Investigation and Enhancement of a Cu-ZSM-5 SCR Catalyst Model

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Abstract

Title: Investigation and Enhancement of a Cu-ZSM-5 SCR Catalyst Model
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Date: 2013 - August

The aim of this study has been to enhance LOGE's semi-detailed Cu-ZSM-5 SCR catalyst model in areas where it lacks to catch important effects. It is important to have an accurate and CPU efficient kinetic model for the catalysis in the work towards minimizing polluting NO_x in the exhaust gas from diesel engines.

Investigations were done on the kinetic model through a few transient experiments including NO oxidation, NH_3 oxidation and a NH_3 SCR experiment. The effects were tested when adjusting different parameters and an adsorption reaction for NO_2 was added to the kinetic model. The simulated results were compared with experimental values. Adjustment on the kinetic parameters in the NO oxidation reaction led to a slight enhancement and results also showed that the additional adsorption reaction was sufficient to catch the desired effects.

This work shows that a semi-detailed kinetic model is sufficient to capture important effects in the catalytic reduction. The model would however need to be validated through more experiments in order to generalize the results. For further improvements on the model a more complex kinetic model would be required, which could include adsorption of more species and alternative reactions.

Key words: Catalyst, Cu-ZSM-5, SCR, modelling, chemical kinetics.

Contents

1   Introduction

In this thesis work LOGE's Cu-ZSM-5 SCR catalyst model is investigated. The model will henceforth be referred to as *LOGE's model* or simply *the model*. The model is used to simulate the aftertreatment of gas from a diesel engine and it captures effects such as external diffusion, storage, inhibition, heat transfer etc. It is important for diesel cars to have a good process for the aftertreatment in order to minimize the exhaust of toxic nitrogen oxides. A model like the one investigated here could be of a great importance in that development. In this work the model has been analysed through transient simulations and includes a parameter sensitivity study.

1.1   Problem Formulation

LOGE's model agrees well with experiments in many areas, but there are some important effect that the model does not capture. There are two main properties in the experimental results from a transient NH_3 SCR experiment executed by Olsson et al. [1] that can not be seen in LOGE's model.

- At the time of the first temperature increase experimental results show a large peak in the ammonia output followed by a large decrease. LOGE's model shows these effects as well. However, where experiments show a rapid drop in ammonia before it increases to a new stable level, the model approaches the same stable level from the peak in a slope-like manner.

- For higher temperatures, experiments show an increasing amount of NO_2 in the outlet gas. The amount of NO_2 increases along with the temperature until it reaches 500°C upon which it decreases slightly. The model, however, shows an increase of NO_2 at this temperature step. This is a very weak effect, but still an interesting one.

The effects described above can be due to various reasons such as missing reactions, incorrect reaction rates, diffusion effects or computational errors. The aim of this work is to investigate which processes are missing and whether they are chemical, physical or something else. When the problems have been located the goal is to highlight the areas where the model differs from experimental results in order to fill the knowledge gap and thereby enhance the accuracy of the model.

1.2 Background

This section presents the background that has motivated this study. This includes results and arguments from previous research such as the chemistry the model is based on and simulations that has been redone in this work.

In *A kinetic model for ammonia selective catalytic reduction over Cu-ZSM-5* written by Olsson et al. [1] an extensive study involving a Cu-ZSM-5 SCR catalyst is presented. The authors have developed a kinetic model which has been calibrated and validated through several experiments. Their kinetic model has a semi-detailed surface chemistry. In practice, this means that they have included a site onto which NH_3 can adsorb as well as surface reactions with NH_3. The paper emphasises the importance of having a good description of ammonia adsorption in the catalyst. In a later paper Sjövall et al. [2] present a kinetic model with a more detailed surface chemistry including adsorption of NO_2, NH_3, O_2 and H_2O. Also Colombo et al. [3] present a detailed surface chemistry where they emphasize on the adsorption of NO_2 and on the details in the reduction reactions.

The importance of oxidation of NO to NO_2 as the rate limiting reaction in the NH_3 SCR has been suggested by M. Wallin et al. [4]. The oxidation is also affected by the adsorption of NO_2 according to M. Colombo et al. [3]. In [3], the authors present a kinetic model that includes a detailed adsorption reaction where NO_2 reacts with adsorbed OH and to produce adsorbed ONO, adsorbed NO_3 and H_2O.

LOGE's model is based on the semi-detailed chemistry from Olsson et al. [1]. Experimental and simulated results from [1] have been compared to results obtained with LOGE's model.

1.3 The Cu-ZSM-5 SCR Catalyst Model

The catalyst investigated in this work is an ammonia selective catalytic reduction (NH_3 SCR) model over Cu-ZSM-5. The simulation tool investigated in this work is a one-dimensional model which simulates the aftertreatment catalytic processes of exhaust gas from a diesel engine. The aim of the model is to do accurate simulations while being numerically fast and comparably easy to simulate. This means that the complexity of the model needs to be high enough to capture necessary effect, while not being too complicated in order to avoid numerous calibration parameters.

The purpose of a catalyst is to increase the reaction rate for certain reactions while not itself being consumed. Catalysis is used in the aftertreatment of exhaust gas with the purpose of having toxic gases undergo chemical reactions and thus minimizing the amount of toxic gas polluting the environment. In order for the catalyst to be as effective as possible it should have a large surface area so as to maximize the amount of gas in contact with the catalytic material. This is achieved by division of the catalyst monolith into channels, each surrounded by a porous washcoat, see Figure 1. In this work, only a single channel is used and therefore heat conduction between channels is not taken into account. The flow of gas and heat transfer is calculated as a function of the distance along the catalyst, see Figure 2.
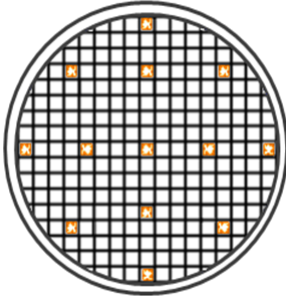

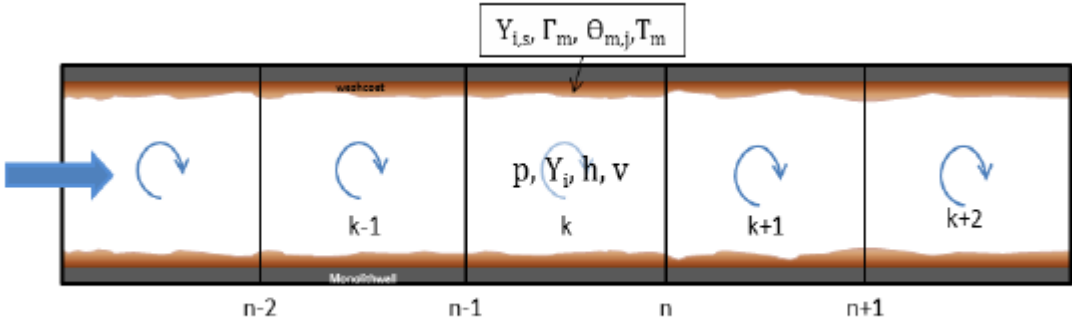Figure 1: Catalyst monolith divided into channels.

Figure 2: Channel model discretized into cells. The pressure p, mass fraction Y_i, enthalpy h and velocity v is calculated in the bulk gas as a function of distance along the catalyst. The adsorbed species mass fraction $Y_{i,s}$, site fraction $\theta_{m,j}$ and temperature T is calculated in the thin film layer. The surface site density Γ_m is assumed to be constant [6].

