

Modelling of NO_x Storage + SCR Exhaust Gas Aftertreatment System with Internal Generation of Ammonia

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ABSTRACT

Combination of an NO_x storage and reduction catalyst (NSRC, called also lean NO_x trap, LNT) and a catalyst for the selective catalytic reduction of NO_x by NH₃ (NH₃-SCR) offers a potential to significantly increase the efficiency of NSRC-based exhaust gas aftertreatment systems. Under most situations the SCR catalyst is able to adsorb the NH₃ peaks generated in the NSRC during the regeneration and utilise it for additional NO_x reduction in the course of the consequent lean phase. This synergy becomes more important with the aged NSRC, where generally lower NO_x conversions and higher NH₃ yields in wider range of operating temperatures are observed (in comparison with the fresh or de-greened NSRC).

In this paper we present global kinetic models for the NSRC (Pt/Ba/Ce/γ-Al₂O₃ catalyst type) and NH₃-SCR (Fe-ZSM5 catalyst type). The NSRC regeneration by a mixture of CO, H₂ and HC is considered with a differentiated activity and selectivity of individual reducing agents in the NO_x reduction. The oxygen storage effects and NH₃ oxidation

reactions are also included in the NSRC model. A non-equilibrium spill-over of the adsorbed NH₃ between the non-reactive and reactive sites is involved in the SCR model. The kinetic parameters are evaluated from transient lab experiments with synthetic gases, individually for the NSRC and SCR, and the models are then validated by engine test data.

The performance of the NSRC+SCR system is simulated in dependence on temperature and rich phase length, and their effects on integral NO_x conversions and NH₃ yields are discussed. Defined periodic lean/rich operation is simulated as well as the test driving cycle FTP. The simulation results show that the added SCR can significantly improve the deNO_x efficiency in a wide range of operating conditions. The mechanistic understanding and modelling of the relevant chemical and physical processes in the NSRC and SCR played a key role in the development of the combined NSRC+SCR system and enabled to bring this technology to series production within the BlueTec I system (2006).

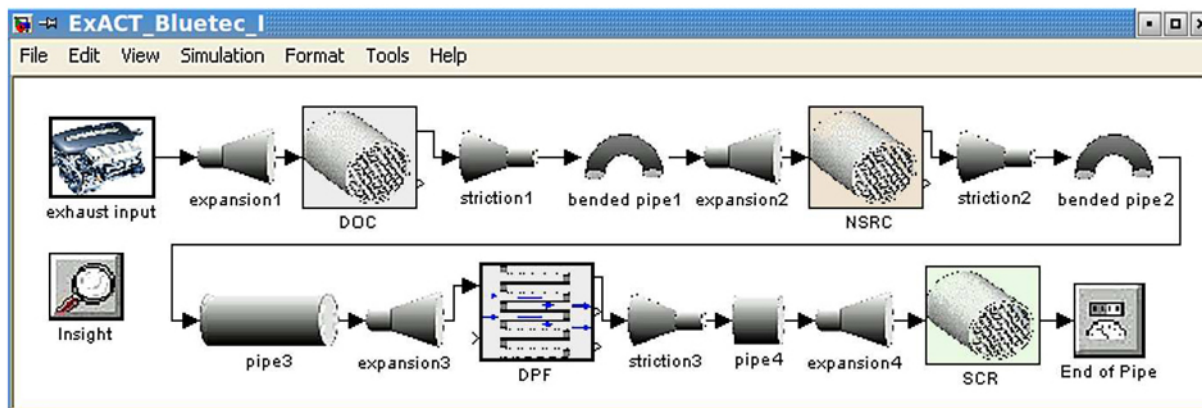


Figure 1. Scheme of the DOC-NSRC-DPF-SCR exhaust gas aftertreatment system BlueTec I in the simulation environment ExACT.

INTRODUCTION

Nowadays there exist two commercially available technologies for the elimination of the NO_x emissions from lean-burn engines: NO_x storage and reduction catalyst (NSRC), and selective catalytic reduction of NO_x by NH_3 , usually generated from urea solution stored in a special tank (NH_3 -SCR, urea-SCR). Even if the raw engine NO_x emissions can be lowered by advanced combustion techniques and exhaust gas recirculation (EGR), exhaust gas aftertreatment in special de NO_x catalytic converters is necessary to meet the most strict emission limits [1, 2].

