Universidade do Porto

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«Kinetic modeling of ammonia selective catalytic reduction for cleaning emissions from vehicles»

Master of Science Thesis

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developed in

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Acknowledgements

I still remember the first day I arrived to Göteborg, when I look into my window I can feel the sensation that embraced my mind in the very first minute I arrived to the room that would host my Erasmus experience. By that time, the floor outside was covered by a stunning white veil that I have never seen before, now is summer and almost midnight but I still can distinguish the sunshine far away in the infinite of the sky. Definitely these five months turned out to be the leading challenge I've ever faced and the life experience that will remain forever in my memory. Not only because it was the first time of many things in my life but also because Göteborg become the comfortable place I love to be, the happy city where every day I feel like home.

I want to start to acknowledge Louise Olsson, my supervisor and examiner, for the support during these months and also for welcoming me in Chalmers. I am also grateful to Bill Partridge, Jae-Soon Choi, both from Oak Ridge National Laboratory, and Xavier Auvray, PhD student from Chalmers, for providing the experimental data that enable my work during these months. I also must acknowledge Supriyanto that helped me, especially in the beginning of my simulation work. To Fuels, Engines and Emissions Research center at Oak Ridge National Laboratory, in USA, special thanks, for all the comments and feedback given to my work. I also want to acknowledge people from Competence Center for Catalysis, in Chalmers University of Technology, not only for the cakes that mysteriously appear on the table but also for the friendly environment that I felt in Chalmers during these months.

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Erasmus memories will always have her face and her laughs, but also our confessions, our music and our crazy moments in Sweden and surroundings (even in international waters). It was really good to meet so many people from so different countries, I am not able to put all of them in the present report once only 50 pages are acceptable, but I will carry them in my memory forever.

Declaration

I declare that I am solely the responsible for the concretization of the present work.

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Abstract

In this work BOOST was employed to develop a kinetic model able to describe ammonia SCR over a Cu-Beta catalyst. On the basis of the steady-state results obtained from experiments conducted earlier at ORNL using the 4-step protocol and the intra-catalyst distributions established by SpaciMS, the kinetic parameters of NO oxidation, NH_3 SCR and NH_3 oxidation were obtained. In addition, a TPD experiment was conducted in order to get more information about the storage and release of ammonia over the catalyst, the kinetic parameters of NH_3 adsorption and desorption were calibrated.

SpaciMS was vital to determine the spatial profiles within the catalyst, it showed that 1/4, 3/8 and 1 L of the total catalyst length were necessary to achieve complete conversion during SCR at 400, 325 and 200 °C, respectively. The effect of ammonia oxidation during SCR conditions was studied to investigate the selectivity of the reaction.

The kinetic model developed can be used successfully to predict SCR mechanism over a broad range of temperatures.

Keywords: Ammonia selective catalytic reduction; Cu-Beta catalyst; Kinetic modeling

Resumo

Neste trabalho BOOST foi utilizado para desenvolver um modelo cinético capaz de descrever a redução seletiva catalítica (SCR), usando amoníaco como redutos, na presença de um catalisador Cu-Beta. Com os resultados experimentais em estado estacionário obtidos usando o protocolo dos 4 passos e as distribuições intra-catalíticas estabelecidas pelo SpaciMS, os parâmetros cinéticos das reações de oxidação de NO, SCR e oxidação de NH_3 foram determinados. Além disso, uma experiência TPD foi conduzida de forma a obter mais informação acerca da capacidade de armazenamento e libertação de NH_3 no catalisador, os parâmetros cinéticos da adsorção e desorção de NH_3 foram calibrados.

SpaciMS foi vital para determinar os perfis espaciais no catalisador, esta técnica demonstrou que 1/4, 3/8 e ½ do comprimento total do catalisador foi necessário para conseguir uma conversão completa durante a reação SCR à temperatura de 400, 325 e 200 °C, respetivamente. O efeito da oxidação do amoníaco nas condições SCR foi estudada de forma a investigar a seletividade da reação.

O modelo cinético desenvolvido pode ser usado com sucesso para descrever o mecanismo SCR numa ampla gama de temperaturas.

Palavras Chave (Tema): Redução seletiva catalítica; Catalisador Cu-Beta; Modelação cinética

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Nomenclature

Parameter	Description	Unit
A_j	Pre-exponential factor for reaction j	
C_i	Concentration of specie i	-
$E_{A,j}$	Activation energy for reaction j	$J \cdot mol^{-1}$
$E_{A,j}(0)$	Activation energy for reaction j for zero coverage	$J \cdot mol^{-1}$
k_j	Rate constant of reaction j	
r_j	Rate of reaction j	$kmol \cdot m^{-3} \cdot s^{-1}$
R	Gas constant	$J \cdot mol^{-1} \cdot K^{-1}$
$S1$	Catalyst-site	-
T_S	Temperature surface	K

Greek symbols	Description
α	Dependence of the ammonia surface coverage
θ_i	Coverage of species i

Subscripts	Description
i	Index

Acronyms

ACEA	European Automobile Manufacturers Association
AVL	Anstalt für Verbrennungskraftmaschinen List (engineering company)
CRADA	Cooperative Research and Development Agreement
DOE	Department of Energy
DPF	Diesel Particulate Filter
EURO	European Emission Standards
FEUP	Faculdade de Engenharia da Universidade do Porto
ICP-AES	Inductively Coupled Plasma and Atomic Emission Spectrometry
LNT	Lean NO_x Traps
ORNL	Oak Ridge National Laboratory
SCR	Selective Catalytic Reduction
SpaciMS	Spatially Resolved Capillary Inlet Mass Spectrometer System
TIER	Emission Regulations
TPD	Temperature Programmed Desorption

1 Introduction

1.1 Master Thesis: Contextualization

Many studies show that a period spent abroad not only enriches students' lives in the academic and professional fields, but can also improve language learning, intercultural skills, self-reliance and self-awareness. Their experiences give students a better sense of what it means to be a European citizen. In addition, many employers highly value such a period abroad, which increases the students' employability and job prospects[1].

In the last semester of the studies of the Integrated Master in Chemical Engineer at FEUP, the students must develop a research project and, at the end, deliver a report and perform an oral presentation. I decided to complete my master thesis work enrolled in the Erasmus programme, I choose Chalmers University of Technology, in Göteborg, Sweden, to host me during these five last months.

I have always wanted to join the Erasmus adventure. I love Europe and the idea of living abroad during five months, meet new people, walk in new streets and among everything depended on my own, seemed the perfect end for my very last year of studies.

This semester I had the chance of growing not only in the personal way but also in the professional manner. I worked with new people from different countries and backgrounds.

Concerning to the master thesis work, I faced the challenge of working for the very first time in simulation work. Although at the beginning I was quiete worried, it turned out to be a fruitful experience. Now I believe that I am able to do everything I want if I am committed and motivated.

More than ever, I believe that it is important to be able to work in a different country and to enjoy the mobility facilities that European Commission offers. During these months I felt myself something like the ambassador of my own country, and I think I did quite well.

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[1] Extrated from European Comission webpage: http://ec.europa.eu/education/lifelong-learning-programme/doc80_en.htm

1.2 Work Plan

In a joint collaboration between Oak Ridge National Laboratory (ORNL), Competence Centre for Catalysis at Chalmers University of Technology and Cummins Inc, Xavier Auvray and co-workers, the former a PhD student at Chalmers, applied Spatially Resolved Capillary Inlet Mass Spectrometry (SpaciMS) to resolve the intra-catalyst distribution of the SCR reaction, and NO and NH_3 oxidation, using a 4-step protocol on a Cu-Beta catalyst [1]. Based on the Xavier Auvray experimental work, the present master thesis work plan was proposed. The aim of the present work thesis is to develop kinetic models and determine rate parameters to simulate correct profiles within the catalyst. The simulations were performed using BOOST AVL and the kinetics described in FORTRAN subroutine script. The results obtained via simulations were analyzed in Matlab and compared with the available experimental data.

TASK 1: Literature review (weeks 1-4)

- Ammonia Selective Catalytic Reduction (NH_3 SCR)

- Standard SCR, Rapid SCR and Slow SCR

- Review of kinetic parameters of different catalysts

- NH_3 Temperature Programmed Desorption (TPD)

TASK 2: Kinetic modeling of NH_3 Temperature Programmed Desorption (weeks 4-6)

TASK 3: Kinetic modeling of NO oxidation- step 1 of 4-step protocol (weeks 6-9)

TASK 4: Kinetic modeling of NH_3 oxidation- step 3 of 4-step protocol (weeks 9-11)

TASK 5: Kinetic modeling of NH_3 SCR- step 2 of 4-step protocol (weeks 11-15)

TASK 6: Writing Report and preparation of oral communication (weeks 15-18)

1.3 Organization of the report

The present report starts with the description of the background of this work (Chapter 2). In the first section, the motivation of this project is stated and contextualized in the actual state of the art (section 2.1). The core idea that led to the development of this work thesis is clarified at the end of the Chapter 2 (section 2.3).

In the third Chapter the aim of the work is specified.

In Chapter 4 the experimental part of the work is presented. It starts with a brief description of the catalyst (section 4.1), then the reactor setup and the analytical technique (section 4.2) followed by the experimental procedure (section 4.3). At the end of this chapter an explanation about BOOST operation is presented (section 4.4).

Chapters 5 to 8 are at the most importance in this report once they state the results obtained and the respective discussion. Each chapter correspond to a specific reaction that was investigated during the master thesis work. The chapters are ordered accordingly to the work plan showed previously (section 1.2). In each chapter the model reactions and species are first described and then the kinetic parameters estimated, along with a brief discussion. Also, a comparison between the simulated results and the values in the open literature is made.

In Chapter 9 the major conclusions are depicted. In addition, some suggestions are done as future work.

In the last section of the present master thesis the references are included. Also, appendixes were added with additional information (although being important in the work context they are not strictly necessary or relevant to include in the main chapters).

2 Background

The number of cars equipped with diesel engines is increasing; these engines have a better fuel economy and enable reduced CO_2 emissions when compared with the conventional gasoline engines. However, the emissions of NO_x from diesel engines are more difficult to catalytically eliminate, which poses some environmental concerns. In order to control the emissions, EURO (in Europe) and TIER (in USA) norms are becoming more restrictive, which represents a challenge for diesel engines and vehicles developers.

Regarding the progressive tightening of emissions standards (Figure 1) it is becoming difficult to comply with these norms without compromising fuel consumption performance levels [2].
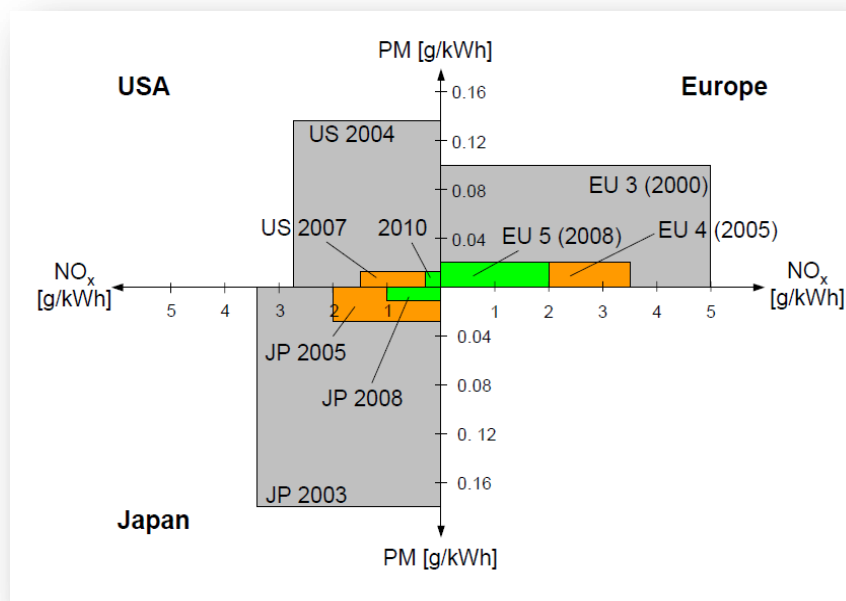
Figure 1 NO_x and PM emission standards for diesel cars [3]

In January 2014, EURO 6 will come into force and emissions from cars must be capped at 0.4 g·kWh^{-1} (a reduction of more than 75% compared with EURO 5).

