Kinetic modeling of NH₃-SCR over a supported Cu zeolite catalyst using axial species distribution measurements

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Abstract

In this work a kinetic model is developed for NH₃-SCR over a honeycomb-monolith-supported Cu-zeolites using intra-catalyst axial species distribution measurements. Ammonia TPD experiment, together with micro calorimetry data were used for tuning the ammonia adsorption and desorption properties. The spatial distribution for NO oxidation, NH₃ oxidation and NH₃ SCR were modeled between 200 and 400°C. Four-step protocol measurements were employed in order to validate the transient functions of the model. The resulting kinetic model provides good spatiotemporal simulation of the SCR reaction and component reactions throughout the monolith catalyst system. This work shows that intra-catalyst spatial data is an asset to developing kinetic models.

Keywords: NH₃ SCR; Kinetic modeling; Spatial distribution measurements; Cu zeolites; Spaci-MS

1. Introduction

With the depletion of fossil fuel resources and the global warming, diesel and lean-burn gasoline engines are increasingly preferred for their advantageous fuel consumption and CO₂ emissions. On the other hand they suffer from high NO_x emissions that contribute to global acidification and air pollution in urban environment. There are different concepts investigated for the catalytic reduction of NO_x into H₂O and N₂. In one technology, urea is injected into the exhausts gas to form NH₃, which is used as a reductant. The selective catalytic reduction (SCR) of NO_x proceeds on a downstream catalyst. In the quest for an

efficient, cheap and non-toxic catalyst for this application, special attention was given to metal-exchanged zeolites[1-6]. Zeolite catalysts are complex since they contain many sites with different properties and activity. The incorporation of metal atoms into the zeolite framework increases this degree of complexity due to the various possible oxidation states of the metal and the heterogeneity of the reactive sites. NH_3 -SCR of NO_x itself is a complex catalytic reaction which can be described by many pathways depending on the NO_2/NO ratio [3, 7] and is often accompanied by side reactions such as NH_3 oxidation, ammonium nitrate formation [8-10] and N_2O production [11]. Spatially resolved experiments have been performed to understand NH_3 -SCR over monolithic catalysts with SpaciMS [12] and Spaci-FTIR [13, 14]. Luo et al. [14] investigated SCR over a Fe/zeolite catalyst and observed that the catalyst zone required to meet 80 % conversion decreases according to Standard SCR > NO_2 -SCR > Fast SCR; i.e., Fast SCR requires the shortest catalyst length. The SCR catalytic zone shifts to the front with increasing temperature up to 400°C, which is in line with observations over a Cu/zeolite catalyst [12]. In addition, Auvray et al. [12] provided information on the NH_3 adsorption and storage throughout the catalyst in SCR condition and observed NH_3 inhibition at low temperature in the front of the monolithic catalyst.

Global and detail kinetic models have been built and developed to understand NH_3 -SCR reaction over the most common catalysts: supported-vanadia catalysts [10, 15], Fe-exchanged zeolites [16] and Cu-exchanged zeolites [17]. These models include side reactions, several possible routes of NO_x reduction, such as “Standard SCR”, “Fast SCR” and “ NO_2 SCR”[17], or are focused on the nature and dynamics of the active sites [18-21]. Catalysts for NO_x -selective reduction are practically coated onto a monolithic support and this system behaves like a plug flow reactor along which chemical species concentrations evolve according to reactions, adsorption and release. The models found in literature are built, fitted and validated based on effluent concentrations in various operating conditions. There is one kinetic model available in literature that is describing spatially resolved MS data for NO_x storage and reduction [22]. However, there are to our knowledge, no kinetic models available for NH_3 SCR that uses spatially resolved experiments. In-catalyst distributed measurements enable kinetic parameters to be determined under actual operating conditions, where regular data for NH_3 SCR gives very high conversion (often 100%) in a significant part of the temperature interval that makes kinetic analysis difficult. Thus, there are large advantages with using spatially resolved measurements. The objective of this work was to develop a kinetic model for NH_3 -SCR using intra-catalyst concentration profiles of species relevant for the process. NH_3 oxidation, NO oxidation, Standard NH_3 -SCR, N_2O formation as well as NH_3 adsorption and desorption were included in the model. The validation of the model was performed by evaluating its capability to capture transient response to changes in the gas composition, i.e. switching NH_3 or NO on and off.

2. Experimental

2.1. Catalyst

The catalyst used was a Cu-Beta, also denoted Cu-BEA, zeolite prepared as described in [23, 24] and washcoated on a 400-cpsi monolithic cordierite support. The silica-to-alumina ratio was 38 and was prepared using Beta zeolite from Zeolyst International. The copper content was 4.3wt-%, measured by inductively coupled plasma and atomic emission spectrometry (ICP-AES). A cylindrical catalyst core sample (25.4-mm long x 7.1-mm diameter) was used for micro reactor analysis. The catalyst was pretreated for 2h at 500°C in a gas stream containing 205 ppm NO, 183 ppm NH₃, 10% O₂, 5% H₂O and Ar balance, to simulate exhaust SCR conditions; this treatment ensures sample thermal stability during subsequent experiments.

