesised global kinetic models of methane oxidation over palladium/alumina. The parameter estimation routine considered different modes of inhibition as

well as mass transfer and applied a semi empirical temperature profile to increase the accuracy of predictions. The best estimated model was considering the following reaction steps:

- $\text{CH}_{4(g)} + \text{O}^* + * \rightarrow \text{CH}_3^* + \text{OH}^*$ (rate determining step)
- $2\text{OH}^* \rightleftharpoons \text{H}_2\text{O}^* + \text{O}^*$
- $2\text{H}_2\text{O}_{(g)} + 2^* \rightleftharpoons 2\text{H}_2\text{O}^*$
- $\text{O}_{2(g)} + 2^* \rightarrow 2\text{O}^*$

Diesel Oxidation Catalyst Session

“Modeling of Two-Step CO Oxidation Light-off on Pt/ γ - Al_2O_3 in the Presence of C_3H_6 and NO_x ” was presented by P. Kočí, A. Arvajová, J. Březina (University of Chemistry and Technology, Prague, Czech Republic). A two-step carbon monoxide light-off phenomenon was observed under slightly rich conditions in the presence of propene. Both formation of intermediate species during propene oxidation and the formation of CO as a byproduct were considered as possible explanations of the phenomenon. Separate propene oxidation experiments showed that CO can be formed as a byproduct but only in small amounts. Results of experiments and simulations revealed that inhibition by an intermediate forming and accumulating on the surface during the early stage of propene oxidation is necessary to describe this effect. Two-step CO light-off was observed both under three-way catalyst (TWC) (near stoichiometric) and DOC (lean) operating conditions, with the highest magnitude at lower O_2 concentrations and in the presence of NO. The developed model correctly predicted the observed trends.

“Low Temperature NO Oxidation Catalysts with Reduced CO Inhibition” was presented by Y. Song, L. C. Grabow (Chemical and Biomolecular Engineering, University of Houston, USA). To guide the design of an improved low temperature oxidation catalyst with minimal CO inhibition the authors conducted a descriptor-based computational screening study, for which linear adsorption and transition state scaling relations for (111) and (211) models of 11 late transition metals were first derived. Results from periodic density functional theory simulations were used as input to the scaling relations, and the binding energies of oxygen and CO were identified as suitable reactivity descriptors for NO and CO oxidation. An analysis of the resulting reactivity trends suggests that alloys containing gold, silver and copper may have better performance than palladium or platinum at 425K. In particular, binary silver/palladium,

copper/palladium and copper/silver alloys were predicted as promising candidates. Notably, these alloys do not efficiently catalyse the $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ reaction, but instead oxidise NO and CO simultaneously.

Diesel Particulate Filter Sessions

“Numerical Investigation of the Impact of Washcoat Deposition on the Performance of Particulate Filters” by I. Belot, D. Vidal, F. Bertrand (Polytechnique Montréal, Canada), R. E. Hayes (University of Alberta, Edmonton, Canada), B. van Setten, M. Votsmeier (Umicore AG & Co KG, Hanau, Germany) aimed to predict how the amount and localisation of the washcoat in a given filter structure can affect filtration efficiency, backpressure and chemical conversion. To do this a three-step numerical model was developed for a washcoated cordierite filter: (i) The model of the porous structure of the filter wall was set up using computed X-ray tomography (CXT) data; (ii) gas flow through the porous wall was modelled using the lattice Boltzmann method; and (iii) filtration performance was predicted by tracking the path of the soot particles through the filter wall by solving the Langevin equation.

“Characterization and Multi-Scale Modeling of Catalytic Filters” by A. Arvajová, M. Václavík, M. Leskovjan, M. Plachá, P. Kočí (University of Chemistry and Technology, Prague, Czech Republic), V. Novák, D. Thompsett (Johnson Matthey, Sonning Common, UK) looked at how the loading and distribution of washcoat has to be controlled in order to achieve optimum performance. A series of particulate filters based on silicon carbide and cordierite substrates were studied. Each sample was examined bare (uncoated) and then coated with catalytic material – zeolite SCR for diesel applications or alumina-based TWC for gasoline applications. Sample structure was characterised by mercury porosimetry (porosity, pore-size distribution), cross-section scanning electron microscopy (SEM) (2D images) and X-ray microtomography (XRT) (3D image). A good match was achieved for different characterisation methods. The 3D image from XRT was transformed into a simulation domain where the gas flow through wall pores was solved (Navier-Stokes equations in OpenFOAM®, and in-house developed Lattice Boltzmann model). The flow distribution was highly non-uniform and followed the largest pores. By contrast, transport in small pores inside the coating was dominated by diffusion. They concluded that too large and compact domains of catalytic material may result

in both diffusion limitations for gas reactants and pressure drop increase.