There are two zones in the channel that are modelled separately; the gas within the channel that is in no contact with the washcoat surface, *the bulk gas*, and the gas near and inside the surface, *the thin film layer* [5].
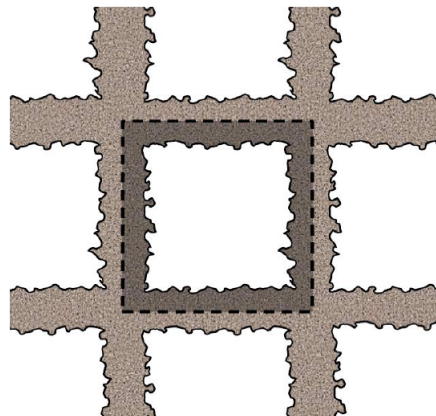
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Figure 3: Cross section of a channel model where the dark grey area indicate the thin film area.

Figure 3 shows the cross section of a channel with the thin film layer illustrated in darker grey. The channel is divided into a series of cells with length Δx. The bulk gas in each cell is modelled as a perfectly stirred reactor (PSR) where species concentration, site fractions, enthalpy and temperature in the cell are solved. Transport between the bulk gas and the thin film layer are calculated by Sherwood and Nusselts numbers [5]. The evolution of the thin film area can be simulated using either a global or a detailed chemistry. A global chemistry implies that there is no adsorption onto the catalytic surface and reactions are described as gas phase reactions. A detailed chemistry however includes adsorption onto the surface as well as surface reactions with the adsorbed species. LOGE's catalyst uses a semi-detailed chemistry for the thin film layer which includes adsorption of ammonia only and surface reactions with adsorbed ammonia. This allows for a good agreement with experiments while still having a CPU efficient model with a comparably low number of parameters to calibrate.

2   Theoretical Background

This section summarizes the theoretical background needed for this work. It involves the chemical kinetics which explain how reaction rates are calculated, the basics of catalysis and especially the selective catalytic reduction which is the main focus of this work. Included in the section about the SCR are the chemical reactions used to describe the catalysis in LOGE's model.

2.1 Chemical Kinetics

The activity of a catalyst is governed by chemical reactions which can be divided into gas phase reactions and surface reactions. Gas phase reactions, as the name suggests, occur while the reacting species are in their gas form while surface reactions requires at least one of the reactants to be adsorbed onto a surface. Which chemical reactions that occur and the rates of these reactions are affected by a number of environmental factors, e.g. the substances in the incoming gas and their concentrations, the shape and composition of the catalytic surface, temperature, pressure etc. Given these factors, the conversion efficiency of the catalyst can be described using chemical kinetics.

The rate of a chemical reaction is determined from the so called rate coefficient, k, which is specific for each reaction. The general case involving species A, B, C...is expressed in equation (1).

$$v_A A + v_B B + v_C C + \ldots \xrightarrow{k} v_D D + v_E E + v_F F + \ldots \tag{1}$$
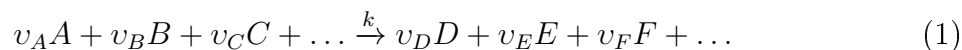
where v_A, $v_B \ldots$ are the stoichiometric coefficients.

The rate coefficient is given by Arrhenius' law [6] and depends on the activation energy E_A, the temperature T, and the so called pre-exponential factor A:

$$k = A T^n e^{-E_A/RT}. \tag{2}$$

where R is the universal gas constant. A and E_A must be determined empirically and the values used in LOGE's model have been obtained from Olsson et al. [1]. The temperature exponent n affects the temperature dependence and is usually set to zero. The reaction rate for reaction (1) is calculated through equation (3).

$$r = k[A]^{v_A}[B]^{v_B}[C]^{v_C} \tag{3}$$

The rate for the backward reaction r_b is determined in an analogous fashion. The forward and the backward reaction rates together create a chemical equilibrium as long as the environmental parameters remain constant. However, as soon as a parameter changes, e.g. the temperature, the reaction rates will change until a new equilibrium is reached. The concentrations of the reacting species will of course also effect the reaction rates and in some cases even other, non-reacting, materials can increase the rate of certain chemical reactions. This modification is called *catalysis* and will be
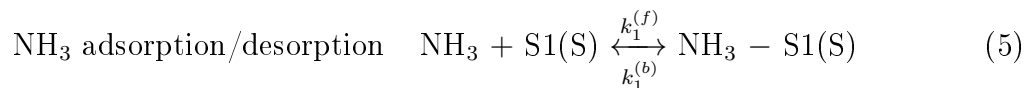
discussed further below.

2.2 Catalysis

Catalysis causes the reaction rate for a certain reaction to increase through a lowering of the activation energy. This can be done in several ways; the most common one which will be discussed here, is by surface reactions. When the reacting species is adsorbed onto the catalytic surface, the bond to that surface causes the internal molecular bond energy to decrease. Thus, reactants will need less energy in order to break that bond and reactions will occur at a higher rate. Adsorption and desorption is also described by Arrhenius' law. The process of a catalysed surface reaction can roughly be described through three steps:

1. Reactants adsorb onto the active surface.

2. Surface reaction occurs.

3. Products desorb from the surface.

The activation energy for adsorption is dependent on the surface *coverage*, denoted θ, according to equation (4). In 4 α is a normalisation constant such that $\alpha\theta$ will be a value between zero and one. Coverage is the amount of adsorbed species on a surface. The coverage dependence falls naturally since more available adsorption sites around lead to higher probability for species to adsorb, in the same way as higher concentration of reacting species lead to higher probability of a reaction to occur.

$$E_A = E_A(0)(1 - \alpha\theta_x) \tag{4}$$

The surface chemistry for the catalyst is quite complex and there are several different species that can adsorb onto the surface with different measure. In LOGE's model one type of adsorption site, S1, is used onto which ammonia is adsorbed. The reaction included in the chemistry for adsorption and desorption is described in reaction (5).

$$\text{NH}_3 \text{ adsorption/desorption} \quad \text{NH}_3 + \text{S1(S)} \underset{k_1^{(b)}}{\overset{k_1^{(f)}}{\longleftrightarrow}} \text{NH}_3 - \text{S1(S)} \tag{5}$$

All values on the Arrhenius' parameters used in this report are included in Appendix A.

2.3 Selective Catalytic Reduction (SCR)

This section will treat the Selective Catalytic Reduction SCR and especially the NH_3 SCR used in LOGE's model. The key mechanisms in the catalytic reduction are discussed, e.g. which the main reactions are and how ammonia can be produced in the upstream of the catalyst.
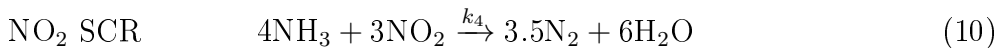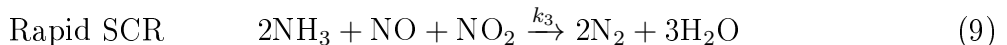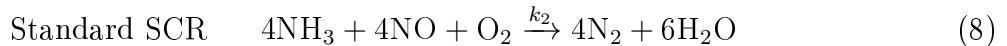
In the SCR the toxic nitrogen oxide gases NO and NO_2 (together referred to as NO_x) are reduced to N_2 and H_2O. The NH_3 SCR uses adsorbed ammonium for the reduction process, as the name implies.