2.2. Reactor setup and analytical technique

The system used to perform the experimental work was described in detail in a previous article [12]. The catalyst core sample was wrapped in fiber glass insulation tape, to minimize gas flow bypassing the catalyst, and placed in a quartz tube positioned in a reactor furnace. Quartz rods were placed in the tube upstream and downstream from the catalyst to reduce axial temperature gradients within the sample (only $\pm 1^\circ\text{C}$ over the 25.4-mm long catalyst). Gases were supplied by mass flow controllers and were preheated and mixed before entering the flow reactor in coiled tubing enclosed in a separate preheater furnace. All the gas lines were maintained at $>200^\circ\text{C}$ and the catalyst internal temperature was measured by a K-type thermocouple inserted in the sample (ca. mid monolith) from the reactor outlet. Analysis of the intra-catalyst gas composition was performed using SpaciMS, an instrument described elsewhere [25-29]. One fused-silica capillary (Polymicro Technologies, 50- μm I.D., 185- μm O.D., ca. 2-m long) was inserted in the monolith from the inlet and mounted on a translating system to sample the gas at any position along the channel. A second capillary was inserted in the reactor to measure the inlet gas composition. The capillaries were connected to a multiport valve, the outlet of which was linked to the mass spectrometer inlet. Thus, switching the valve allowed selecting the gas feed for the mass spectrometer. The capillaries were maintained at ca. $> 200^\circ\text{C}$ throughout their entire length. The experiment was carried out at the catalyst exit and six target intra-catalyst locations: 1/2, 3/8, 1/4, 3/16, 1/8 and 1/16 of the total monolith length. For the exit measurement, the capillary was actually positioned just inside the catalyst outlet; this allowed exclusive sampling from the measurement catalyst channel and not adjacent channels, which would complicate the analysis due to channel-to-channel performance (e.g., washcoat loading) differences. The experimental sampling positions were corrected using ammonia oxidation and SCR conversion as described in detail in [12]. The m/z ratios monitored were 15 for NH₃, 28 for N₂, 30 for NO, 44 for N₂O, 46 for NO₂ and 84 for Kr; despite these signal assignments, there were numerous cross sensitivities which were considered in our analysis.

2.3. Experimental procedure

The Cummins 4-step protocol [30] was used for analysis and consists of four successive steps at constant flow and temperature:

- Step 1 (NO oxidation): 205ppm NO, 10% O₂ and 5% H₂O in Ar
- Step 2 (Standard SCR): 205ppm NO, 183ppm NH₃, 10% O₂ and 5% H₂O in Ar
- Step 3 (NH₃ Saturation): 183ppm NH₃, 10% O₂ and 5% H₂O in Ar
- Step 4 (NO oxidation): 205ppm NO, 10% O₂ and 5% H₂O in Ar

A low concentration of Kr was included for analytical purposes. The total flow was 510 sccm (0°C & 760 Torr standard conditions) providing a space velocity of 30000h⁻¹. To assess repeatability, the 4-step protocol was repeated twice at each location and temperature, and the second was typically used for analysis. The catalyst nature was studied at 200°C, 325°C and 400°C.

3. Model

3.1. Reactor model

The model aims at reproducing the intra-catalyst evolution of the reactions occurring during NH₃-SCR. To simulate the behavior of a honeycomb-type catalytic converter, the “Aftertreatment analysis” mode of a commercial software, AVL BOOST, was used. The dimensions of the monolith used led to the following geometric surface area, GSA=2649.6 m²/m³_{monolith}. In order to optimize the computation time, several assumptions were made. All the channels were assumed similar, which reduced the system to a one dimension single channel model. The 1D channel was discretized in 15 elements in series, in which the mass balance (Eq. 1) equation was solved [31].

$$\varepsilon_g \cdot \frac{\partial \rho_g \cdot w_{k,g}}{\partial t} = \varepsilon_g \cdot \frac{\partial \rho_g \cdot w_{k,g} \cdot v_g}{\partial z} + \varepsilon_g \cdot \frac{\partial}{\partial z} \left(\rho_g \cdot D_{eff} \cdot \frac{\partial w_{k,g}}{\partial z} \right) + M_{G_{k,g}} \cdot \sum_i^I v_{i,k} \cdot \dot{r}_i(c_k^L, T_s) \quad (\text{Eq.1})$$

ε_g is the volume fraction of gas phase in entire system (-), ρ_g is the density of the gas phase (kmol/m³), $w_{k,g}$ is the mass fraction of species k in gas phase (-), $v_{i,k}$ is the stoichiometric coefficient of species k in reaction i , $\dot{r}_i(c_k^L, T_s)$ represents the molar reaction rate of the surface reaction i , and $M_{G_{k,g}}$ is the molar mass of gas phase species k (kg/kmol). The transport of species from the bulk gas phase to the surface was included and described by the film model. Considering the low working temperature range, homogeneous gas phase reactions were negligible and not taken into account in the model.

The reaction heat associated with NH₃ SCR is very small and therefore the simulations were considered isothermal, which also was the case in several earlier models for NH₃ SCR.[16-22]

BOOST allows the user to define the axial position of the simulation output. This option was convenient and enabled us to extract the simulated concentrations at the axial positions where the capillary inlet was experimentally placed for an easy comparison.