2.1 Aftertreatment technologies

The improvement of combustion systems that limit the formation of pollutants during the combustion process do not seem to be efficient enough, so in the past years exhaust gas **aftertreatment systems** have been developed in order to meet the legislative emissions

standards described above. Diesel particulate filters (DPFs), lean NOx traps (LNTs) and Selective Catalytic Reduction systems (SCRs) are some of the strategies that are now under investigation.

2.1.1   Diesel particulate filters

Particulate filters are used after diesel engines to remove diesel particulate matter or soot from the exhaust of diesel engines. The particles are kept on the interior walls of the filter, as it is shown in Figure 2. Trapped particulates are burnt at normal exhaust temperatures using the powerful oxidative properties of NO_2 (passive regeneration) or at higher temperatures using O_2 (active regeneration). In order to remove the particles from the filter walls, the filter must be sporadically regenerated by active or passive regenerations processes. [4]
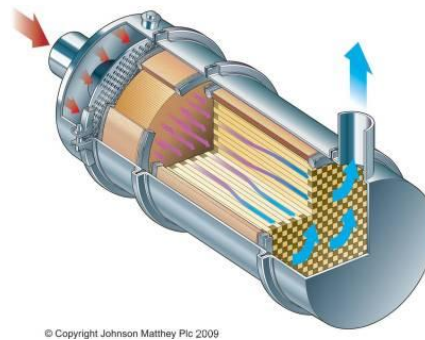
Figure 2 Johnson Matthey diesel particulate filter [5].

2.1.2   Lean NO_x traps

Figure 3 shows the working principle of NO_x traps: under lean conditions (excess of oxygen in the air:fuel ratio) NO_x is chemically bound to the adsorbent (Figure 3a), and when it is saturated the system must be regenerated, which happens under rich conditions (excess of fuel), where NO_x is reduced to nitrogen (Figure 3 b) [6].
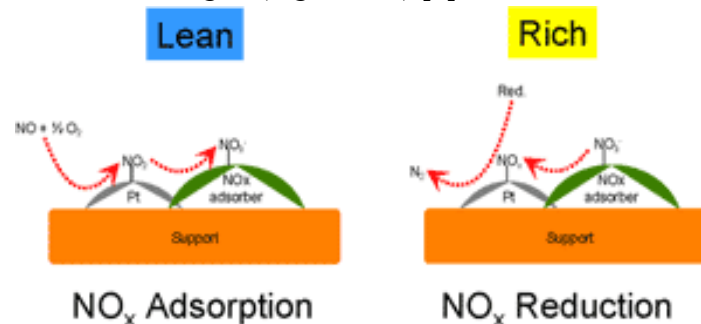
Figure 3 The NOx adsorber system, NOx adsorption a) and NOx reduction b) [5]

2.1.3 Selective Catalytic Reduction (SCR)

SCR processes aim to continuously reduce NO_x from the gas exhaust to molecular nitrogen in the presence of oxygen. Many reductants have been used in the conversion of NO_x, investigation has been done in order to study the performance of different catalysts in SCR reactions.

2.2 Most Promising Technology

The choice of the best technology, able to reduce efficiently the combustion emissions, must take into account costs, reliability, driving performance, fuel consumption and compatibility with other technologies.

The Selective Catalytic Reduction of NO_x, using NH_3 as a reductant, was chosen by the European HD vehicle manufacturers as the most promising technology able to comply with the strict emissions standards for heavy-duty diesel vehicles. In July 2003 this was confirmed and stated in a report issued by the European automobile manufacturers association (ACEA) [7].

ACEA [7] stated «SCR technology corresponds to the best compromise between fuel consumption and formation of pollutants during combustion process. With SCR it is possible to meet the EURO IV and V emission standards and achieve fuel consumption levels 5% to 6% lower than those of equivalent EURO 3 engines». It has also been confirmed that SCR has the potential for emissions reduction to comply with EURO VI norms. [8]

Recently, manufactures announced that they are now starting to use this technology in light duty vehicles in US and in Europe as well. [9]

2.3 SCR- Selective Catalytic Reduction

The study of the NH_3 SCR is the focus of this thesis work. Ammonia is obtained from the decomposition of urea ($NH_2 - CO - NH_2$) according to the following reactions:

$$NH_2 - CO - NH_2 \rightarrow NH_3 + HNCO \qquad (1)$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \qquad (2)$$
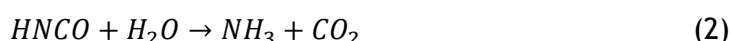
The ammonia produced by the hydrolysis of urea reacts with NO in the presence of O_2, at different rates, to obtain N_2 and H_2O. Besides the well-established "Standard SCR" (3), it is also described in the literature two more SCR reactions, the "Fast SCR" reaction with NO and NO_2 (4) and NO_2 SCR with NO_2 only (5). Many authors [10,11] have been studying the effect of NO_2 feed in SCR rate, but this present work will focus on the "Standard SCR".

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (3)$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \qquad (4)$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \qquad (5)$$
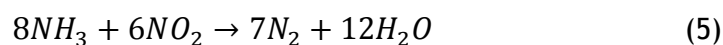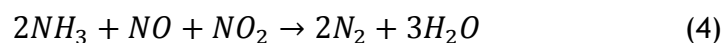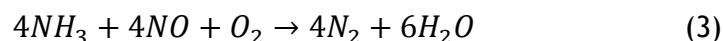
High levels of NO_x conversion can be obtained using ammonia SCR over a wide range of temperatures, and various types of catalysts. In recent years, three major catalysts have been widely employed for this reaction: vanadium [12,13,14], Cu-zeolites [15,16] and Fe-zeolites [17,18]. Vanadium supported on titanium catalysts have been broadly used in the last decades. V_2O_5/TiO_2 is the most active at 350-450°C. At higher temperatures vanadium catalysts lose selectivity due to the enhanced oxidation of ammonia [19]. In addition, vanadia is toxic, which is a major concern [19]. In this context it is necessary to develop new materials that respond to the actual needs in the automobile sector, concerning the real driving conditions. In the past years, new materials have been developed based on Fe- and Cu-exchanged zeolites. These catalysts present many advantages due to its great stability and activity. On the other hand due to its much higher NH_3 storage capacity, ion-changed zeolites are proved to be more difficult than vanadium catalysts to operate transiently on the road, but the large ammonia storage also has several advantages.

Hence, to understand and characterize the behaviour of zeolite-based catalysts during NH_3-SCR operation, Kamasamudram et al [20] proposed a 4-Step protocol of alternating periods of NO and NH_3 combinations. With this method Kamasamudram et al increased the knowledge of multiple catalytic functions, steady state and transient, relevant to mobile SCR applications.

3 Aim of the work

There are no kinetic models or kinetic parameters in the open literature on ammonia SCR on Cu-Zeolites that describe the intra-catalyst profiles. The focus of this work is to develop a kinetic model able to describe the ammonia SCR mechanism over Cu-Beta catalyst. Ammonia SCR was studied over Cu-Beta catalyst, the 4-step protocol (section 4.3) was applied to study NO oxidation, NH_3-SCR and NH_3 oxidation. The intra-catalyst distribution of reactions was established using SpaciMS- Spatially Resolved Capillary Inlet Mass Spectrometer (section 4.2). This experimental data was collected at Oak Ridge National Laboratory and it was used in the kinetic modeling of ammonia SCR.

The simulations were performed using BOOST AVL and the kinetics described in a FORTRAN script routine. The simulations results were analyzed in Matlab.

4 Experimental

The catalyst preparation was conducted at Chalmers University of Technology and the measurements done at ORNL. These experiments were done prior to this master thesis work and in the following sections a short description of them is added.

4.1 Catalyst

The catalyst used was Cu-Beta zeolite, its preparation is described in [21]. The catalyst powder was prepared with silica to alumina ratio of 38, manufactured by Zeolyst International.

The catalyst powder was washcoated on a 400 cpsi cordierite monolith (7.4 mm in diameter and 25.4 mm in length). A thin layer of alumina was inserted to make the attachment of the zeolite easier. Thereafter, the incipient wetness method was applied.

Using an Inductively Coupled Plasma and Atomic Emission Spectrometry (ICP-AES) it was found that the copper content of the zeolite was 4.3%. Specific surface area was also measured according to BET technique and it was measured to be 378.8 $m^2 \cdot g^{-1}$. It is important to bear in mind that the alumina content in the catalyst lowers the BET area compared to pure zeolite. [21]

To ensure thermal stability of the sample, the catalyst was aged for 2h at 500°C in a gas stream using 205 ppm of NO, 183 ppm of NH_3, 10% of O_2, 5% of H_2O in Ar, to simulate SCR conditions.

4.2 Reactor setup and analytical technique

A detailed description of the reactor set up can be found in [1]. Briefly, the catalyst sample was placed in a quartz tube. The gases were pre-heated in coiled pipes and mixed before entering the flow reactor and were supplied by mass flow controllers. A K-type thermocouple was used to control and measure the catalyst internal temperature.

The intra-catalyst gas composition was analyzed using SpaciMS developed in the Fuels, Engines and Emissions Research Center at Oak Ridge National Laboratory in a DOE-funded Cooperative Research and Development Agreement (CRADA) with Cummins Inc. Two fused-silica capillaries were introduced in the reactor tube from the inlet. The capillaries were connected to a multiport valve, and the outlet was linked to the mass spectrometer inlet. The SpaciMS measurements were performed at the catalyst inlet, exit and at six target

intra-catalyst locations: 1/2, 3/8, 1/4, 3/16, 1/8 and 1/16 of the total monolith length. [1] This technique has proved to be minimally invasive [22].

4.3 Experimental Procedure

In order to study the intra-catalyst distributions, the Cummins 4-step protocol [20] was applied. This method consists of four successive steps, exhaust gas (10% O_2, 5% H_2O in Ar) were present in the whole experiment while NO and NH_3 are switched on and off, at constant flow and temperature, as it is represented in the figure below. The duration of each step depends on the required time to reach steady-state.

- **Step 1 (NO oxidation):**
    205 ppm NO, 10% O_2, 5% H_2O in Ar
- **Step 2 (Standard SCR):**
    205 ppm NO, 183 ppm NH_3, 10% O_2, 5% H_2O in Ar
- **Step 3 (NH_3 oxidation)**
    183 ppm NH_3, 10% O_2 and 5% H_2O in Ar
- **Step 4 (NO oxidation):**
    205 ppm, 10% O_2 and 5% H_2O in Ar
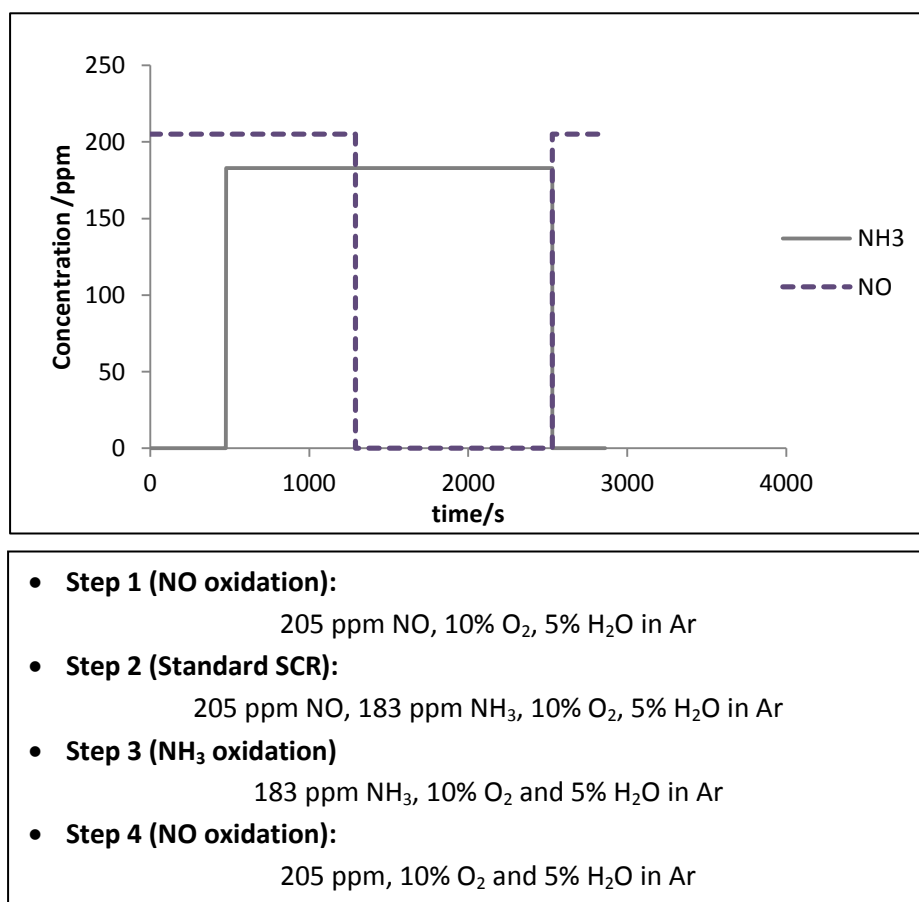
Figure 4 Schematic representation of the 4-Step experimental protocol.