There are several ways to get the ammonia into the catalyst tube, e.g. by injecting anhydrous ammonia (without water), aqueous ammonia (with water) or urea. Anhydrous ammonia has the advantage that it does not need any conversion before being used as a reductant but it is however classified as toxic and dangerous to the environment. Aqueous ammonia is safer to store but must be hydrolysed before it can be used. The most commonly used reductant is urea (NH_2-CO-NH_2), which is decomposed into ammonium through reactions (6) and (7).

$$NH_2\text{-CO-}NH_2 \rightarrow NH_3 + HNCO \tag{6}$$

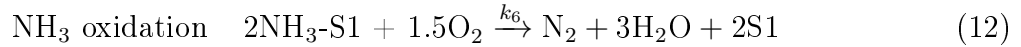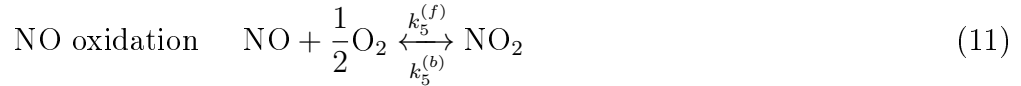$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{7}$$
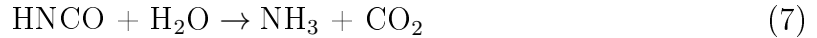
In the catalyst model ammonia is used as a direct input to the catalyst and there will be no further focus on the origin of it.

The catalytic reduction is governed by three reactions, *standard SCR*, *rapid SCR* and *NO_2 SCR* - reaction (8), (9) and (10) respectively. The standard SCR uses NO only while the rapid SCR (which is much faster) consumes equal parts NO and NO_2. The NO_2 SCR uses NO_2 only and is slower than the other two.

$$\text{Standard SCR} \quad 4NH_3 + 4NO + O_2 \xrightarrow{k_2} 4N_2 + 6H_2O \tag{8}$$

$$\text{Rapid SCR} \quad 2NH_3 + NO + NO_2 \xrightarrow{k_3} 2N_2 + 3H_2O \tag{9}$$

$$\text{NO}_2 \text{ SCR} \quad 4NH_3 + 3NO_2 \xrightarrow{k_4} 3.5N_2 + 6H_2O \tag{10}$$

The reactions 8-10 will occur to varying extent depending on circumstances such as the relative concentration of NO and NO_2 and also on the temperature. It has been shown

that the maximum reduction occurs when the ratio of NO and NO_2 is one-to-one [1]. Therefore the oxidation of NO to NO_2 (reaction (11)) plays an important role in the reduction process. As the temperature increases the NH_3 will start to oxidise (reaction (12)) leaving less NH_3 for the SCR.

$$\text{NO oxidation} \quad NO + \frac{1}{2}O_2 \underset{k_5^{(b)}}{\overset{k_5^{(f)}}{\longleftrightarrow}} NO_2 \tag{11}$$

$$\text{NH}_3 \text{ oxidation} \quad 2NH_3\text{-S1} + 1.5O_2 \xrightarrow{k_6} N_2 + 3H_2O + 2S1 \tag{12}$$

3   Research Process

The first part of the research process involved analysing the model with the aim of figuring out how the chemistry in the catalyst model works. There are three different cases, listed below, that have been used in the investigations. All cases were simulated before any alternations had been made to LOGE's model. The cases are transient with stepwise increasing temperature:

NO oxidation - Inlet of 500 ppm NO, 5 % H_2O, 8 % O_2.

NH$_3$ oxidation - Inlet of 500 ppm NH_3, 5 % H_2O, 8 % O_2.

NH$_3$ SCR - Inlet of 500 ppm NH_3, 500 ppm NO, 5 % H_2O, 8 % O_2.

In each of the cases the temperature began at 100°C and was then increased in steps of 50°C up to 500°C. The inlet gas concentrations were constant throughout all experiments. The NO oxidation, the NH_3 oxidation and the NH_3 SCR have been both simulated and experimentally executed by Olsson et al. [1] and the results were used to analyse the similarities and differences between the model and the experiments.

The sudden decrease of NH_3 by the first temperature step in the NH_3 SCR experiment indicates that there is a reaction which rapidly consumes ammonia. Such a reaction could be the rapid SCR (9) which requires NO_2. A hypothesis was presented that NO_2 is adsorbed onto the catalytic surface; this is also suggested by Colombo et al. [3]. If this is the case then the temperature increase could lead to desorption of NO_2 which would enable the rapid SCR reaction. In the NO oxidation experiment by Olsson et al. [1] there seems to be some oxidation even at lower temperature. There are also peaks of NO_2 that could be due to desorption at the first two temperature steps.

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For any NO_2 to be adsorbed onto the surface at lower temperature the activation energy for NO oxidation (11) had to be decreased. This process is explained further below.

The second part of the research process involved alterations of the model. This was a way to understand how the different parameters affected the results and also to locate the problem. These changes can be categorised according to whether the problem is computational, physical, chemical or due to missing reactions. Within these categories the following things were done:

Computational parameters
The number of cells were increased and the time step length was decreased. This was a method to make sure that the model did not miss the effects due to imprecision. The number of cell was doubled, from 10 to 20, and the time step length was changed from $3.0 \cdot 10^{-3}$ seconds to $1.0 \cdot 10^{-3}$ seconds.

Physical parameters
The washcoat thickness, solid heat transfer and solid density were changed. The physical properties had not been specified in Olsson's paper [1] and were therefore a potential source of error in LOGE's model. The washcoat thickness was changed from $1.00 \cdot 10^{-3}$ m to $1.12 \cdot 10^{-3}$ m. This would enable a higher volume gas to participate in the catalytic reactions. Changing the solid density (i.e. the density of the catalytic main material) was motivated by the fact that the heating of the catalyst was slow (based on comparisons of the input temperature and the output temperature) and the reaction rate is highly dependent on the temperature. The solid density was changed in two runs, one from 2000 to 1000 and the other to 500 (kg/m^3). The solid heat capacity was changed for the same reason as the solid density, from 800 to 200 (J/(kg·K)). The large decrease of the solid density was done so that any effect would be noticeable and clear. The physical parameters were changed and tested in the NH_3 oxidation simulation. The aim of this investigation was to get the ammonia desorption peaks more symmetric. Before the changes, the peaks have a steep increase and a smooth slope-like decrease.

Chemical parameters
Different values were tested for A and E_A in the Arrhenius equation for NO oxidation, reaction 11. These parameters were originally obtained from Olsson's calibration. The parameters were systematically altered around the original value and different combinations were tested.

Chemical reactions

In a first attempt to investigate the hypothesis presented above, a "fake" desorption peak was added at the first temperature increase in the NH_3 SCR experiment. This was done in order to test the effect when the rapid SCR was enabled. In two different simulation experiments 300 ppm and 400 ppm NO_2 was added to the inlet gas 50 minutes into the experiment during 30 seconds. Further, an adsorption and desorption reaction (13) was added to the kinetic model.

$$NO_2 \text{ adsorption/desorption} \quad NO_2 + S1(S) \underset{k_7^{(b)}}{\overset{k_7^{(f)}}{\longleftrightarrow}} NO_2 - S1(S) \tag{13}$$
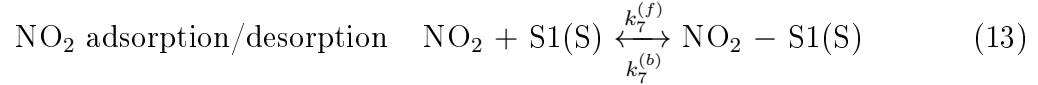
There are no Arrhenius' coefficients available for these reactions so they were estimated based on the kinetic parameters for the NH_3 adsorption and desorption reactions. These parameters were tested and altered through simulations of NO oxidation and the NH_3 SCR experiment.

4   Results

The presentation of the results is divided into three parts; the first part shows simulations done by the model before any modifications had been made, the second part presents the effect when different parameters were changed and in the last part the final results are illustrated.