<figure 1 here>

The selective catalytic reduction of NO_x by NH_3 (SCR)-originally developed for stationary emission sources [3]-soon turned out to be a promising technology for the de NO_x in the automotive industry as well [4]. It was introduced in Europe for commercial heavy-duty vehicles in 2005, and more recently also for passenger cars [5]. Different types of catalysts, mainly $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ or zeolite based formulations (Fe-ZSM5 and Cu-ZSM5) are used in the automotive industry. The NH_3 -SCR converter needs an external source of the selective reducing agent (ammonia). In a standard configuration, the vehicle is equipped with a special tank containing urea solution (marketed under different names, e.g., AdBlue) that need to be re-filled periodically [2]. Ammonia is generated from urea solution injected in a controlled way into the exhaust line, where it is thermally decomposed into NH_3 and CO_2 [6]. Ammonia then reacts selectively with NO_x under lean (oxidizing) conditions, giving mostly N_2 as the final product.

The NO_x storage and reduction catalyst has been derived from classical three-way catalyst by adding the NO_x adsorbing components into the active washcoat layer [7, 8,

9]; it was first implemented by Toyota with lean-burn gasoline engines. Typical formulation of the NSRC catalyst is $\text{NM/EA/OS}/\gamma\text{-Al}_2\text{O}_3$, where NM denotes noble metals (Pt,Rh,Pd), EA denotes earth alkaline or alkali metals serving as active components for the NO_x chemisorption [10, 11], and OS denotes oxygen storage compounds (typically Ce oxides). In the course of a longer lean phase (economical engine operation with a lean fuel mixture lasting a couple of minutes) the NO_x are chemisorbed on the catalyst surface. The accumulated NO_x need to be periodically reduced within a controlled short rich phase (enrichment of the fuel mixture leading to temporarily increased concentrations of the reducing components normally present in fuel or exhaust gas- CO , H_2 , and HC) [1, 2]. While the NSRC is primarily being used in passenger cars, the SCR is well established for heavy-duty vehicles [12].

For quite a long time it was not much reflected in the open literature (cf., e.g., review [11]) that besides the N_2 , desired main product of the NO_x reduction, also significant amounts of NH_3 can be formed depending on the regeneration phase length, temperature and gas composition. In the stand-alone NSRC, the regenerations must be properly calibrated with respect to actual catalyst conditions (amount of NO_x stored, temperature, etc.) to avoid excessive NH_3 formation. However, there exist a possibility to combine the NH_3 by-production in the NSRC with the ammonia capture and utilization in the SCR, cf. Figure 2. The NSRC+SCR concept had been developed since late 1990's [13, 14] and the system was launched into series production in 2006 with Mercedes E320 CDI BlueTec I [2, 15]-cf. Figure 1. After that, several integrated designs with multiple washcoat layers and/or multifunctional catalysts using the NSRC/SCR principle were proposed, e.g., [16].

<figure 2 here>

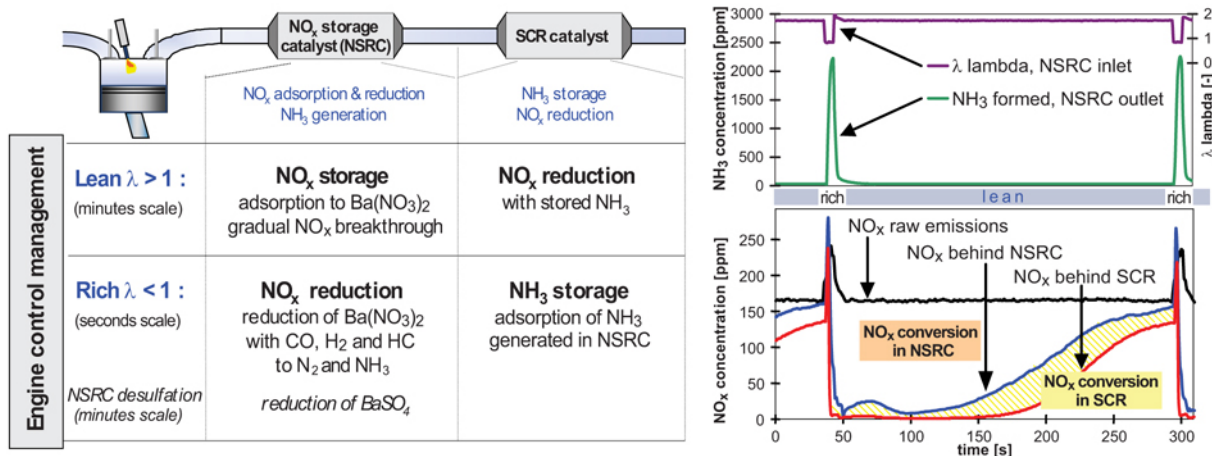


Figure 2. Principle of the combined exhaust gas aftertreatment system consisting of NO_x storage & reduction catalyst (NSRC) and selective catalytic reduction of NO_x by NH₃ (SCR).