The total flow was 510 sccm (0°C and 760 Torr standard conditions) giving a space velocity of 30000 h^{-1}. The protocol was applied at three temperatures: 200°C, 325°C and 400°C. More details of the experimental procedure can be found in [1].

In order get more information about the adsorption and desorption of ammonia over the catalyst, one TPD-Temperature Programmed Desorption experiment was performed. The

catalyst was first degassed at the temperature of 500°C and then the temperature was lowered to 40°C. After 120 min the catalyst was exposed to 183 ppm of NH_3, 5% of O_2 and 10% of H_2O for about 50 min, followed by a period of exposure to Ar alone for purging. Thereafter, the temperature started to increase at a rate of 5.1C°min^{-1} until reaching 600°C.

4.4 BOOST

"AVL BOOST is an advanced and fully integrated "Virtual Engine Simulation Tool" with advanced models for accurately predicting engine performance, acoustics and the effectiveness of exhaust gas after treatment devices."[2]

BOOST was employed to develop the kinetic model for SCR mechanism and determine the respective rate parameters. BOOST is a user friendly and powerful tool that enables the user to analyze the transient and steady-state performance of the aftertreatment system.

The procedure for tuning kinetic parameters, using BOOST, is described below:

1. The user defines the type specification of the catalyst, in terms of cell density, wall thickness and washcoat thickness (Figure 21- Appendix I); also the catalyst physical properties must be characterized (density, thermal conductivity and specific heat) (Figure 22- Appendix I). This step was only necessary in the beginning of the work, since the same catalyst was used in all the experiments performed.

2. As it was described in the previous section (section 4.2) SpaciMS allowed the analysis of the intra-catalyst distributions, so the specific intra-catalyst locations had to be specified in BOOST, in order to get an accurate simulation of the experimental results. (Figure 23- Appendix I)

3. Before running each simulation the aftertreatment boundaries (Figure 24- Appendix I) must be updated in terms of:

   - temperature: as it was stated previously (section 4.3), the catalyst behaviour was investigated at three temperatures: 200, 325 and 400°C.
   - gas composition: in section 4.3 the 4-step protocol was explained, it consists in alternating periods of NH_3 and NO, 10% O_2, 5% H_2O in

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[2] extracted from AVL website https://www.avl.com/boost1

balance of Argon. The characterization of gas composition is highly important, since it defines each step that is being simulated.

- total flow: it is only necessary to define in the beginning, since the same total flow was used in the whole set of experiments.

4. BOOST enables to link sub-routines defined in FORTRAN to the BOOST-code, so the user can freely define the chemical species, the reaction stoichiometry and the rate laws of the specific chemical reactions that are matter of investigation. Before each run, the parameters of the defined reactions must be specified, it is an important task in kinetic modeling (Figure 25- Appendix I).

5. After running the simulation, BOOST gives a detailed picture of the physical and chemical behavior of the catalyst (Figure 26- Appendix I). These results can be easily exported to Matlab in a text file. Once in Matlab, the simulation results and the experimental results are compared. In these kinetic studies only the steady-state cases were considered; the results of each location at each temperature were plotted and compared. A good result was obtained if the maximum difference between the calculated concentration and the experimental was 10 ppm (relative error of 5%-10%).

The kinetic studies followed this order: first ammonia adsorption/desorption kinetic parameters were modeled, then NO oxidation, followed by ammonia oxidation and finally NH_3 SCR. The kinetic modeling of SCR mechanism is divided in subsystems in order to decrease the correlation between the parameters. The specific order must be tracked since some parameters are vital in the simulation of the new ones (this will be explained further in this report).

The ammonia adsorption/desorption kinetic parameters were the first parameters to be calibrated. Some information from previous studies on this catalyst [21], is available in the literature.

NO and NH_3 simulations were first conducted for one temperature (325°C) and then, after getting a good result the same parameters were used at the higher temperature. The simulations started at 325°C because it is in the middle of the temperature interval. The simulated activity at 400°C was however higher than the experimental value. As it is well-known from chemical reaction engineering that the activation energy is not dependent on temperature and according to Maxwell-Boltzmann distribution diagram, the reaction rate

increases with temperature due to disproportionately large increase in high energy collisions. So, a new activation energy leading to better simulation results both at 325 and 400 °C had to be found. To this end, the activation energy was changed and the pre-exponential factor recalculated, these parameters were then applied in BOOST until a successful simulation was achieved at 400 °C in a trial-and-error method. After getting a good result, the same parameters were applied at 325°C. It is known from the literature [10-19] that at 200°C NO and NH_3 oxidation is not active, nevertheless in order to validate the results the simulation at 200°C was run to confirm that the conversion of NO or NH_3 was zero. This method worked very well.

NH_3 SCR was the last reaction to simulate, since it required all the parameters that had been determined before. This set of experiments turned out to be the most difficult to model, since NO and NH_3 must be considered together at all the three temperatures and six locations. The method described above was applied in this set of experiments (SCR). The experimental results showed that SCR is very active in the catalyst front, which means that it is the first locations that are more sensitive in the simulation. In this context, two locations (in the front of the catalyst) were chosen and the results at these locations, were analysed for both NO and NH_3 at the three temperatures, and the SCR kinetic parameters were changed until getting a good result. After that all locations were simulated.

Unlike the classic model that only analyses the catalyst outlet, in this kinetic work six locations must be considered together, which is challenging. However, good and reliable results were obtained that can describe the intra-catalyst distribution.

5 NH$_3$ Temperature Programmed Desorption

5.1 Kinetic Model

A good description of ammonia storage and release over the catalyst surface is a crucial part of the overall SCR model. Therefore, a good model for the ammonia adsorption and desorption is important in order to get an accurate understanding of transient SCR activity.

Ammonia adsorbs both on the copper sites [23] and Brönsted acid sites. Nevertheless, in this model only one type of active surface sites will be taken into account, designated by S1. This assumption has been used by other authors [15,24] in order to make the model simpler.

The adsorption and desorption of NH$_3$ on an active site are described by the following forward and backward reactions:

$$NH_3 + S1 \leftrightarrow NH_3 \cdot S1 \tag{6}$$

(symbol S1 denotes an active surface site, as explained before)

The rate expressions for NH$_3$ adsorption and desorption are described, respectively, as

$$r_a = k_a C_{NH_3} \theta_{S1-vacant} \tag{7}$$

$$r_d = k_d \theta_{NH_3-S1} \tag{8}$$

The temperature dependence of each rate constant can be depicted using the Arrhenius equation:

$$k_i = A_i e^{-E_{A,i}/RT_s} \qquad i = a, d \tag{9}$$

Temperature Programmed Desorption experiments show that the desorption peak of ammonia is very broad which means that NH$_3$ adsorbs on the catalyst surface with different energies. Many authors [15,17,21,24] use a coverage dependent activation energy:

$$E_{A,d} = E_{A,d}(0)(1 - \alpha_1 \theta_{NH_3-S1}) \tag{10}$$

where θ_{NH_3-S1} is the surface coverage of ammonia and α_1 is a constant describing coverage dependent activation energy for NH$_3$ in this reaction.

5.2 Results and Discussion

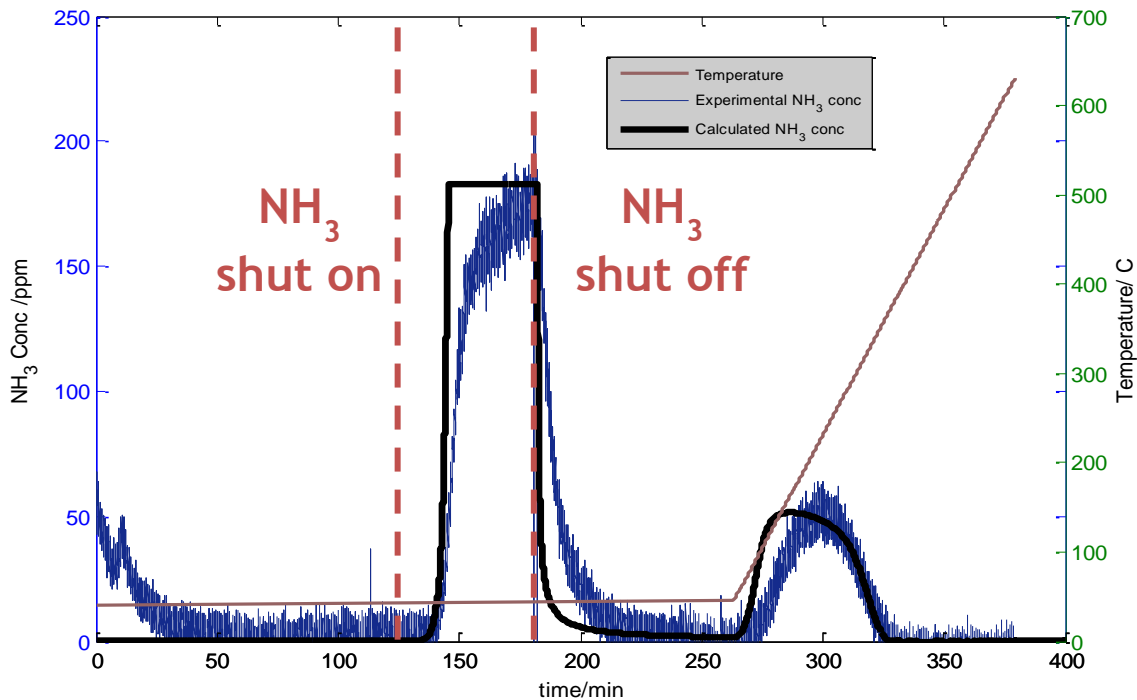The results from both the experiment and simulation are represented in Figure 5.

Figure 5 Experimental and calculated NH₃ concentration during NH₃ TPD. Catalyst is exposed to 183 ppm of ammonia, 10% O₂ and 5% H2O for 60 min at 40°C followed by Ar purge and a temperature ramp.

After NH$_3$ was fed to the catalyst (t=120 min), no ammonia was observed in the gas outlet, which means that ammonia was absorbed on the catalyst. Ammonia has very "sticky" properties, which results in high NH$_3$ uptake in the catalyst front and zero breakthrough at the outlet initially [21]; NH$_3$ front then moved down the bed and broke through after 13 min (t= 135 min). As it can be seen in the figure above, the increase of concentration in the experimental curve is slower than the simulated one when the concentration is high, this might be explained by a slower adsorption when the catalyst is close to saturation [15].

After the adsorption phase, the catalyst is exposed to Ar only and desorption of loosely bound ammonia is observed. After 10 min the temperature started to increase and a desorption peak was observed. The desorption peak is very broad, which means that ammonia desorbs the catalyst surface with different energies. At 400°C, all ammonia has desorbed from the surface.

The model can describe the storage and release of ammonia well over the catalyst due to the coverage dependent activation energy for ammonia desorption (10) that was included in the model.

BOOST was employed to get a detailed picture of the catalyst physical and chemical behavior during transient operation. The simulation results were achieved changing the pre-exponential factors for NH_3 adsorption and desorption until the deviation between simulation and experiment was minimized. The value for α_1 and activation energy for ammonia desorption were determined by Wilken et al [21], in the calorimetric experiments performed. NH_3 adsorption is assumed to be a non activated process [15,25], so $E_{a,f}$ is set to zero. The kinetic parameters are presented in Table 1.