4.1   Model Analysis

NO oxidation

Figure 4 shows the oxidation of NO run with LOGE's model before any alterations were made. There was 500 ppm NO, 8% O_2 and 5% H_2O in the inlet gas. The results from the model are compared with experimental values from Olsson et al. [1]. The experimental result in Figure 4 shows a low activity of NO oxidation when the temperature is low. LOGE's model however shows no oxidation at all when $T = 100°C$ and barely any when $T = 150°C$. Thereafter the oxidation increases stepwise along with the temperature until the temperature reaches $500°C$ and the oxidation of NO decreases. The experimental result shows NO_2 peaks by the first temperature steps that does not show at all in LOGE's model.
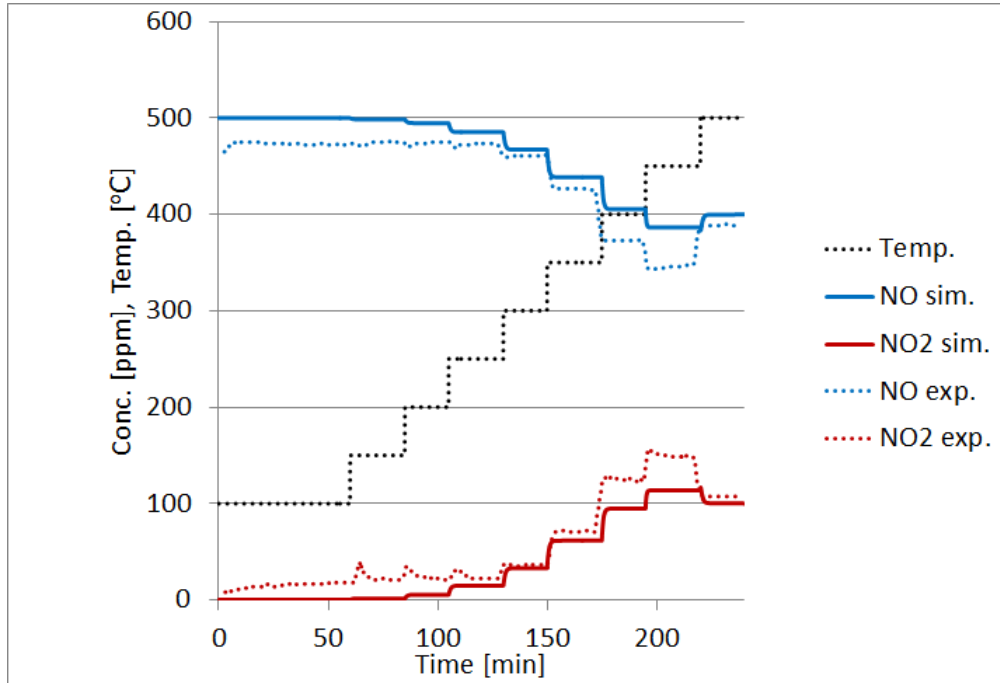
Figure 4: NO oxidation before any modifications. Inlet: 500 ppm NO, 8% O_2 and 5% H_2O.

NH_3 oxidation

The oxidation of NH_3 was simulated with the unaltered kinetic model and compared to the experimental results from [1], see Figure 5. The inlet of 500 ppm NH_3, 8% O_2 and 5% H_2O was constant throughout the experiment and the temperature was increased stepwise as shown in the figure. The absence of ammonia during the first 20 minutes is due to adsorption onto the catalytic surface. When the surface is saturated and the same outlet as inlet can be seen. When the temperature increases there are peaks of ammonia which are caused by desorption. When the temperature reaches 300°C ammonia starts to oxidise and there is a decrease of ammonia in the gas outlet. As the temperature increases further the oxidation approaches 100%.
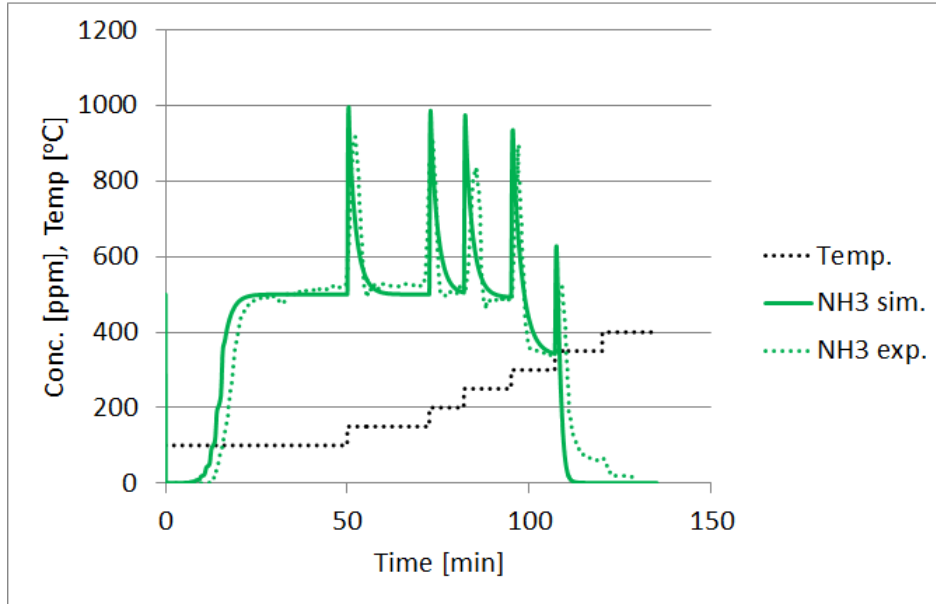
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Figure 5: NH$_3$ oxidation before any modifications. Inlet: 500 ppm NH$_3$, 8% O$_2$ and 5% H$_2$O.

NH$_3$ SCR experiment

In the NH$_3$ SCR experiment there was an inlet of 500 ppm NH$_3$, 500 ppm NO, 8% O$_2$ and 5% H$_2$O and the temperature was increased stepwise. The result can be seen in Figure 6. The solid lines show the simulation with the unaltered model and the dashed lines show the experimental results from [1]. As for the NH$_3$ oxidation, the model shows results similar to the experimental ones for the ammonia adsorption. However, when the temperature increases the model has a larger desorption peak than the experimental data, 980 ppm compared to about 800 ppm. After the peak the experimental data dip to about 250 ppm whereas the model instead simulates a smooth decrease until a new steady level of 335 ppm is reached. The second desorption peak is also too high in the simulation, 730 ppm compared to 500 ppm. Within the temperature interval 200-300°C almost all NO is reduced by SCR. When the temperature reaches 350°C the SCR is inhibited since the NH$_3$ is consumed by direct oxidation (12) to N$_2$. The NO instead oxidises to NO$_2$ according to the NO oxidation experiment (4). This oxidation process does not exactly follow experiments or more specifically, the amount of NO$_2$ in the outlet gas.
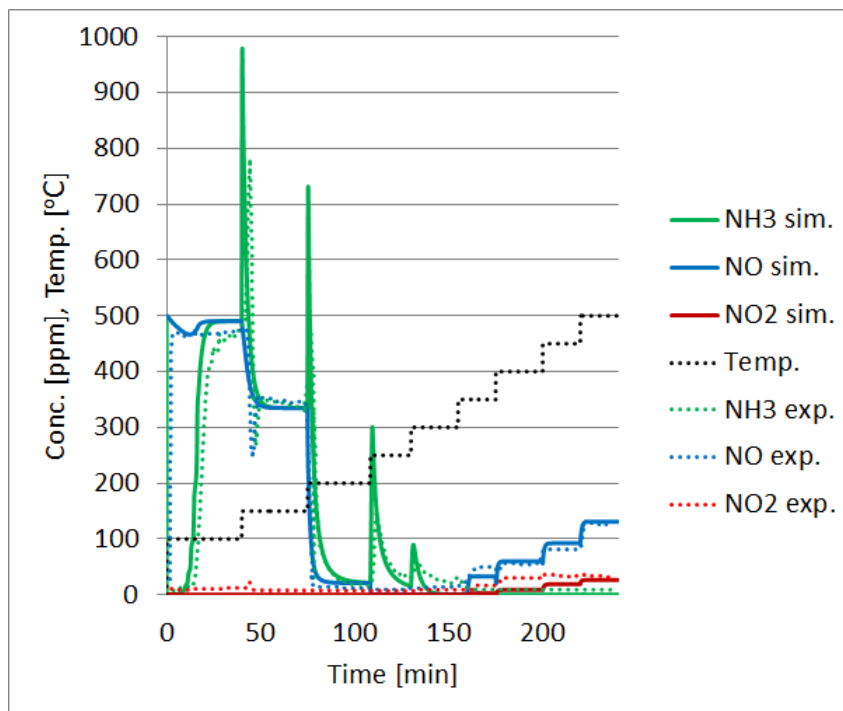
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Figure 6: NH$_3$ SCR experiment, before any modifications. Inlet: 500 ppm NH$_3$, 500 ppm NO, 8% O$_2$ and 5% H$_2$O.