In this paper we present mathematical models for the NSRC+SCR system consisting of the two catalysts in series (Figure 2). The independently developed NSRC and SCR models are based on global reaction kinetics, calibrated according to lab experimental data obtained with individual catalyst samples, and validated by engine test driving cycle data. The models are then used for simulations of the NSRC+SCR system operation under varying conditions, calculation of spatio-temporal concentration profiles in the monoliths, analysis of the dynamic behaviour, and evaluation of local and overall conversions.

MATHEMATICAL MODEL

In order to simulate combined exhaust aftertreatment systems a modular and flexible software structure is required. A system simulation tool ExACT (Exhaust Gas Aftertreatment Components Toolbox) developed at Daimler [1, 17] has been used to perform the simulations presented in this paper. Each catalytic monolith model together with the respective reaction kinetics and optimised numerical solver is written in Fortran and compiled into a respective library block. These library blocks can be arranged in sequence or in parallel exchanging all the relevant information like exhaust mass flow, temperature und species concentration.

The NSRC and SCR libraries employed in this work were developed in co-operation with Prague Institute of Chemical Technology (NSRC), and Politecnico Milano (SCR). ExACT includes also models for the connecting pipes between engine and aftertreatment systems and between the aftertreatment components. The connecting pipes become important when the temperature loss between the individual aftertreatment components has to be considered. An example of the ExACT environment is given in Figure 1, where a complete BlueTec I system is shown, consisting of the DOC, NSRC, DPF and

SCR in series. In this paper we specifically focus on the NSRC+SCR subsystem.

A standard, spatially 2D(1D+1D) heterogeneous model of catalytic monolith channel with plug-flow and surface deposition of components is employed in the simulations, cf. e.g. [1]. The following balances are considered: Mass balances in the flowing gas, including accumulation, convection, and external mass transfer (1); mass balances in the washcoat pores, including accumulation, internal diffusion, and catalytic reactions (2); mass balances on the catalyst surface, including accumulation, and catalytic reactions (3); enthalpy balance of the flowing gas, including accumulation, convection, and gas-solid heat transfer (4); enthalpy balance of the solid phase, including accumulation, axial heat conduction, gas-solid heat transfer, heat exchange with the surroundings, and heat source from catalytic reactions (5):

$$\frac{\partial c_k(z,t)}{\partial t} = -\frac{\partial(v \cdot c_k)}{\partial z} + \frac{k_c(z)a}{\varepsilon^g} c \left(y_k^s|_{r=\delta} - y_k \right), \quad k = 1, \dots, K \quad (1)$$

$$\frac{\partial c_k^s(z,r,t)}{\partial t} = \frac{D_k^{\text{eff}}}{\varepsilon^s} \frac{\partial^2 c_k^s}{\partial r^2} + \frac{1}{\varepsilon^s} \sum_{j=1}^J v_{k,j} R_j, \quad k = 1, \dots, K \quad (2)$$

$$\frac{\partial \psi_m(z,r,t)}{\partial t} = \frac{1}{\Psi_m^{\text{cap}}} \sum_{j=1}^J v_{m,j} R_j, \quad m = 1, \dots, M \quad (3)$$

$$\rho c_p \frac{\partial T(z,t)}{\partial t} = -v \frac{\partial T}{\partial z} \rho c_p + \frac{k_h(z)a}{\varepsilon^g} (T^s - T) \quad (4)$$

Table 1. Parameters of the used commercial NSRC and SCR monoliths (both catalysts coated on a cordierite substrate with square channels).