Table 1 Parameters of NH3 Adsorption and Desorption

site density (mol-sites·m^{-3}$_{cat}$)	Pre-exp factor adsorption, A_a (s^{-1})	Activation energy adsorption, $E_{A,a}$ (kJ·mol^{-1})	Pre-exp factor desorption, A_d (s^{-1})	Activation energy desorption, $E_{A,d}$ (kJ·mol^{-1})	α_1
60.9	9279	0	6.76 x 10^9	113.0	0.39

The heat of desorption for zero coverage obtained in this model is in line with the results obtained from other authors for acid zeolites. Busco et al. [26], for instance, studied the heat of adsorption at 303K and obtained 130 kJ·mol^{-1} at zero coverage for both H-Beta and H-ZSM-5; Felix et al. [27] investigation resulted in ΔH for zero coverage of about 120 to 130 kJ·mol^{-1} for H-ZSM-5 ; as mentioned above the calorimetric experiments of Wilken et al [21] in Cu-Beta catalyst resulted in an heat of desorption of ammonia at zero coverage of 113.0 kJ·mol^{-1}, which is the value used in this study.

6 NO oxidation- Step 1

6.1 Kinetic Model

In the first step of the protocol, NO is fed alone to the catalyst and the oxidation of nitric oxide is studied. NO oxidation was described by a global reversible reaction, which has been previously used for models for zeolite based-catalysts [15,16]:

$$NO + 1/2\,O_2 \leftrightarrow NO_2 \qquad\qquad (11)$$

This reaction is important in the SCR mechanism; it is shown that NO_2/NO ratio has a major effect on the catalytic efficiency of zeolite-based SCR catalysts. It has been appointed that 50% NO_2 and 50% NO is much more reactive with NH_3 than NO only [10-12,29]. The rate expression for reaction (11) is described as:

$$r_{NO} = k_{NO,f}C_{O_2}{}^{1/2}C_{NO} - k_{NO,b}C_{NO_2} \qquad\qquad (12)$$

where the rate constants are modeled using Arrhenius equation:

$$k_{NO,i} = A_{NO,i}e^{-E_{A,NO,i}/RT_s} \qquad\qquad i = f,b \qquad\qquad (13)$$

At higher temperatures the rate of NO oxidation is controlled by the thermodynamics, the backward rate constant, $k_{NO,b}$, is determined by the equilibrium constant, using ΔH= -58.279 kJ·mol^{-1} and ΔS=-76.1 J·mol^{-1}·K^{-1}.

6.2 Results and Discussion

The catalyst was exposed to 205 ppm NO, 10% O_2 and 5% H_2O in Ar at three different temperatures 400°C, 325 °C and 200 °C. The results obtained for each temperature can be observed in Figures 6-8. At the lowest temperature (200 °C) no NO conversion was observed, as it is shown in Figure 6; at 325°C a maximum concentration of 195 ppm was observed at the catalyst outlet, which gives a conversion of 5% (Figure 7). For the experiment performed at 400°C the concentration in the catalyst outlet was 159 ppm, which corresponds to a conversion of 22%. Figure 8 shows an inhibiting effect of NO_2 on the oxidation of NO in the second half of the catalyst length. It is maybe due to a competitive adsorption of NO_2 on the available active sites for NO oxidation reaction [18]. If this is added in the reaction rate, it results in an increase in the apparent activation energy [20,29].
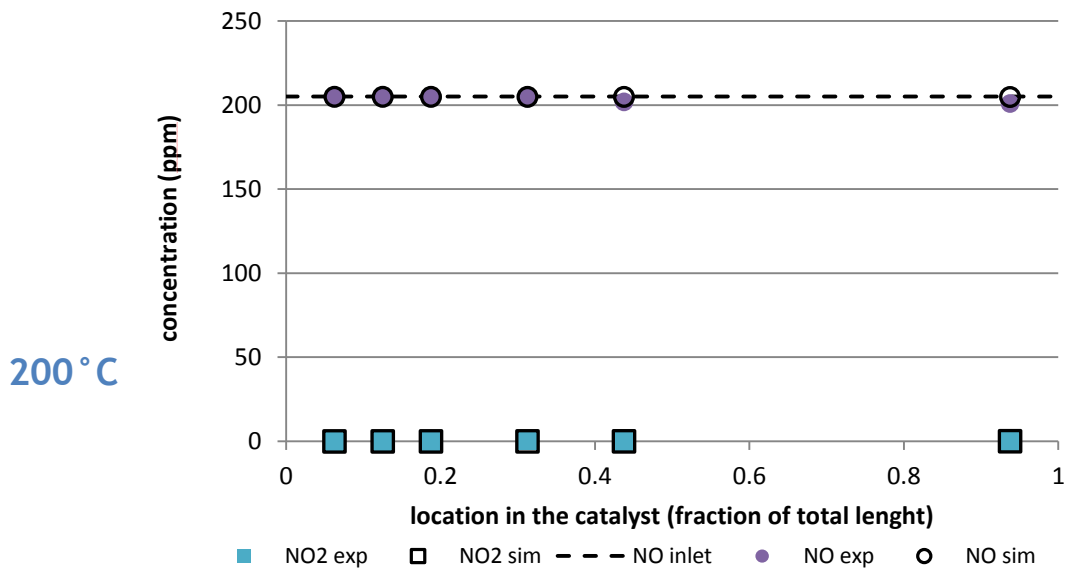
200°C

Figure 6 Comparison between the calculated and measured NO and NO_2 concentration within the catalyst, during Step 1 of the 4-step protocol at temperature of 200°C

325°C

Figure 7 Comparison between the calculated and measured NO and NO_2 concentration within the catalyst, during Step 1 of the 4-step protocol at temperature of 325°C
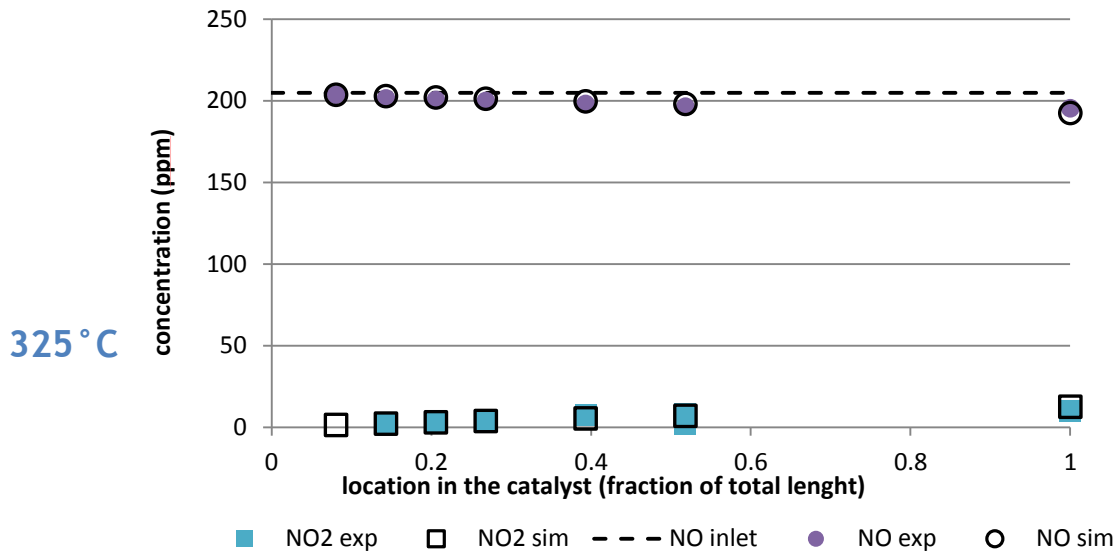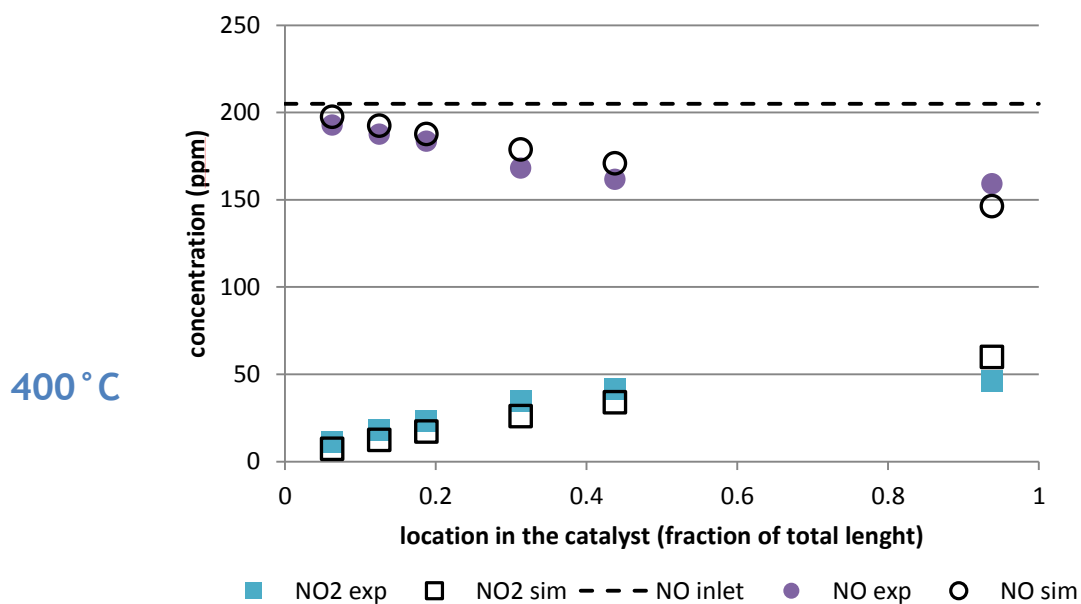
400˚C

Figure 8 Comparison between the calculated and measured NO and NO₂ concentration within the catalyst, during Step 1 of the 4-step protocol at temperature of 400˚C

The agreement between the measured and the calculated results is good, which confirms that the model, with one reversible rate for NO oxidation, is adequate to describe this reaction. Using BOOST, the kinetic parameter calibration was achieved for NO oxidation, on the basis of the steady-state experimental results. The result of the tuned parameters for the reversible NO oxidation is presented in Table 2. To obtain these results an iterative calculation was maintained until the deviation between the simulated concentrations and the experimental values was minimal.

Table 2 Estimated parameters for NO oxidation, step 1 of 4-step protocol

Rate	Rate Constant	Pre-exponential Factor, $A_{NO,f}$ $(kmol^{-1/2} \cdot m^{-3/2} \cdot s^{-1})$	Activation Energy, $E_{A,NO,f}$ $(kJ \cdot mol^{-1})$
NO oxidation (r_{NO})	k_{NO}	1.473×10^8	88.0

The activation energy obtained for Cu-Beta zeolite was 88 kJ·mol⁻¹ with the presented model. Olsson [15] studied ammonia SCR over Cu-ZSM5 and obtained Ea= 48 kJ·mol⁻¹ for NO

oxidation reaction. Mulla [29] found an activation energy of 82 kJ·mol^{-1} in the kinetic studies of NO oxidation using Pt catalysts.

7 NH$_3$ oxidation- Step 3

7.1 Kinetic Model

During the third step of the protocol the feed consists of only NH$_3$, O$_2$ and H$_2$O, and in this section pure ammonia oxidation is investigated. It is vital to include NH$_3$ oxidation in the SCR model since ammonia is related to a variety of NO$_x$ reactions and to NH$_3$ slip. In this step it will be possible to quantify steady-state ammonia oxidation by oxygen alone, without NO$_x$. This process can, theoretically, produce species such as N$_2$, N$_2$O, NO and NO$_2$, however today zeolite based catalysts are very selective towards N$_2$, even at high temperatures [18]. Ammonia oxidation is a non desirable reaction in SCR mechanism, it represents a competition with SCR reaction as both reactions consume ammonia.

The detailed mechanism of NH$_3$ oxidation is not well-known. Some authors believe that ammonia is directly oxidized to N$_2$ [30], others suggest that the oxidation of ammonia to NO is an intermediate step and the nitric oxide produced will react with additional NH$_3$ to produce NH$_3$ and N$_2$ [31].