4.2 Parameter Sensitivity Study

This part will present and illustrate the effects when changing the parameters mentioned in Section 3.

Computational Parameters
Increasing the number of cells and decreasing the time step length did not improve the results.

Physical Parameters
The NH$_3$ oxidation experiment was investigated when altering physical parameters. Changing the washcoat thickness, the solid density and the solid heat capacity did not give any significant effects. This approach was abandoned.

Chemical Parameters
The original kinetic parameters for NO oxidation was $A = 8.0 \cdot 10^7$ and $E_A = 48.0$ kJ/mol. The first three images 7(a)-7(c) illustrate the effects of changing the pre-exponential factor A and the activation energy E_A from the Arrhenius equation (2).

Figure 7(d) shows the simulation with the final parameters $A = 9.0 \cdot 10^7$ and $E_A = 47.4$ kJ/mol. These are the values that will be used further on.

(a) $A = 6.0$, $E_A = 48.0$ kJ/mol

(b) $A = 10.0$, $E_A = 48.0$ kJ/mol

(c) $A = 8.0$, $E_A = 46.0$ kJ/mol
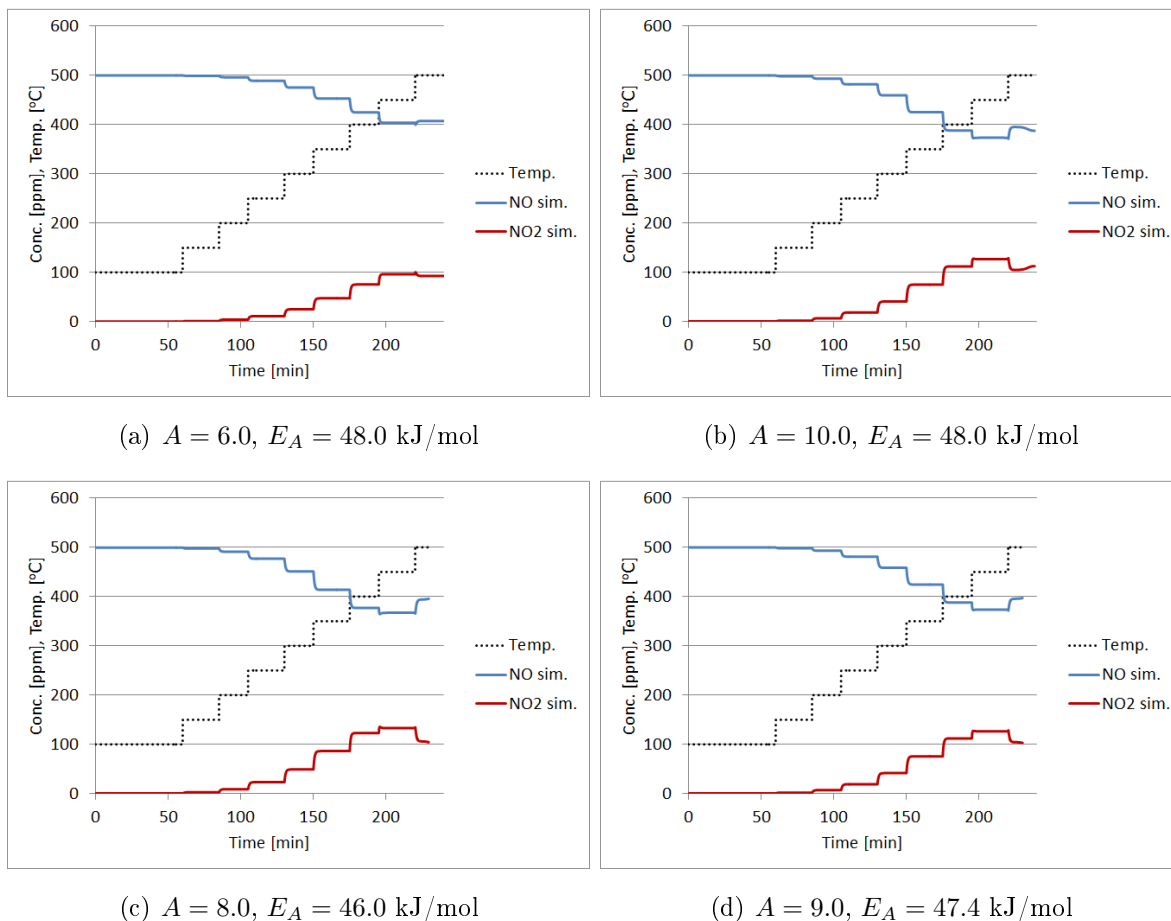

(d) $A = 9.0$, $E_A = 47.4$ kJ/mol

Figure 7: NO oxidation experiment with modified chemical kinetic parameters for the NO oxidation. For the result with original parameters see Figure 4.

Chemical Reactions

To see if the oscillating behaviour in the NH_3 concentration (see Figure 6) could be captured, NO_2 was added to the inlet gas by the time of the first temperature increase. The result can be seen in Figures 8(a) and 8(b) where 300 ppm and 400 ppm have been added respectively. The effect is an ammonia dip which indicate that the large decrease of ammonia is likely due to storage and desorption of NO_2. Not all of the added NO_2 is consumed which can be seen by the peak of NO_2 in the outlet gas. Another effect of the NO_2 input is that the ammonia peak is decreased. This is a desired effect, though not to the observed extent.

