

The NH₃ Inhibition Effect in the Standard SCR Reaction over a Commercial Fe-zeolite Catalyst for Diesel Exhaust Aftertreatment: An Experimental and Modeling Study

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ABSTRACT

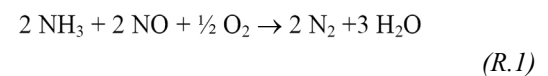
Transient and steady-state kinetic data are herein presented to analyze the inhibiting effect of ammonia on the NH₃-SCR of NO at low temperatures over a Fe-zeolite commercial catalyst for vehicles. It is shown that in SCR converter models a rate expression accounting for NH₃ inhibition of the Standard SCR reaction is needed in order to predict the specific dynamics observed both in lab-scale and in engine test bench runs upon switching on and off the ammonia feed. Two redox, dual site kinetic models are developed which ascribe such inhibition to the spill-over of ammonia from its adsorption sites, associated with the zeolite, to the redox sites, associated with the Fe promoter. Better agreement both with lab-scale intrinsic kinetic runs and with engine test-bench data, particularly during transients associated with dosing of ammonia to the SCR catalyst, is obtained assuming slow migration of NH₃ between the two sites. In addition to a satisfactory description of the observed transient features, the resulting kinetic model granted absolute errors generally less than 5% for the predicted steady-state NOx conversions in all the operating points of test-bench validation maps, and performed well in the predictive simulation of the highly dynamic hot part of a WHTC test cycle.

INTRODUCTION

The Selective Catalytic Reduction (SCR) of NOx with NH₃/urea is the most widespread technology for the control of

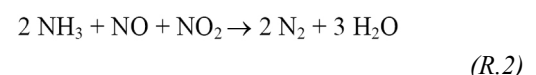
NOx in the emission of stationary sources; however, it has recently gained more and more interest in the aftertreatment of exhausts from Diesel vehicles, as well. Indeed, in Europe it is currently implemented on both heavy duty vehicles and passenger cars in order to meet the emission limits associated with the EUROV regulations.

In the case of the application of the technology to stationary sources, mainly V₂O₅-WO₃/TiO₂ catalysts are used: they typically work between 300-400°C where the Standard SCR reaction



is the prevailing reaction.

In the case of mobile applications, the need of higher DeNOx activities in a wider T-window is satisfied by the presence of the Diesel Oxidation Catalyst upstream of the SCR system, which partially converts NO to NO₂. This permits the occurrence of the Fast SCR reaction, associated with greater DeNOx efficiencies than reaction (R.1) particularly at low temperatures, in which an equimolar mixture of NO and NO₂ reacts with NH₃ to form nitrogen and water:



One of the most suitable catalysts for NH_3 - SCR reactions for mobile applications is the Fe-promoted zeolite system, which is known for its very high activity in the presence of NO_2 , high selectivity to dinitrogen also at high temperatures, and high thermal durability.

SCR converters are one part of usually complex aftertreatment systems. Optimization of design and operation of the integrated system is a challenging and expensive task, as it involves many topics like temperature and NH_3 /urea (as AdBlue® solution) dosing strategy for minimal emissions at reasonable costs. Therefore the development of simulation tools has become a key factor in order to accelerate the development process of aftertreatment systems and to reduce related costs and effort.

In this context, the development of SCR kinetic schemes and converter models has received growing attention in the last few years. Indeed, the catalytic mechanism and in particular transient kinetics of the SCR reactions over Fe promoted zeolites have been recently investigated in the literature by different groups. Malmberg et al. [1] presented a model able to reproduce steady state and transient operation of the main SCR reactions; particular attention was paid to the Standard SCR reaction (R. 1), that was found to be temporarily inhibited by excess NH_3 at low T, and thus the authors had to use a specific rate expression originally proposed by Chatterjee et al. [2] for a V-based catalyst to reproduce such transient effects. Iwasaki et al. [3] developed a transient kinetic scheme for NH_3 SCR reactions over an Fe/ZSM-5 catalyst; they found that for the Standard SCR reaction the N_2 production rate was transiently promoted in the absence of gaseous NH_3 , and described such an effect assuming a rate expression with a negative reaction order in the NH_3 concentration. Sjoval et al. [4] presented a global transient kinetic model for a commercial Fe-zeolite catalyst, which included NH_3 storage and oxidation, NO oxidation, the Standard, the NO_2 and Fast SCR reactions; they also found that the DeNO_x activity associated with the Standard SCR reaction was enhanced at low NH_3 coverages, and they accordingly empirically modified the rate expression by including a dependence of the reaction rate on the number of vacant sites.

