

Transient Simulation of NO_x Reduction over a Fe-Zeolite Catalyst in an NH₃-SCR System and Study of the Performance under Different Operating Conditions

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ABSTRACT

The NO_x reduction in an ammonia SCR converter has been simulated by a 1D+1D model for a single representative channel to parametrically study the characteristics of the system under typical operating conditions. An appropriate model has been selected interpreting the chemical behavior of the system and the parameters are calibrated based on a comprehensive set of experiments with an Fe-Zeolite washcoated monolith for different feed concentrations, temperatures and flow rates. Physical and chemical properties are determined as well as kinetics and rate parameters and the model has been verified by experimental data at different operating conditions. Three different mechanisms for the surface kinetics to model NO_x reduction have been assessed and the results have been compared in the cases of steady DeNO_x performance and transient response of the system. Ammonia inhibition is considered in the model since it has a major effect specifically under transient operating conditions. Effects of the operating temperature, the gaseous flow rate and the species concentrations such as ammonia dosage and the ratio of NO and NO₂ have been investigated. It has been shown that recently proposed dual site chemical kinetics for Fe-Zeolite catalysts are especially suited to predict the transient operation of the system during ammonia feeding and the inhibition effect after shutting off ammonia. Accurate numerical results for various cases are a strong indication for the validity of the model under the typical operating conditions of an SCR system. This study helps to find the optimum performance of the system under different conditions including a wide range of working temperatures with different flow rates and concentrations.

INTRODUCTION

The Selective Catalytic Reduction (SCR) of NO_x has been established in the automotive industry as an efficient technique for the abatement of NO_x from the

exhaust of Diesel engines. In view of shortening the vehicle development cycles and reducing the costs, numerical simulation is a powerful tool to optimize the complex design processes of an SCR system.

A variety of modeling approaches are in use today depending on the process of interest. There are different ways to deal with simulations of fluid flow and surface kinetics, which have been developed in the past twenty years and reported in a previous publication [1]. To briefly mention the current state of the art, 1D+1D model are a good choice in most cases, when not only the fluid flow has to be considered but also the convective mass transfer in the channel and the intra-porous diffusion within the washcoat layer on the channel walls. Simulations are most often performed for a single channel of a honeycomb SCR converter. The most significant progress in the simulation of the SCR system behavior is achieved by improving the modeling of the surface kinetics. Various surface kinetics and species have been implemented in new models to explain the detailed mechanisms [2-5]. One of the most recently proposed kinetics [6] has been applied in this work and results in a very good prediction of the SCR system performance.

Operating conditions of SCR converters in mobile applications are strongly transient and a broad temperature window is covered during regular use. Under such highly transient conditions also the urea dosage is highly dynamic and, as a consequence, the concentration of the urea decomposition product NH₃ can change considerably during an NH₃ shutdown phase [2]. NH₃ inhibition effects are more significant at low temperatures and affect the dynamic response of the SCR systems. The traditional standard Eley-Rideal rate law for the SCR reaction [7] does not consider the inhibiting effect of NH₃ on the SCR reaction [8]. However, this inhibition effect has pronounced practical consequences and should,

therefore, be included in the kinetic model of SCR systems in vehicles.

A modified dual-site redox rate law was developed in 2005 [8], which effectively accounts for the NH_3 inhibition effect observed during transient experiments at low temperatures (below 250 °C). The study was based on the Standard SCR reaction between NO and NH_3 performed over a commercial powdered $\text{V}_2\text{O}_5/\text{WO}_3\text{--TiO}_2$ catalyst. Two different types of sites were proposed on the surface and the kinetics included NH_3 spill-over between the sites. It was demonstrated that the implementation of this novel modified redox kinetics into a fully predictive 1D+1D model of SCR monolith reactors significantly improves simulations of SCR transient runs at different scales.

The oxygen influence on the ammonia inhibition effect at low temperatures was specifically addressed in [2]. The higher oxygen content did not alter the dynamic features of the transient experiments in the case of ammonia inhibition. The main effect of the higher oxygen concentration was a slight enhancement of the SCR conversion compared to the steady state. Since a redox mechanism governs the SCR reaction, in which the active site has to be reoxidized by oxygen, the kinetic depends on the oxygen content. The developed dual-site kinetic model described well the experimental oxygen effect.