Parameter	NSRC	SCR
Catalyst type	PtRh/Ba/Ce/ γ -Al ₂ O ₃	Fe-ZSM5
Ageing state	aged	de-greened
Ageing procedure	160 000 km on road	HT 5h at 600°C
Channels per cross-section area (cpsi)	400	300
Equivalent channel diameter (mm)	1.10	1.22
Wall thickness (μ m)	110	170
Mean washcoat thickness δ (μ m)	30	40
Open frontal area fraction ε^g (1)	0.750	0.688
Lab sample monolith diameter (cm)	2.54	powder
Lab sample monolith length (cm)	1.52	powder
Full-size monolith diameter (cm)	14.4	14.4
Full-size monolith length (cm)	19.7 / 9.85 ^a	19.7

a- In driving cycle simulations a half-size NSRC was used.

$$\rho^s c_p^s \frac{\partial T^s(z,t)}{\partial t} = \lambda^s \frac{\partial^2 T^s}{\partial z^2} + \frac{k_h(z)a}{1-\varepsilon^g} (T - T^s) - \Omega (T^s - T^e) - \frac{a}{(1-\varepsilon^g)} \sum_{j=1}^J \int_{r=0}^{\delta} \Delta H_j R_j dr \quad (5)$$

The boundary conditions are in the form of Eqs. (6,7,8,9,10):

$$T \Big|_{z=0} = T_{in}, \quad v \Big|_{z=0} = v^{in} \quad (6)$$

$$\frac{\partial T^s}{\partial z} \Big|_{z=0+} = 0, \quad \frac{\partial T^s}{\partial z} \Big|_{z=L-} = 0 \quad (7)$$

$$c_k \Big|_{z=0} = c_k^{in}, \quad k = 1 \dots K \quad (8)$$

$$D_k^{eff} \frac{\partial c_k^s}{\partial r} \Big|_{r=\delta-} = k_c(z) c(y_k - y_k^s \Big|_{r=\delta}), \quad k = 1 \dots K \quad @ \quad r = \delta \quad (9)$$

$$\frac{\partial c_k^s}{\partial r} \Big|_{r=0} = 0, \quad k = 1 \dots K \quad (10)$$

The axial coordinate $z=0$ is located at the monolith inlet and $z=L$ corresponds to the monolith outlet. The transverse coordinate $r=\delta$ is at the top of the catalytic washcoat layer, while $r=0$ corresponds to the bottom of the layer.

The reaction rates R_j employed in the NSRC and the SCR model will be discussed in detail in the next sections. If not explicitly stated, the local reaction rate coefficients k_j are calculated in dependence on temperature according to the Arrhenius-type equation:

$$k_j = k_{j,0} \exp \left(\frac{-E_{a,j}}{R^g T^s} \right) \quad (11)$$

The inhibition coefficients K_{inh} are evaluated in a similar way. Different approaches regarding washcoat diffusion modeling have been used for the SCR and the NSRC simulation. To keep facile computation times for the more complex NSRC reaction system, a simplified 1D balance of the catalytic washcoat layer (without explicit solution of internal diffusion) has been used. In this case transverse coordinate r was lumped, i.e., Eq. (2) was replaced by Eq. (12).

$$\frac{\partial c_k^s(z,t)}{\partial t} = \frac{k_c(z)a}{\varepsilon^s(1-\varepsilon^g)\phi^s} c(y_k - y_k^s) + \frac{1}{\varepsilon^s} \sum_{j=1}^J v_{k,j} R_j, \quad k = 1 \dots K \quad (12)$$

The parameters of the studied NSRC and SCR monoliths are given in Table 1.

<table 1 here>

NH₃-SCR, THE SELECTIVE CATALYTIC REDUCTION OF NO_x

The automotive application of SCR systems has lead to a fundamental investigation of both the standard and the fast

SCR reaction mechanisms [19, 20, 21, 22, 23]. It seems that a similar approach can be used for global modelling of the catalytic processes on the most commonly used SCR materials like V_2O_3 - WO_3 /TiO₂, Fe-ZSM5 and Cu-ZSM5 [17, 24, 25]. The global SCR reaction kinetics presented in Table 2 is based on an extensive study of the reaction mechanisms on SCR catalysts of the types V_2O_3 - WO_3 /TiO₂ [26, 27] and Fe-ZSM5 [22].

The initial step in the SCR reaction is the NH_3 adsorption onto the catalyst surface (R^{SCR}_1 and R^{SCR}_2). Here a non-activated NH_3 adsorption process and a Temkin-type NH_3 desorption are assumed [28]. By means of a simple Arrhenius expression (R^{SCR}_3) the NH_3 oxidation is accounted for. A small NO-to- NO_2 oxidation activity is usually observed on an automotive SCR catalyst-this reaction is modeled by the rate expression R^{SCR}_4 taking into account the NO/ NO_2 thermodynamic equilibrium [17].