The reaction of NH$_3$ oxidation is described as:

$$4NH_3 \cdot S1 + 3O_2 \rightarrow 2N_2 + 6H_2O + 4S1 \tag{14}$$
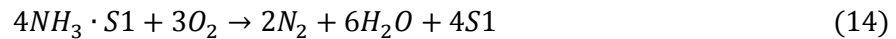
The rate of NH$_3$ oxidation can be expressed as:

$$r_{NH_3} = k_{NH_3} \theta_{NH_3-S1} C_{O_2}^{0.6} \tag{15}$$

where the rate constant is described by the Arrhenius form:

$$k_{NH_3} = A_{NH_3} \, e^{-E_{A,NH_3}/RT_s} \tag{16}$$

7.2 Results and Discussion

The reaction of ammonia oxidation takes place from the adsorbed NH$_3$ on the active sites, so the capability of oxidizing ammonia is dependent on the characteristics of ammonia storage and release. Therefore, the simulation of the kinetic parameters of NH$_3$ oxidation reaction must be considered together with the already tuned parameters for NH$_3$ adsorption and desorption.

Using BOOST, the kinetic parameters for ammonia oxidation were calibrated on the basis of the steady-state experimental results for step 3. In Figures 9-11, next presented, the experimental and simulated results of the steady-state concentration of NH$_3$ of Step 3 of the 4-step protocol [20] are compared.
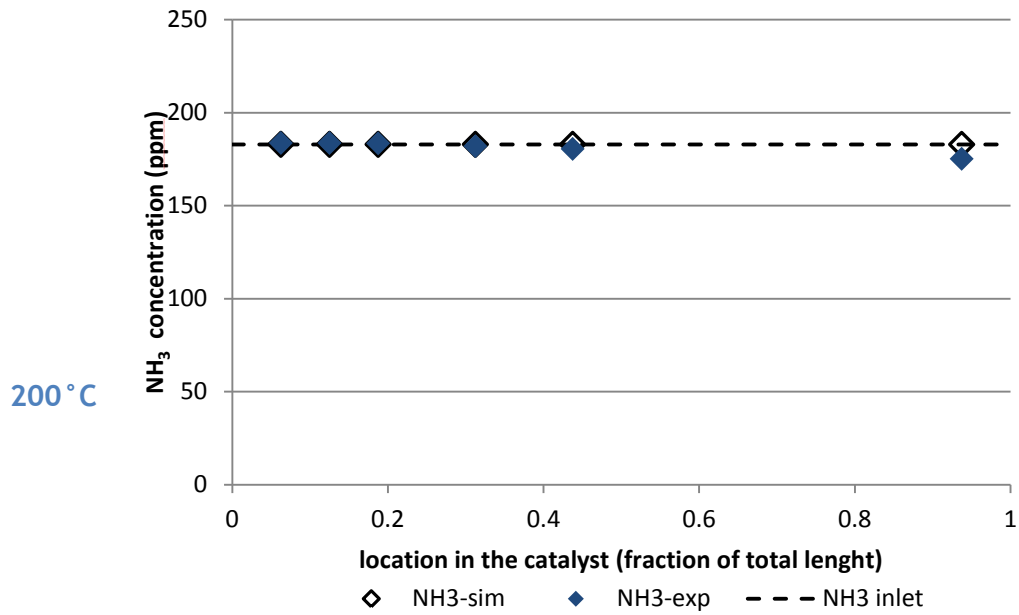
Figure 9 Comparison between the calculated and measured NH$_3$ concentration within the catalyst, during Step 3 of the 4-step protocol at temperature of 200˚C
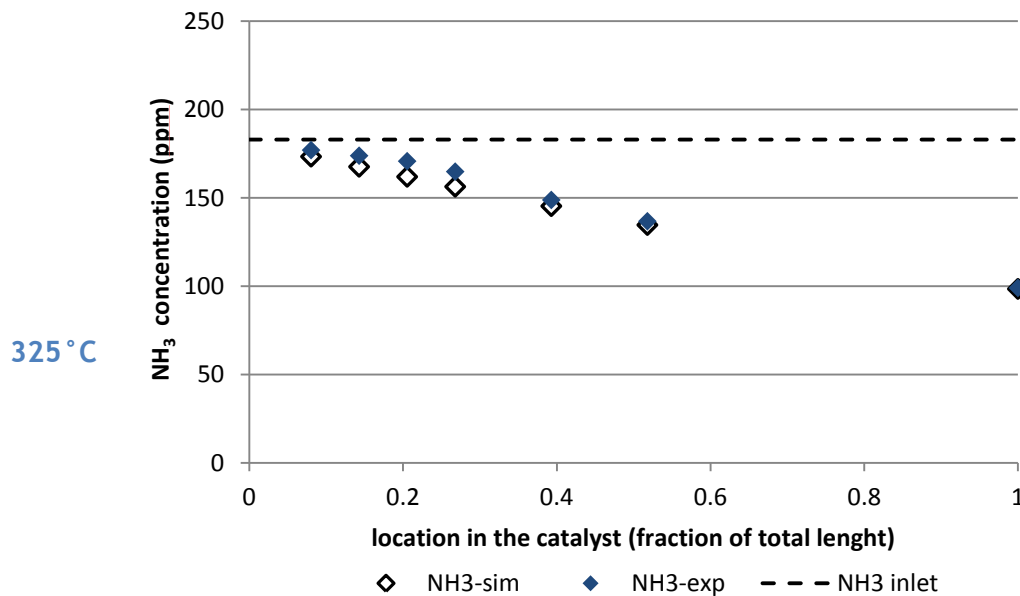

Figure 10 Comparison between the calculated and measured NH$_3$ concentration within the catalyst, during Step 3 of the 4-step protocol at temperature of 325˚C
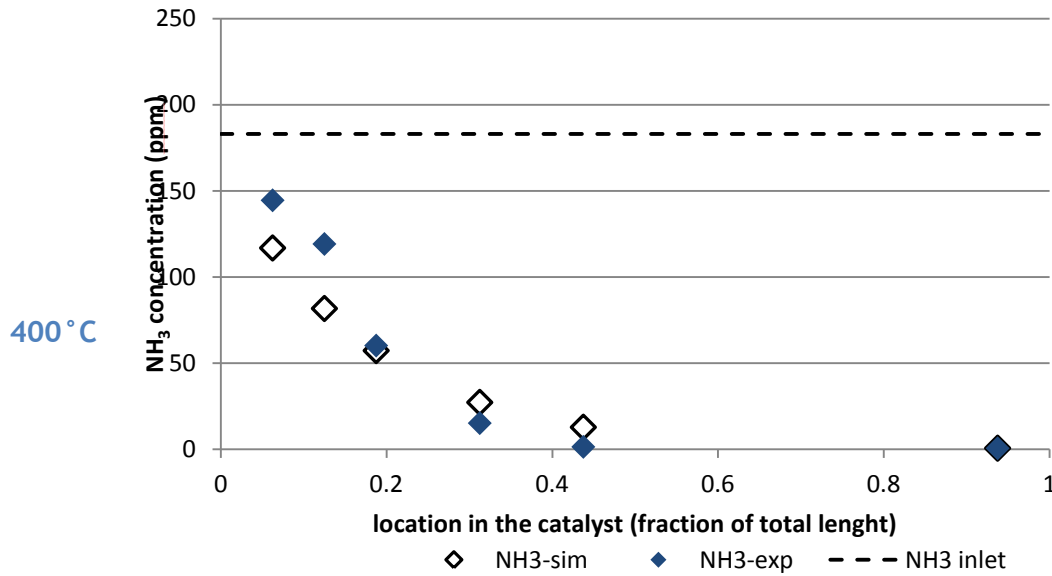
Figure 11 Comparison between the calculated and measured NH$_3$ concentration within the catalyst, during Step 3 of the 4-step protocol at temperature of 400˚C

The results reveal that ammonia oxidation rate increases as temperature becomes higher. At the lowest temperature investigated (200℃) there was no oxidation of ammonia (Figure 9). At 325℃ a conversion of almost 45% of ammonia was achieved at the catalyst outlet (Figure 10). A noteworthy ammonia oxidation was observed at 400℃ since there was a complete conversion of NH$_3$ at half length of the catalyst (Figure 11). The model shows a good agreement with the experimental results, although at the temperature of 400℃ there are some discrepancies in the front of the catalyst, maybe due to inaccuracy of ammonia coverage prediction.

The rate parameters for step 3 are presented in Table 3.

**Table 3 Estimated parameters for NH$_3$ oxidation, step 3 of the 4-step protocol**

Rate	Rate Contant	Pre-exponential Factor $(kmol^{0.4} \cdot m^{-1.2} \cdot s^{-1})$	Activation Energy $(kJ \cdot mol^{-1})$
NH$_3$ oxidation (r_{NO})	k_{NH3}	3.501×10^{11}	157.1

With the model proposed the activation energy for ammonia oxidation was found to be 157 kJ·mol^{-1}. This value is in line with the values in the literature: Baik et al. [16] obtained Ea= 166 kJ·mol^{-1} using Cu-ZSM-5; Olsson et al [15] reported an Ea= 162 kJ·mol^{-1} for ammonia oxidation reaction with Cu-ZSM5 catalyst; Chatterjee et al [32] found a value of 178 kJ·mol^{-1} for the activation energy using a commercial zeolite.

8 NH$_3$ SCR- Step 2

8.1 Kinetic Model

In the second step of the protocol, 205 ppm of NO flows together with 183 ppm of NH$_3$ over the catalyst and ammonia selective catalytic reduction is investigated. The model for NH$_3$ SCR, the so-called standard SCR, is described by the reaction that includes adsorbed ammonia and gas phase NO:

$$4NH_3 - S1 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O + 4S1 \tag{17}$$
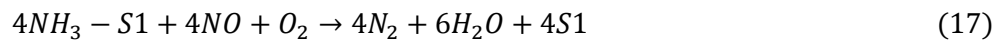
Its rate can be expressed as:

$$r_{SCR} = k_{SCR} C_{NO} \theta_{NH_3-s1} \tag{18}$$

The rate constant dependence on temperature can be depicted by Arrhenius equation:

$$k_{SCR} = A_{SCR}\, e^{-E_{A,SCR}/RT_s} \tag{19}$$

8.2 Results and Discussion

For a realistic simulation of NH$_3$ SCR, NH$_3$ adsorption/desorption, NO and NH$_3$ oxidation must be consider together. Hence, the estimation of SCR kinetics was carried out using the parameters already tuned in the previous sections of this report.

Employing BOOST, the kinetic parameters of ammonia SCR were investigated on the basis of the experimental steady-state results. Figures 12-17 compare the calculated and measured results for ammonia SCR for the three temperatures studied: 200°C, 325°C and 400°C. In this experiments NH$_3$ is used in deficit, once it was proved [20] that, under this range of temperatures, ammonia gets utilized very selectively if the ammonia/NO$_x$ molar ratio is less than 1. Figures 18-20 show the NH$_3$ limited steady-state conversions for NH$_3$ and NO, calculated as the percentage available of NH$_3$ (183 ppm) owing to the stoichiometric use of NH$_3$.