3.2. Kinetic model

The rate equations and the kinetic parameters were user-defined in a FORTRAN script executed by BOOST. The rate constants were described by the Arrhenius equation:

$$k = A \exp\left(-\frac{E_A}{RT}\right) \quad (\text{Eq. 2})$$

where A is the pre-exponential factor, E_A the activation energy (J/mol), R the gas constant (8.314 J/(mol K)) and T the temperature (Kelvin). The pre-exponential factor and the activation energy of each simulated reaction were tuned to fit the experimental data and are tabulated (Tables 1-5).

3.2.1. NH_3 adsorption and desorption

The model included NH_3 adsorption and desorption on catalytic sites of the Cu-BEA, denoted S1 (see table 1). It was considered as a non-activated step and the activation energy of adsorption was set to 0, which has been the case in many models for NH_3 SCR [16, 17]. Unlike adsorption, the ammonia desorption is an activated process, the activation energy of which is coverage dependent. The activation energy of NH_3 desorption was expressed using a Temkin isotherm, which considers the adsorbate-adsorbate interactions:

$$E_{\text{NH}_3, \text{des}} = E_{\text{NH}_3, \text{des}}^0 (1 - \alpha \theta_{\text{NH}_3}) \quad (\text{Eq. 3})$$

where α is a constant fitting parameter, θ_{NH_3} the NH_3 coverage and $E_{\text{NH}_3, \text{des}}^0$ the activation energy for 0 coverage. An alternative explanation for the coverage dependent activation energy is that in zeolites there is a range of acidity for the sites, and a coverage dependent barrier reflects this inhomogeneity. A coverage dependent activation energy for NH_3 desorption has been used in many kinetic models [16, 19, 20, 32] and is in line with micro-calorimetric experiments by Wilken et al. [23]. Micro-calorimetry experiments on Cu-BEA powder from the same batch as is used in this study resulted in heat of adsorption of 112.75 kJ/mol with a coverage-dependence α of 0.39. These values were used in the model. NH_3 adsorption followed by TPD was performed in order to experimentally measure the number of copper sites and to fit the adsorption/desorption parameters, which are reported in table 1. Since no storage of nitric oxide was observed, even at 200°C, NO adsorption was not taken into account.

3.2.2. NH_3 and NO oxidation

Zeolites are active for oxidation of NO and NH_3 [6, 33]. Oxidation of NH_3 by oxygen leads to an overconsumption of NH_3 [14] while NO_2 , produced by NO oxidation, improves the SCR process via the “Fast SCR” mechanism. The oxidation of NH_3 was modeled by the reaction of NH_3 , adsorbed on S1, and O_2 present in the gas phase. However, this is a global model and does not mean that physically the oxygen is in the gas phase. The only product formed during the experiment was N_2 , therefore only one reaction was included in the model to describe ammonia oxidation. The steady-state concentrations of NH_3 and N_2 at various intra-catalyst axial positions during the step 3 were used to tune the parameters. The tuning of NO oxidation parameters followed the same approach. In the model, NO oxidation was described as a global reaction dependent on NO and O_2 concentration (table 2). In the same

way as for NH_3 oxidation, this is a global kinetic model using gas phase concentrations but in reality, the reaction occurs on the surface. These two reactions were studied independently to determine their kinetic parameters, which were subsequently used in the simulation of NH_3 SCR and of the whole 4-step experiments aiming at validating the model. The activation energies were taken from the experimental kinetic study of Mihai et al. [34] over a Cu-BEA catalyst containing 4 wt.% Cu. The pre-exponential factors were determined by manual tuning.

3.2.3. NH_3 SCR

NH_3 SCR in excess oxygen was modeled by only one reaction corresponding to the “Standard SCR”. The “Fast SCR” and the NO_2 -SCR reactions were not added to simplify the model since NO_2 was not present in the gas feed and NO oxidation was significant only at 400°C, however with significantly low rate compared to NH_3 SCR. Activation energy for NH_3 SCR was taken from Arrhenius experiments presented by Mihai et al. [34] and the pre-exponential factor was manually tuned, as for the NO and NH_3 oxidation reactions, to fit the experimental steady state distributed concentrations of N_2 , NH_3 , and NO. Since NO oxidation and NH_3 oxidation may occur in lean SCR conditions, these reactions were accounted for in the modeling of the SCR step using the parameters determined in these previous sub-models.