The so called “standard” SCR reaction rate (R^{SCR}_5) is based on a dual-site modified redox (MR) mechanism [26]. It assumes that two different types of sites are present on the catalyst surface: acidic non-reducible sites for NH_3 adsorption (denoted by *, with NH_3 coverage θ_{NH_3} , and the sites concentration $\Psi^{cap}_{NH_3}$), and redox sites for the NO + NH_3 activation/reaction (denoted by x, with NH_3 coverage σ_{NH_3} , and the sites concentration Ψ^{cap}_x). It is further assumed that ammonia can block the active redox sites (x), leading to NH_3 inhibition of the “standard” SCR reaction.

An equilibrium state of the NH_3 spillover from the acidic sites (*) sites to the redox (x) sites can be assumed for many SCR technologies. However, it has been revealed that this assumption is not valid for the Fe-ZSM5 SCR technology used within this study. Therefore a finite $NH_3^* \rightleftharpoons NH_3^x$ spillover rate (R^{SCR}_{10}) needs to be introduced [26]. Based on the transient experimental data discussed later in this section, the mutual concentration ratio of the two surface sites was estimated to be 450:1 ($\Psi^{cap}_{NH_3} : \Psi^{cap}_x$)-there are obviously more NH_3 adsorption sites than the reactive ones (that are correlated with Fe).

The partial conversion of NO to NO_2 in the upstream DOC and/or NSRC leads to a higher NO_x conversion rate in the SCR. This is due to the “fast” SCR reaction (R^{SCR}_6). However, high NO_2 / NO_x ratios can lead to the formation of NH_4NO_3 and N_2O (cf. R^{SCR}_7 and R^{SCR}_8 , respectively). In the presented model it is assumed that NH_4NO_3 transfers directly into the gas phase, which is true only for temperatures higher

than 200°C. More detailed approach to NH_4NO_3 formation with high NO_2 concentrations was discussed in [29]. In fact the NH_4NO_3 is not solely a byproduct-recent findings have pointed out that surface nitrates and nitrites play an important role in the overall SCR mechanism [20, 27, 22, 30, 31]. Finally, NO_2 can react directly with NH_3 (R^{SCR}_9). This reaction is significant only at higher temperatures.

A powder microreactor with a crushed commercial Fe-ZSM5 catalyst (cf. Table 1) was used for the kinetic experiments in order to avoid any transport effects. A hydrothermal conditioning was applied for 5h at 600°C prior the measurements to de-green the Fe-ZSM5 catalyst. A typical example of a transient response measurement (TRM) is depicted in Figure 3. This experiment was conducted to obtain the calibration data for the NH_3 adsorption/desorption dynamics while adding/removing NH_3 to the inlet feed. After removing ammonia from the

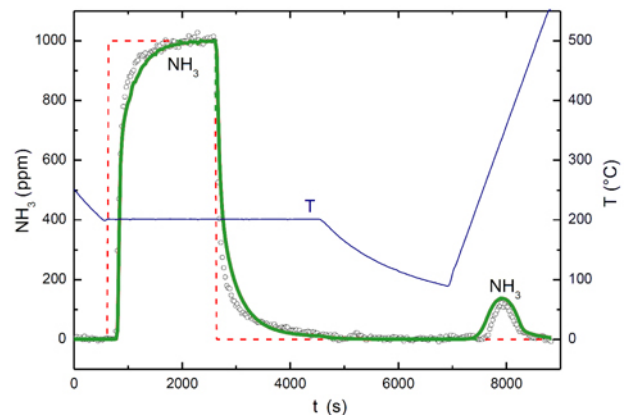


Figure 3. NH_3 adsorption/desorption experiment, crushed SCR monolith powder. Dashed red line: NH_3 inlet concentration, open circles: measured NH_3 outlet concentration, thick solid green line: simulated NH_3 outlet concentration, thin solid blue line: temperature. Inlet gas composition: 0/1000 ppm NH_3 , 2 % O_2 , 3 % H_2O , balance He.

inlet, the reactor is cooled down to 100°C, and this is followed by a temperature ramp. The comparison with the simulation data reveals an excellent correlation between the model and experiment. More details about the experimental and calibration procedure can be found in [1, 17].