In [9], an experimental study of the $\text{NH}_3\text{--NO--NO}_2$ SCR reactivity over a commercial washcoated Fe-Zeolite catalyst was presented in view of its use in Diesel exhaust aftertreatment technologies. The effects of the main operating conditions were tested and experiments showed that oxygen concentration (2-10% v/v) has no effect on NH_3 adsorption and Fast SCR (reaction between NO/ NO_2 in a 1:1 ratio and NH_3), however it promotes NH_3 and NO oxidation as well as Standard SCR and inhibits NO_2 decomposition. Compared to a V-based SCR catalyst, zeolite systems are characterized by a higher activity in the Standard SCR reaction at low temperature, a higher activity in the Fast SCR reaction and a higher selectivity to N_2O in the presence of excess NO_2 [9].

The elementary steps of the Fast SCR reaction over Fe-ZSM-5 were identified based on transient model gas experiments at realistic conditions for removal of NO_x from mobile Diesel exhausts [10]. It was established that the mechanistic pathways demonstrated for V-based catalysts widely apply also for Fe-exchanged zeolites and a general mechanism was considered to describe the Fast SCR reaction at low temperature over V-based and zeolite catalysts.

A dynamic Mars-van Krevelen kinetic model that unifies Standard and Fast SCR reactions into a single redox approach was proposed for V-based catalysts for NO_x removal from Diesel exhausts in [3], where a global kinetic model was derived for the full $\text{NH}_3\text{--NO--NO}_2$ SCR reacting system by extending the dual site redox kinetics presented in [2] for the $\text{NH}_3\text{--NO--O}_2$ reacting subsystem. The kinetic model expressed the overall reduction rate of NO associated with both the Standard and Fast SCR reaction.

The activity of a commercial copper-exchanged zeolite SCR catalyst for heavy and light duty Diesel engines was investigated by both steady state and transient experiments and the results were compared with Fe-zeolite catalysts in [11]. With respect to the iron-based catalyst, the copper zeolite system showed a higher ammonia storage capacity, a higher activity in the ammonia oxidation reaction and in the Standard SCR reaction, and its De NO_x activity was found less sensitive to the NO_2 feed content. As opposed to the iron zeolite, no inhibiting effect of ammonia on the Standard SCR reaction was observed over the copper zeolite, while formation of some N_2O was detected even in the absence of NO_2 in the gas feed mixture.

NO_x reduction in ammonia SCR was simulated for a combined NO_x storage and $\text{NH}_3\text{--SCR}$ catalytic system in [6] by using the dual site modified redox rate reaction for Standard SCR [2]. It was revealed that only a finite spill-over reaction rate is able to reproduce the transient NH_3 inhibition effects with the Fe-ZSM-5 catalysts. However, for many other SCR catalysts (such as Cu-ZSM-5) the equilibrium assumption regarding NH_3 spill-over is acceptable.

The aim of this work is simulation of the NO_x reduction over a Fe-zeolite catalyst by considering a finite rate for the ammonia spill-over reaction. The effect of the NH_3 spill-over rate on transient behavior after ammonia shutoff has been studied. The strong influence of NH_3 spill-over on ammonia inhibition plays a determinant role in simulation of the system under fast transient condition. Intra-porous diffusion within the washcoated layer has been simulated in the direction of the washcoat thickness. The diffusion resistance limits ammonia adsorption and consequently influences NO_x reduction. Responses of the SCR system have been investigated in several transient conditions and the importance of different reactions and parameters have been identified. The simulation results have been validated by experimental data for a wide range of operating conditions and the performance of the SCR system has been examined for different cases.

EXPERIMENTAL

The catalyst used in the experiments was a commercially available Fe-BEA zeolite, which is widely used in automotive SCR catalysts. The powder Fe-BEA material was coated at the Paul Scherrer Institute on a standard 400 cpsi cordierite monolith from Corning Incorporated (catalyst loading = 135 g/L) with wall thickness 0.165 mm and calcined at 550 °C for 4 h prior to testing.

For the parameterization of the catalyst model, the catalyst performance had to be measured in dependency of the parameters $\text{NO}_{x,\text{in}}$, $\text{NO}_{2,\text{in}}/\text{NO}_{x,\text{in}}$, $\alpha = \text{NH}_{3,\text{in}}/\text{NO}_{x,\text{in}}$, temperature and GHSV. For that purpose three small monolith samples with a volume of 6.4 cm³, 8.9 and 13.3 cm³ were cut out of the brick and tested with model Diesel exhaust gas in the laboratory test apparatus described in [12].