In the present paper we investigate the transient kinetics specifically of the $\text{NO} + \text{NH}_3$ SCR reaction over a commercial Fe-zeolite catalyst for mobile applications, particularly addressing the NH_3 inhibition at low temperatures. In order to take into account such an effect, two different rate expressions for the Standard SCR reaction have been derived and results are herein compared: both kinetic models were fitted to transient data collected over the powdered catalyst under a chemical regime, then validated first against data collected over full scale monolith systems,

thus taking into account also mass transfer effects, and eventually in test bench facilities using real engine exhaust gases.

METHODS

1. LAB SCALE EXPERIMENTS

For the purposes of the present study dedicated unsteady kinetic SCR experiments of various nature were performed in the 200 - 300°C T-range over a commercial Fe-zeolite catalyst, originally supplied by Daimler AG in the form of a washcoated 400 CPSI honeycomb monolith. The monolith catalyst was crushed and ground to powder (140-200 mesh); a sample of the so-prepared powder (80 mg) was diluted with 80 mg of quartz and loaded in a flow-microreactor consisting of a quartz tube (6 mm i.d.) directly connected both to a UV analyzer (ABB Limas 11-HW) and to a quadrupole mass spectrometer (Balzers QMS 200), which operated in parallel.

The reactor was placed into an electric furnace and a thermocouple, directly immersed in the catalyst bed, measured the reaction temperature. NH_3 , NO, NO_2 , O_2 and He feed streams were dosed by mass flow controllers, while water vapour was added by means of a saturator. Helium was used as inert carrier gas in order to allow evaluation of N_2 . The N-balances always closed within $\pm 5\%$ at steady-state.

Catalyst conditioning consisted in a temperature ramp of 5 K/min from room temperature up to 600°C in 10% O_2 v/v + 10% H_2O , followed by hold at 600°C for 5 h.

The reaction dynamics were investigated by TRM runs (Transient Response Method, involving a step change of reactant feed concentrations at isothermal conditions) within the 200-300°C T-range. Typical feed contents of NO_x and NH_3 were 500 ppm, always in the presence of O_2 (2% v/v) and water (3% v/v). TPD (Temperature Programmed Desorption) experiments were also performed by heating the catalyst in a T-ramp at 15 K/min from 150°C up to 600°C.

The system was operated at atmospheric pressure with flow rates ranging from 71 to 327 cm^3/min (STP), corresponding to gas hourly space velocities (GHSV) referred to the active phase between 194,000 and 890,000 $\text{cm}^3/(\text{h g}_{\text{cat}})$ (STP). A detailed description of the experimental equipment and procedures can be found in [5, 6, 7].

Intraparticle gradients and gas-solid mass transfer limitations were ruled out by theoretical diagnostic criteria [8].

2. TEST BENCH EXPERIMENTS

The developed and calibrated model has been validated with heavy duty engine test bench measurement data from several

experiments performed at Daimler AG. The exhaust aftertreatment system always consisted of a DOC, DPF, SCR and ASC (NH₃ oxidation catalyst), thermally isolated against the environment. Two different setup configurations have been considered, as described in the following.

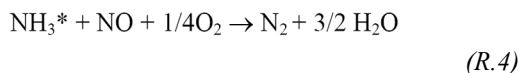
In the first configuration, gaseous NH₃ as reducing agent was fed to the system upstream of the SCR catalyst, followed by a mixing device. Good uniformity of the NH₃ concentration at SCR inlet has been confirmed experimentally. Data were measured directly before and after the SCR catalyst by means of a chemiluminescence detector for NO and NO₂ and a diode laser spectrometer for NH₃ [2, 9]. For each experimental run the engine was operated at constant load and speed.