After the calibration the model is able to predict the NO_x conversion and selectivity in a wide range of operation conditions. Figures 4a-e depict measured and simulated powder microreactor outlet concentrations for several different NO_2 / NO_x inlet feed ratios in the temperature range from 180°C to 550°C. Some deviations can be noted for high NO_2 / NO_x ratios and temperatures below 200°C. Under those

Table 2. Reactions on Fe-ZSM5 catalyst for selective NO_x reduction by NH₃ (SCR). Derived from [32, 17, 26, 22]. Local molar concentrations c^s in washcoat pores are considered in all reactions-the superscript “s” was omitted below for sake of brevity.

Reaction step	Reaction rate
$\text{NH}_3 + * \rightarrow \text{NH}_3^*$	$R_1^{\text{SCR}} = k_1^{\text{SCR}} \Psi_{\text{NH}_3}^{\text{cap}} c_{\text{NH}_3} (1 - \theta_{\text{NH}_3})$
$\text{NH}_3^* \rightarrow \text{NH}_3 + *$	$R_2^{\text{SCR}} = k_{0,2}^{\text{SCR}} \Psi_{\text{NH}_3}^{\text{cap}} \exp[-E_{a,2}^{\text{SCR}}(1 - \gamma\theta_{\text{NH}_3})/(R^g T^s)] \theta_{\text{NH}_3}$
$4\text{NH}_3^* + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$	$R_3^{\text{SCR}} = k_3^{\text{SCR}} \Psi_{\text{NH}_3}^{\text{cap}} \theta_{\text{NH}_3} [\gamma_{\text{O}_2}^{\beta_3}]$
$\text{NO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{NO}_2$	$R_4^{\text{SCR}} = k_4^{\text{SCR}} (c_{\text{NO}} c_{\text{O}_2}^{0.5} - c_{\text{NO}_2}/K_4^{\text{eq}}) [\gamma_{\text{H}_2\text{O}}^{\beta_4}]$
$4\text{NH}_3^* + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$	$R_5^{\text{SCR}} = k_5^{\text{SCR}} \Psi_{\text{NH}_3}^{\text{cap}} \Psi_x^{\text{cap}} c_{\text{NO}} \gamma_{\text{O}_2}^{\beta_5} \theta_{\text{NH}_3} (1 - \sigma_{\text{NH}_3})$
$4\text{NH}_3^* + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$	$R_6^{\text{SCR}} = k_6^{\text{SCR}} \Psi_{\text{NH}_3}^{\text{cap}} c_{\text{NO}} c_{\text{NO}_2} \theta_{\text{NH}_3} [\gamma_{\text{H}_2\text{O}}^{\beta_6}]$
$2\text{NH}_3^* + 2\text{NO}_2 \rightarrow \text{NH}_4\text{NO}_3 \uparrow + \text{N}_2 + \text{H}_2\text{O}$	$R_7^{\text{SCR}} = k_7^{\text{SCR}} \Psi_{\text{NH}_3}^{\text{cap}} c_{\text{NO}_2}^2 \theta_{\text{NH}_3}$
$2\text{NH}_3^* + 2\text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{N}_2 + 3\text{H}_2\text{O}$	$R_8^{\text{SCR}} = k_8^{\text{SCR}} \Psi_{\text{NH}_3}^{\text{cap}} c_{\text{NO}_2} \theta_{\text{NH}_3}$
$2\text{NH}_3^* + \frac{3}{2}\text{NO}_2 \rightarrow \frac{7}{4}\text{N}_2 + 3\text{H}_2\text{O}$	$R_9^{\text{SCR}} = k_9^{\text{SCR}} \Psi_{\text{NH}_3}^{\text{cap}} c_{\text{NO}_2} \theta_{\text{NH}_3}$
$\text{NH}_3^* + x \rightleftharpoons \text{NH}_3^x + *$	$R_{10}^{\text{SCR}} = k_{10}^{\text{SCR}} \Psi_{\text{NH}_3}^{\text{cap}} \Psi_x^{\text{cap}} [\theta_{\text{NH}_3} (1 - \sigma_{\text{NH}_3}) - \sigma_{\text{NH}_3} (1 - \theta_{\text{NH}_3})/K_{\text{LH}}]$

The factors $[\gamma_{\beta 3\text{O}_2}]$, $[\gamma_{\beta 4\text{H}_2\text{O}}]$ and $[\gamma_{\beta 6\text{H}_2\text{O}}]$ were used only for scaling the reaction rates from the lab experiments with lower O₂ and H₂O amounts (2 % and 3 %, respectively) to the high O₂ and H₂O concentrations observed in the exhaust gas (≈ 10 %). At the high O₂ and H₂O concentrations a saturation level is achieved and zero reaction orders β_3 , β_4 and β_6 are used.

conditions the formation and storage of NH₄NO₃ plays an important role [22, 29] which is not treated in detail in the model used for the presented study (Table 2).