3.2.4. N_2O formation

During SCR of NO with NH_3 , formation of N_2O has been observed on various metal-exchanged zeolite catalysts [3, 8, 11]. The source of N_2O is unclear and several pathways have been proposed. Nevertheless, there is a correlation between NO_2 and N_2O since the production of the latter increases with NO_2 concentration [3, 4]. N_2O release has been explained by formation and subsequent decomposition of ammonium nitrate, direct oxidation of NH_3 or SCR with a different stoichiometry. These side reactions should be avoided since they consume NH_3 and produce N_2O , the emission of which is an environmental issue due to its significant greenhouse gas potential. The type of SCR catalyst as well as the operating temperature is among the factors influencing N_2O selectivity. On Cu-BEA zeolites, a high N_2O selectivity at low temperature (200°C) and high (400°C) temperature has been noticed [12]; however, at 325°C, the N_2O formation was less. Two pathways were therefore included in our model to simulate the N_2O production: the low-temperature pathway, involving the formation of an adsorbed NH_3 -NO complex, and the high-temperature pathway, involving reaction between adsorbed NH_3 and NO, see Table 5. The reaction mechanism for N_2O production used in this work was developed in an earlier study, using a broad range of temperatures and varying NO_2/NO_x ratio [35].

3.3. Model validation

Whereas the steady state distributed experimental data from the 4-step protocol were used to determine the kinetic parameters of the individual reactions, the transients associated

with the various gas-composition steps in the protocol were used to validate the model. The whole protocol was therefore simulated and compared to the experimental results.

4. Results and discussion

4.1. NH₃ Temperature Programmed Desorption (TPD)

After exposing the catalyst until saturation to a gas stream containing 183 ppm NH₃ at low temperature (40°C), the NH₃ flow was shut off. During the NH₃ step, the catalyst stored a substantial amount of ammonia. A fraction of the stored amount was released when NH₃ was removed from the flow, forming a long tail on the NH₃ profile, which is in line with earlier studies [17, 32, 36]. Next, the temperature was progressively increased at 5°C/min to 600°C in order to release the remaining of NH₃ stored during the exposure. The quantitative NH₃ outlet concentration profile is shown in Figure 1. The amount adsorbed and released ammonia was calculated and used to fit the number of active sites, which is a crucial parameter for the kinetic model. Adsorption was considered as a non-activated step and the activation barrier was set to zero, which was done in several other studies [19]. The pre-exponential factors for adsorption and desorption were fitted to reproduce the shape of the associated data in Figure 1. Due to interaction between ammonia molecules, or alternatively non-homogeneous strength of the acid sites, a coverage-dependent expression was used for the activation energy of desorption (Eq. 3). As described in section 3.2.1, the coverage dependent activation energy was determined using micro-calorimetry. The fitted parameters are reported in table 1 and the results in Figure 1 shows good agreement between the experimental and simulated NH₃ TPD profile. The number of S1 sites in the model was 0.0257 mol/m², i.e. 68.1 mol/m³_{monolith} (Geometric surface area, GSA=2649.6 m²/m³_{monolith}).

Figure 1: NH₃ adsorption and Temperature programmed desorption. 183 ppm NH₃, T=40°C (T_{cat}=56°C).

Table 1: Equations and kinetics parameters for NH₃ adsorption and desorption from TPD experiments.

Reaction	Equation/ Reaction rate	Pre-exponential factor ^a (kmol/(m ³ ·s))	Activation energy (kJ/mol)
NH₃ adsorption	$\text{NH}_3 + \text{S1} \rightarrow \text{NH}_3\text{-S1}$ (r.1f) $r_{1f} = k_{1f} * \theta_v * [\text{NH}_3]$	9279 ^b	0
NH₃ desorption	$\text{NH}_3\text{-S1} \rightarrow \text{NH}_3 + \text{S1}$ (r.1b) $r_{1b} = k_{1b} * \theta_{\text{S1-NH}_3}$	$6.8 \cdot 10^8$ ^b	113.0 ^c

^a The unit for the reaction rate is kmol/(m³·s) and the gas phase concentrations are dimensionless.

^b Fitted.

^c Parameters from micro-calorimetry experiments. $\alpha=0.39$.

4.2. NO oxidation

In step 1 of the 4-step protocol, NO was flowed together with oxygen and water vapor. In these conditions, oxidation of NO into NO₂ could take place provided that the temperature was high enough. Oxidation of some NO was observed at 400°C (Figure 2 b) and, to a less extent, at 325°C (Figure 2 a), whereas no activity was noted at 200°C. The extent of reaction could be measured along the catalyst and then modeled. The activation energy of 39.6 kJ/mol, reported by Mihai et al. [34] for NO oxidation over Cu-BEA catalyst containing 4 wt.%

259 Cu, was used and yielded a good agreement with the experimental data as shown in Figure
 260 2. This value was close to the activation energy reported by Olsson et al. [17] on Cu-ZSM-5
 261 (48 kJ/mol) and Metkar et al. on Fe-ZSM-5 (48 kJ/mol) and Cu-chabazite (56 kJ/mol) [32]. The
 262 model predicts a rather linear evolution of NO and NO₂ in the monolith, especially at 325°C.
 263 However, the experiment conducted at 400°C showed a linear evolution in the front half of
 264 the catalyst followed by constant NO and NO₂ concentration in the rear half catalyst. The
 265 decrease in NO oxidation rate experimentally observed at the monolith end is likely due to
 266 NO₂ inhibition of NO oxidation. This has been suggested for NO oxidation over Fe-ZSM-5 and
 267 Cu-chabazite [37]. NO₂ inhibition was not included in the model because the experiments
 268 were carried out feeding only NO; our intra-catalyst results suggest the necessity of including
 269 the inhibition effect and more data would be needed for describing the trend such as the
 270 apparently greater inhibition at 325 °C than 400 °C. The parameters used in the simulation
 271 are shown in Table 2.