In the second configuration, liquid urea-water solution (AdBlue®) was injected into the exhaust stream after the DPF, followed by a mixing device and a urea-processing tube of specific length for optimal NH₃-generation and distribution. According to the real system configuration, the exhaust stream was then split symmetrically into two lines, each containing SCR- and ASC-bricks. The experimental run used for model validation was the hot part of a WHTC. Gas analysis was carried out after DPF before AdBlue®-injection and after the SCR before ASC.

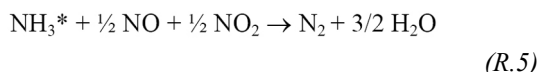
3. KINETIC ANALYSIS

The transient data collected over the powdered SCR catalyst were analyzed according to a dynamic one-dimensional isothermal isobaric heterogeneous plug-flow model of the test microreactor [10] in order to obtain estimates of the relevant SCR rate parameters.

To describe the NH₃-NO/O₂ reacting system in the T-range from 150 up to 300°C, NH₃ adsorption-desorption, and SCR DeNOx reaction have been considered, namely:



Ammonia oxidation reactions were ruled out because of the low T range, while the “Fast SCR” reaction



was also considered, since in engine test bench runs relevant amounts of NO₂ could be present at the SCR inlet.

Accordingly, the test reactor model comprises the mass balances of adsorbed NH₃ and of gaseous NH₃, NO, NO₂ and N₂, as reported in the following:

adsorbed phase: NH₃

$$\Omega \frac{\partial \theta_{\text{NH}_3}}{\partial t} = r_{\text{ads}} - r_{\text{des}} - r_{\text{NO}} - r_{\text{Fst}} \quad \text{Eq. (1)}$$

gas phase: NH₃, NO, NO₂ and N₂

$$\varepsilon \frac{\partial C_{\text{NH}_3}}{\partial t} = -v \frac{\partial C_{\text{NH}_3}}{\partial z} - (1 - \varepsilon)(r_{\text{ads}} - r_{\text{des}}) \quad \text{Eq. (2)}$$

$$\varepsilon \frac{\partial C_{\text{NO}}}{\partial t} = -v \frac{\partial C_{\text{NO}}}{\partial z} - (1 - \varepsilon)(r_{\text{NO}} + 1/2 \cdot r_{\text{Fst}}) \quad \text{Eq. (3)}$$

$$\varepsilon \frac{\partial C_{\text{NO}_2}}{\partial t} = -v \frac{\partial C_{\text{NO}_2}}{\partial z} - (1 - \varepsilon)(1/2 \cdot r_{\text{Fst}}) \quad \text{Eq. (4)}$$

$$\varepsilon \frac{\partial C_{\text{N}_2}}{\partial t} = -v \frac{\partial C_{\text{N}_2}}{\partial z} + (1 - \varepsilon)(r_{\text{NO}} + r_{\text{Fst}}) \quad \text{Eq. (5)}$$

The set of ODEs (1), (2), (3), (4), (5), with obvious initial and boundary conditions, was solved numerically according to the method of lines, based on spatial (axial) discretization with backward finite differences and on time integration by Gear's algorithm [11, 12].

To account for the delayed NH₃ evolution, Eq.(2) was coupled with an empirical model describing the NH₃ response function of the rig and of the analyzers. Blank NH₃ step change experiments (not shown) were used to fit the NH₃-delay model, which consisted of two continuous stirred tanks in parallel.

The rate parameters appearing in the rate expressions herein considered, to be discussed below, have been estimated in this work by global multiresponse nonlinear regression of isothermal concentration step change runs, taking the temporal evolutions of the outlet NH₃, NO, NO₂ and N₂ concentrations as the fitted responses: a robust multi-method regression routine was used for this purpose [13].