<table 2 here>

<figure 4 here>

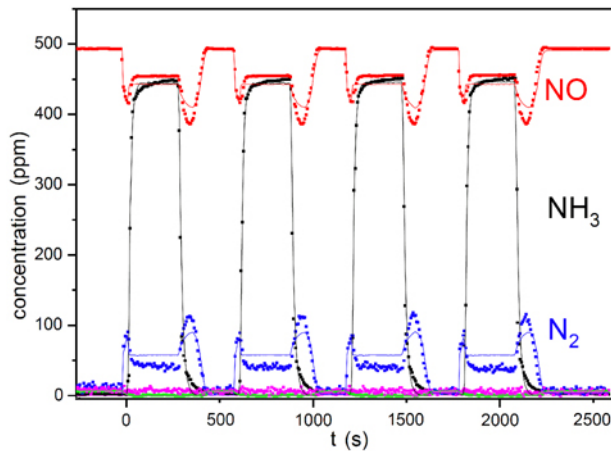


Figure 5. Outlet concentrations during a dynamic NH₃ dosing experiment in microreactor with the crushed SCR monolith. Symbols: measurement, lines: simulation (including the NH₃ spill-over reaction at finite rate). $T=250^\circ\text{C}$, inlet gas concentrations: 500 ppm NO, 0/500 ppm NH₃ (periodic alternation each 300 s), 2 % O₂, 3 % H₂O, balance He.

depicts the dynamic response of the microreactor outlet by applying 300 s NH₃ pulses. The start of NH₃ dosing is indicated by the decrease of the NO_x concentration at the reactor outlet. The decrease of the NH₃ concentration at the reactor outlet indicates the NH₃ shut off. It can be noted that the steady state NO_x conversion is lower compared to the levels during the NH₃ shut off/on phases. This can be explained by the fact that the build-up of the stored NH₃ led to an increasing inhibition of the SCR reaction. After removing NH₃ from the feed, the stored NH₃ is consumed by the SCR reaction, which reduces the inhibition effect and leads to an increased reaction rate until the stored NH₃ is completely consumed. The good correlation between simulation and experiment proves that the model is able to predict these inhibition effects.

It has already been confirmed that combination of the reaction kinetics studied on SCR catalyst powders with the monolith model described in section Mathematical Model, and consequent up-scaling to full-scale monolith dimensions is possible [29, 32]. The comparison between simulation and experiments for full-scale SCR monolith is shown in Figure 6a. During these engine test bench measurements, the engine was running at constant speed and load. Around the time 750 s, ammonia was injected in excess into the exhaust line. As a result, the NO_x concentration at the SCR outlet decreased. However, after a certain time the NO_x outlet concentration increased partly. Thus, similar dynamic features like in the laboratory experiment (Figure 5) are observed, which confirms the practical relevance of the NH₃ inhibition effect.

The Fe-ZSM5 catalyst studied in this work exhibits a significant NH₃ inhibition effect. As an example Figure 5

