Modelling and Simulation of NOx Abatement with Storage/Reduction Catalysts for Lean Burn and Diesel Engines

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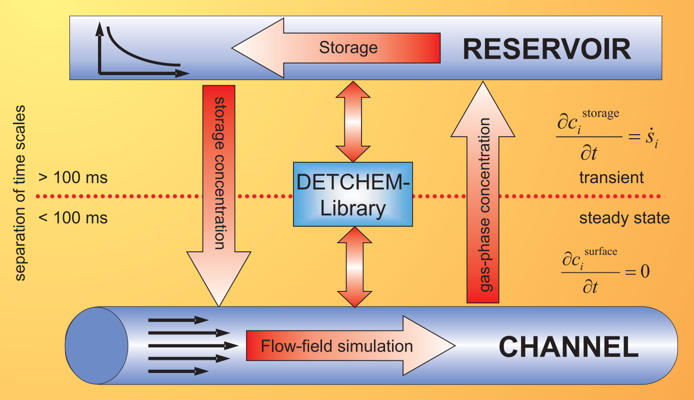
Introduction

In spite of the enormous achievements in the aftertreatment of exhaust gas emissions, the worldwide increasing number of vehicles represent a serious environmental problem due to vehicles' raw emissions, in particular, carbon dioxide, which has a strong impact on the greenhouse effect. A more efficient fuel consumption can be realized in Diesel and lean-operated engines, i.e., in excess of air (oxygen). Here, the problem is the formation of nitrogen oxides (NOx). Since improvements of the combustion process itself are not sufficient to meet future legislative limits, the development of a technique for the aftertreatment of NOx is urgently needed.

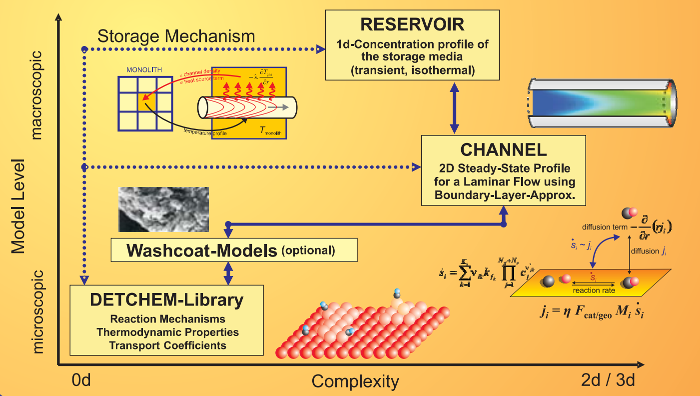
One of the most promising approaches is the NOx Storage and Reduction Catalyst (NSR) which utilizes the NOx storage on barium sites to form nitrates during the lean phase and their reduction to nitrogen in a rich atmosphere [1]. Detailed models, which are based on physical and chemical processes on the molecular level, are indispensable to exploit the full potential of this technique.

The numerical simulations are carried out using the software package DETCHEM, which uses detailed reaction mechanisms. DETCHEM is a FORTRAN based package that is designed to couple chemistry models with CFD programs. The core is a library for the description of species properties based on atomistic models and for reactions among gas-phase and surface species based on elementary step reaction mechanisms.

DETCHEM^RESERVOIR



Numerical Model, DETCHEM Package



Elementary-step Mechanism for Platinum

HC-Decomposition:

- $C_3H_6 + 2* \leftrightarrow C_3H_6*$
- $C_3H_6* \leftrightarrow C_3H_5* + H*$
- $C_3H_5* + * \leftrightarrow C_2H_3* + CH_2*$
- $CH_3* + * \leftrightarrow CH_2* + H*$
- $CH_2* + * \leftrightarrow CH* + H*$
- $CH* + * \leftrightarrow C* + H*$
- $C_2H_3* + O* \leftrightarrow CH_3CO* + *$
- $CH_3CO* + * \leftrightarrow CH_3* + CO*$
- $CH_3* + O* \leftrightarrow OH* + CH_2*$
- $CH_2* + O* \leftrightarrow OH* + CH*$
- $CH* + O* \leftrightarrow OH* + C*$
- $C_3H_6 + * + O* \leftrightarrow C_3H_5^+ + OH*$
- $C_3H_5^+ + O* \rightarrow C_3H_4^+ + OH*$
- $C_3H_4^+ + 4 O* + 2* \rightarrow 3 C* + 4 OH*$

N-O-Reactions:

- $NO + * \leftrightarrow NO*$
- $NO* + * \leftrightarrow N* + O*$
- $2 N* \rightarrow N_2 + 2*$
- $NO + O* \leftrightarrow NO_2*$
- $NO* + N* \leftrightarrow N_2O*$
- $NO* + H* \leftrightarrow N* + OH*$
- $NO_2* + H* \leftrightarrow NO* + OH*$

C-O-Reactions:

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

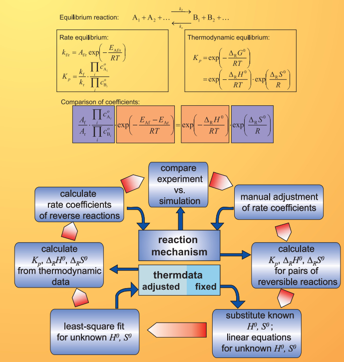
H-O-Reactions:

- $O_2 + 2* \leftrightarrow 2 O*$
- $H_2 + 2* \leftrightarrow 2 H*$
- $H_2O + * \leftrightarrow H_2O*$
- $H* + O* \leftrightarrow OH* + *$
- $OH* + H* \leftrightarrow H_2O* + *$
- $2 OH* \leftrightarrow H_2O* + O*$

75 elementary reactions
22 surface species
10 gas-phase species

see Ref. [3] and [4]

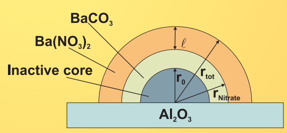
Thermodynamic Consistency



NOx Storage/Reduction Model

Shrinking Core Model

Modelling Approach[4,5]



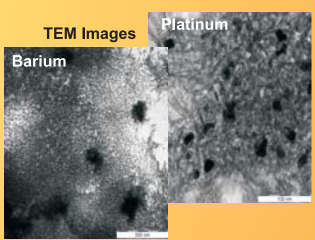
$$\dot{r}_{NO2-O2-Ba} = \tilde{k}_f * c_{NO2} * c_{O2}^{1/4} * \Theta_{BaCO3} - \tilde{k}_b * c_{CO2}^{1/2} * \Theta_{Ba(NO3)2}$$

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

$$k_f = A_f * T^{\beta} * e^{-\frac{Ea,f}{RT}} \qquad k_b = \frac{k_f}{K_{NO2-O2-Ba}^{eq}} = \frac{k_f}{\exp(-\frac{\Delta_R H}{RT} + \frac{\Delta_R S}{R})}$$

$$\tau = \frac{\ell}{D_S} * \frac{r_{Nitrate}}{r_{tot}}$$

Model Catalyst Charaterization



Particel Dimensions

$\varnothing_{Platinum} \approx$ 20nm
$\varnothing_{Barium} \approx$ 100nm

No spill-over reaction between Pt and Ba due to spatial separation of both phases on the catalyst

Storage Reactions

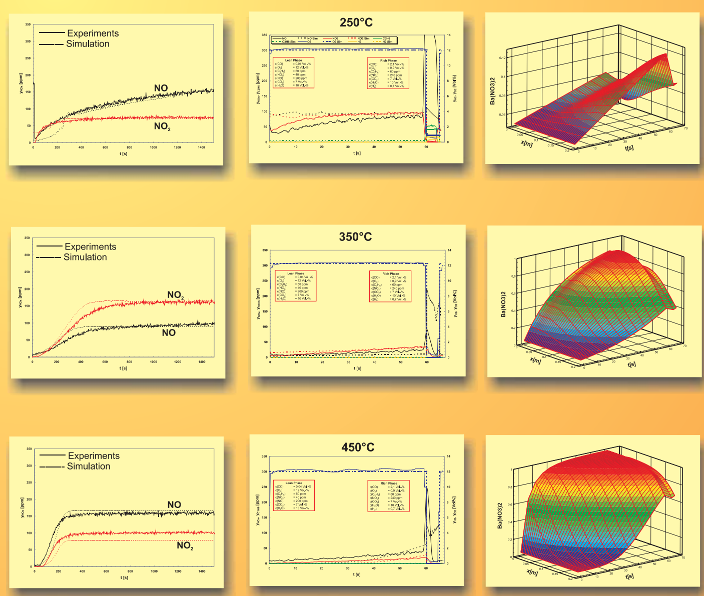
- $BaCO_3 + 2NO_2 + ½O_2 \leftrightarrows Ba(NO_3)_2 + CO_2$
- $BaCO_3 + 2NO + ½O_2 \leftrightarrows Ba(NO_2)_2 + CO_2$
- $BaCO_3 + 3NO_2 \leftrightarrows Ba(NO_3)_2 + NO + CO_2$

Reduction Reactions

- $Ba(NO_3)_2 + 3 CO \leftrightarrows BaCO_3 + 2 NO + 2 CO_2$
- $Ba(NO_3)_2 + 3H_2 + CO_2 \leftrightarrows BaCO_3 + 2NO + 3H_2O$
- $Ba(NO_3)_2 + {}^1/_3C_3H_6 \leftrightarrows BaCO_3 + 2NO + H_2O$

Simulation Results for $Pt/Ba/Al_2O_3$

Long-Term Storage | **Lean/Rich Cycle (60s/5s)** | **Coverages of $Ba(NO_3)_2$**



Literature

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