4. MONOLITH REACTOR MODEL

The intrinsic kinetics determined over the SCR catalyst in powdered form have been incorporated into a transient two-phase 1D+1D adiabatic mathematical model of SCR monolith reactors [2] specifically adapted for mobile SCR applications. The model assumes identical conditions within each channel of the monolith catalyst with negligible axial dispersion and pressure drop, and accounts explicitly also for

intra-porous diffusion of the reacting species within the porous catalytic washcoat of the monolith.

Unsteady mass and enthalpy balances for a single monolith channel are provided by the following equations:

gaseous phase:

$$\frac{\partial C_i}{\partial t} = -\frac{v}{L} \frac{\partial C_i}{\partial z^*} - \frac{4}{d_h} k_{mt,i} (C_i - C_i^w) \quad \text{Eq. (6)}$$

$$\frac{\partial T_g}{\partial t} = -\frac{v}{L} \frac{\partial T_g}{\partial z^*} - \frac{4}{d_h} h (T_g - T_s) / (\rho_g C_p) \quad \text{Eq. (7)}$$

solid phase:

$$0 = k_{mt,i} (C_i - C_i^w) + R_{eff,i} \quad \text{Eq. (8)}$$

$$\frac{\partial T_s}{\partial t} = \frac{h(T_g - T_s) - \sum_{j=1}^{NCG} \Delta H_j R_{eff,j}}{\rho_s C_{p,s} E_w (1 + E_w / d_h)} \quad \text{Eq. (9)}$$

where C_i is the gas-phase concentration of species i , C_i^w is the concentration of species i at gas-solid interface, v is the gas linear velocity in the monolith channels, d_h is the hydraulic diameter of the washcoated monolith channel, and

T_g and T_s are the gas and the catalyst temperatures; $z^* = \frac{z}{L}$ where z is the axial coordinate and L is the monolith length. E_w represents the total half-thickness of the monolith wall (including washcoat), while $R_{eff,i}$ is the effective surface rate of formation of species i .

Gas-solid mass and heat transfer coefficients (k_{mt} and h) are evaluated by analogy with the thermal Graetz-Nusselt problem for developing laminar flow in square ducts [14].

The following equations for diffusion-reaction of the reactant and product species in the catalytic monolith washcoat take into account intra-phase diffusional limitations which can be associated with NH_3 -SCR reactions in monolith catalysts:

$$0 = D_{eff,i} \frac{\partial^2 C_i^*}{\partial x^{*2}} + S_w^2 R_i \quad \text{Eq. (10)}$$

$$R_{eff,i} = -\frac{D_{eff,i}}{S_w} \frac{\partial C_i^*}{\partial x^*} \Big|_w \quad \text{Eq. (11)}$$

C_i^* is the intraporous concentration of species i , while R_i represents the volumetric intrinsic rate of formation of

species i ; $x^* = \frac{x}{S_w}$ where x is the intraporous coordinate and S_w represents the washcoat thickness.

Build up of reactants in the gas phase inside the catalyst pores is neglected, whereas accumulation/depletion of NH_3 adsorbed onto the catalyst surface, which is typically the controlling factor in the dynamics of SCR monolith reactors, is described by

$$\Omega_{\text{NH}_3} \frac{\partial \theta_{\text{NH}_3}}{\partial t} = R_{\text{NH}_3^*} \quad \text{Eq. (12)}$$

In addition to rate parameters and reaction conditions, the model requires the physicochemical, geometrical and morphological (porosity, pore size distribution) characteristics of the monolith catalyst as input data. Effective diffusivities, $Deff,j$, are then evaluated from the catalyst morphological data according to a modified Wakao-Smith random pore model, as specifically recommended in the literature for V-based SCR monolithic catalysts [15].

TRANSIENT EXPERIMENTS ON POWDERS AND KINETIC ANALYSIS

1. AMMONIA ADSORPTION-DESORPTION

Feeding only NH_3 and oxygen to the reactor at low temperatures results in NH_3 adsorption-desorption at the catalyst surface.