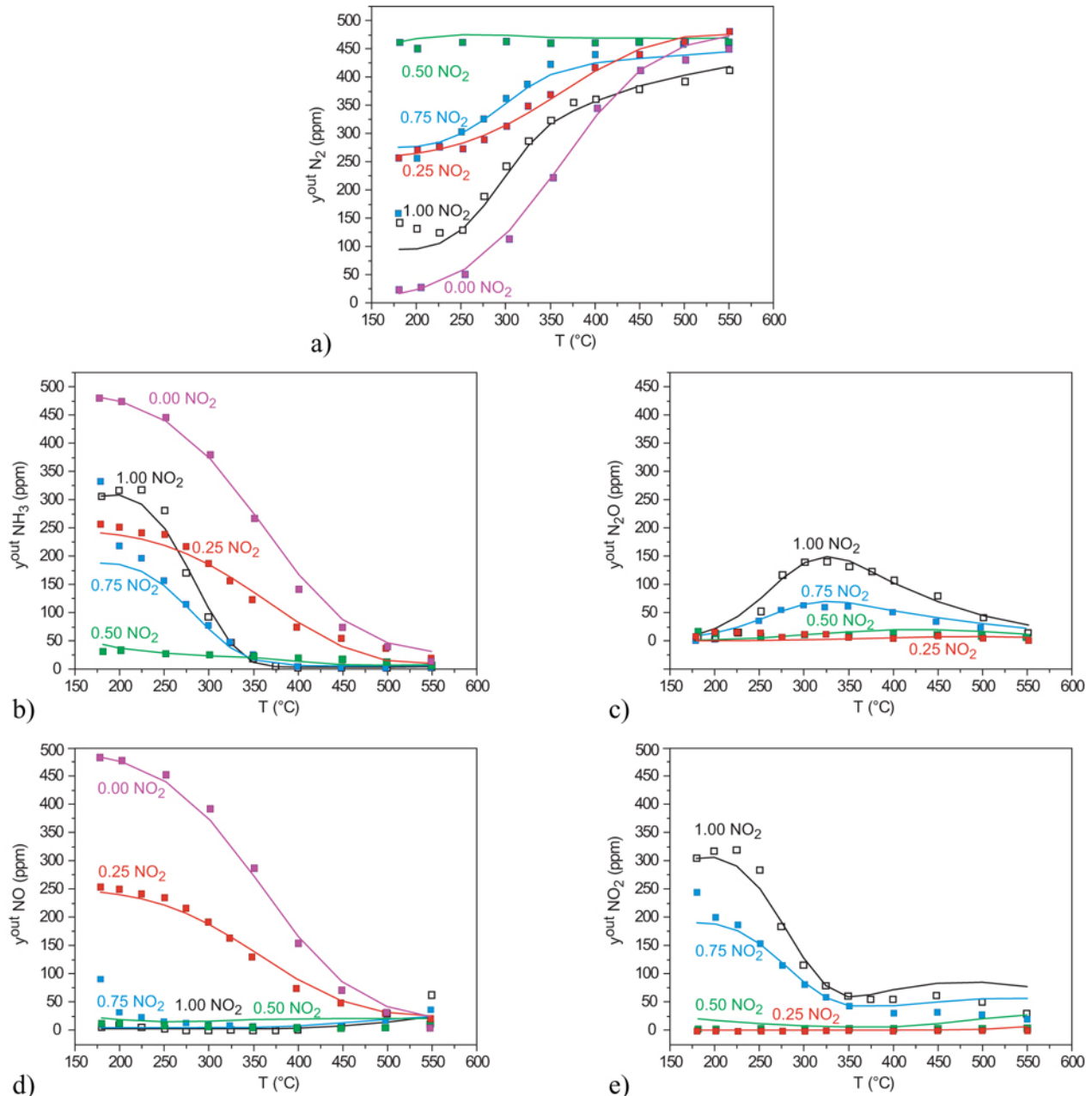


Figure 4. Steady state outlet concentrations in a microreactor with the crushed SCR monolith for several inlet NO_2/NO_x molar ratios: 0.00, 0.25, 0.50, 0.75 and 1.00. (a) outlet N_2 , (b) outlet NH_3 , (c) outlet N_2O , (d) outlet NO , and (e) outlet NO_2 . Symbols: experimental data, lines: simulations. Inlet gas composition: 500 ppm NO_x (varied NO_2 content), 500 ppm NH_3 , 3 % H_2O , 2 % O_2 , balance He.

The comparison of Figures 6a and 6b underlines the influence of the NH_3 spill-over reaction (R_{10}^{SCR}). The simulation data in Figure 6a are calculated using the reaction kinetics listed in Table 2. However, Figure 6b depicts the situation when equilibrium with respect to the $\text{NH}_3^* \rightleftharpoons \text{NH}_3$ spill-over is assumed in the SCR model. Under this assumption all the rate laws used for the simulations remain identical to Table 2, but

the R_{10}^{SCR} is omitted and the “standard” SCR reaction rate R_5^{SCR} becomes [17, 26]:

$$R_{5,\text{eq.spill}}^{\text{SCR}} = k_5^{\text{SCR}} c_{\text{NO}} y_{\text{O}_2}^\beta \theta_{\text{NH}_3} / [1 + K_{\text{LH}} \theta_{\text{NH}_3} / (1 - \theta_{\text{NH}_3})] \quad (13)$$