

# Effective Global Kinetic Model for Dynamic Regeneration of NO<sub>x</sub> Storage and Reduction Catalyst

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## Introduction

Several nitrogen compounds can be produced during the regeneration phase in NO<sub>x</sub> storage and reduction catalyst (NSRC), also called lean NO<sub>x</sub> trap (LNT). Periodically operated NSRC is used for NO<sub>x</sub> abatement from lean-burn automobile engines (mainly Diesel). In the course of a longer lean phase (economical engine operation with lean fuel mixture, typically lasting for several minutes) the NO<sub>x</sub> are adsorbed (stored) on the catalyst surface in the form of nitrites and nitrates [1]. Several NO<sub>x</sub> adsorbing components (Ba, K, Na, Ca, Li, Mg, etc.) can be used simultaneously in the NSRC washcoat, with particular temperature dependence of the effective NO<sub>x</sub> storage capacity related to the basicity of the used components [2].

Then, the accumulated NO<sub>x</sub> are desorbed and reduced within a short rich phase (excess of reducing components - CO, H<sub>2</sub> and hydrocarbons - in the exhaust gas, lasting several seconds). Besides the main product N<sub>2</sub>, also NO, N<sub>2</sub>O, and NH<sub>3</sub> can be formed, depending on the regeneration phase length, temperature, and gas composition [3]. Particular attention is devoted to the formation of ammonia that is identified as a main by-product and an important intermediate of the NO<sub>x</sub> reduction under rich conditions [4,5,6]. The exhaust gas enrichment can be realized by controlled (post-)injection of rich fuel mixture or other techniques [7].

## NSRC model

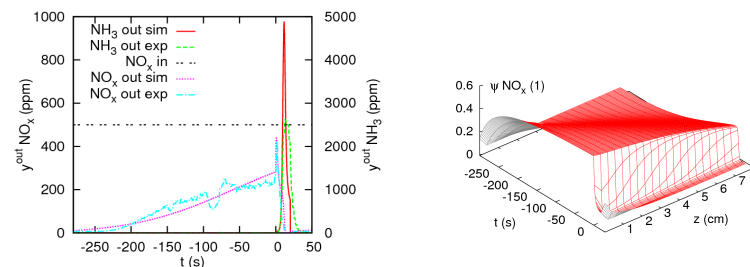
This contribution focuses on modelling of the NO<sub>x</sub> reduction dynamics during catalyst regeneration phase. Effective, spatially 1D distributed NSRC model with global kinetics has been developed [5,8]. It can be employed for simulations of the real NSRC converter operation with reasonable computation times [9]. The reaction scheme has been constructed with minimum set of reactions and kinetic parameters that need to be evaluated from experimental data, while keeping the essential level of model reliability. Regeneration of the catalyst by CO, H<sub>2</sub> and HC is considered [5,8].

The following ammonia reactions are included: NH<sub>3</sub> is formed by the reaction of H<sub>2</sub> with NO<sub>x</sub> [3,4,5,6], as well as by the reaction of CO with NO<sub>x</sub> in presence of water (formation and consequent hydrolysis of isocyanates [10]. Furthermore, water gas shift and steam reforming reactions enable *in situ* H<sub>2</sub> production from CO and HC [8]. The formed ammonia can then react with oxygen and NO<sub>x</sub> deposited on the catalyst surface, producing N<sub>2</sub> [5]. Only minor N<sub>2</sub>O formation is observed experimentally under common NSRC operating conditions [3,4,5,6], thus it has been neglected in the model.

## Results and Discussion

The model exhibits a good agreement with experimental data obtained in a lab mini-reactor with industrial PtRh/Ba/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> NSRC monolith sample in the temperature

range 100-500 °C [5]. An example is given in Fig. 1. Reduction front traveling in the flow direction along the reactor is predicted, with the NH<sub>3</sub> maximum on the moving boundary. When the front reaches the reactor outlet, the main NH<sub>3</sub> peak is observed in the exhaust gas [5]. The actual NO<sub>x</sub> and oxygen storage capacities, their saturation, operating temperature, concentrations of the reducing agents, and the flow-rate determine the breakthrough time of the reducing front and the selectivity of the NO<sub>x</sub> reduction towards N<sub>2</sub> or NH<sub>3</sub> [3,5].



**Figure 1.** One lean (300 s) + rich (20 s) cycle of the NSRC operation at  $T^{\text{in}}=200$  °C, GHSV=30 000 h<sup>-1</sup>. Time  $t=0$  s corresponds to the beginning of the rich (regeneration) phase. Left: Experimentally observed and simulated evolution of the outlet NO<sub>x</sub> and NH<sub>3</sub> concentrations. Right: Calculated spatiotemporal concentration profile of the NO<sub>x</sub> adsorbed on the catalyst surface ( $z=0$  cm: monolith inlet,  $z=7.5$  cm: monolith outlet,  $\psi$ : coverage).

## Significance

The developed model of NO<sub>x</sub> storage and reduction catalyst can be effectively used for the simulations under real operating conditions. It forms an efficient tool for basic computer design and control of complex exhaust gas aftertreatment devices in automobile industry.

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