NH_3
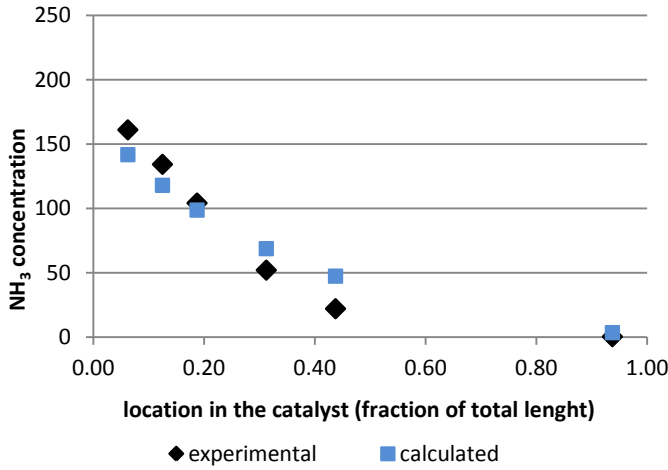
200°C

Figure 12 Comparision between experimental and calculated steady-state concentrations of NH_3, from Step 2 of the 4-Step protocol at 200°C
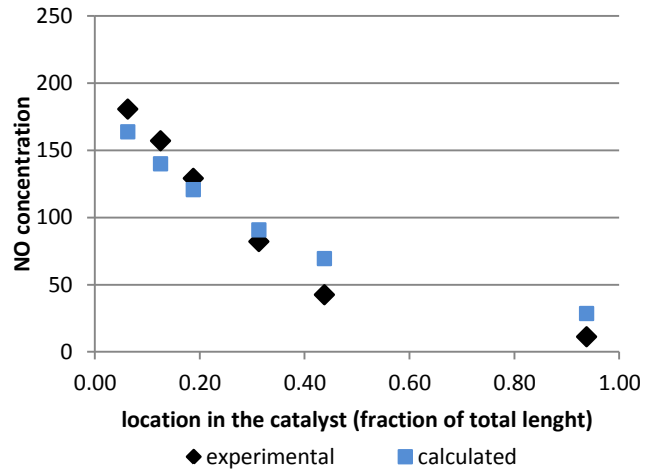
NO

Figure 13 Comparison between experimental and calculated steady-state concentrations of NO, from Step 2 of the 4-Step protocol at 200°C

325°C

Figure 14 Comparision between experimental and calculated steady-state concentrations of NH_3, from Step 2 of the 4-Step protocol at 325°C
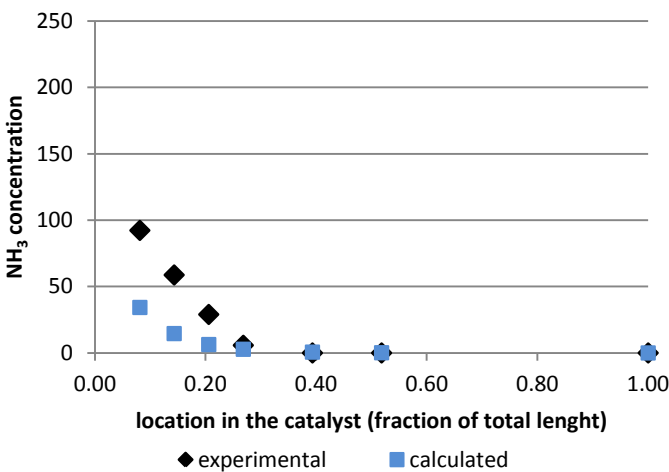

Figure 15 Comparison between experimental and calculated steady-state concentrations of NO, from Step 2 of the 4-Step protocol at 325°C

400°C

Figure 16 Comparison between experimental and calculated steady-state concentrations of NH$_3$, from Step 2 of the 4-Step protocol at 400°C
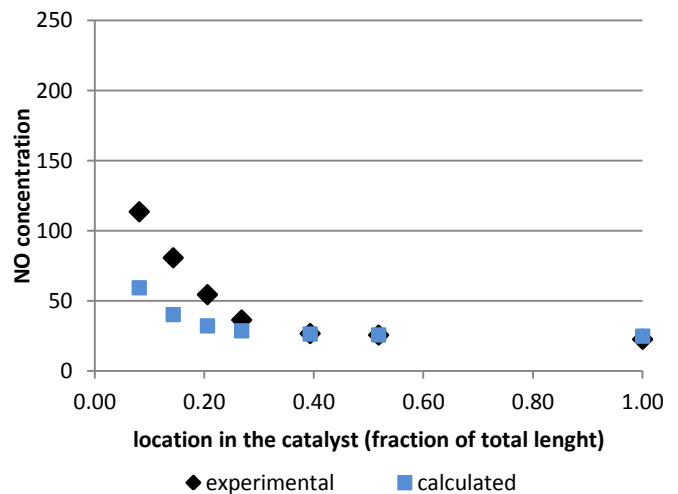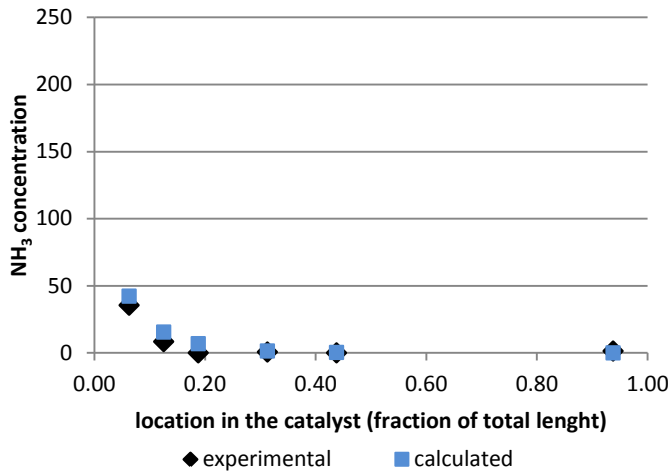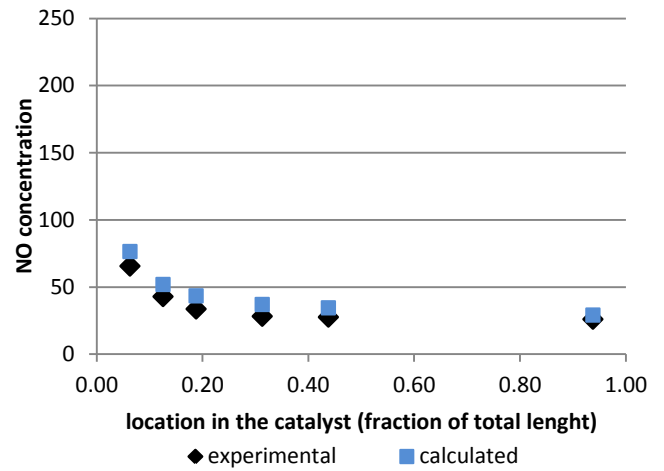

Figure 17 Comparison between experimental and calculated steady-state concentrations of NO, from Step 2 of the 4-Step protocol at at 400°C

At 200°C the concentrations of NH$_3$ and NO decrease linearly at the front of the catalyst, ammonia is fully converted only at the catalyst outlet (Figure 12). However, since there were no measuring points between half length of catalyst and the outlet it is not possible to say exactly in which location the conversion of ammonia reached 100%. Figure 18 shows that ammonia-limited NO and NH$_3$ conversions indicate a stoichimetry of 1:1, which is in agreement with the Standard SCR reaction (17).

At 325°C, the initial slopes of the curves are higher than the ones for 200°C, which indicates that the consumption of NH$_3$ and NO was faster at this temperature (Figures 14 and 15). SCR took place mostly at the front of the catalyst and by 3/8 of the total length of the catalyst ammonia was fully consumed. The 1:1 NO:NH$_3$ stoichiometry was consistent with the Standard SCR, as it can be seen in Figure 19. The ammonia-limited NO-conversion was similar to the ammonia conversion, which means that despite the significant NH$_3$ oxidation measured in Step 3 (Figure 10, section 7.2) at this temperature, ammonia was mainly reacting in the SCR reaction. This high selectivity for SCR reaction indicates that at 325°C ammonia SCR is faster than NH$_3$ oxidation.

At 400°C, the apparent SCR rate is even higher, about 80% of ammonia is consumed at the very front of the catalyst (1/16 of the total length). At the first quarter of catalyst length all ammonia has been consumed (Figure 16). At this temperature the conversion of ammonia is larger than the NO conversion (Figure 20), which indicated that ammonia

oxidation started to compete with SCR at 400℃. However, SCR selectivity was still not significantly affected and it can seen that the NO:NH_3 stoichiometry was close to 1:1, despite the significant oxidation of ammonia at 400℃ in the absence of NO (Figure 11, section 7.2).
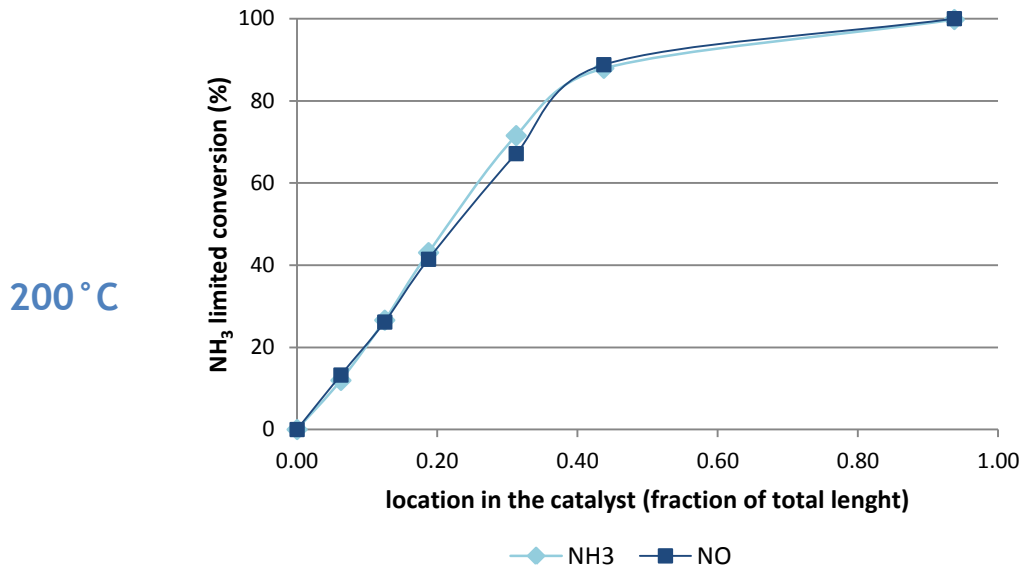
200°C

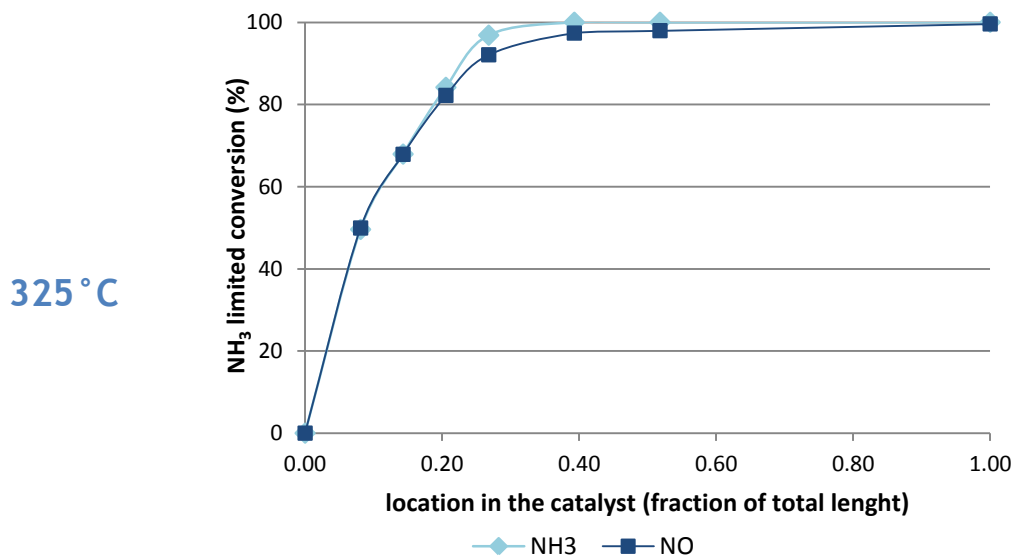**Figure 18 NH₃-limited conversion of NH₃ and NO during SCR step at 200°C**

325°C

Figure 19 NH₃-limited conversion of NH₃ and NO during SCR step at 325°C
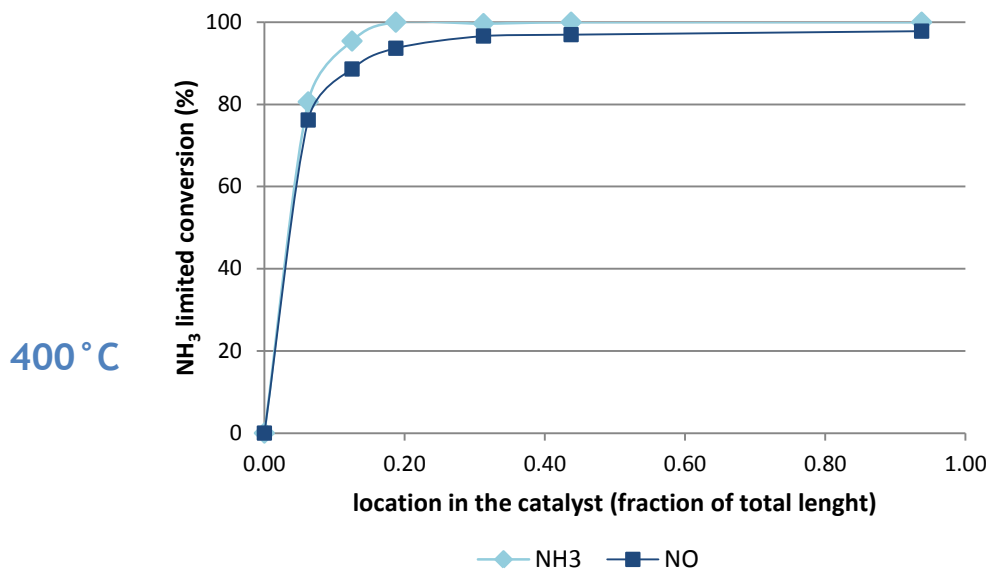
400°C

Figure 20 NH$_3$-limited conversion of NH$_3$ and NO during SCR step at 400°C

The comparison between the SCR NO-conversion profiles within the catalyst at the three temperatures studied highlights the temperature-induced kinetic differences. Although the conversion of ammonia is identical (100%) for all the three temperatures, the experiments performed allowed to quantify the SCR zone variations. At 400°C ammonia was fully consumed within a quarter of the catalyst, while at 325°C and 200°C the total conversion of NH$_3$ was reached at 3/8L and 1L, respectively. This analysis was only possible to conclude due to SpaciMS, that is able to detect the kinetic variation inside the catalyst.