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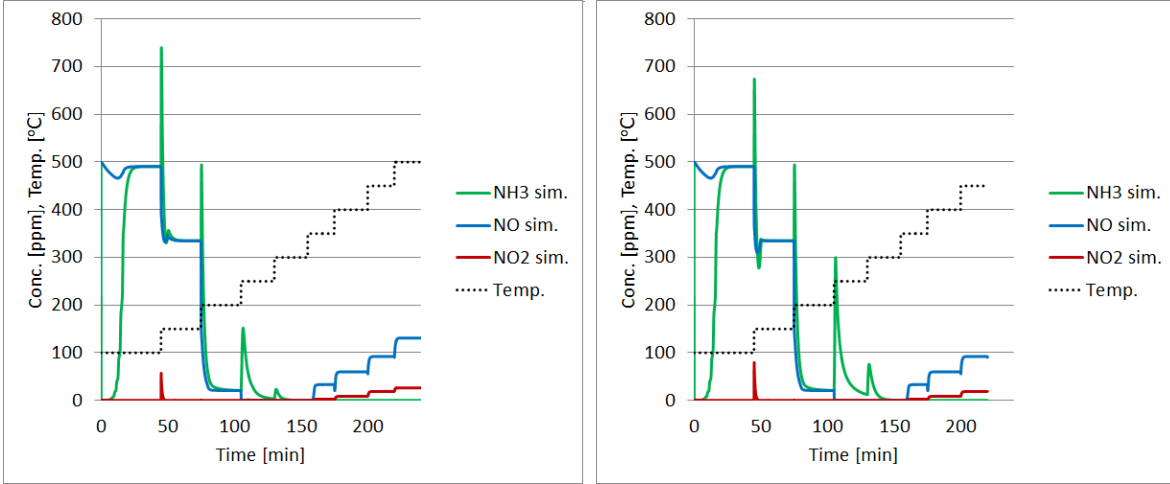
(a) 300 ppm NO$_2$ inlet. (b) 400 ppm NO$_2$ inlet.

Figure 8: Effect of NO$_2$ inlet 50 minutes into the experiment during 30 seconds.

Reaction (13) was added to the kinetic model and different values of the Arrhenius parameters were tested. Figures 9(a) and 9(b) show the results when simulating the NO oxidation and the NH$_3$ SCR experiment, respectively, using pre-exponential factor $A^{(f)} = 1.0 \cdot 10^7$ and activation energy $E_A^{(f)} = 0.0$ for the adsorption and $A^{(b)} = 1.0 \cdot 10^{11}$ and $E_A^{(b)} = 100$ kJ/mol for the desorption reaction. The Arrhenius parameters chosen where based on the adsorption and desorption reactions for NH$_3$ (5).
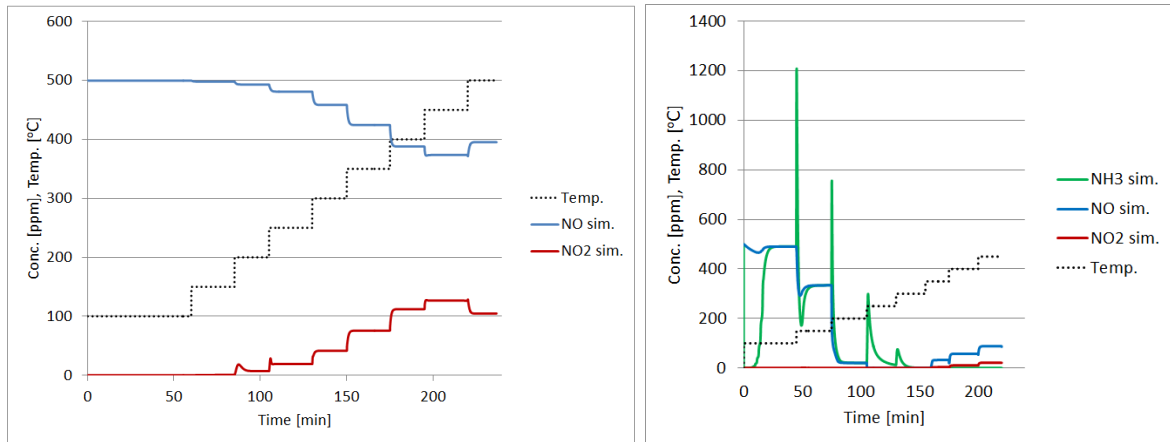
(a) NO oxidation experiment. (b) NH$_3$ SCR experiment.

Figure 9: NO oxidation experiment and NH$_3$ SCR experiment with modified kinetic parameters for adsorption (f) and desorption (b) of NO$_2$:
$A^{(f)} = 1.0 \cdot 10^7$, $E_A^{(f)} = 0.0$, $A^{(b)} = 1.0 \cdot 10^{11}$, $E_A^{(b)} = 100.0$ kJ/mol.

After some modifications the result looked as in Figure 10(a) and 10(b) where the following Arrhenius coefficients: $A^{(f)} = 1.0 \cdot 10^5$, $E_A^{(f)} = 0.0$, $A^{(b)} = 1.0 \cdot 10^5$ and $E_A^{(b)} = 110.0$ kJ/mol have been used. These are the parameters used in the simulations illustrated in Section 4.3.
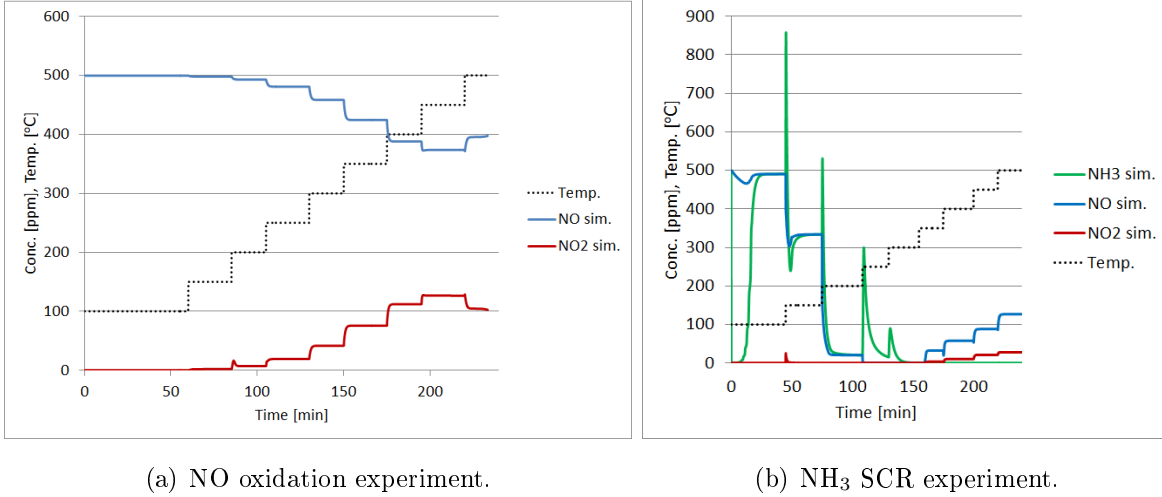

(a) NO oxidation experiment.

(b) NH$_3$ SCR experiment.

Figure 10: NO oxidation experiment and NH$_3$ SCR experiment with modified kinetic parameters for adsorption (f) and desorption (b) of NO$_2$:
$A^{(f)} = 1.0 \cdot 10^5$, $E_A^{(f)} = 0.0$, $A^{(b)} = 1.0 \cdot 10^{11}$, $E_A^{(b)} = 110.0$ kJ/mol.

4.3   Final Results

Final simulations of the NO oxidation and NH$_3$ SCR experiments have been done with these parameters and the result can be seen in Figures 11 and 12, respectively. Experimental results from Olsson et al. [1] are compared with the final simulations.