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Figure 2: NO oxidation (205 ppm NO, 10% O₂, 5% H₂O): experimental (solid lines) and simulated (dotted lines) intra-catalyst NO and NO₂ concentration profiles. (a) 325°C, (b) 400°C.

Table 2: Estimated kinetic parameters for NO oxidation, step 1 of the 4-step protocol.

Reaction	Equation/ Reaction rate	Pre-exponential factor ^a (kmol/(m ³ ·s))	Activation energy (kJ/mol)
NO oxidation	$\text{NO} + 0.5 \text{O}_2 \rightleftharpoons \text{NO}_2 \quad (\text{r.2})$ $r_2 = k_{2f} * [\text{NO}] * [\text{O}_2]^{0.5} - k_{2b} * [\text{NO}_2]$	$2.5 \cdot 10^4$ ^b	39.6 [34]

^a The unit for the reaction rate is kmol/(m³·s) and the gas phase concentrations are dimensionless.

^b Fitted.

4.3. NH₃ oxidation

In the presence of O₂ and water, ammonia was oxidized on Cu-BEA at 325 and 400°C. This reaction can occur in parallel during NH₃-SCR and it is therefore important to accurately determine its kinetic parameters. Figure 3 shows the spatial evolution of NH₃ and nitrogen concentrations during step 3 (NH₃ oxidation) at both 325 (Figure 3 a) and 400°C (Figure 3 b). The activation energy was fixed to a literature value [34]. Hence, by tuning only the pre-exponential factor, very good agreement at both temperatures was difficult to get. Since the NH₃ oxidation was more significant at high temperature, the data obtained at 400°C were the focus of the fitting procedure. At 325°C, the parameters reported in Table 3 resulted in a slightly faster NH₃ consumption compared to the experimental results. It should be noted that, at 325°C, the last experimental point (position=1 catalyst length) shows unexpected

high N_2 value ($N_2/NH_3_{consumed}=1.27$), which might be due to measurement uncertainties; nevertheless, all other NH_3 and N_2 data points from the experiments and modeling indicate the 2-to-1 $NH_3:N_2$ stoichiometry, which is given by r.3 in Table 3. At 325°C, both the model and the experiments show a rather linear NH_3 consumption and N_2 formation along the monolith (Figure 3 a). At 400°C, the concentrations evolved rapidly in the front half of the catalyst until full conversion was reached. The model was able to simulate intra-catalyst concentrations of N_2 and NH_3 during NH_3 oxidation adequately (Figure 3). The activation energy value used for NH_3 oxidation (99.5 kJ/mol) was obtained by Mihai et al. using Arrhenius plots for 4% Cu/BEA. This value was close to the 97.36 kJ/mol reported by Sjövall et al. [19] on Cu-ZSM-5. The reaction order of oxygen (β_1 in Table 3) was, in the simulations, 0.6 and was tuned to separate experiments with varying O_2 concentration (results not shown here).

Figure 3: NH₃ oxidation (183 ppm NH₃, 10% O₂, 5% H₂O): experimental (solid lines) and simulated (dotted lines) intra-catalyst NH₃ and N₂ concentration profiles. (a) 325°C, (b) 400°C.

Table 3: Estimated kinetic parameters for NH₃ oxidation, step 3 of the 4-step- protocol.

Reaction	Equation/ Reaction rate	Pre-exponential factor ^a (kmol/(m ³ ·s))	Activation energy (kJ/mol)
NH₃ oxidation	$4\text{NH}_3\text{-S1} + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} + 4\text{S1}$ (r.3) $r_3 = k_3 * \theta_{\text{S1-NH}_3} * [\text{O}_2]^{\beta_1}$	$3.0 \cdot 10^6$ ^b	99.5 [34]

^a The unit for the reaction rate is kmol/(m³·s) and the gas phase concentrations are dimensionless. ^bFitted.

4.4. NH₃ SCR

The parameters determined previously for NO and NH₃ oxidation as well as for NH₃ adsorption and desorption were held constant and used when tuning the NH₃-SCR parameters. The reaction order of oxygen (β_2 in Table 4) was determined as described for β_1 , and the value of 0.5 was used in the simulations. The catalyst was active for SCR at all three temperatures. In addition, side reactions occurred, yielding N₂O. During the SCR step, ammonia is the key component since it is involved in NH₃ storage, NH₃ oxidation, NH₃-SCR and N₂O formation. A good agreement between the model and measurements was observed for the intra-catalyst concentration profiles of NH₃, NO and N₂. The experimental concentration profiles at 200°C (Figure 4 a) show a rather linear evolution in the front half of the monolith. At 325°C (Figure 4 b), this trend applies only through the front quarter of the catalyst where almost complete consumption of ammonia is reached. At both temperatures,