It was shown that at the highest temperature (400°C) ammonia oxidation occurs during SCR reaction, however it is not clear if NO oxidation takes place under SCR conditions. Nevertheless if NO oxidation occurs, the enrichment of NO$_2$ is beneficial in the SCR rate [10-12].

A good agreement between the calculated concentrations and the steady-state experimental results was observed for both species (NH$_3$ and NO). However some discrepancies were found at 325°C for the results in the front of the catalyst (Figures 14 and 15), possibly due to either some experimental uncertainty in the exact location of measurement points within this high gradient catalyst region or ammonia inhibition which was not considered in the model, it is an issue that is still under investigation. The values of the kinetic parameters estimated are presented in the following table:

Table 4 Estimated parameters for ammonia SCR, step 2 of the 4-step protocol

Rate	Rate Contant	Pre-exponential Factor (s^{-1})	Activation Energy ($kJ \cdot mol^{-1}$)
NH3 SCR (r_{SCR})	k_{SCR}	5.876×10^{10}	81.0

The activation energy of SCR reaction derived in this model, 81 $kJ \cdot mol^{-1}$, is in the range of values found in literature. Baik et al [16] obtained an Ea of 52 $kJ \cdot mol^{-1}$ for ammonia SCR using Cu-ZSM5 catalyst; for this reaction Olsson et al [15] estimated a value of 85 $kJ \cdot mol^{-1}$ for activation energy with Cu-ZSM5; Wang et al [24] found activation energy of 77 $kJ \cdot mol^{-1}$ in their studies with Fe-zeolite.

9 Conclusions and future work

Selective catalytic reduction of NO with NH_3 was studied over Cu-Beta catalyst. In order to understand the multiple catalytic functions relevant in SCR mechanism, the 4-step protocol developed by Kamasamudram et al. [20] was applied. SCR reaction, NO and NH_3 oxidation reactions were monitored using spatially resolved capillary inlet mass spectrometer (SpaciMS). The experiments were carried out at 200, 325 and 400°C and the gas composition was analysed at about 1/16L, 1/8L, 3/16L, 1/4L, 3/8L, 1/2L and 1 L, in which L is the catalyst total length. In addition, one NH_3 TPD was performed to get information about the adsorption and desorption of ammonia over the catalyst. These experiments were conducted at ORNL prior to this master thesis work.

The focus of the present work was to develop a kinetic model able to describe ammonia SCR mechanism over Cu-Beta catalyst. BOOST was employed to determine the respective kinetic parameters using the experimental steady-state results from 4-step protocol. In addition, BOOST allowed the calibration of the kinetic parameters of ammonia adsorption and desorption on the basis of the TPD experiment.

A good description of ammonia storage and release is crucial to get an accurate understanding of the SCR mechanism, thus the kinetic study started with the calibration of NH_3 adsorption/desorption parameters. The model was able to describe well the storage and release of ammonia due to the inclusion of the coverage dependent activation energy for ammonia desorption in the model. The TPD experiment showed that ammonia desorbs from the surface with different energies, the catalyst could keep some of stored NH_3 until the temperature reached 400°C.

In step 1 of the 4-step protocol NO and oxygen were passed over the catalyst and NO oxidation was investigated. This reaction can have a major effect on SCR rate since NO_2 /NO mixtures are known to be more reactive than NO alone [10-12]. However, it is possible that the presence of ammonia suppresses the NO oxidation reaction. The experimental results showed that at lower temperatures the conversion is kinetically limited and the conversion of NO into NO_2 increases with temperature. At 400°C an inhibition of NO conversion was observed, probably due to the blockage of the active sites by the NO_2 produced . A good agreement was observed between the experimental steady-state results and the kinetic parameters for NO oxidation.

In step 3 of the protocol, the oxidation of NH_3 can be studied. For a realistic simulation of NH_3 oxidation, ammonia adsorption and desorption were considered together, as the ammonia oxidizing capability is dependent on its storage and release characteristics. The

experimental results demonstrated that the oxidation of ammonia increases with the temperature; at 325°C the conversion of ammonia was 40% and at the highest temperature (400°C) full conversion was observed. However, there was no oxidation of ammonia at 200°C. The kinetic parameters for NH_3 oxidation, based on the steady-state results, can predict well the experimental concentrations.

In step 2 the so-called 'Standard SCR' reaction takes place, where NH_3 on the surface reacts with NO in the gas phase. For an accurate simulation of SCR, NH_3 adsorption/desorption and NO and NH_3 oxidation results were considered together. At 400°C ammonia was fully consumed within a quarter of the catalyst, and at 325°C and 200°C the total conversion of NH_3 was reached at 3/8L and 1L, respectively. This analysis was only possible to conclude due to SpaciMS that is able to detect the kinetic variation inside the catalyst. The effect of ammonia oxidation was also investigated in this step, the results for the ammonia-limited conversion of NO and NH_3 showed that the NO:NH_3 stoichiometry was practically 1:1 despite the significant oxidation of ammonia in step 3, especially at the highest temperature (400°C). The kinetic parameters for SCR, calculated using the experimental steady-state results, were in line with results obtained by other authors and can describe the experiments well.

SpaciMS proved to be very useful to determine the spatial profiles within the catalyst. Unlike the classic method that only measure the conversion of the species at the outlet of the catalyst, with the method described in this thesis work it is possible to examine the kinetic variation inside the catalyst, despite the fact that the conversion at the outlet is the same (100%) for the three studied temperatures.

The detailed information provided by SpaciMS was vital to determine the rate parameters presented in this report. The resulted kinetic model was able to describe well the SCR mechanism. Nevertheless, there were some discrepancies (Figure 11, section 7.2 and Figure 14 and 15, section 8.2) in the model that can be investigated further. In this context, kinetic modeling of transient experiments will be done and the dynamic ammonia inhibition will be studied.

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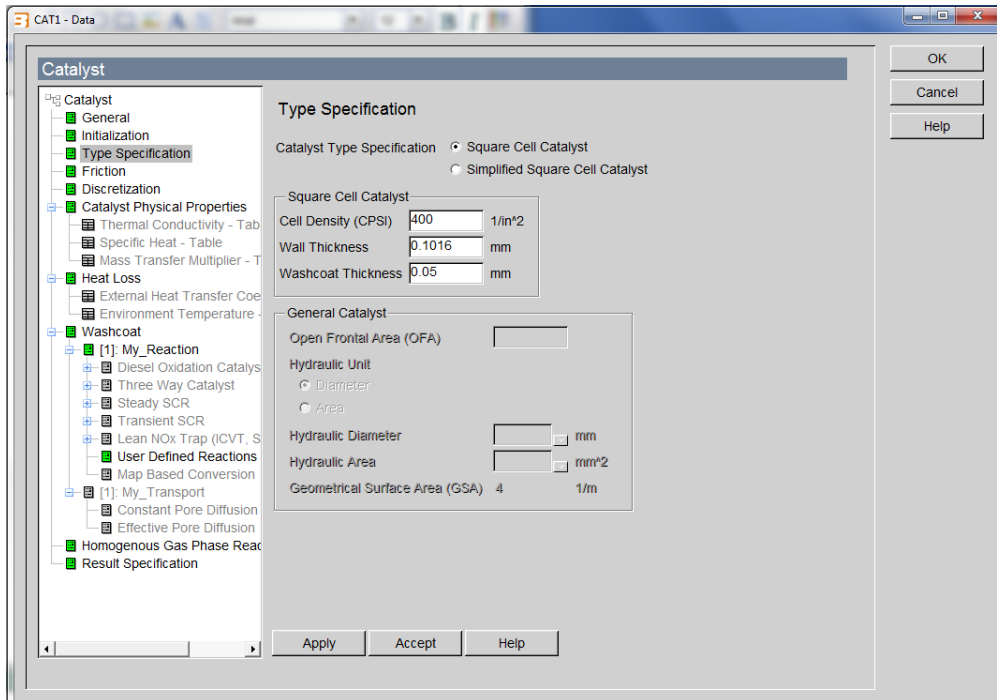
Appendix I - BOOST
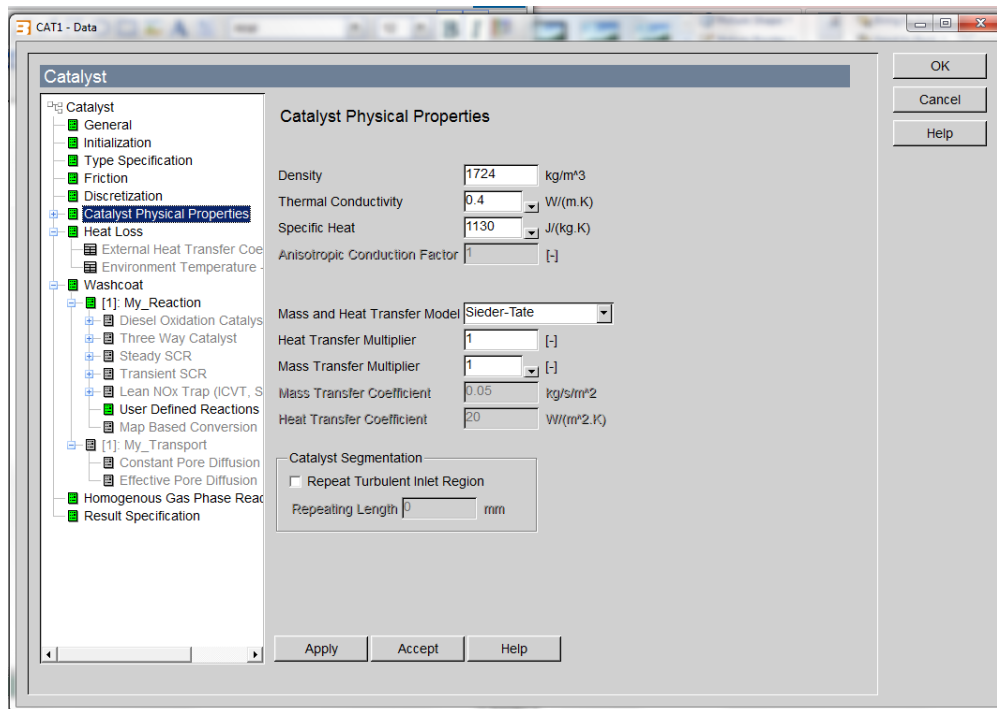

Figure 21 BOOST window- catalyst type specification.