When comparing the results in Figure 11 with those in Figure 4 a few things are worth pointing out. One subtle effect is that the oxidation level is higher throughout the simulation and it matches the experimental result better even if there is room for further improvement. The other effect is a small NO$_2$ peak by the second temperature step. There is still no peak at the first temperature step.
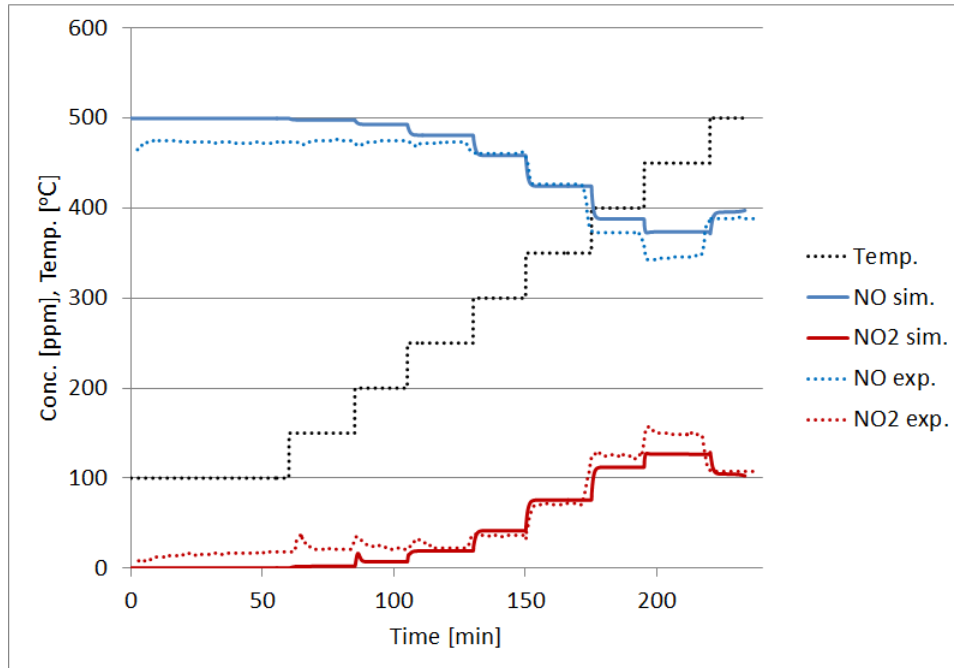
Figure 11: NO oxidation after modification.

The results in Figure 12 show the NH$_3$ SCR simulations after modification. It is the same simulation as in Figure 10(b) but with the experimental results from Olsson et al. [1] plotted for comparison. It can be seen that LOGE's model overall follows the experimental results with more precision after the modifications. The ammonia peaks are lower and the ammonia dip has a good depth. There is also a small but distinguishable NO$_2$ peak by the first temperature increase that is also seen in the experiment. Furthermore, for higher temperatures the amount of NO in the simulation also agrees better with experiment when using the altered kinetic parameters.
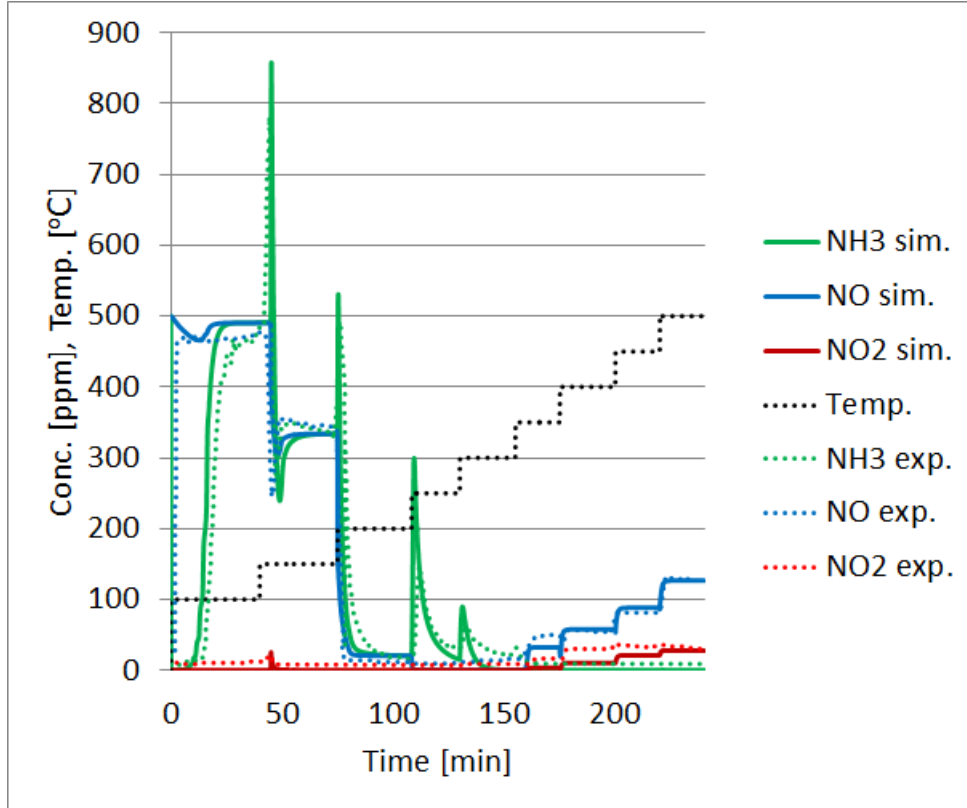
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Figure 12: NH$_3$ SCR experiment after modification.

The pre-exponential factor A and the activation energy E_A for the modified and added reactions are listed in Table 1.

Table 1: Resulting kinetic parameters for NO oxidation and NO$_2$ adsorption and desorption.

Reaction, rate constant	Pre-exponential factor, A	Activation energy, E_A [kJ/mol]
NO oxidation, k_5	$9.0{\cdot}10^7$	47.4
NO$_2$ adsorption, $k_7^{(f)}$	$1.0{\cdot}10^5$	0
NO$_2$ desorption, $k_7^{(b)}$	$1.0{\cdot}10^{11}$	110.0

5 Discussion

The first step of changing the *computational parameters* was a way to ensure that the problem was not due to inaccurate discretisation. Since there was no improvement when increasing the number of cells and decreasing the time step length this possibility was ruled out. The changes made on the *physical parameters* did not improve the results

either. However, the possibility that physical parameters have some significance should not be dismissed entirely. The shape of the peaks in Figure 5 in the simulations are different than in the experimental results, especially as the outlet of NH_3 approaches a stable level again.

Since the NO_x reduction with NH_3 is dependent on the oxidation of NO to NO_2 it is of great importance that the kinetic model of the oxidation is correct and includes the effects that can affect the SCR. The goal when changing the *kinetic parameters* is to approach the oxidation rate of the experiment in the paper by Olsson et al. [1]. It should be noted though that the activity seen in the experimental results at low temperatures can be due to noise in the measurements. According to Figure 4 a change in the kinetic parameters needs to result in an increase of the oxidation rate. Increasing the pre-exponential factor has this effect (Figure 7(b)) and so does decreasing the activation energy (Figure 7(c) and 7(d)). Decreasing the activation energy also leads to a larger temperature dependence due to the exponential $e^{E_A/RT}$ in equation (2). The simulated NO oxidation experiments with the final kinetic parameters mean improvements on most points, although it is a bit disappointing that there is no noticeable desorption peak at the fist temperature step. The final parameters are however the ones that generate the best overall results compared to the experiments.

If the hypothesis that the ammonia dip is due to NO_2 desorption is correct, then it is of great importance that the apparent NO_2 desorption peaks in the NO oxidation experiment are caught by LOGE's model. To add the adsorption and desorption reaction (13) was an important part in that process. However, if there is no NO oxidation (11) at low temperatures there will be no NO_2 in the catalyst to adsorb onto the surface and thus no desorption at the first temperature step. So another contribution toward the goal was to change the kinetic parameters for the NO oxidation such that there was activity even for $T = 100°C$. This was done by decreasing the activation energy so that less energy is required for oxidation to occur and also to increase the pre-exponential factor in order to amplify the effect.