To analyse this process, TRM experiments at constant temperature (200°C) feeding 500 or 1000 ppm of NH_3 along with oxygen (2%) and water (3%) were performed, followed by a TPD run when the catalyst was heated from 100 to 550°C at 15 K/min in inert atmosphere.

Figure 1A shows the corresponding results in terms of inlet (dashed line) and outlet (thin line) NH_3 concentration profiles during the adsorption phase.

For the first 150 s after NH_3 feed, a “dead time” was observed in the NH_3 outlet concentration profile, indicating that the whole amount of NH_3 fed to the system was being adsorbed onto the catalyst surface. Then, the NH_3 outlet concentration grew with time approaching saturation after 1000 s. At NH_3 shut-off ($t = 3100$ s), the outlet ammonia concentration rapidly decreased, showing a desorption tail associated with the desorption of weakly adsorbed NH_3 .

species. Figure 1B shows the following TPD, where a desorption peak was observed due to the release of NH_3 species still stored onto the catalyst. Data analysis showed a storage capacity of about $0.35 \text{ mmol NH}_3/\text{g}_{\text{active phase}}$ at 200°C .

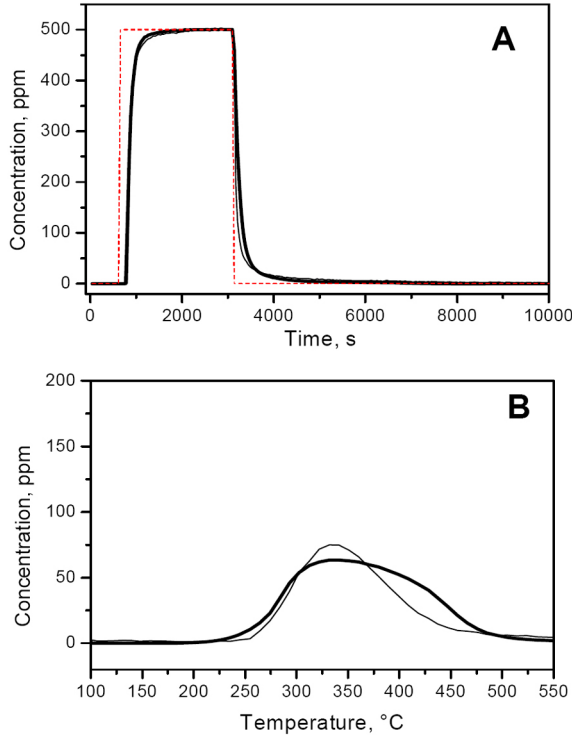


Figure 1. NH_3 adsorption-desorption + TPD run. $\text{NH}_3 = 500 \text{ ppm}$, $\text{O}_2=2\%$ (0% during TPD), $\text{H}_2\text{O}=3\%$, He carrier gas, $Q=71 \text{ Ncc/min}$. (A) Gas phase ammonia concentration during adsorption phase $T=200^\circ\text{C}$; (B) gas phase ammonia concentration during TPD (from 100°C up to 550°C). Thin lines = experimental data; thick lines = kinetic fit using the Double Horn model

The kinetic analysis of the NH_3 adsorption-desorption was addressed using the dynamic one-dimensional isothermal heterogeneous plug-flow model of the test micro reactor described in the Methods section, simplified in order to account only for the occurrence of the NH_3 adsorption-desorption (R.3).

Concerning the rate expressions, a non-activated NH_3 adsorption and a coverage-dependent desorption energy were adopted, in line with previous findings [16, 17]:

$$r_{\text{ads}} = k_{\text{ads}} C_{\text{NH}_3} (1 - \theta_{\text{NH}_3}) \quad \text{Eq. (13)}$$

$$r_{\text{des}} = k_{\text{des}}^0 \exp\left[-\frac{E_{\text{des}}^0}{RT} (1 - \alpha \theta_{\text{NH}_3})\right] \cdot \theta_{\text{NH}_3} \quad \text{Eq. (14)}$$

The kinetic parameters for NH_3 adsorption-desorption in Eq.s (13) - (14) were estimated by regression on the TRM and TPD runs presented above.