the model slightly overestimates the reaction rate in the catalyst front and could not capture the linear aspect. At 400°C, the rapid consumption of NO and NH₃ in the catalyst front as well as the exponential shape of the profiles (Figure 4 c) are accurately reproduced by the model. The model slightly overestimates NO consumption throughout the catalyst while the gap between experimental and simulated N₂ profiles is mostly due to experimental uncertainties on N₂ measurements, leading to an N-balance of ≈110% through the whole catalyst. In general, the model agrees well with the SCR experimental data. The activation energy of SCR (107.8 kJ/mol) measured by Mihai et al. [34] was relatively high for a 4 wt.% Cu-BEA zeolite catalyst while lower values were obtained for Cu/BEA with lower copper loadings. The high activation energy resulted in a high pre-exponential factor in order for the SCR to occur with a significant rate at low temperature. Using this pre-exponential factor ($4 \cdot 10^{13}$ kmol/(m³s)) resulted in a good agreement of the model at 200°C (Figure 4 a) and a similarly good fitting at 325°C (Figure 4 b). Figure 4 c shows excellent results for the 400°C case.

Figure 4: NH₃-SCR (183 ppm NH₃, 205 ppm NO, 10% O₂, 5% H₂O): experimental (dotted lines) and simulated (solid lines) intra-catalyst NO, NH₃ and N₂ concentration profiles. (a) 200°C, (b) 325°C, (c) 400°C.

Table 4: Equation and estimated kinetic parameters for ammonia SCR, step 2 of the 4-step protocol.

NH ₃ SCR equation/ Reaction rate	Pre-exponential factor ^a (kmol/(m ³ ·s))	Activation energy (kJ·mol ⁻¹)
$4 \text{ NH}_3\text{-S1} + 4 \text{ NO} + \text{O}_2 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O} + 4 \text{ S1} \quad (\text{r.4})$ $r_4 = k_4 * \theta_{\text{S1-NH}_3} * [\text{NO}] * [\text{O}_2]^{\beta_2}$	$4 \cdot 10^{13} \text{ }^b$	107.8 [34]

^a The unit for the reaction rate is kmol/(m³·s) and the gas phase concentrations are dimensionless.

^b Fitted.

4.5. NH₃ coverage

The SCR catalyst is able to store ammonia as observed in our experiment during step 2 and 3. Simultaneously, our model includes the consumption of surface NH₃ by the reaction with NO and oxygen and the equilibrium of surface NH₃ with gas phase NH₃. According to these factors, NH₃ surface coverage, defined by the number of sites occupied by NH₃ divided by the total number of sites was calculated along the catalyst length. Figure 5 presents the calculated NH₃ coverage and the fraction of vacant sites during SCR (step 2), at steady state. It can be seen that ammonia coverage decreases through the catalyst from the inlet to the outlet. In parallel, the concentration of vacant sites increases. The operating temperature has a major effect on the NH₃ surface coverage since desorption becomes faster at higher temperature, and the equilibrium is shifted towards the gas phase. The NH₃ SCR reaction also occurs with a higher rate at higher temperature, in the studied temperature range. In addition, ammonia oxidation might occur, although the rate was significantly lower compared to SCR in the studied interval. A correlation can be established between the location where the NH₃ coverage reaches zero and the location where NH₃ is fully consumed, at all three temperatures. At 200°C (Figure 5 a), the ammonia coverage was very near zero close to the outlet where the ammonia gas phase concentration was zero; note that the distributions in the catalyst back are limited by the reported data density, and the actual distribution in this region is not expected to be linear. At 325°C (Figure 5 b), the null ammonia coverage and ammonia concentration were observed from 3/16 of the total length. The coverage at 400°C was very close to zero already at the inlet position (Figure 5 c). At 200°C, the NH₃ coverage was over 0.5 in the whole front half while at 325°C, it was significant only in the front of the SCR catalyst. These coverage simulation results are consistent with our experimental measurements of distributed coverage at 200 and 325°C in terms of both shape and spatial extent [cf. Fig.9 and associated discussion in reference 12].

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Figure 5: Simulated NH₃ coverage and fraction of free sites during NH₃ SCR at (a) 200°C, (b) 325°C, (c) 400°C. Steady state profile throughout the catalyst.

4.6. N₂O formation

NH₃-SCR catalysts convert NO into N₂ and may produce N₂O as side-product. N₂O formation should be minimized to obtain the N₂ selectivity as close to 100 % as possible. The Cu-BEA catalyst tested in the present study produced N₂O during SCR in various proportions depending on the temperature (Figure 6). The outlet N₂O concentration was 18 ppm at 200°C, 11 ppm at 325°C and 15 ppm at 400°C. The production of N₂O has therefore no linear temperature dependence and cannot be explained by only one reaction following Arrhenius' kinetic law. Instead, N₂O concentration is higher at 200°C and 400°C than at 325°C, describing two peaks of formation, at low and high temperature. Delahay et al. [11] correlated the presence of CuO aggregates to the low temperature N₂O formation. Centi et al. [38] suggested that N₂O formation originates from the decomposition of ammonium nitrate intermediate, at low temperature. At high temperature, Delahay et al. [11] postulated copper ions or copper dimers [CuOCu]²⁺ as active species in the formation of N₂O. Thus, two paths are proposed to model N₂O formation and a mechanism developed by Supriyanto et al. [35] was used in this work. The low temperature path involves the formation of a surface NH₃-NO complex that decomposes into N₂O. This complex is, in the model, formed on the sites S1 (see Table 5, r6f). This complex formation is reversible and the backward reaction, r6b, is also shown in Table 5. The reversibility is crucial to describing the lower N₂O formation at 325°C. The NH₃-NO complex can also decompose to form N₂O (see Table 5, r7). The lower thermal stability of the NH₃-NO complex at 325°C vs. 200°C is the