The addition of the *chemical reactions* NO_2 adsorption and desorption had a great effect in the NH_3 SCR experiment. The "fake" desorption peak generated the desired ammonia dip. The ammonia desorption peaks were also suppressed slightly. However, the fact that the 300 ppm inlet gave such a small effect gave reason for concern since experiments had shown a very small NO_2 "bump" in the NO oxidation experiment.

There are two effects that could explain how a small amount of NO_2 in the gas could lead to a large ammonia dip. The main effect is that the chemical equilibrium will be forced to shift if the NO_2 is consumed right away. More correctly, the reaction rate for the NO oxidation has to be much higher to uphold the chemical equilibrium. This would lead to *a lot* of NO_2 being produced if the consuming reaction is fast as is the case with the rapid SCR. The other explanation is that the desorbed NO_2 is close to the surface (within the thin film area) where also the SCR reactions occur. Therefore there would be no NO_2 spill like there is in Figure 8 and instead nearly all NO_2 would be consumed.

The decision to add an adsorption/desorption reaction for NO_2 was based on the article by Sjövall et al. [2] and Comondo et al. [3] where they suggest this type of reaction. Although they both have more complicated reactions for NO_2 adsorption than what was used in this work. In this work only one reaction was added and the rate was empirically determined. The fact that this method with a simple model gives such nice results is positive since it keeps the model CPU time efficient as well as easy to calibrate.
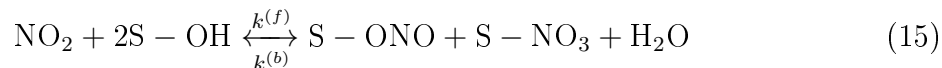
Figure 9(b) shows one of the first simulations where the adsorption reaction is added. As can be seen, the ammonia peak is much higher and the ammonia dip much lower than in the later version (Figure 10(b)). Between the versions two alterations have been done. First of all, the activation energy for the desorption reaction, $E_A^{(b)}$, was lowered. This step decreased the depth of the dip since not all NO_2 was desorbed off the surface. The manipulation did however not affect the height of the peak. In the second step the pre-exponential factor for the adsorption, $A^{(f)}$, was decreased which resulted in a lower ammonia peak and a more shallow dip. Why this modification would lead to a lower ammonia peak is a bit unclear and a point for future investigations. A decrease of $A^{(f)}$ would be likely to result in less adsorbed NO_2 onto the catalytic surface but there is no apparent connection between that and a lower amount of ammonia desorption.

The model is now likely almost as good as it gets with such a simple chemistry. There is still room for a bit of fine tuning of the parameters but in order to really improve the model further a more complex surface chemistry would be required. A suggestion in that direction could be to add adsorption of O_2 and H_2O as suggested by Sjövall et al. [2]. In [2] they also model the NO oxidation as a surface reaction with adsorbed oxygen which results in adsorbed NO_2 (14). This could be a way to have a more chemically correct reaction for the NO_2 adsorption. It is also possible that NO itself is adsorbed

to some extent onto the surface. That could also add to the oxidation effect at low temperatures.

$$\text{NO} + \text{O} - \text{S} \overset{k^{(f)}}{\underset{k^{(b)}}{\longleftrightarrow}} \text{NO}_2 - \text{S} \tag{14}$$

Another suggestion would be to try the approach of Comondo et al. [3] where they have NO_2 adsorbed through a reaction with adsorbed OH (15). This would also require some reaction for OH adsorption.

$$\text{NO}_2 + 2\text{S} - \text{OH} \overset{k^{(f)}}{\underset{k^{(b)}}{\longleftrightarrow}} \text{S} - \text{ONO} + \text{S} - \text{NO}_3 + \text{H}_2\text{O} \tag{15}$$

In the NO oxidation experimental results show a decrease in the amount of NO_2 as the temperature reaches 500°C. To obtain that effect focus is again required on the oxidation of NO (11). It becomes clear when observing Figure 4 that it is not so much a decrease in the last temperature step that is needed, as an increase in the second to last temperature step. So a higher amount of oxidation is required when $T = 450$°C and only a tiny bit less oxidation when $T = 500$°C. This is achieved to some extent in the final NO oxidation experiment, Figure 11, but not enough to actually generate the decrease in the final NH_3 SCR experiment, Figure 12. As mentioned above, this might be the best as can be done without implementing a more complex chemistry. It would, for example, be interesting to see how exchanging (or complementing) reaction (11) with (14) would affect the NO oxidation experiment.

A detailed kinetic model does not however guarantee a more accurate model. In the two papers by Olsson et al. [1] and Sjövall et al. [2] corresponding NH_3 SCR experiments have been executed using a semi-detailed and a detailed kinetic model respectively. The overall results are not more accurate for the detailed model than the semi-detailed in this experiment. Some of the effects are better caught in the detailed model and some in the semi-detailed model.

6 Conclusions

A catalyst is an extremely complicated system with many affecting factors. It is not possible to theoretically calculate the reaction rates for all reactions in the catalysis without complete knowledge on the material composition and the site distribution. This information is never available for industrial systems. An alternative approach is to have a simple, global chemistry to save CPU time and a few additional reactions

to capture important effects. LOGE's model before this work included adsorption and desorption of ammonia, as an addition to the global model. This reaction was enough to capture many effects in the catalysis but not all. The additional NO_2 adsorption and desorption reactions included in this work had a large positive effect on the simulated results when comparing with experimental results. The modified Arrhenius parameters for the NO oxidation (11) were also important to enable the oscillation of NH_3. Improvement in the NO oxidation experiment were achieved as well, although not as significant.

In the light of the results from this thesis work one can claim that LOGE's enhanced semi-detailed model works well when a CPU time efficient model is required for the aftertreatment of exhaust gas from a diesel engine. It will be useful in the work towards minimizing pollution with toxic nitrogen gases. It is however important to note that the enhancements presented here has been calibrated through the NO oxidation and NH_3 SCR experiments and no new experiments have executed done to validate the model. In order to generalize the results the model would need validation through additional experiments. There could be effects that this model does not capture correctly but which are not shown in the experiments. Olsson et al. [1] have good examples of such validation experiments. One could for example have a varying inlet gas concentration such as an increasing amount of NH_3 or vary the ratio between NO and NO_2 while keeping the NO_x concentration constant.

A next interesting step would be to execute a full motor experiment, i.e. to implement the kinetic model from this work into a full motor system including engine combustion. A full motor experiment would enable a comparison between experimental and simulated results which has more significance than the calibration experiments done in this work. This would be method to determine how much the model has been improved. The integrated outlet gas should differ less then 5 % between simulations and experiments in order to be regarded as a satisfying catalyst.

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A Kinetic Parameters

Kinetic parameters used in LOGE's model, obtained from Olsson et al. [1]. The backward reaction for the NO oxidation is calculated through the enthalpy. In table

Reaction, rate constant	Pre-exponential factor, A	Activation energy, E_A [kJ/mol]
NH$_3$ adsorption, $k_1^{(f)}$	$9.3\cdot10^5$	0
NH$_3$ desorption, $k_1^{(b)}$	$1.0\cdot10^{11}$	181.5
Standard SCR, k_2	$2.3\cdot10^{14}$	84.9
Rapid SCR, k_3	$1.9\cdot10^{24}$	85.1
NO$_2$ SCR, k_4	$1.1\cdot10^{13}$	72.3
NO oxidation, k_5	$8.0\cdot10^7$	48.0
NH$_3$ oxidation, k_6	$1.2\cdot10^{17}$	162.4