The kinetic fit (thick line) resulted in a good prediction of the TRM phase of the experiment, both during the NH_3 feed and shut-off transients. Focusing on the TPD phase, a fairly good agreement between model and experiments can be claimed but for the fact that the model predicts the desorption of the previously adsorbed NH_3 over a slightly wider T-range if compared to the experimental data.

2. STANDARD SCR DYNAMICS

Several sets of isothermal step feed runs were performed to investigate the dynamic behavior of the catalyst in the Standard SCR reaction in the low T-range. In each run 500 ppm of NH_3 were stepwise fed to the reactor while continuously flowing NO (500 ppm), oxygen (2%), water (3%) and balance helium. Different sets of data were collected by changing temperature (in the range $200\text{--}300^\circ\text{C}$) and duration of the NH_3 step (in the range 150–2700 s).

Figure 2 shows one typical result obtained at 200°C by feeding NH_3 for 2700 s in a flow of NO, oxygen and water (thin lines in A and B). The outlet concentration profiles of NH_3 , NO, N_2 and N_2O are displayed as a function of time.

At $t = 0\text{s}$, while continuously flowing NO, NH_3 was stepwise fed to the reactor. It appears, that the NH_3 outlet concentration trace exhibited about 25s of dead time and then slowly grew with time on stream, eventually approaching a steady-state value of about 480 ppm. At the same time, the NO signal rapidly went through a minimum after which it eventually approached the steady state value of about 480 ppm; the nitrogen signal mirrored that of NO, presenting an identical transient effect. During both the dynamic phase and the steady state condition the concentration of NO, NH_3 and N_2 were consistent with the stoichiometry of the Standard SCR, indicating a NOx conversion of $\sim 4\%$. A maximum in the DeNOx activity, with the simultaneous nitrogen peak, was also observed at NH_3 shut-off, while the NH_3 concentration rapidly decreased with time recovering the 0 value. Such temporary enhancements in the DeNOx activity observed over the Fe-zeolite catalyst both at NH_3 opening and shut off, could be associated with a negative effect played by excess NH_3 present onto the catalyst surface or in the gas phase.

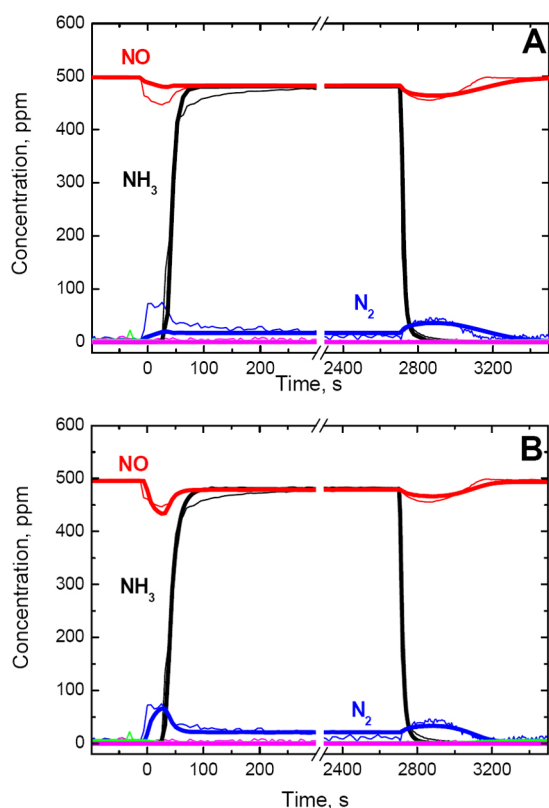


Figure 2. Transient experiments with step feed of NH_3 at 200°C. $\text{NH}_3 = 500 \text{ ppm}$, $\text{NO} = 500 \text{ ppm}$, $\text{H}_2\text{O} = 3\%$, $\text{O}_2 = 2\% \text{ v/v}$, He carrier gas, $Q = 327 \text{ cm}^3/\text{min}$. Thin lines (A, B): measured concentrations of NH_3 , NO , N_2 at reactor outlet. Thick lines (A): kinetic fit using the Single Horn model Thick lines (B): kinetic fit using the Double Horn model