reason for the lower N₂O at 325°C in the model and measurements. The second N₂O formation path is active at high temperature and described by the reaction of NH₃ adsorbed on S1 sites with gas phase NO and O₂ to produce N₂O; this is shown in Table 5 as the ‘direct – high temperature’ reaction. Since this is a global reaction step, gas phase NO and O₂ were used for simplification. However, the real mechanism is through adsorbed species. By using these two N₂O mechanisms, it was possible to account for the relatively high N₂O formation at low (200°C) and high (400°C) temperatures and the lower production at intermediate temperature (325°C). The reaction equations and the optimized kinetic parameters are reported in Table 5, where the activation energies were taken from Supriyanto et al. [35].

Table 5: Equations and estimated kinetic parameters for N₂O formation during NH₃-SCR.

Reaction	Equation/ Reaction rate	Pre-exponential factor ^a (kmol/(m ³ ·s))	Activation energy (kJ/mol)
N₂O formation (direct - high temperature)	2NH ₃ -S1 + 2NO + O ₂ → N ₂ O + 3H ₂ O + 2S1 (r.5) $r_5 = k_5 * \theta_{S1-NH_3} * [NO] * [O_2]$	1.7·10 ¹⁶ ^b	140.0 [35]
N₂O formation (indirect - low temperature)			
surface complex formation	NH ₃ -S1 + NO → S1-NH ₃ -NO (r.6f) $r_{6f} = k_{6f} * \theta_{S1-NH_3} * [NO] * \theta_v$	1·10 ⁴ ^b	0 [35]
surface complex dissociation	S1-NH ₃ -NO → NH ₃ -S1 + NO (r.6b) $r_{6b} = k_{6b} * \theta_{S1-NH_3-NO}$	1·10 ⁸ ^b	34.0 [35]
surface complex decomposition	2S1-NH ₃ -NO + O ₂ → N ₂ O + N ₂ + 3H ₂ O + 2S1 (r.7) $r_7 = k_7 * \theta_{S1-NH_3-NO} * [O_2] * \theta_v$	2·10 ⁶ ^b	29.0 [35]

^aThe unit for the reaction rate is kmol/(m³·s) and the gas phase concentrations are dimensionless. ^bFitted.

The results in Figure 6 suggest that N₂O formation, like the SCR reaction, becomes faster when the temperature increases. Indeed, the slope of the N₂O profile at the catalyst inlet increases with temperature. However the outlet N₂O concentration did not follow the temperature since the highest integral N₂O production occurred at 200°C (Figure 6 a) and the lowest at 325°C (Figure 6 b), as previously discussed. At 200°C the low temperature route mostly contributes to N₂O production while at 400°C, N₂O profile was not affected by the low temperature mechanism. The N₂O profiles, calculated by our model, match well the experimental profiles at all three temperatures.

Figure 6: N₂O formation as a by-product of NH₃-SCR. The inlet feed consisted in 183 ppm NH₃, 205 ppm NO, 10% O₂, 5% H₂O. Experiment (solid lines) and simulation (dotted lines) intra-catalyst N₂O concentration profiles. (a) 200°C, (b) 325°C, (c) 400°C.

4.7. Model validation: 4-step protocol transient behavior

The transient aspects of the 4-step protocol were used to validate the model. Each step showed transient phenomena like NH₃ storage (Step 2 and 3), non-steady state reaction (all steps) and reaction between gas species and stored species (Step 4). The full transient protocol was simulated using the optimized kinetic parameters fit to the steady state intra-catalyst axial concentration profiles. The NO, NH₃, N₂ and N₂O profiles at 0.5L and 200°C were compared to the simulation results (Figure 7). The comparison is shown for position 0.125L and 0.25L at 325°C (Figure 8) and 400°C (Figure 9), respectively. The results shown are representative of different settings, namely temperature and axial position. In addition, these positions are all within the SCR zone of the catalyst at their respective temperature, which means that NH₃ concentration during SCR step was not null and can be compared. In the first example, at 200°C and 0.5L, the model yields a very good agreement with the experiments (see Figure 7). At this position, both the steady-state spatial profiles and the transient curves of NO (a), NH₃ (b), N₂ (c) and N₂O (d) match well. In the first step, NO oxidation was not significantly occurring, which was accurately described by the model. Thereafter, ammonia was added to the feed gas mixture, resulting in SCR reaction. Large ammonia storage is apparent and only small amounts (ca. 20 ppm) of ammonia were passing through the catalyst at this location. Since the ammonia coverage was increasing during Step 2, the reaction rate for SCR was increasing. This resulted in an increased NO conversion with

446 time, which the model predicted very well. In addition N_2O was observed during this step. In
447 Step 3, NO was turned off and further ammonia storage was visible followed by a
448 breakthrough. In Step 4, ammonia was shut off and NO started, causing the stored ammonia
449 to react with NO forming N_2 and N_2O . The N_2O peak was slightly over-predicted, but in
450 general the model described the transient features of the four-step protocol very well.