Modelling and Performance

“Modeling the Impact of Non-Uniform Coating Thickness on Catalyst Performance” was given by D. Dimopoulos, I. Markomanolakis (Exothermia SA, Pilea, Greece), G. C. Koltsakis (Aristotle University Thessaloniki, Greece). A common modelling assumption for catalytic reactors is that the washcoat has a uniform thickness around the channel perimeter. However, during the washcoat deposition the coating tends to accumulate in the corners of the honeycomb channels. This group’s model allowed the effect of coating uniformity on the catalyst performance to be investigated. To isolate the effect of coating geometry, the model was applied initially to ideal isothermal conditions for a single first-order reaction. In a next step, more realistic conditions were investigated, involving non-isothermal, multi-component, multi-reaction systems with highly non-linear rate expressions. Finally, the model was applied in fully transient driving cycles. The results illustrated that the impact of non-uniform coating may be quite important when the catalyst operates in the regime of ‘internal diffusion’ control, i.e. with relatively thick and highly tortuous washcoats at temperatures above light-off.

“Application of Surrogate Modelling to the Optimisation of Kinetic Parameters in an Emissions Control Catalyst Model using Vehicle Drive Cycle Data” by J. E. Etheridge, T. C. Watling (Johnson Matthey, Sonning Common, UK), G. John, (Johnson Matthey, Royston, UK) describes the use of surrogate modelling to optimise kinetic parameters in a vehicle emissions control catalyst model using engine or vehicle test data. The method is faster compared to conventional methods as it reduces the number of evaluations required of the detailed (full) model. The surrogate model (a quadratic response surface, in this case) approximates the behaviour of the full model; this sacrifices some accuracy for speed of evaluation. After a few runs of the detailed model to train the initial surrogate, it is used in place of the detailed model in a simplex optimisation method. Since evaluation of the surrogate is computationally inexpensive, the optimisation runs rapidly. The new kinetic

parameters thus obtained are then tested in the full model. The surrogate model can then be updated with new information; thus the surrogate model is improved with each iteration. As an illustration, the model was used to extend an existing kinetic model for a diesel oxidation catalyst to predict the effect of platinum group metal (pgm) loading (30 g ft^{-3} to 120 g ft^{-3}) with drive cycle data.

“Studies of the Turbulence Inside of an Automotive Catalytic Converter” by I. Cornejo (University of Alberta, Canada, and Santa Maria University, Valparaiso, Chile), P. Nikrityuk, R. E. Hayes (University of Alberta, Canada) studied turbulence inside the monolith of an automotive catalytic converter. Turbulence inside the channels of the monolith affects the heat and mass transfer, as well as the pressure drop, thus also the performance of the catalytic converter and the engine. Even at the low Reynolds number inside the channels of the monolith there was an appreciable turbulence penetration on the entrance of channels; however, the turbulence decays rapidly and the flow becomes laminar along the length of the monolith.

“Real-Driving Emissions – System Modeling for Office and Hardware-in-the-Loop Application” by J. C. Wurzenberger, C. Triebel, S. Kutschi, C. Pötsch, (AVL List GmbH, Graz, Austria) was focused on real world driving. The presentation discussed, for the example of a diesel passenger car, a vehicle modelling framework suitable to address real driving emissions in office and in hardware-in-the-loop (HiL) environments. The system model comprised the domain engine thermodynamics including combustion, pollutant formation and exhaust gas aftertreatment and the domains drivetrain, cooling and control. The group demonstrated there could be good agreement between the model and engine data.

Conclusion

The conference reinforced the importance of modelling to help improve the design of advanced efficient autocatalysts, but it also emphasised the need for detailed experimental studies. The importance of computer simulation for optimising emissions control systems and for helping to understand the working of these complex systems is growing. This conference highlighted the breadth of activity going on in this area and the progress that is being made.

The Reviewers



Djamela Bounechada joined Johnson Matthey, Sonning Common, UK, in 2014, as part of the reaction engineering research team following two years as a post-doctoral Fellow at Chalmers University of Technology, Sweden.



Iain Hitchcock is a Principal Scientist in the Emissions Control Research Department at Johnson Matthey, Sonning Common. His work is focused on the porosity of catalysts and diffusion of gasses.



Tim Watling is a Senior Principal Scientist in the Emissions Control Research Department at Johnson Matthey, Sonning Common, where he leads a team focused on the development of computer models for the simulation of vehicle emissions control systems.