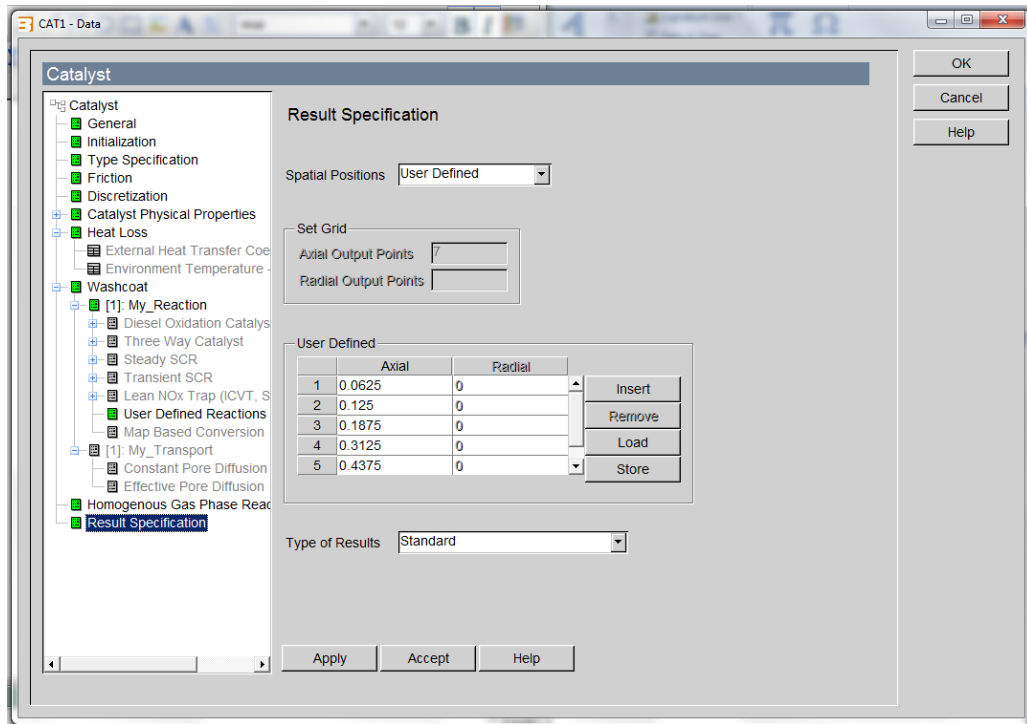**Figure 22 BOOST window- catalyst physical properties.**
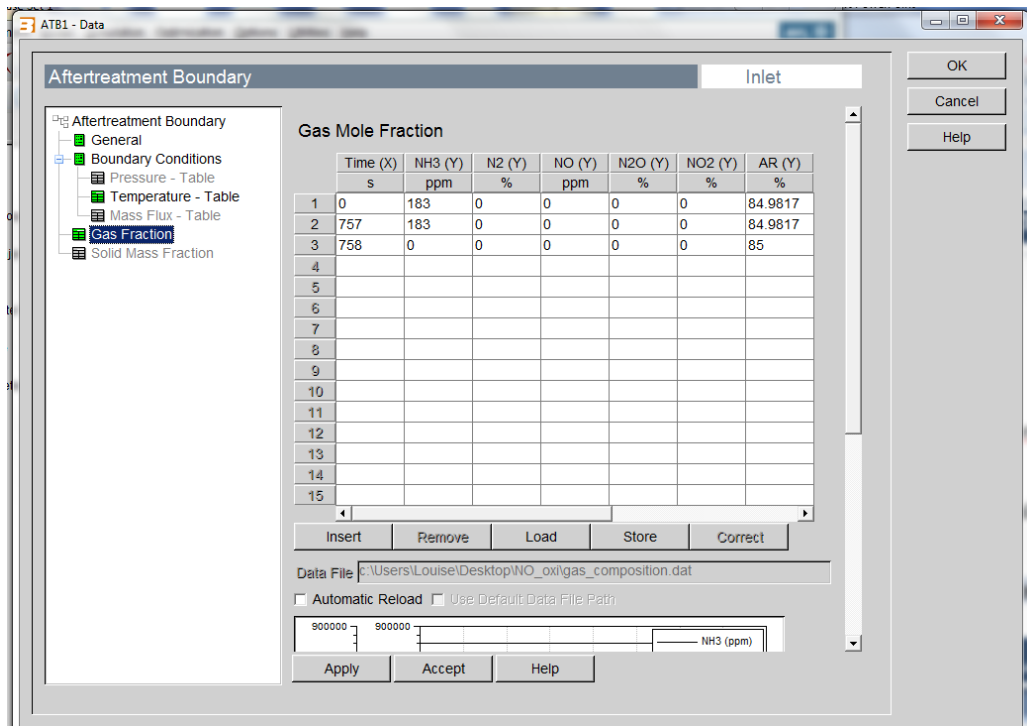
Figure 23 BOOST window- result specification.
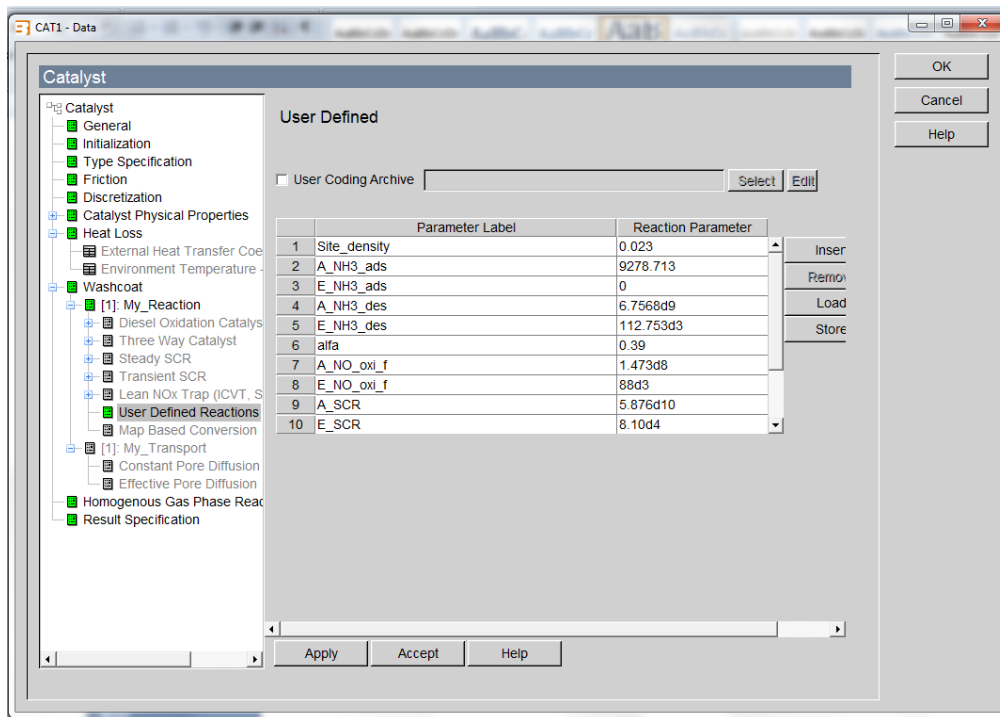

Figure 24 BOOST window- aftertreament boundary.

Figure 25 BOOST window- user defined reaction parameters.
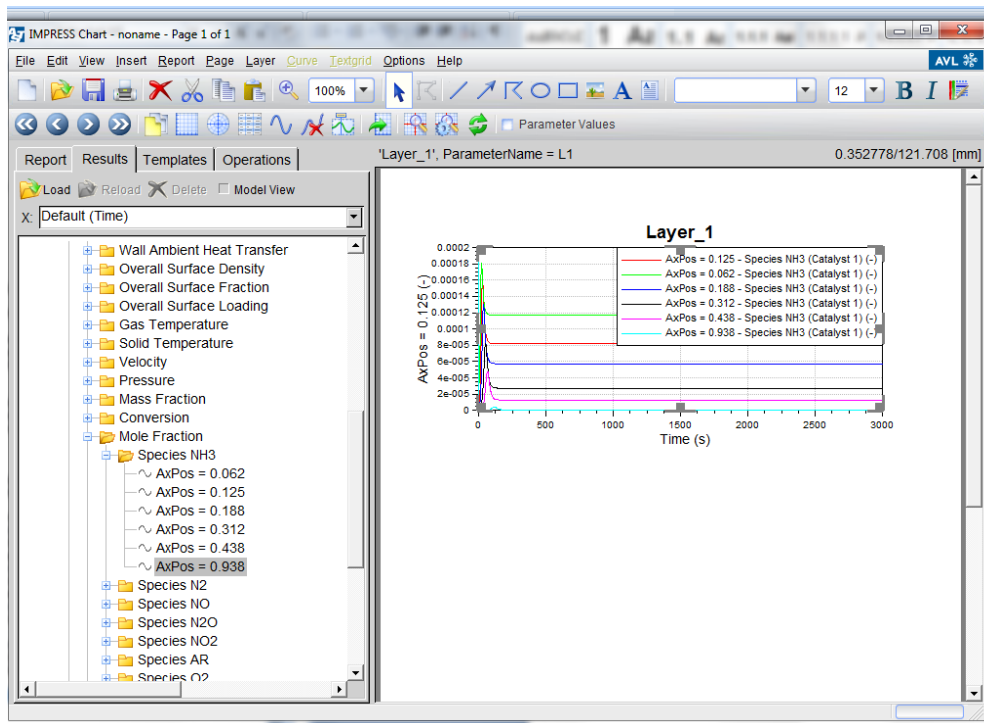

Figure 26 BOOST window- results.

Short *Curriculum Vitae*

Identification

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Education

1st cycle completed of Integrated Master in Chemical Engineer in the Faculty of Engineering of University of Porto (FEUP), Portugal, with the classification of 14 out of 20. Presently finishing master thesis in Chalmers University of Technology in Göteborg, Sverige.

Scientific activity

IJUP Project

Young Research in University of Porto 2010/11 IJUP Project, "Utilization of keratin from animal hair, leather and human hair for film production to agriculture applications", in Requimte-Department of Chemical Engineering, Faculty of Engineering of University of Porto

BII – Integration into research grant

Project CEFT/2009/03 2009/10 , "Production and Storage of Hydrogen through the catalyzed hydrolysis of sodium borohydride solutions" in CEFT-Transport Phenomena Research Center- Department of Chemical Engineering, Faculty of Engineering of University of Porto

Publications

Papers in international scientific periodicals with referees:

1- M.J.F. Ferreira , F. Coelho , C.M. Rangel , A.M.F.R. Pinto, "Batch sodium borohydride hydrolysis systems: Effect of sudden valve opening on hydrogen generation rate", Int J Hydrogen Energy 2012; 37:1947-53

Papers in conference proceedings (and <u>oral communication</u>):

4- <u>F. Coelho</u>, J.Bessa, L. Barbosa, S. Neto, C. Sousa, J. Costa, C. Rocha, O. M. Freitas, A. Crispim, C. Delerue-Matos and M.P. Gonçalves. "Production and characterization of keratin films to be used as an alternative to synthetic plastic" 12th National Meeting of 'Sociedade Portuguesa de Química1, 3-6 July 2011 Braga, Portugal

3- M.J.F. Ferreira, F. Coelho, C.M. Rangel and A.M.F.R. Pinto, "Batch sodium borohydride hydrolysis systems: effect of sudden valve   opening on hydrogen generation rate", in Proceedings of the 10th International Conference on Clean Energy, Famagusta, N. Cyprus, 15-17 September, paper 3-43 (2010)

2- M.J.F. Ferreira, F. Coelho, C.M. Rangel and A.M.F.R. Pinto, "On-demand   hydrogen generation by hydrolysis of sodium borohydride in batch reactors: effect of the buffer presure", in Proceedings of Hydrogen Energy and Sustainability – Advances in Fuel Cells and Hydrogen Workshop Torres Vedras, Portugal, 28-29 April (2010)

1- F. Coelho, M.J.F. Ferreira, C.M. Rangel and A.M.F.R. Pinto, "Hydrogen generation and storage by successive loadings of reactant   stabilized sodium borohydride solutions to feed a PEM fuel cell for portable applications", in the 3rd Meeting of Young Researchers at UP, Porto, 17-18 February 2011

Languages

English* – *Reading*: Excellent; *Writing*: Very good; *Speaking*: Very good

French – *Reading*: Good; *Writing*: Basic; *Speaking*: Basic

Portuguese – Mother Tongue

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