In fact, such a dynamic behavior has been already reported on vanadium-based catalysts [18](and references therein), on H-ZSM-5 zeolites [19, 20] and on various Fe zeolites [1, 3, 4]. In the case of vanadium based catalysts, it was proposed that the increase in the DeNOx activity observed at NH_3 opening and shut-off was associated with an inhibiting effect of NH_3 on the standard SCR reaction [18]. It was, indeed, speculated that the Standard SCR rate-limiting step that occurs on V-sites involving a redox catalyst function, may be adversely affected by NH_3 adsorbed onto nearby acidic sites either due to electronic interaction or possibly due to direct blocking of the redox sites.

The similarities between the dynamics observed in the case of vanadium based catalysts and over the present Fe-zeolite system suggests that the inhibition effect invoked for the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ can apply to Fe-promoted zeolites as well. It is well known in the literature that the presence of suitable metals in the zeolite framework greatly enhances the SCR activity [21], while it is well established that NH_3 easily

adsorbs onto the acidic sites of the zeolite [22, 23, 24, 25]. However it has been reported in the literature that NH_3 is able to adsorb on Fe sites, too [26]. We can thus speculate that, in analogy with vanadium based catalysts, the Standard SCR rate-limiting step occurs on Fe-sites involving a redox catalyst function. The adsorption/interaction of NH_3 with these sites may result in blocking of the redox function, thus causing a decrease of the DeNOx activity.

The effect of temperature on the dynamics observed at both NH_3 feed and shut-off is presented in Figures 3 A and B (thin lines), which show the results collected feeding NH_3 for 2700s at $T = 250$ and 300°C , respectively. It appears that, qualitatively, the same transient effects were present in the outlet concentration profiles of NO and nitrogen. However, such dynamics became less pronounced as the temperature was increased. In parallel, the temperature positively affected the NO_x conversion, which increased from 4% at 200°C up to 20% at 300°C .

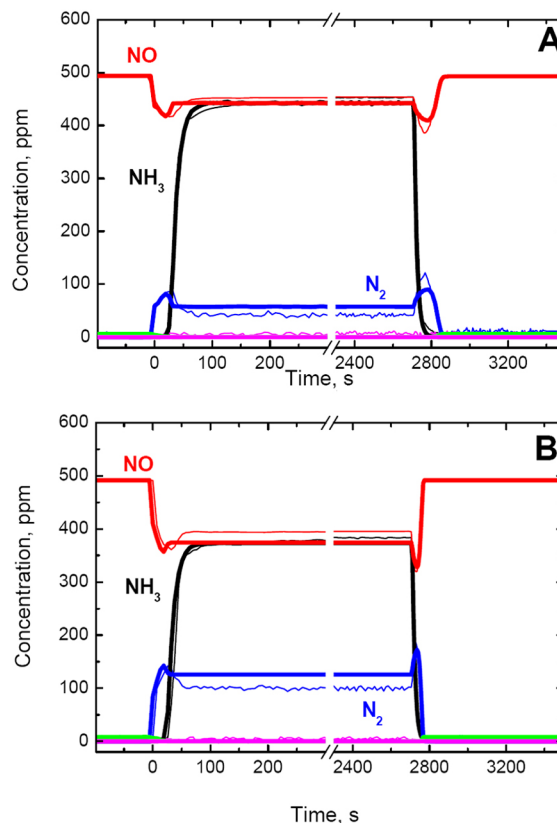


Figure 3. Transient experiments with steps feed of NH_3 at 250°C (A) and 300°C (B). $\text{NH}_3 = 500 \text{ ppm}$, $\text{NO} = 500 \text{ ppm}$, $\text{H}_2\text{O} = 3\%$, $\text{O}_2 = 2\% \text{ v/v}$, He carrier gas, $Q = 327 \text{ cm}^3/\text{min}$. Thin lines (A, B): measured concentrations of NH_3 , NO , N_2 at reactor outlet. Thick lines: kinetic fit using the Double Horn model