The characterization experiments were designed such that the catalyst behavior was covered over a practice-relevant parameter space with a minimum number of experiments: $\text{NO}_{x,\text{in}}$ was kept constant at 500 ppm in most of the experiments, the $\text{NO}_{2,\text{in}}/\text{NO}_{x,\text{in}}$ ratio was switched between 0%, 25%, 50% and 75%, the temperature was varied between 200 °C and 450 °C in 50 °C steps and the GHSV was adjusted to 30000 h⁻¹, 50000 h⁻¹, and 70000 h⁻¹. α_{OD} denotes the optimum dosage ratio of $\text{NH}_{3,\text{in}}/\text{NO}_{x,\text{in}}$ under practice-relevant conditions which results in a slip of 10 ppm ammonia downstream of the catalyst. This ratio α_{OD} significantly differs from the ideal 1:1 ratio for NO-SCR (Standard SCR), for which it was determined at each temperature and then varied stepwise. There are 10% oxygen and 5% water vapor in the base feed and the rest is nitrogen.

In a first set of step-response experiments the Standard SCR performance and NH_3 oxidation was measured at given temperature and GHSV by switching NH_3 on and off at 0.8 α_{OD} , 1.0 α_{OD} and 1.2 α_{OD} . Moreover, NH_3 was switched on and off without NO_x in the feed in order to determine the dynamics of the NH_3 storage and release. The Fast SCR performance was measured with the same procedure. As equilibration was awaited after the concentration steps, the steady-state performance of the catalyst is included in the recorded data.

MODEL

A typical SCR converter has a large number of parallel channels in a honeycomb monolith structure with catalytically washcoated walls. To simulate the behavior of the SCR process one representative channel is selected. The model, which is described in detail in [1], accounts for the convective mass transfer through the channel, the diffusive mass transfer and the chemical reactions within the catalytic layer coupled together via the mass transfer boundary condition at the wall.

$$k_m(C_i - \hat{C}_i|_{\text{interface}}) = D_{\text{eff}} \frac{\partial \hat{C}_i}{\partial y} \Big|_{\text{interface}} \quad (1)$$

where k_m is the convective mass transfer coefficient of the channel calculated based on Sherwood number from Graetz-Nusselt analogy for a developing laminar flow in a square duct and by employing the default model constants [13, 14].

The flow inside the channel is modeled by means of a hyperbolic equation for a step flow into the channel,

$$\frac{\partial C_i}{\partial t} = -u \frac{\partial C_i}{\partial x} - \frac{4k_m}{D_h} (C_i - \hat{C}_i|_{B.C.}) \quad (2)$$

where u denotes the average velocity and C_i the species concentrations in each section of the channel. The last term in eq. (2) describes the mass transfer at the boundary condition between channel and wall.

The physical processes within the catalytic layer comprise several steps including diffusion and surface reactions. The gaseous flow inside the channel contains the species O_2 , NO , NO_2 , NH_3 , N_2 . The gaseous species diffuse into the washcoated layer and ammonia inside the wall pores adsorbs strongly on the catalytic surface. The adsorbed ammonia reacts with NO_x and O_2 , which have diffused into the pores. As a result water vapor and nitrogen are produced and diffuse back into the channel.

Intra-porous diffusion limits ammonia adsorption on the catalytic surface within the washcoated layer and consequently influences NO_x reduction as is clearly demonstrated e.g. in [13, 15]. The diffusion within the catalytic layer is described by the following equation:

$$\frac{\partial \hat{C}_i}{\partial t} = D_{\text{eff}} \frac{\partial^2 \hat{C}_i}{\partial y^2} + r_i \quad (3)$$

where $\hat{C}_i$ denotes the concentration of the species inside the pores and r_i shows the formation rate of species i due to the surface reactions.

CATALYTIC SURFACE REACTIONS

To calculate the formation rate of species inside the pores, ten surface reactions are taken into account for the Fe-zeolite catalyst according to ref. [6] (Table 1).

Table 1. Surface reactions

(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	$\text{NH}_3^* \leftrightarrow \text{NH}_3^*$
(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	$2 \text{NH}_3^* + 2 \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{N}_2 + 3 \text{H}_2\text{O}$