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Figure 7: Full transient 4-step protocol as model validation: experiment (solid lines) and simulation (dashed lines) intra-catalyst concentration profiles at 200°C and 0.5L location; the three vertical dashed lines indicate the progressive transition times between protocol steps 1, 2, 3 & 4. (a) NO, (b) NH₃, (c) N₂, (d) N₂O.

At 325°C and the 1/8L position (Figure 8), the model had a somewhat too high NH_3 SCR rate illustrated by the lower steady-state concentrations of NO and NH_3 (Figure 4 b). The slight overproduction of N_2 in step 2 and step 4 is consistent with this prediction. NH_3 oxidation was also overestimated using an activation energy of 99.5 kJ/mol [34], as shown by the NH_3 level during step 3 on Figure 3 b. These offsets at the steady state portions of the protocol are consistent with the steady state spatial results in Figure 4. Nonetheless, the transient progression of the three species to reach steady state was in good agreement with the experimental profiles during all four steps. The concentration profile features for N_2 were particularly well-captured by the model. The N_2 peak at the beginning of step 4 matched well the experiment and the N_2 level during SCR was also very close to the experimentally measured values. N_2O is, at 325°C, well-described by the simulation in step 4 (Figure 8 d), as shown by the appearance of the characteristic peak immediately after the change of the gas composition. This peak at the beginning of Step 4 is the result of NO in Step 4 reacting with the large quantity of stored ammonia on the catalyst surface from Step 3 to form N_2 and N_2O until the surface ammonia is depleted.

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Figure 8: Full transient 4-step protocol as model validation: experiment (solid lines) and simulation (dashed lines) intra-catalyst concentration profiles at 325°C and 0.125L location. (a) NO, (b) NH₃, (c) N₂, (d) N₂O.

Figure 9 shows the experimental and simulated concentrations at 400°C after the front quarter of the catalyst. The transient concentration changes were again captured well by the model. The steady state concentrations of all compounds including N₂O were in general agreement with the experiments during SCR and consistent with the steady state spatial results in Figure 4. Note that, at this high temperature, the coverage of ammonia (Figure 5 c) on the surface is low, which results in rapid outlet gas changes when changing the inlet gas composition, which was not the case at low temperature (compare with Figure 7).

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495 **Figure 9: Full transient 4-step protocol as model validation: experiment (solid lines) and simulation**
 496 **(dashed lines) intra-catalyst concentration profiles at 400°C and 0.25L location. (a) NO, (b) NH₃, (c)**
 497 **N₂, (d) N₂O.**

498

499 **Conclusions**

500 The NH_3 -SCR of NO over a honeycomb-monolith-supported Cu-BEA catalyst was modeled at
501 three temperatures: 200, 325 and 400°C. In this work, intra-catalyst spatially resolved gas
502 composition data were used instead of integral effluent values to determine kinetic
503 parameters of the various reactions. Several reactions were also studied separately in order
504 to determine their kinetic parameters for inclusion in the full SCR simulation. The kinetic
505 parameters of NH_3 adsorption and desorption were determined with an ammonia TPD
506 experiment and earlier calorimetric measurement. NO oxidation was described by a global
507 reaction depending on NO and oxygen concentration. In addition, the spatial profile of NH_3
508 oxidation was modeled separately. These submodels were used together when the
509 simulation of NH_3 -SCR was performed. The steady state concentration of NH_3 , NO and N_2 at
510 different positions along the catalyst during NH_3 -SCR were well predicted by the model.

511 Two routes were envisaged to model the N_2O formation. To predict the low temperature
512 N_2O production, the formation of a surface complex was proposed. According to this route,
513 N_2O production decreases with temperature due to thermal decomposition of the NH_3 -NO
514 surface complex, which agrees well with the lower N_2O concentration at 325°C. The reaction
515 between NO, NH_3 and O_2 yielding N_2O with the adequate stoichiometry represents the
516 second route and is responsible for the N_2O production at high temperature.

517 To validate the model, the whole experiment, composed of a series of concentration steps,
518 was simulated. The model could reproduce, with a good temporal agreement, the transition
519 from NO oxidation (Step 1) to SCR (Step 2), the NH_3 storage in the NH_3 oxidation step (Step
520 3) following the SCR step and the reduction of NO by the stored ammonia in Step 4
521 ($\text{NO} + \text{O}_2 + \text{H}_2\text{O}$), yielding a characteristic N_2 and N_2O puff. Our spatially-resolved results point
522 out that some disagreements may exist between model predictions and experimental data
523 at intra-monolith position, while good agreement is reached at outlet conditions. This fact
524 emphasizes the necessity to consider spatial measurements and kinetic modeling for a
525 better characterization of catalytic performance of monolithic catalysts.

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